TREATISE ON POWDER METALLURGY

VOLUME II

Applied and Physical Powder Metallurgy

TREATISE ON POWDER METALLURGY *in three volumes*

by Claus G. Goetzel

Volume I:
Technology of Metal Powders and Their Products

Volume II:
Applied and Physical Powder Metallurgy
Part 1. Applied Powder Metallurgy—Industrial Materials and Products
Part 2. Physical Powder Metallurgy—Practical Evaluations and Theoretical Analyses of the Materials, Products, and Processes

Volume III:
Classified and Annotated Bibliography
Part 1. Literature
Part 2. Patents

TREATISE ON POWDER METALLURGY

By

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Volume II

Applied and Physical Powder Metallurgy

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PREFACE

Powder metallurgy is still very much in a state of flux. It is therefore not surprising that the amount of information that has appeared in the literature—both on technical and on theoretical issues—during the last few years alone is truly tremendous. Neither is it surprising that much of this information is controversial or preliminary in character, and subject to revision in coming years.

These circumstances have made difficult, and in many instances most trying, the completion of the first two volumes of *Treatise on Powder Metallurgy*. The influx of over one hundred reports from Field Investigators covering Occupied Europe, which dealt solely with topics concerned with the technology of the process, coincided with the last stages of preparing the book. The incorporation of pertinent material, especially in the field of powder manufacture, into the text would have necessitated complete rewriting of Chapters III to VI. Instead, only brief mention of the references was made in these chapters, and more space allotted for them in Volume II. This refers especially to the many interesting methods of manufacturing iron powder that were perfected during World War II in Germany; the reader will find considerable space devoted to this subject in Chapter XXV. Likewise, in Chapter XXII, powder production in the hard metal field is treated extensively, and the latest British and German experiences are given due consideration.

Turning now to the theoretical phase of Volume II, some remarks beyond those in the Preface to Volume I appear to be in order.

In Chapter XXXV, a summary of the theories of bonding and sintering is given. A major part of it constitutes a review of the many theories that have been advanced to date, and which amount to no less than twenty-two contributions of major significance, not to speak of a number of less outstanding ones, that may, however, eventually rank with the others in importance.

Naturally, the author was tempted to follow the vogue of the last five years by presenting a theory of sintering of his own. But it was felt that this would only have added more controversy and confusion to the already profuse and contradictory subject matter. Instead, it was the author's considered opinion that the reader would be helped more by an impartial presentation of the highlights of the different theories in form of brief synopses, to which cross references to coinciding theoretical concepts by others are appended. Thus, many of the controversial aspects of the different theories could readily be illuminated.

Among those to be considered of particular significance at this date are the theories dealing with the dispute over viscous flow *versus* volume diffusion as the primary process governing sintering. While the former—originated by Frenkel and energetically propagated by Shaler and Wulff—has lately lost considerable ground in favor of the latter—as formulated by Kuczynski and supported by Alexander, Nabarro, Rhines and others, the final word has not yet been spoken. Even the *Symposium on the Physics of Powder Metallurgy,* sponsored last year by Sylvania Electric Products Company and organized for the specific purpose of clarifying some of the issues involved, has failed to do so in this controversy. It should be recognized that the late theoretical discourses are still so transient in most of their basic concepts and interpretation of test results that the same experimental evidence may serve to prove or disprove the theoretical postulations. It is interesting to note that Shaler, for example, provided certain test data which were then used by his opponents to support some of their own theories.

The reader will probably not fail to notice that the author, in presenting the historical development of the different theoretical concepts and the composite theory based on the available, reliable experimental observations, has indicated his preference for the more conservative concepts of the mechanism of bonding and sintering. These concepts are based primarily on diffusion processes, supported by the action of surface tension forces, and are, perhaps best elucidated in Rhines' comprehensive theory presented at the *Seminar on Sintering* at the 1946 Meeting of the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers.

ACKNOWLEDGMENTS

The completion of this Second Volume of *Treatise on Powder Metallurgy* in its present form would not have been possible without the generous assistance and expert counsel of a number of prominent men connected with the field.

Once more, I should like to express my sincere gratitude to Dr. Paul Schwarzkopf for his offer of various illustrations and data that have been used throughout this volume.

The unselfish help of Dr. Richard Kieffer and his associate, Mr. Fritz Benesovsky, is especially appreciated in view of their sacrifice of time and effort in reviewing the entire text of Volume II, and in making most valuable suggestions for revision and additions, including a member of original illustrations.

I am grateful to Professor Gustav Hüttig for his thorough review and valuable assistance in reshaping the chapter on the summary of the theories of bonding

and sintering; the section on the theories of atomic migration during sintering was added at his suggestion.

I should like to thank Dr. Frederick N. Rhines for his permission to use substantial parts of his composite theory of sintering in the same chapter. Mr. Walter Kingston's generous help in placing at my disposal the manuscript of his theory of sintering, and in arranging for several translations of other theories, which were used in the same chapter, is also deeply appreciated.

I am very grateful to Dr. Werner H. Simon for his help in preparing the chapter on the physical properties of sintered *versus* fused metals and alloys and that surveying the sintered metals and alloys for potential industrial use.

Likewise, my gratitude is expressed to Dr. John T. Norton, Dr. Robert Steinitz, and Mr. R. W. Yancey for reviewing some of the chapters dealing with theoretical aspects or with applications in the refractory metal, electrical and magnetic fields.

To the impressive list of those who have helped me in the more technical tasks of completing this volume, and of which most have already been duly acknowledged in Volume I, I should like to add Mrs. Dorothy Trauberman, whose invaluable aid in proofreading is greatly appreciated. To the others I should like to express once again my sincere thanks.

I am most indebted to Mr. Erwin Loewy who, through his generosity and confidence, has greatly facilitated the liberal approach taken in this volume.

Lastly, I should like to take this opportunity to express my gratitude to the personnel, especially Mr. Allen Kent, and the management of Interscience Publishers, Inc., for their sacrificial aid and innumerable contributions which alone have made possible the completion of this volume—with its very broad scope and the difficult technical layout of the voluminous tabular and illustrative material.

My everlasting gratitude goes once more to my family for their forbearance and sacrifices during the years needed in producing this work.

C. G. G.

New York
June, 1950

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CONTENTS, VOLUME II

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PART TWO. PHYSICAL POWDER METALLURGY—PRACTICAL EVALUATIONS
AND THEORETICAL ANALYSES OF THE MATERIALS,
PRODUCTS, AND PROCESSES

ERRATA, VOLUME I

Page 20, line 10, change to read : “powdered lead alloys for assaying.”

Page 23, footnote 26, change to read: “W. H. Wollaston, *Phil. Trans. Roy. Soc., 119,* 1 (1829).”

Page 32, line 28, change to read: “in tuning inductance coils . . .”

Page 32, line 30, change to read: “core of a radio inductance coil . . .”

Page 37, lines 2 to 4 from bottom of page, change to read: “eners in concrete are often produced by this method. Machining costs are high and the method is practicable only when”

Page 50, footnote 31, change “Stablein” to “Stäblein”

Page 50, footnote 36, change “Offerman” and “Buchholz” to “Offermann” and “Buchholtz”
Make this same change for: footnote 55, page 52; footnote 13*b*, page 96; footnote 35, page 120
Correct the spellings in the text on pages 96, 119, 120

Page 50, footnote 38, change to read: “. . . *Bull. soc. chim. France, 41,* 1041 (1927).”

Page 50, footnote 40, change “Fieldauer” to “Fieldner”

Page 52, line 8, transpose this line with line 5 from the bottom of page 53

Page 86, Fig. 21, change “Maldau” to “Meldau”

Page 121, line 29, change “Bludar” to “Bludau”

Page 250, footnote 22, line 2, change “712,575” to 712,675”

Page 427, heading for Table 41, change to read: “Pressure–Temperature Relationship on Density of Hot-Pressed Copper, Brass, and Iron”

Page 428, heading for Table 42, delete “Electrolytic”

Page 463, Table 50, last value under “Yield point, psi,” change “46,900” to “36,900”

Page 470, footnote 11, change “137,815” to “137,185”

Page 476, last line, and page 477, lines 4 and 5, change “500°C. (930°F.)” to “600°C. (1110°F.)”

Page 566, Fig. 231, magnification is ×1500.

Part 1

APPLIED POWDER METALLURGY

Industrial Materials and Products

CHAPTER XXI

Refractory Metals and Alloys

REFRACTORY METALS

Tungsten

The present day manufacture of ductile tungsten wire stems largely from the work on refractory metal filaments for incandescent lamps initiated at the turn of the century. Because of the high melting point of this metal, it must be prepared from powders, and the practices of producing tungsten, molybdenum, and other refractory metals have formed the nucleus of the entire technique of powder metallurgy.

The historic development of tungsten and other refractory metals in ductile form has been described in some detail in Volume I, Chapter II. A comprehensive account of this history can also be found in the books by Smithells,[1] and—emphasizing the work done in Germany—by Skaupy,[2] and Kieffer and Hotop,[3] as well as in the publications by Hoyt[4,5] and Sykes.[6,7] Here, it may suffice to describe briefly the procedure developed by Coolidge,[8,9] which was first employed successfully in 1909, and which essentially is still in use. Coolidge compressed fine and very pure tungsten powder into bars without the aid of the previously used organic addition agents or metallic binders (*e.g.*, nickel, copper or amalgams). Thus he was able to use considerably higher temperatures for sintering. A strong sinter bar, which could be deformed in the heat, resulted from sintering near the melting point of tungsten by passing a direct current through the bar. Hot swaging at relatively high temperatures (1600 to 1800°C., 2910 to 3275°F.) produced a fibrous structure and improved the ductility to such an extent that the production of very fine wires and thin sheets

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[1] C. J. Smithells, *Tungsten*, 2nd ed. Chapman & Hall, London, 1945.

[2] F. Skaupy, *Metallkeramik*, 3rd ed. Verlag Chemie, Berlin, 1943.

[3] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe*. Springer, Berlin, 1943.

[4] S. L. Hoyt, *Metals & Alloys, 6*, No. 1, 11 (1935).

[5] S. L. Hoyt, *Metal Progress, 32*, 749 (1937).

[6] W. P. Sykes, *Metal Progress, 25*, 24 (1934).

[7] W. P. Sykes, *J. Chem. Education, 17*, 190 (1940).

[8] W. D. Coolidge, *J. Am. Inst. Elec. Engrs., 29*, 953 (1909)

[9] U. S. Pats. 1,026,429; 1,077,674; 1,082,933.

became possible. In contrast to the relatively porous structures obtained when using the paste process (employing organic binders) or lower melting metal additions that were later removed by volatilization, the sinter bars produced by the Coolidge method provided for more contact areas and better bonding between the individual crystallites, thereby improving the deformability of the metal during hammering. With progressing hot working, additional contact areas were created by closing of residual pores, and the formation of the fiber structure imparted a high degree of ductility to the metal. Incidentally, it may be of interest to know that the process developed by Coolidge for tungsten had its beginnings in the technique of producing sintered platinum developed nearly eighty years earlier by Wollaston (for details see Volume I, Chapter II, pages 23–25).

The Coolidge method was the foundation for the truly revolutionary development of incandescent lighting and its connected lamp industry, and remains to date the exclusive method for producing ductile refractory metals on an industrnal scale. The only other method (used later in Germany to a small extent) is the Pintsch single-crystal process as developed by Orbig and Schaller[10] in 1913. In this process, a paste made of very fine tungsten powder (average particle size 0.5 μ) mixed with approximately 2% thoria is extruded into filaments which are then heated indirectly by passing them through a tungsten coil kept at about 2200°C. (4000°F.) at a transport rate of about 10 ft. per hour—corresponding to the rate of crystal growth at the particular temperature used.

MANUFACTURE OF DUCTILE TUNGSTEN

Powder Production. The preparation of tungsten powder by reduction of pure tungsten oxides obtained from wolframite, $(Fe,Mn)WO_4$, scheelite, $CaWO_4$, or tungstenite, WS_2, has been described in some detail in Volume I, Chapter VI. The treatment of the ores is complicated, and the production of the metal powder can be summarized in seven steps: (*1*) pulverization of the ore; (*2*) treatment of the ore with caustic alkali at about 800°C. (1470°F.); (*3*) purification of the alkali tungstate by repeated crystallization; (*4*) precipitation with hydrochloric acid for the formation of tungstic acid, H_2WO_4; (*5*) filtration, drying and heating in air, for the formation of pure tungstic oxide, WO_3; (*6*) pulverization of the oxide; and (*7*) reduction by hydrogen.

The reduction of the tungstic oxide according to the reaction:

$$WO_3 + 3\ H_2 \rightleftharpoons W + 3\ H_2O$$

is conventionally conducted in tubular push furnaces (see Volume I,

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[10] German Pats. 291. 994; 296, 191.

Chapter XVI) at a temperature between 800 and 1000°C. (1470 and 1830°F.). The water vapor formed by the reaction is removed from the hydrogen by passage over a dryer, and the gas not used by the reaction is recirculated and used again together with fresh supply (see Volume I, Chapter XVII). During the reduction process the yellow-green tungstic oxide is transformed into varicolored lower oxides, namely, W_4O_{11}, violet; W_2O, chocolate-brown; or intermediate colors for mixtures of these oxides with WO_3 or with each other. The various reduction steps are reproduced from Smithells[1] in Table 83.

TABLE 83

Reduction Temperatures of Tungsten Trioxide (Smithells[1])

Temperature			
°C.	°F.	Appearance	Approximate composition
400	750	Green-blue	$WO_3 + W_4O_{11}$
500	930	Dark blue	$WO_3 + W_4O_{11}$
550	1020	Violet	W_4O_{11}
575	1065	Red-brown	$W_4O_{11} + WO_2$
600	1110	Chocolate-brown	WO_2
650	1200	Black-brown	$WO_2 + W$
700	1290	Black-gray	W
800	1470	Gray	W
900	1650	Metallic gray	W
1000	1830	Coarse metallic luster	W

TABLE 84

Production Conditions of Tungsten Powder (Smithells[1])

Particle size produced, μ	Reduction temperature		Moisture content of hydrogen	Tap density of WO_3, g./cc.
	°C.	°F.		
0.5	800	1470	Dry	0 05
2	830	1530	Dry	0.5
4	900	1650	Dry	1.0
8	1130	2070	Saturated with water at 75°C. (167°F.)	1 5
10	1200	2190	Saturated with water at 85°C. (185°F.)	2.0

The particle size of the tungsten powder depends on various factors, including temperature of reduction, moisture content of the hydrogen, flow rate of the gas, and history and particle size distribution of the oxide. The powder tends to become coarser with coarser tungstic acid, with higher temperature of reduction, with greater moisture content of the gas, and with a lesser flow rate for the gas. In Table 84, these relationships are reproduced from Smithells' work. The most suitable particle size distribution of tungsten powder to be used in the filament, x-ray, and hard-metal industries ranges from 0.5 to 10 μ.

TABLE 85

Growth Rates of Tungsten and Tungsten Oxide Powders of Different Particle Size (Kopelman[11])

Material	Initial particle size, μ	Lowest temperature required for growth, °C. (°F.)	Initial behavior at 850°C. (1560°F.)	Over-all behavior with time at 850°C. (1560°F.)	Remarks
WO_3....	0–1	About 400 (750)	Rapid growth	Growth, then some shrinkage	Commercial WO_3 is in the 0–1 μ range
WO_3...	1–5	About 600–800 (1110–1470)	Slow growth	Rather constant size	—
WO_3....	>5	Over 900 (1650)	Shrinkage	Continuous shrinkage	—
W_2O_5...	0–1	About 600 (1110)	Fairly rapid growth	Growth, then shrinkage	Blue oxide used was a mixture of the latter two groups with some WO_3 in solution
W_2O_5...	1–5	700–900 (1290–1650)	Slow growth	Rather constant size	
W_2O_5...	>5	Over 900 (1650)	Shrinkage	Continuous shrinkage	
WO_2....	0–1	About 700 (1290)	Slow growth	Very slight growth	Material used mainly of this size
WO_2....	1–2	About 800 (1470)	Very slow growth	Rather constant size	—
WO_2....	>5	About 1000 (1830)	Shrinkage	Shrinkage	Shrinkage only
W.....	0–2	1050 (1920)	No change	No change	Over 1200°C. (2190°F.) required for growth
W......	2–4	1200 (2190)	No change	No change	
W......	>4	Over 1200 (2190)	No change	No change	—

The effects on particle size of time and temperature of reduction, and concentration of water vapor in the hydrogen have recently been studied by Kopelman.[11] The raw materials used in this work included WO_3 (yellow oxide), mixtures of WO_2 and W (brown oxide), and mixtures (or more likely solid solutions) of WO_3 and W_2O_5 (blue oxide): in each instance about 0.4% SiO_2 and 0.4% K_2O plus KCl were added to the oxides prepared by usual commercial methods. In Table 85, growth rates of tungsten oxide and tungsten powders are given for different particle sizes. Based on the experimental results obtained by determining (microscopically) the size distribution obtained, and on published data of other investigators, a general theory of the mechanism of particle growth and shrinkage has been offered.

The particle size changes occurring during the hydrogen reduction cycle may be considered as related to the presence of pores of an extremely small size. After failing to detect such pores under the electron microscope at a magnification of 10,000 diameters, Kopelman and Gregg[11a] concluded that the pores are of a size of 100 Å. or less, and established supporting evidence to this effect by particle density determinations in liquids varying in molecular diameter (individual molecules of a liquid having diameters larger than that of the pores are unable to penetrate them, resulting in a particle density lower than in the case of penetration). An evaluation of the particle size of tungsten powders by specific surface measurements was also reported recently by Burden and Barker.[11b]

Pressing and Presintering. The tungsten powder is cold-pressed into bars in split dies (see Volume I, Chapter X) and in hydraulic presses (see also Volume I, Chapter XI), as shown in Figure 301. The cross section of the bars is either square or rectangular, and, depending upon the end use, the dimensions vary from about $^1/_4 \times ^1/_4 \times 8$ in. to $1^1/_4 \times 2^1/_2 \times 30$ in. The pressures lie in the range of 10 to 40 tsi, usually in the neighborhood of 20 tsi. The compactibility is sometimes improved by additions of lubricants, such as camphor dissolved in ether, or paraffin wax in benzene.

After removal of the bars from the mold they are too fragile for clamping into the sinter bell. For this reason they are first presintered in hydrogen at 1000–1200°C. (1800–2200°F.). The operation is usually performed in push-type or conveyor furnaces heated by molybdenum resistors. Slight grain growth occurs during this treatment and the conductivity is increased, thereby reducing the span of resistance of the bar during final sintering and simplifying the transformer needed for the sinter bell.

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[11] B. Kopelman, *Trans. Am. Inst. Mining Met. Engrs.*, *171*, 457 (1947).
[11a] B. Kopelman and C. C. Gregg, *ibid.*, *180*, 666 (1949).
[11b] H. Burden and A. Barker, *J. Inst. Metals*, *75*, 51 (1948).

Sintering. The sintering of tungsten and other refractory metal bars for wires, contacts, and x-ray targets in bell jars by passing a direct current through the bar has already been described in connection with sintering methods and furnaces (Volume I, Chapters XV and XVI). The bell-type furnace generally employed has been shown in Figure 239 and its cross section in Figure 253 of Volume I. The bell jar to be used for this purpose is sufficiently large to prevent overheating of the water-cooled walls. The upper contact clip which holds the bar in suspension is also water cooled. Since sintering results in appreciable shrinkage and sometimes warpage of the bar, the lower clip must be arranged in such manner as to give flexibility without breaking the contact. This is achieved by dipping the clip into water-cooled mercury. As protection against

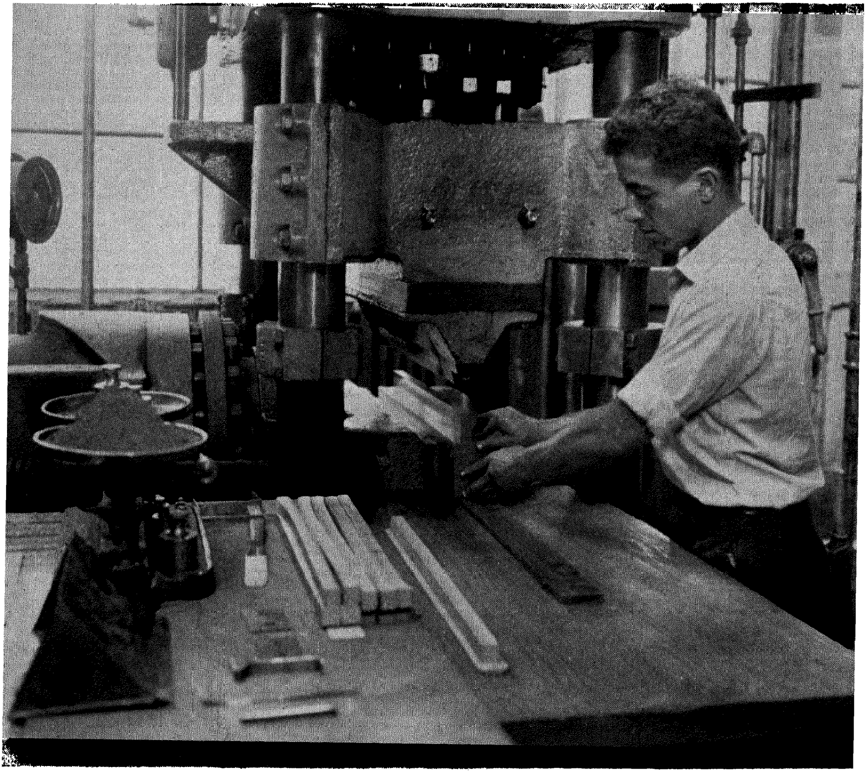
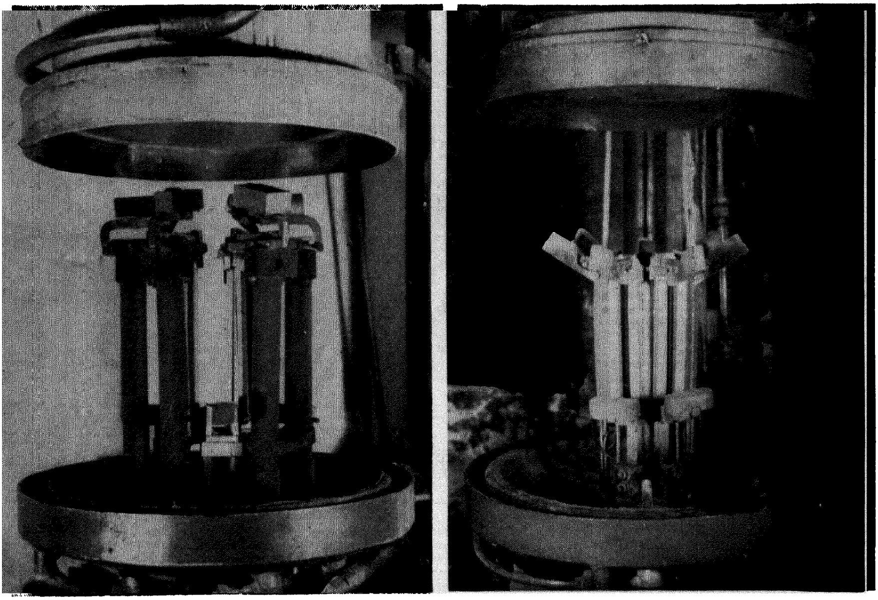


Fig. 301. Pressing of tungsten powder ingots. On scale is allotment of powder for one bar. In foreground is stack of sintered bars for comparison purposes. (Courtesy of American Electro Metal Corp.)

oxidation, the bell is sealed at the bottom by another mercury bath, and the bar is surrounded by pure hydrogen throughout the heating, sintering, and cooling cycle. In modern sinter bell constructions, the toxic mercury contacts are replaced by flexible molybdenum or tungsten contacts with molybdenum springs. The construction permits the simultaneous sintering of several bars, the number of bars depending on the capacity of the transformer.[11e] Figure 302*A* shows a late model six-bar sinter bell in which the bars are held in pairs by molybdenum clips.



A *B*

Fig. 302. Multiple-bar bell-jars for sintering of refractory metals by direct passage of high-amperage current; bells in raised position: *A*, six-bar arrangement for sintering tungsten (according to Kieffer and Benesovsky[11e]); *B*, sixteen-bar arrangement for sintering molybdenum. (Courtesy of R. Kieffer.)

The voltage applied to the upper clamp and the mercury pot ranges between 10 and 50 volts, while the currents amount to several thousand amperes. It is important that the electric current is carefully regulated, and that sharp temperature increments are avoided; especially in rods for incandescent lamp filaments, which contain certain additives, the current densities should not be too high at the beginning of the sintering

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[11e] R. Kieffer and F. Benesovsky, *Elektrotechnik und Maschinenbau, 65,* No. 1/2, 17 (1948).

cycle, for local fusion in the grain boundaries might occur because of the high resistance of the additives. The current density can be gradually increased as the additives volatilize and sintering progresses. The maximum current density is about 95% of that required for fusion, corresponding to some 1000 amp./cm.[2] (6500 amp./in.[2]); the maximum temperature exceeds 3000°C. (5400°F.). The energy input required for the sintering operation depends primarily upon the surface area of the bar, since the radiation energy received by the bell and carried off by the cooling water constitutes the principal energy loss at these high temperatures. The power input usually ranges between 60 and 300 watts per sq. cm. (400 and 2000 watts per sq. in.) of the surface of the bar.

Changes in voltage, current, and resistivity of the bar with increased sintering time are schematically shown in Figure 303.[12] The high initial resistance of the bar due to limited contacts of the particles at a few points decreases rapidly as sintering proceeds, and after approximately 20 minutes a constant value corresponding to the ultimate sintering temperature is reached. The bar is usually kept at the peak temperature for 5 to 20 minutes, and the total time consumed by heating and holding at temperature does not exceed 45 minutes—even for the largest bars. Because of limited convection, cooling is slow and takes usually 1 to 2 hours. In the production of certain wires of the "non-sag" type (see p. 19 ff.), the sintering process is repeated after the cross section of the bar has been reduced by about 50% by swaging, and sometimes is repeated once more after further reduction of the cross section.[13]

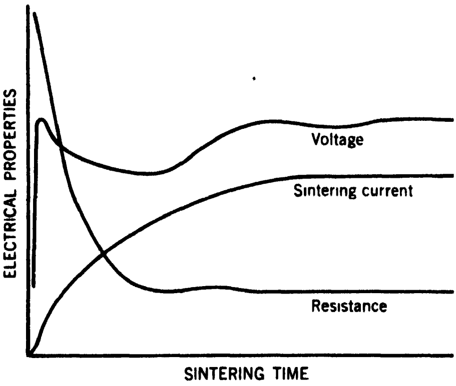

Fig 303 Changes in voltage, current, and resistance with time during sintering of tungsten or molybdenum bars (according to Kieffer and Hotop[12]).

During sintering the density increases from about 10–13 g./cc. for

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[12] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe.* Springer, Berlin, 1943, p. 231 ff.

[13] P. Schwarzkopf, *Powder Metallurgy,* Macmillan, New York, 1947, p. 171.

the presintered bar to 17–18 (the theoretical density being 19.3). This is accompanied by a linear shrinkage of about 15% and considerable distortion of the bar, as shown in Figure 304.[14] Grain growth begins at about 1000°C. (1830°F.) and, according to Jeffries,[15] reaches a maximum at about 2600–2800°C. (4700–5000°F.) as shown in Figure 305; during this grain growth the finest particles are absorbed and a structure of fairly uniform grain size results, as shown in Figure 306*A*. Under certain conditions, *i.e.*, extensive sintering at temperatures close to the melting point and with moist hydrogen gas as protective atmosphere, even single crystal bars can be obtained.[16] According to Kieffer and Hotop,[12] very fine powders of a particle size between 0.5 and 2μ and containing traces of oxygen usually lead to a coarse grain size in the sintered bar; somewhat coarser powders with a particle size ranging between 5 and 10 μ lead under identical sintering conditions to bars with a fine grain structure. Foreign oxide additions, such as ThO_2, Al_2O_3, CaO, SiO_2 or alkali

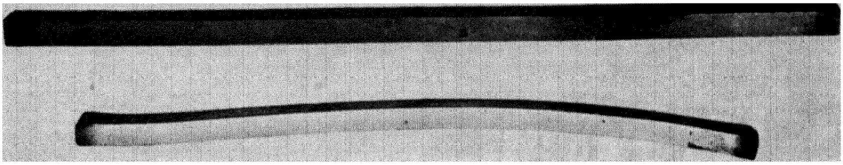

Fig. 304. Comparison of a pressed (top) and sintered (bottom) tungsten bar (according to Smithells[14]).

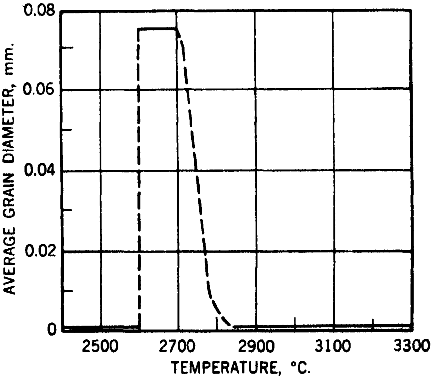

Fig. 305. Effect of sintering temperature on grain size of sintered tungsten rod (according to Jeffries[15]).

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[14] C. J. Smithells, *Tungsten*, 2nd ed., Chapman & Hall, London, 1945, pp. 54–59.
[15] Z. Jeffries, *Chem. & Met. Eng.*, *16*, 503 (1917).
[16] H. Alterthum, *Z. physik. Chem.*, *10*, 1 (1924).

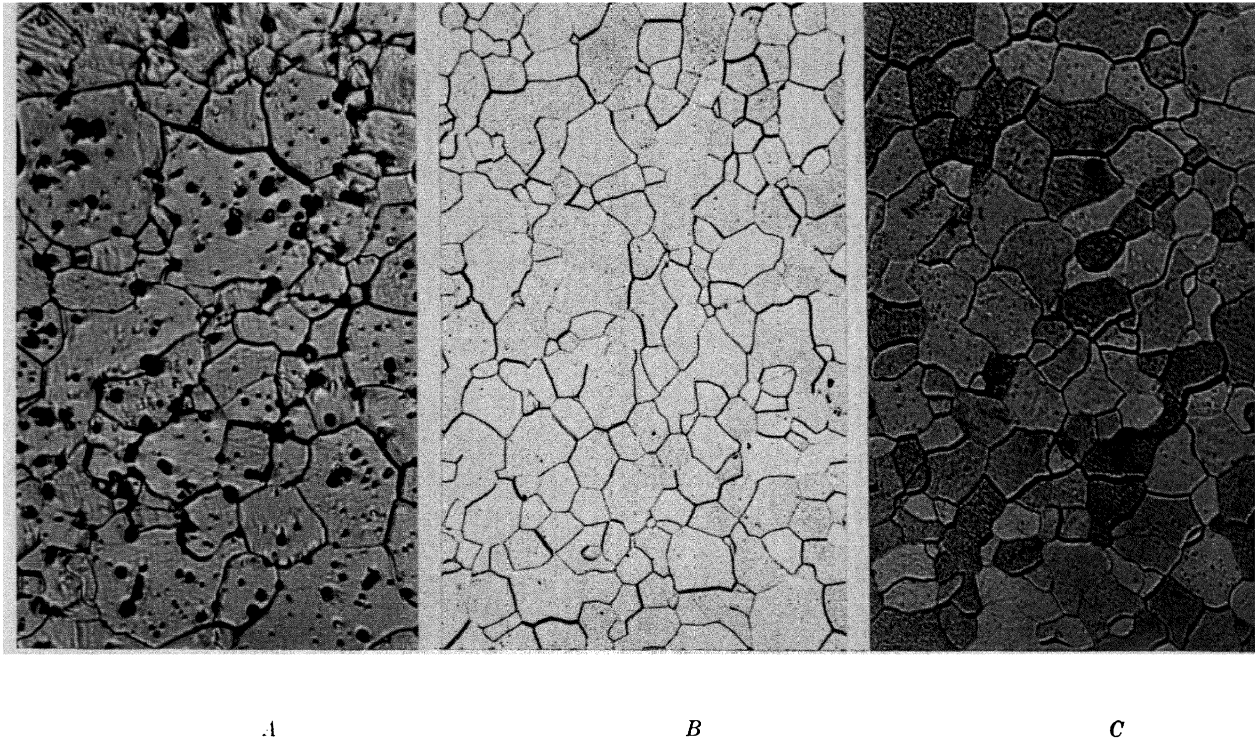

Fig. 306. Microstructures of sintered tungsten bar and swaged and annealed tungsten rod: *A*, sintered tungsten bar showing porous structure of fairly uniform and equiaxed grains. ×500. Courtesy of Callite Tungsten Corp. *B*, swaged and annealed tungsten rod, showing dense and recrystallized structure with very uniform and equiaxed grains. ×100. Courtesy of Sylvania Electric Products, Inc. *C*, same; annealing by resintering in bell jar for 30 min. at 1700°C. (3100°F.). ×200. Courtesy of Callite Tungsten Corp.

oxides reduce grain growth, whereas the lower tungsten oxides promote grain growth. Smithells[14] found an increase in grain growth with increasing molding pressure in bars pressed from a powder of 0.6 μ average particle size, but Kieffer and Hotop could not observe the same effect for coarser, oxygen-free powders of particle sizes ranging from 5 to 20 μ and conclude that Smithells' results are due to the higher oxide content that is always present in the fine powders. A recent report on studies in Germany has indicated that not only the particle size, but also the source of the powder, has a profound effect on the sintering characteristics.[16a] When tungsten powders of different origin but of similar particle size range (0.5–2 μ) were processed under identical conditions, sintering at 1700°C. (3090°F.) resulted in shrinkage values varying from 3.0 to 23.6% ! This comparatively wide spread is believed to be caused primarily by variations in the particle surface conditions.

By proper control of the particle size distribution, Kurtz[16b] was able to produce virtually fully dense metal (19.2 g./cc.) when sintering in pure hydrogen at the comparatively low temperature of 1350–1400° (2460–2550°F.). The patent claims of Hall and Ramage,[16c] on the other hand, are based on *wet* hydrogen (containing water vapor in amounts corresponding to saturation between 20 and 40°C.; 68 and 104°F.) as chief criterion for the production of high-density tungsten or molybdenum (see page 33) at low sintering temperatures.

Swaging of Tungsten Rod. The deformability of a metal in the solid state, as a rule, is dependent upon the temperature. Wretblad[17] distinguishes three cases:

(*1*) A low temperature zone in which the metal is brittle and the fracture is usually intercrystalline.

(*2*) An intermediate temperature zone in which the metal can be deformed plastically, the deformation causing an increase in hardness (cold working). For pure metals the fracture is generally transcrystalline.

(*3*) A high temperature zone above the recrystallization temperature in which deformation does not cause any increase in hardness (hot working). Again, the fracture is intercrystalline.

The zone of low temperature brittleness (considerably below room

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[16a] Studiengesellschaft Hartmetall, *B. O. T. German Division* (Documents Unit), F. D. 3881/47; see also *Met. Powd. Rept.*, *2*, No. 8, 119 (1948).

[16b] J. Kurtz, *Proc. Second Annual Spring Meeting of Metal Powder Association*, New York, June 13, 1946, p. 40.

[16c] U. S. Pat. 2,431,690.

[17] P. E. Wretblad, in J. Wulff, *Powder Metallurgy*. Am. Soc. Metals, Cleveland, 1942, p. 425.

temperature for common metals) extends far above room temperature for the high melting metals molybdenum and tungsten. The sintered tungsten bar is therefore completely brittle when cold. Deformation of the tungsten bar by swaging, forging, rolling or slight bending, is possible, however, if the bar is heated to a temperature of 1300–1700°C. (2400–3100°F.). This operation, although far above room temperature, must be considered "cold working" rather than "hot working," because the recrystallization temperature is not yet reached. The recrystallization temperature (and possibly the range of cold brittleness[18]) is lowered by the energy invested in the metal by the cold work. Hence, with increasing deformation, the zone at which cold work can be performed moves toward lower temperatures. By lowering the range of cold brittleness of tungsten through progressive reduction in cross section, a status is reached in which cold working makes the metal *ductile* at ordinary temperatures. The fabrication of the brittle bar into ductile wire or sheet is governed strictly by this mechanism. The metal first is worked at a high temperature (above the low-temperature brittleness range of sintered tungsten). A progressively lower working temperature is not only permitted by the gradual decrease in the cold brittleness temperature, but is actually demanded by the fact that the recrystallization temperature is also lowered. If the metal is heated above the recrystallization temperature, working must be resumed at the original high temperature above the cold brittleness range of the sintered, nonworked metal.

The tungsten bar is worked in swaging machines (Fig. 307A), in which rotating dies of semicylindrical surfaces are forced together by cams. The dies are of hardened high-speed steel, Stellite, or cemented carbide or of Stellite or carbide-surfaced steel. The square sinter bar is rounded by about 10,000 hammer blows per minute. The bars must be preheated before swaging, and the swaging must often be interrupted by reheating. The swaging temperatures generally used are:[14]

Diameter, mm.	Swaging temperature	
	°C.	°F.
11–6	1350	2460
5.5–2.5	1250	2280
2.5–1.0	1175	2150

The bars cool considerably while being transferred (with tongs) from the heating furnace to the swaging machine and require overheating to about 1500°C. (2700°F.) for a swaging temperature of 1350°C. (2450°F).

According to Wretblad[17] the following procedure is used in the fabrication of incandescent lamp wire from tungsten, containing alkaline and

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[18] Z. Jeffries and R. S. Archer, *Chem. & Met. Eng.*, 27, 747 (1922).

silica additions. The sintered rod is first heated in an air furnace to about 1600°C. (2900°F.), and the rod is then immediately hammered. The reheating during the first stages of swaging often reaches 2000°C.

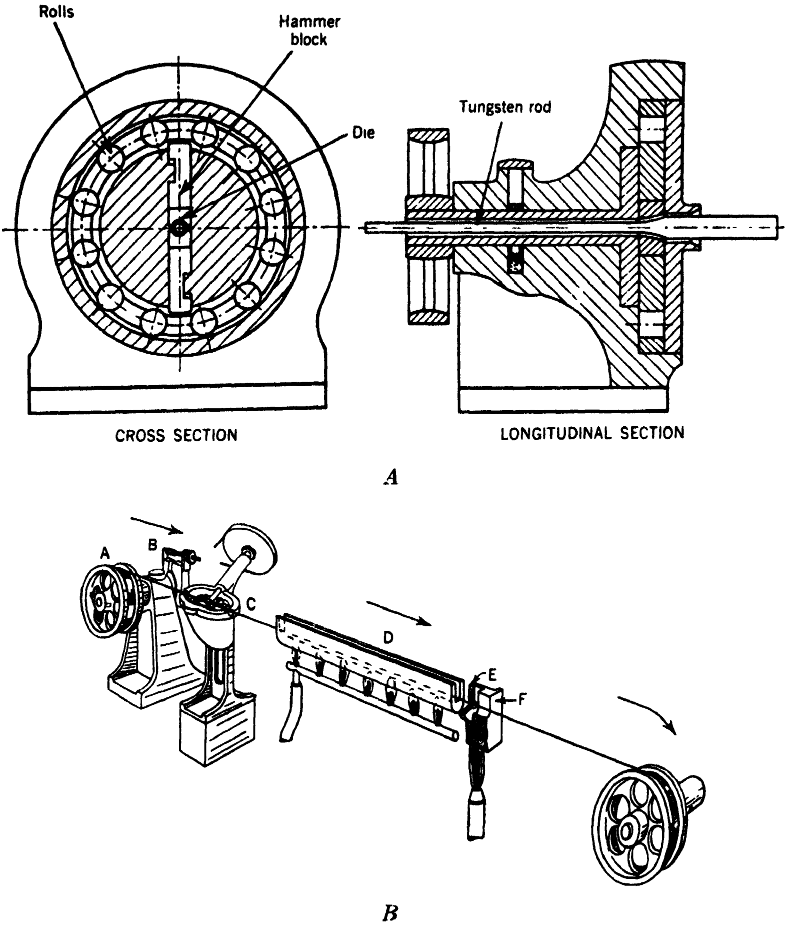

Fig. 307. (*A*) Diagrammatic view of cross section and longitudinal section of swaging machine as used in the working of tungsten rod (according to Kieffer and Hotop[12]). (*B*) Diagrammatic view of arrangement of tungsten wire drawing machine (according to Smithells[14]): A, takeoff drum; B, brake; C, Aquadag pot; D, heater; E, die; and F, heated die block.

(3600°F.). Reduction in cross section of the bar is obtained with progressively smaller swaging dies. When the bar has been reduced to 3 to 4 mm. in diameter, it has become long enough for swaging in a machine having feed rolls which pull the rod through a heating furnace and the swager. A coating of colloidal graphite is usually applied to the bars at this stage in order to form an adherent film that acts as a lubricant in the subsequent drawing operation and protects the bar against oxidation. The reduction in diameter during each pass is less than 5%, yielding a final diameter of about 1 mm. The last swaging passes are carried out at about 1000°C. (1800°F.). This bar, ready for wire drawing, has a density of about 18.5 g./cc.

During swaging the tensile strength increases from about 18,000 to above 100,000 psi. The hardness increases from about 200 Brinell units for the sintered bar (18 × 18 mm. cross section) to about 400 Brinell for the bar swaged to a diameter of 5 mm. A complete densification of the microstructure is achieved in the early stages of the swaging operation, and the annealed rod displays a uniform and equiaxed grain structure, as shown in the photomicrographs of Figures 306 *B* and *C*.

Wire Drawing and Coiling. Since tungsten wire of 1 mm. diameter is not sufficiently ductile to be wound on a feed roll, it is first drawn in a chain bench to 0.7 mm. Then the wire is drawn by power-driven reels which pull the wire horizontally through a gas furnace and the drawing die, as illustrated schematically in Figure 307*B*, according to Smithells.[14] Dies made from cemented carbides are used for diameters down to about 0.3 mm.; finer wires are obtained by drawing through diamond dies. The reduction takes place in steps of about 10%, and the wire is frequently dipped into an aqueous graphite suspension. The temperatures to which the wires are heated during drawing are gradually reduced from about 800 to 400°C. (1500 to 750°F.), while the drawing speed is increased at the same time, thereby reaching values of 700 ft./min. for the finest wires. To permit threading through the die, the end of the wire is pointed by chemical etching with fused sodium nitrite as long as the wire remains fairly thick. The very fine diameters are etched either by dipping into a fused 50–50 sodium nitrite–sodium nitrate bath, or by alternating-current electrolysis in dilute acid.[14]

A careful inspection of the last diamond dies is necessary to assure a sufficiently round wire. The difficulties in making diamond dies for the very thin wires limit the wire size to about 8 μ. Incandescent lamp wires of decreasing diameter are used for lower lamp currents, and the finest wires used in 300-volt, 15-watt lamps, are about 12 μ in diameter. This wire is too fine to be measured accurately, and determinations are made by weighing on a torsion balance a length wound around a cylinder of 200 mm. The weight of a 12 μ wire of the specified length is about 0.5

mg., and the wire is generally known as "0.5 mg. wire."[17] Experimentally, still finer wires can be produced, and, according to Kieffer and Hotop,[19] filaments 7 to 2μ in diameter have been obtained by etching or electrolytic pickling in a fused sodium nitrite or caustic soda solution. After the drawing operation is completed, the wire is cleaned by removing the oxide-graphite layers introduced by the drawing process: in boiling, dilute or concentrated alkali hydroxide or sodium carbonate solutions; by passing through trichloroethylene; by electrolytic pickling, in the case of coarser wires; by etching with fused sodium nitrite; or by annealing in nitrogen containing traces of oxygen, or in commercial hydrogen.[19]

The density of the fine tungsten wires is practically equal to the theoretical density of tungsten, 19.3 g./cc. The tensile strength is the highest of any material known, 850,000 psi, *i.e.*, more than twice that of the hardest steel. The modulus of elasticity is 60,000,000 psi for tungsten wire, twice that of steel, and the linear coefficient of thermal expansion is 4.6×10^{-6} per °C., the lowest of any pure metal.

Finally, the wire is coiled into the form of the filaments used in the modern incandescent lamps. This operation is performed either at room temperature or at about 500°C. (930°F.), this temperature being obtained by passing an electric current through it. A common single coil is wound on a straight iron core wire which is afterward dissolved in a diluted acid. The so-called "coiled-coil" filament for gas-filled lamps and for cathodes in fluorescent lamps is produced by winding a spiral of tungsten around a straight molybdenum wire which itself is subsequently coiled into a spiral. Since in a coiled-coil filament the clearance between the turns is extremely small, the slightest sagging during recrystallization would cause short circuiting of part of the filament. Hence, the wire is recrystallized on the molybdenum core wire by heating it in a tube furnace in hydrogen to about 1600°C. (2900°F.). The molybdenum is then dissolved in a mixture of hot sulfuric and nitric acids.[17]

Forging, Rolling, and Other Fabrication Methods. Forging of tungsten is usually conducted at temperatures somewhat above those used during swaging. The sintered ingot is first heated to about 1800°C. (3300°F.), and the temperature is reduced to 1100°C. (2000°F.) toward the end of the operation. After each reduction in thickness, the ingot must again be reheated to the forging temperature. A variety of forms can be machined from the forged blanks. High-speed silicon carbide cutoff wheels are necessary for cutting, and punching, grinding, and

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[19] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe.* Springer, Berlin, 1943, p. 234.

machining with hard metal tools are possible. Joining to tungsten or other metals is made possible by spot welding, electric arc welding, or by brazing after the tungsten has been coated with copper.

In the production of very thin tungsten sheets, forging is followed by hot rolling down to about 1-mm. thickness. The sheet must be reheated between each pass. The sheet is then pickled in a potassium nitrite solution and subsequently cold-rolled to the desired size. Intermediate heating facilitates the process, but the temperature must not reach the recrystallization temperature of about 1000°C. (1830°F.).

In general, oxidation occurring during the heating process makes it difficult to produce sheets thinner than about 0.1 mm. Considerably thinner sheets (0.02–0.03 mm.) can, however, be obtained by stacking them into multiple sheets.[20] A still more elaborate method in which a tungsten sheet is placed between oxidized or asbestos-covered iron sheets that are closed at the end to exclude air, has reportedly produced foils 3–5 μ thick.[21]

In the fabrication of formed products such as x-ray targets or electric contacts the cylindrical shapes are often already machined after presintering. To obtain high density parts, the bars are swaged in the aforementioned manner. Tungsten tubes can be produced by subjecting tungsten powder, placed between two rubber tubes, to a hydrostatic pressure of about 30 tsi and afterward sintering the hollow compact on a tungsten support at about 2000°C. (3600°F.).[22] The manufacture of seamless thin-walled tubes is also possible by applying tungsten powder wetted by collodion into a slurry to a magnesia rod, presintering followed by dissolving the rod, and final sintering by direct resistance heating.[22a]

MICROSTRUCTURE AND PROPERTIES

Control of Grain Structure Through Additives. In contrast to most engineering metals and alloys, tungsten is used commonly at temperatures above recrystallization (*e.g.*, at 2500°C., 4500°F. for incandescent lamp filaments) so that a close control of the recrystallization phenomena is of very great importance. Furthermore, tungsten differs from other metals in having a greater transcrystalline than intercrystalline (boundary) strength. The tensile strength of tungsten wire is, therefore, considerably reduced when recrystallization produces boundary areas that occupy a relatively large proportion of the cross section. The

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[20] Brit. Pat. 247,507.

[21] P. Schwarzkopf, *Powder Metallurgy*. Macmillan, New York, 1947, p. 177.

[22] U. S. Pat. 1,081,618.

[22a] German Pat. 750,464.

original equiaxed grain structure of the sintered bar (Fig. 306*A*) is changed into a fibrous structure of high strength by the swaging and drawing process (Figs. 308*A*, 309*A*). If the filament is heated above 2000°C. (3600°F.), the fibrous structure is destroyed and again a polycrystalline structure is formed by the recrystallization (Figs. 308*B*, 309*B*). The newly formed crystallites engulf the entire cross section after a comparatively short time (Fig. 309*C*). In addition, during heating by alternate current the larger crystals slide along the grain boundaries and display a characteristic "off-setting" effect, that causes sagging of the filaments under the influence of gravity, and eventually fusion by overheating due to local contractions of the cross section of the wire. This off-setting effect is shown schematically in Figure 309*D*.


A *B* *C* *D*

Fig. 308. Microstructures of tungsten wire (×150): *A*, 110μ wire as drawn before recrystallization; *B*, 135μ wire recrystallized at 2500°C. (4500°F.), commercially pure tungsten metal, containing 0.05% impurities; *C*. 100μ wire recrystallized at 2500°C., containing 0.75% ThO_2; and *D*, 145μ wire recrystallized at 2500°C. (non-sag wire). Courtesy of General Electric Co.

Two principally different approaches are taken in the lamp industry to prevent sagging. The first method (formerly used exclusively) is now only used in straight-wire lamps. It was originally developed by Jeffries and consists of adding a small percentage (0.7–1%) of powdered ThO_2 to the tungsten, which simply retards the diffusion of tungsten atoms and inhibits grain growth, as shown in the photomicrograph Figure 308*C*.

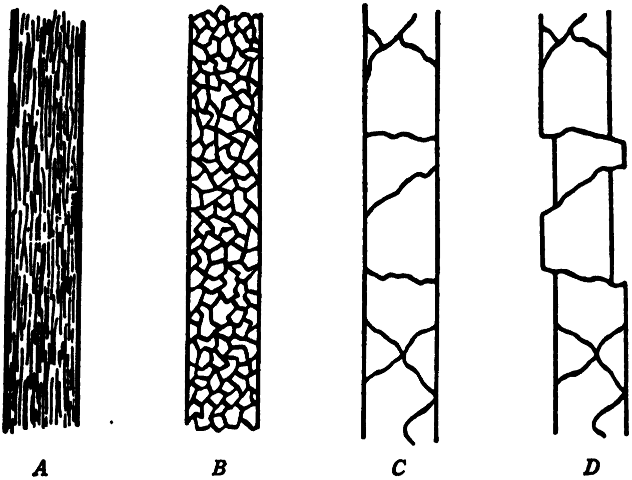

Fig. 309. Diagrammatic presentation of "off-setting" or sagging process in pure tungsten wire heated above recrystallization temperature (according to Smithells[14]): *A*, fiber structure of swaged and hard drawn wire; *B*, equiaxed grain structure after recrystallization during heating to high temperature; *C*, excessive grain growth during prolonged heating at high temperature; and *D*, "off-setting" of crystals in suspended wire.

However, a critical quantity of thoria lying below the range mentioned stimulates grain growth. The second method, now used exclusively for coiled filaments, causes the formation of a special macrocrystalline structure through small additions of mixtures of at least partly volatile alkali silicates and such nonvolatile substances as SiO_2, Al_2O_3, ThO_2, or CaO. These double additives may be combined in one salt, as, for instance, sodium-silico-tungstate. The addition agents are often mixed wet with tungstic oxide and the mixture reduced after drying. The function of these double additives is not to restrict grain growth but rather to promote the proper *orientation* of the grain boundaries with respect to the wire axis. Thus, although grain growth is excessive, a special overlapping sag-proof structure is obtained, as shown in the photomicrograph of Figure 308*D*. This structure of overlapping grains constitutes a crystal arrangement of great hot-strength and gives the filament the required nonsag property.

Wretblad[23] explains the mechanism of the action of the double additives by considering singly the effect of each additive. Nonvolatile additives used alone usually inhibit grain growth, while the volatile alkalis alone cause exaggerated grain growth without overlapping of grains. This excessive grain growth occurs at temperatures at which the alkali additives commence to decompose. Diffusion across grain boundaries becomes probable, and exaggerated grain growth may occur in different directions. However, with the other component of the double additive the same effect is only possible at very high temperatures, *e.g.*, 2500°C. (4500°F.) in the case of ThO_2. Consequently, additives of the two types added in proper proportions act in conjunction and cause exaggerated grain growth in a preferred direction. This is due to the fact that during the drawing operation at elevated temperatures, the inhibiting additive has been forced into stringlike arrangement parallel to the wire axis, thereby inhibiting *lateral* diffusion, while diffusion and grain growth progress

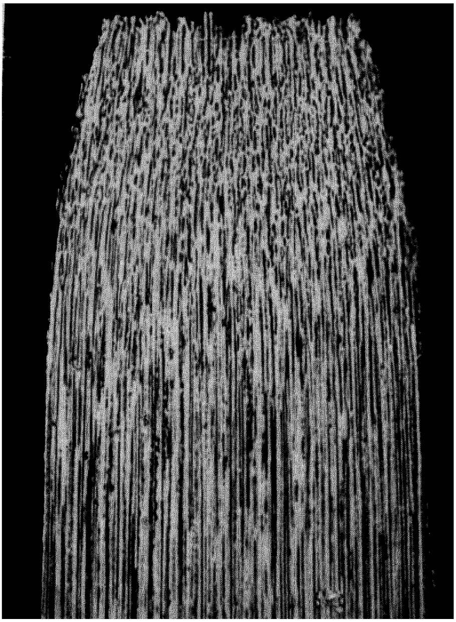

Fig. 310. Ductile tensile break of 0.007-in. (175 μ) diameter tungsten wire (according to Woods[24]).

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[23] P. E. Wretblad, in J. Wulff, *Powder Metallurgy*. Am. Soc. Metals, Cleveland, 1942, p. 433.

TABLE 86. Characteristics of Tungsten[a]

PHYSICAL PROPERTIES

Crystal lattice, type	Body-centered, cubic
Parameter, Å	3.158
Atomic weight	184
Density, g./cc.	
Theoretical	19.3
Presintered to about 1500°C. (2730°F.)	10 0–13 0
High sintered to about 3000°C. (5430°F.)	16.5–17 0
Swaged (15 → 4 mm.)	17 6 → 19 2
Drawn (0.15 → 0.01 mm.)	19 2 → 19 3
Tensile strength, psi.	
Sintered ingot	16,000
Swaged bar, 5 mm	57,000
3 mm	107,000
Hard drawn wire, 1 mm	200,000
0.5 mm	263,000
0.3 mm	313,000
0.15 mm	384,000
0.1 mm	426,000
0.05 mm	490,000
0.03 mm	547,000
0.015 mm	670,000
Annealed wire (recrystallized)	150,000
Single crystal wire, nondeformed (thoriated)	165,000
deformed (thoriated)	250,000
Elongation, %	
Hard drawn wire, 1.0 mm	1–4
0.1 mm	1–4
Annealed wire (recrystallized)	0
Single crystal wire, nondeformed (thoriated)	About 20
Yield point, psi.	
Hard drawn wire, 0.5–1 mm	213,000
Annealed wire, 0.5–1 mm	102,000–118,000
Modulus of elasticity, psi	
Hard drawn wire, 0.3 mm	12,800,000
0.15 mm	37,000,000
0.10 mm	45,000,000
0.05 mm	47,000,000
0.03 mm	48,500,000
Single crystal wire	51,000,000–60,000,000
Modulus of torsion, psi	
Single crystal wire	21,000,000–31,000,000
Tensile strength at elevated temperature, psi	
Wire, 0.6 mm., 400°C. (750°F.)	170,000–225,000
800°C. (1470°F.)	112,000–142,000
1200°C. (2190°F.)	57,000–85,000
1800°C. (3270°F.)	14,000–42,000
Elongation at elevated temperature, %	
Wire, 6 mm., 400° C. (750°F.)	2–3
800°C. (1475°F.)	5
1200°C. (2200°F.)	6
Brinell hardness	
Sintered bar 18 × 18 mm	250
Swaged bar to 5 mm	350–400

THERMAL PROPERTIES

Melting point, °C. (°F.)	3370 (6100)
Boiling point, °C. (°F.)	About 5900 (10,650)

TABLE 86 (*concluded*)

THERMAL PROPERTIES (*continued*)	
Vapor pressure, mm. Hg	
1530 °C. (2790 °F.)	1.93×10^{-15}
2130 °C. (3870 °F.)	7.90×10^{-9}
2530 °C. (4590 °F.)	5.10×10^{-6}
2730 °C. (4950 °F.)	6.55×10^{-5}
3230 °C. (5850 °F.)	4.68×10^{-3}
Vapor pressure of metallic oxide, mm. Hg at 1400 °C. (2550 °F.)	760
Linear coefficient of thermal expansion, per °C.	
30 °C.	4.44×10^{-6}
1030 °C.	5.19×10^{-6}
2030 °C.	7.26×10^{-6}
Heat conductivity, cal./cm./sec./°C. at 20 °C.	0.38
Specific heat, cal./g./°C.	
20–100 °C.	$3\ 4 \times 10^{-2}$
1000 °C.	3.65×10^{-2}
Heat of fusion, cal./g.	About 60
Heat of vaporization at normal boiling point, cal./g.	About 1150

ELECTRICAL PROPERTIES	
Electrical resistivity, microhm-cm.	
20 °C. (68 °F.)	5.5
750 °C. (1380 °F.)	25.5
1200 °C. (2190 °F.)	40
2400 °C. (4350 °F.)	85
Electrical conductivity, megmho-cm., at 20 °C. (68 °F.)	About 0.18
Temperature coefficient of resistivity	4.8×10^{-3}
Work function, volts	4.5
Electrolytic potential against hydrogen electrode, volts	0.0
Ionization voltage, volts	8.1
Thermionic emission, ma/cm.^{2} at 1950 °K.	1

RADIATION PROPERTIES	
Total radiation, watts/cm.^{2}	
800 °K.	About 0.3
1400 °K.	About 4.0
2000 °K.	About 25.0
2600 °K.	About 84.0
Radiation for 5500 Å., per cent of the radiation of the black body, at 20 °C.	48
Reflectivity for 5500 Å., per cent at 20 °C.	50
Wave length of the characteristic x-ray radiation, Å.	
K-series	About 0.21
L-series	About 1.48

ACOUSTIC PROPERTIES	
Velocity of sound, m./sec.	About 4300

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[a] This table is a composite of data from R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe*, 2nd ed., Springer, Berlin, 1948, p. 237, Table 44; H. W. Highriter, in J. Wulff, *Powder Metallurgy*, Am. Soc. Metals, Cleveland, 1942, pp. 410, 411, Tables 26 and 27; P. Schwarzkopf, *Powder Metallurgy*, Macmillan, New York, 1947, p. 178, Table 38; and "Elmet Molybdenum, Tungsten and Alloys," catalog of North American Philips Co., Inc., New York, pp. 24, 25.

TABLE 87

Chemical Behavior of Tungsten[a]

Substance	Reaction of Tungsten
Air or oxygen	Practically none at 20°C. (68°F.); oxidation starts at 400–500°C. (750–930°F.); strong oxidation (WO_3) at higher temperatures and in oxygen; oxidation above 900°C. (1650°F.) at very low pressure
Ammonia, aqueous	Practically none
Carbon dioxide	Formation of oxide at about 1200°C. (2200°F.)
Carbon monoxide	Formation of oxide at 1000°C. (1830°F.)
Halogens	Bromine and iodine: reaction at bright red heat Chlorine: reaction above 250–300°C. (480–570°F.) Fluorine: reaction at 20°C. (68°F.)
Hydrogen	None
Hydrogen sulfide	Superficial reaction at red heat
Nitrogen	None up to 1500°C. (2730°F.); formation of nitride at 2300°C. (4170°F.)
Nitric oxide	N_2O, NO, NO_2: oxidation to WO_3 at higher temperatures
Sulfur dioxide	Oxidation at higher temperatures
Water	None
Water vapor	Fast oxidation at red heat
Aqua regia	Superficial oxidation to WO_3 at room temperature
Hydrochloric acid	
Aqueous	No reaction at 500–600°C. (930–1110°F.) if free from oxygen
Gaseous	Cold: practically none; warm: slight reaction
Hydrofluoric acid	Cold and warm: none
Hydrofluoric acid mixed with nitric acid	Rapid solution
Nitric acid	Cold: practically none; warm: slight reaction
Sulfuric acid	Cold: practically none; warm: slight reaction
Ammonium hydroxide	Practically none
Potassium hydroxide or sodium hydroxide	
Aqueous	Practically none
Molten	Slow oxidation in air; fast solution if oxidizing agents present such as KNO_3, KNO_2, $KClO_3$, PbO_2
Oxidizing solutions	Soluble in basic solution of $K_3Fe(CN)_6$; soluble in saturated solution of $NaClO_3$; slight reaction with water containing chlorine; soluble in sodium nitrite at 300°C. (570°F.)
Carbon, solid (soot, coal, graphite) and hydrocarbons	Formation of carbide above 1200°C (2200°F.) (enrichment of carbon from W_2C to WC); complete formation of carbide at about 1400–1500°C. (2550–2730°F.)
Mercury	Very slight amalgamation
Sulfur, molten or boiling	Slow reaction

Etching agents for metallographic specimens:

1. Basic solution of $K_3Fe(CN)_6$.
2. Hydrogen peroxide with ammonia.
3. Nitric acid with hydrofluoric acid.

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[a] "Elmet" catalog, North American Philips Company, Inc., New York, pp. 22, 23.

unhampered in the *longitudinal* direction, and grain boundary areas tend to favor an acute-angle orientation with the wire axis.

An interesting approach to the problem of producing tungsten filament coils exhibiting high resistance to sagging, endurance to vibration, and high extensibility (in the direction of filament axis) has recently been disclosed by Van Liempt.[23a] This is accomplished in large-grained, nonsagging-type wire by a special heat treatment which effects a readjustment of the space lattice prior to recrystallization.

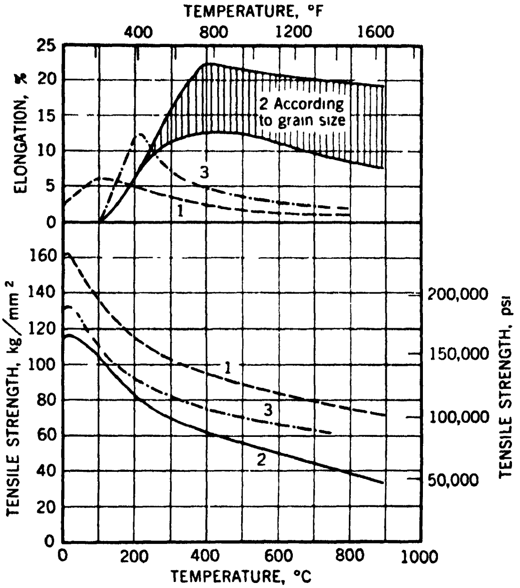

Fig. 311. Tensile properties of tungsten wire containing 0.75% ThO_2 (according to Jeffries[15]): curve 1 is for wire cold drawn 97.5% to 0.63-mm. diameter, not recrystallized; curve 2 is for same, but recrystallized in hydrogen at 2000°C. (3625°F.); and curve 3 is for wire cold drawn 56% to 0.7-mm. diameter, not recrystallized.

The high degree of ductility obtained in the fibrous tungsten wire is best illustrated by the typical neck-shaped tensile break, as shown in Figure 310 for a 0.007-in. (175 μ), ductile tungsten wire, according to Woods.[24]

[23a] U. S. Pat. 2,439,913.

[24] H. W. Woods, *Metal Progress*, *51*, 261 (1947).

In order to facilitate production control, Zapffe and Landgraf[24a] have recently suggested the use of fractographic examination, since this method gives a clear indication of the degree of densification and homogenization by the characteristic cleavage patterns in hot-swaged tungsten rods.

Properties of Tungsten. The various applications of tungsten are governed by the unique physical and chemical properties of the metal. Most important are its extremely high melting point, its low vapor pressure in vacuum, its high hot-strength and hardness, its comparatively good electrical and heat conductivity, its paramagnetic behavior, its chemical purity, and its relatively effective resistance against acids and inert or reducing gases. In Table 86 the physical properties of tungsten are reproduced, while in Table 87 the chemical behavior of the metal is indicated. The tensile properties of tungsten wires at elevated temperatures are shown in Figures 311 and 312. The oxidation behavior, volatility of thin oxide films, and reducibility of these films with pure hydrogen have been studied by Gulbransen and Wysong[25] in connection with

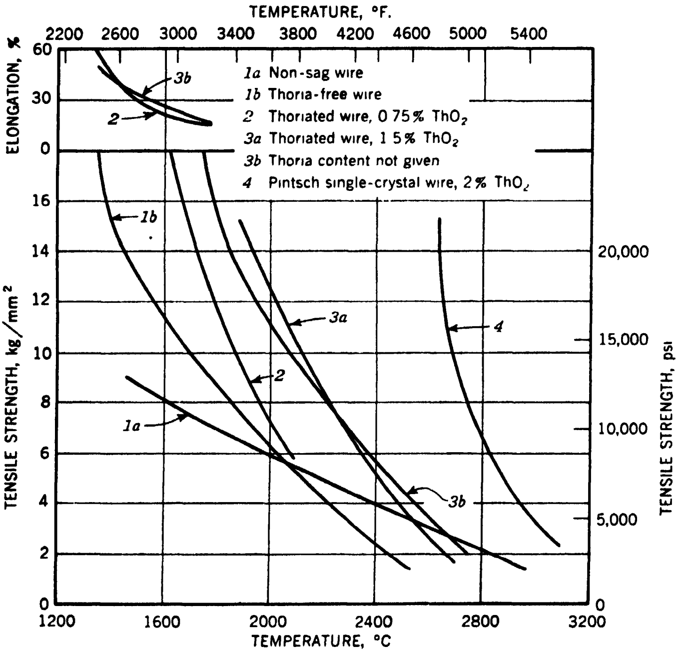

Fig. 312. Tensile properties of tungsten wire at 1200–3000°C. (2190–5430°F.). According to Espe and Knoll[25a]

[24a] C. A. Zapffe and F. K. Landgraf, *Trans. Am. Soc. Metals, 41,* 396 (1949).

[25] E. A. Gulbransen and W. S. Wysong, *Trans. Am. Inst. Mining Engrs., 175,* 611 (1948).

the question of the behavior of tungsten and its surface oxides at elevated temperature under various atmospheric conditions. The reactivity of tungsten with oxygen was also investigated by Huff, Squitieri, and Snyder,[25a] who determined the heat of formation of WO_3 (—200.16 ± 0.10 kcal./mole under standard conditions); that of tungsten with carbon was investigated by Pirani and Sandor,[25b] who carburized arc-melted and granulated tungsten at different temperatures and determined the respective values of the diffusion coefficient; and that of tungsten with hydrogen was studied by Halsey and Taylor,[25c] who analyzed available data for adsorption.

INDUSTRIAL APPLICATIONS

In addition to the application of tungsten filaments in incandescent lamps, they are also used as cathodes for electronic tubes. In this case, 2% ThO_2 are added to the metal to increase the thermionic emission. X-ray targets for radiographic and therapeutic use are made from tungsten disks, where the high atomic number of the metal favors a greater yield of x-rays than obtainable with elements of a lower atomic number. Another application is that of lead-in wires in large lamps, x-ray tubes, etc. requiring closely matching coefficients of expansion between the metal and the hard borosilicate glasses (Pyrex). A considerable amount of tungsten rod and sheet is used for electrical contacts; for certain applications where higher conductivity is required, tungsten is used in conjunction with another metal such as copper or silver (see Chapter XXIII). In the case of pure tungsten, disks are cut out from rod or punched from sheet, and are brazed to supports. They are used in a variety of relays, automotive and airplane ignition systems, and other devices where inductive loads of high voltage are encountered. Tungsten is also used for electrodes in "arcatom" welding, where (in the presence of atomic hydrogen) temperatures up to 4000°C. (7200°F.) can be reached. Structural parts in the high vacuum technique constitute another application, as do furnace parts, vessels, or other supports for high temperature treatments. Finally, tungsten in the form of wires, bars, sinus loops or ribbons can be used as heating elements for high temperature vacuum or hydrogen muffle furnaces. The perfection of tungsten–molybdenum thermocouples, another application related to high-temperature furnace work, has recently been reported by Potter and Grant.[25d] An excellent description of the uses of tungsten

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[25a] G. Huff, E. Squitieri, and P. E. Snyder, *J. Am. Chem. Soc.*, *70*, 3380 (1948).

[25b] M. Pirani and J. Sandor, *J. Inst .Metals*, *73*, 385 (1947).

[25c] G. Halsey and H. S. Taylor, *J. Chem. Phys.*, *15*, 624 (1947).

[25d] R. D. Potter and N. J. Grant, *Iron Age*, *163*, No. 13, 65 (1949).

in the high-vacuum field can be found in the standard work by Espe and Knoll.[25e]

Wartime development resulted in an eightfold expansion of the tungsten production in the United States. In addition to the use in the above-mentioned applications, tungsten products were also required in large amounts in radar and U. S. Army Signal Corps radio equipment, and in vast quantities for the atomic bomb project.[26]

In Table 88, a variety of commercial forms of ductile tungsten are listed.

TABLE 88

Commercial Tungsten Shapes[a]

Applications	Sizes		Normal tolerance, %		Finish
	Inch	Mm.	Weight	Diameter	
Support rods. . . .	0.040–0.500	1.02–12.7	—	±3	Cleaned and annealed
Drawing to fine wire	0.040–0.500	1.02–12.7	—	±3	Black and swaged
Contacts.	0.040–0.500	1.02–12.7	—	±3	Smooth hammered or ground
Glass to metal seals.	0.180–0.500	4.57–12.7	—	±2	Centerless ground and polished
Glass to metal seals	0.040–0.500	1.02–12.7	—	±2	Centerless ground
Pure tungsten for supports and leads	0.010–0.080	0.254–2.00	—	±3	
Special processed tungsten wire of high density, nontwist and nonsag	0.0004–0.020	0.010–0.50	±1 1/2	—	
Annealed pure tungsten wire prepared for straight filament lamps . . .	0.0004–0.020	0.010–0.50	±1 1/2	—	
1 1/2% thoriated wire	0.0007–0.020	0.018–0.50	±2	—	
2% thoriated wire tested for emission	0.0007–0.020	0.018–0.50	±2	—	
Seal finish wire, especially treated for glass to metal seals	0.040–0.080	1.02–2.03	—	±3	

[a] "Elmet" catalog, North American Philips Company, Inc., New York, pp. 20, 21.

Molybdenum

The historic development of ductile molybdenum production followed closely that for tungsten. In 1907, several years before Coolidge's dis-

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[25e] W. Espe and M. Knoll, *Werkstoffkunde der Hochvakuumtechnik.* Springer, Berlin, 1936.

[26] M. H. McClement, *Steel, 118,* No. 9, 141 (1946).

closure of the manufacture of ductile tungsten, Skaupy[27] produced molybdenum by extrusion of paste. Filaments thus obtained could even be hot-drawn to very fine size. After the Coolidge method had been introduced for tungsten, it was also employed for molybdenum, and to date constitutes the principal method of manufacture for this metal.

MANUFACTURE OF THE DUCTILE METAL

The production of molybdenum powder has been described in Volume I, Chapter VI. Sulfidic ores or commercially pure ammonium molybdate serve as raw materials. The sulfide may also be obtained as a by-product of copper flotation. The roasted concentrate is transformed into molybdenum trioxide by either chemical or physical means. The chemical process

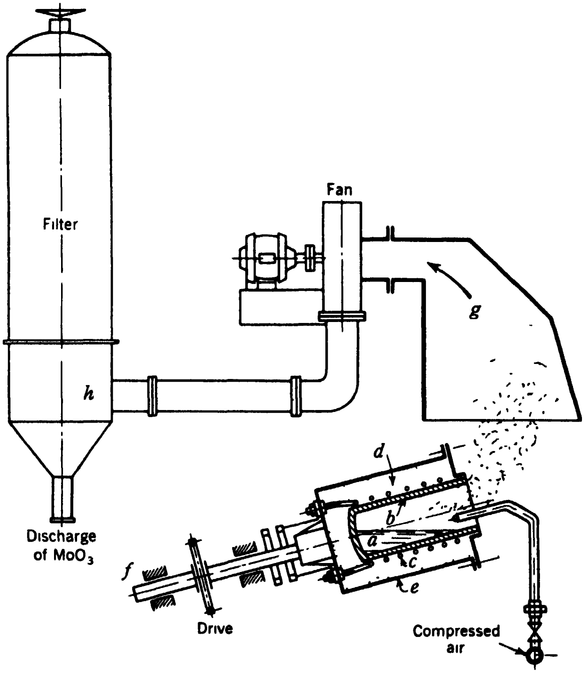

Fig. 313. Diagrammatic sketch of a distillation system for molybdenum trioxide (according to Kieffer and Hotop[28]): *a*, liquid molybdenum concentrate; *b*, quartz retort; *c*, molybdenum heating element; *d*, insulation; *e*, furnace shell; *f*, rotating shaft of furnace; *g*, hood, and *h*, collector.

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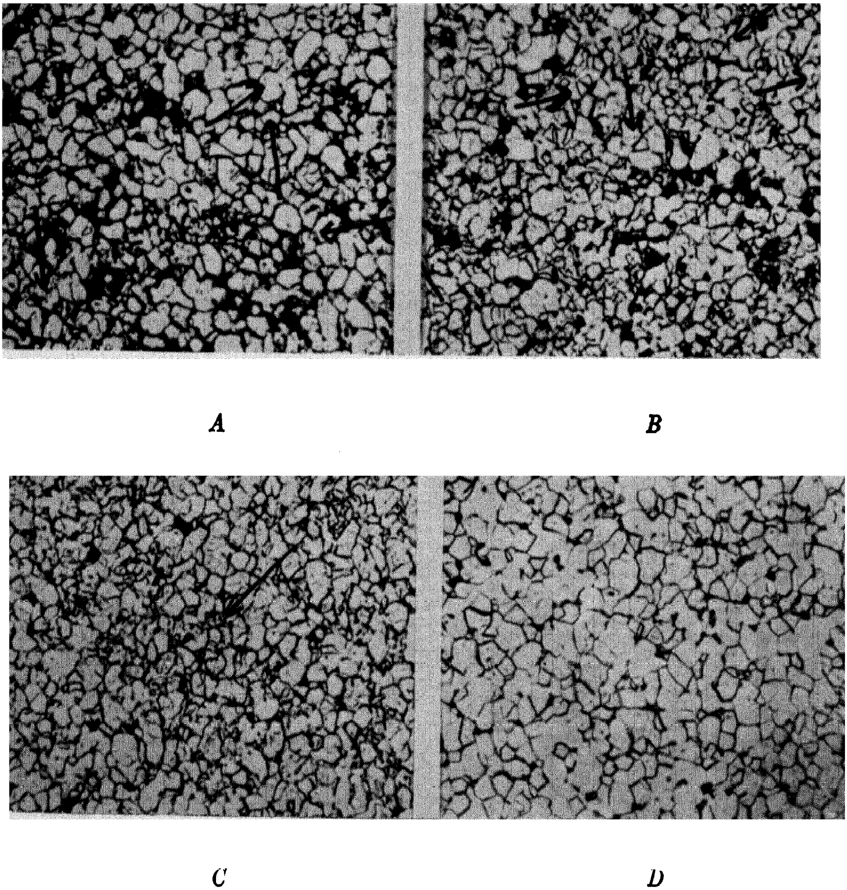
[27] F. Skaupy, *Wegscheider Festschrift Monatsh.*, *53*, 73 (1929).

[28] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe.* Springer Berlin, 1943, pp. 245, 251.



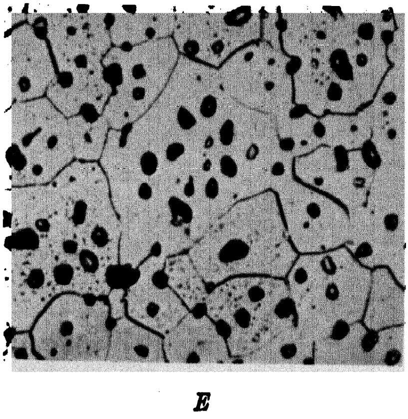


Fig. 314. Change in microstructure of sintered molybdenum with rising sintering temperature (according to Kingston[31]): *A*, hydrogen-reduced molybdenum powder of 4 to 6 μ particle diameter after pressing at 24 tsi for 15 sec. (×675); *B*, same after sintering at 1000°C. (1830°F.) ×675; *C*, same after sintering at 1200°C. (2190°F.) ×675; *D*, same after sintering at 1500°C. (2730°F.) ×675; and *E*, same after sintering at 1800°C. (3270°F.) ×675. Grain growth from room temperature to 1800°C. (3270°F.) about tenfold (grain size at 1800°C.; 3270°F. about 6000 per square millimeter).

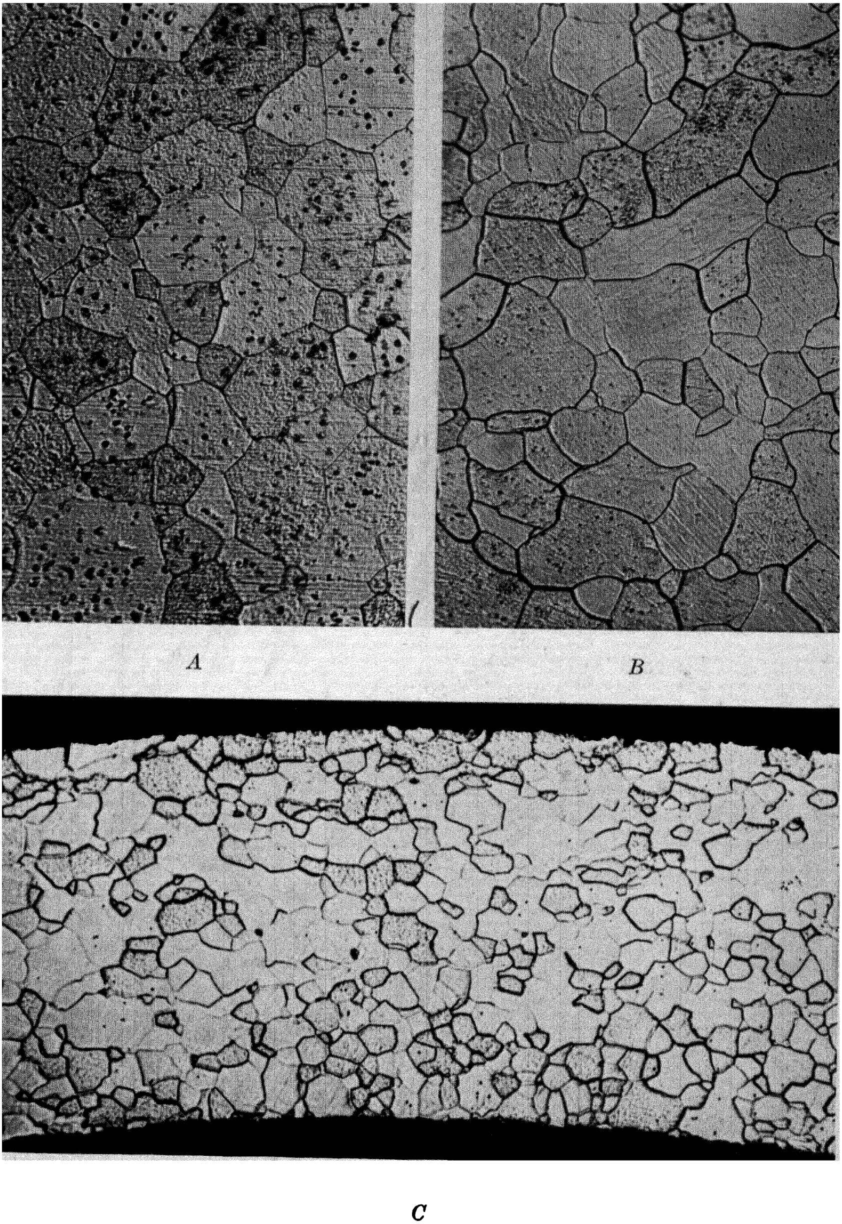


Fig. 315. Change in microstructure of sintered molybdenum caused by working and annealing: *A*, after sintering at about 2350°C. (4260°F.) ×200. Courtesy Callite Tungsten Corp.; *B*, after swaging and annealing for 20 min. at 1200°C. (2190°F.). ×200. Courtesy Callite Tungsten Corp.; and *C*, after wire drawing and complete

changes the roasted concentrate (containing 80–90% MoO_3, remainder Fe_3O_4, as well as SiO_2, and other gangue) into alkali molybdates through reaction with fused or aqueous alkalis. The solutions are then transformed into technically pure molybdic acid, from which chemically pure molybdenum trioxide is gained by precipitation with ammonium molybdate. The physical process is based on the distillation of MoO_3 from the sulfide, favored by a high vapor pressure and ready volatilization of the trioxide at higher temperatures. Very pure oxide (99.97%) can be obtained in large-scale production simply by heating the sulfidic ore in air, distilling the MoO_3 and condensing and collecting it in bag filters. A schematic view of the installation is reproduced from Kieffer and Hotop[28] in Figure 313.

The reduction to metal is carried out in a process similar to that used for tungsten except that the reaction is often carried out in two steps:

$$MoO_3 + H_2 \rightleftharpoons MoO_2 + H_2O \qquad (1)$$

$$MoO_2 + 2\,H_2 \rightleftharpoons Mo + 2\,H_2O \qquad (2)$$

This duplex reduction is favored because it avoids the formation of coarse metal powder through the action of water vapor that has been produced by the reaction. However, reduction of MoO_3 may also be performed in a continuous operation.[28a]

The powder is pressed into bars or ingots which are sometimes presintered at about 1000°C. (1830°F.) to provide additional strength. The green strength of the bars is superior to that of bars made from tungsten, because the powder is somewhat softer, and sintering in the bell jar often can follow molding directly. The current input is usually in the order of 90% of that required for fusion of the bar. The design features of the sintering equipment are the same as those for tungsten. Figure 302*B* shows a modern 16-bar sinter bell with the hood raised, as now being used by the Metallwerk Plansee in Austria.[11c]

Sintering is followed by swaging and drawing or rolling. The rods are first heated to about 1400°C. (2550°F.) and then swaged at about 1200°C. (2200°F.). With progressive reduction in cross section the swaging temperature is lowered to about 1000°C. (1830°F.). Molybdenum, in contrast to tungsten, can be worked at room temperature in the final stages of drawing or rolling, since its ductility is better. Wire of 5-mm. diameter can already be bent cold without danger of breaking, and foils as thin as 10μ can be produced by cold rolling.

The production of seamless tubes requires special techniques, one of which[28b] involves pressing the powder around a core of borosilicate glass,

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[28a] U. S. Pats., 2,398,114; 2,402,084.

[28b] Canadian Pat. 440,231.

sintering between the melting points of the metal and the glass, inserting a metal rod into the hollow space, and finally rolling, swaging, and drawing the compact before chemically dissolving the metal core. Extrusion is another method of producing tubes of pure molybdenum, and products weighing about 20 pounds and having a length of 43 in., an outside diameter of 2 in., and a wall thickness of $^1/_4$ in. have been produced thereby.[28c]

A new manufacturing process for molybdenum products which results in components of considerably increased size and of a greater variety of shapes has been disclosed in patents by Hall and Ramage[29] and Newman.[30] The principal difference between the process and conventional practice lies in sintering the compacted refractory metal powder at considerably lower temperatures, permitting the production of parts in the final shape and sintering in pusher-type furnaces. Complete consolidation of the compacts is achieved at the lower temperature if the compacts are exposed to an atmosphere of hydrogen conditioned with water vapor, and if a comparatively lengthy sintering period is employed. If the hydrogen atmosphere is saturated with water vapor between 20° and 40°C. (68° and 104°F.), and sintering is performed at a temperature between about 50 and 70% of the melting point (as measured in degrees centigrade), a reversible reaction between the metal powder and the atmosphere takes place, according to equation (2), page 32. This reaction adds "chemical agitation" to the thermal agitation—increasing atomic mobility and promoting sintering and shrinkage. A molybdenum ingot pressed under standard conditions and sintered for 2 hours at 1630°C (2965°F.) in hydrogen saturated with water vapor at about 40°C. (104°F.) is completely dense, fully sintered, and of normal susceptibility to working such as hot forging. The grain size of the metal thus treated is small and uniform, and the material is in all respects equivalent to an ingot treated in the conventional manner. Where very large sizes (*e.g.*, 24 × $1^1/_2$ × 1-in. compacts) are to be sintered according to this method, Newman[30] suggests the use of transversely corrugated resilient molybdenum plates as supports. By applying the same principle of treatment in wet hydrogen to intermediate annealings during metal working, grains of a length-to-width ratio of less than 4:1 are obtained which are claimed to be advantageous as far as machinability is concerned.[30a]

Machining was also recently discussed by Gelok,[30b] and welding

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[28c] Anonymous, *Chem. Eng. News*, *27*, 644 (1949).

[29] U. S. Pat. 2,431,690.

[30] U. S. Pat. 2,431,691.

[30a] Brit. Pat. Appl. 407/48 (1947).

[30b] J. Gelok, *Iron Age*, *162*, No. 24, 106 (1948).

TABLE 89

Characteristics of Molybdenum[a]

PHYSICAL PROPERTIES	
Crystal lattice, type	Body-centered, cubic
Parameter, Å	3.140
Atomic weight	96
Density, g./cc.	
Theoretical	10.2
Compacted, unsintered	6.1–6.3
Sintered at about 1800–2000°C. (3270–3630°F.)	9.2–9.4
Swaged (15 → 4 mm.)	9.7 → 10.0
Drawn (0.15 → 0.01 mm.)	10.0 → 10.2
Tensile strength, psi.	
Hard drawn wire, 1.2 mm.	140,000–170,000
0.4 mm.	210,000–240,000
0.05 mm.	250,000–350,000
Annealed wire (recrystallized), 1.25 mm.	115,000–140,000
0.4 mm.	115,000–170,000
0.03 mm.	115,000–170,000
Single crystal wire	About 50,000
Elongation, %	
Hard drawn wire, 1.2 mm.	2–5
0.4 mm.	2–5
0.05 mm.	2–5
Annealed wire (recrystallized), 1.25 mm.	10–20
0.4 mm.	10–25
0.03 mm.	20–30
Single crystal wire	About 30
Yield point, psi	
Hard drawn wire, 0.1–0.5 mm.	85,000
Annealed wire, 0.1–0.5 mm.	55,000
Modulus of elasticity, psi	
Hard drawn wire	About 47,500,000
Single crystal wire	About 42,500,000
Modulus of torsion, psi	
Single crystal wire	About 21,000,000
Tensile strength at elevated temperature, psi	
Wire, 0.6 mm., 200°C. (400°F.)	115,000–140,000
400°C. (750°F.)	85,000–100,000
800°C. (1470°F.)	70,000–85,000
1200°C. (2190°F.)	28,000–42,000
Elongation at elevated temperature, %	
Wire, 0.6 mm., 200°C. (400°F.)	4–5
400°C. (750°F.)	4–5
800°C. (1470°F.)	4–5
1200°C. (2190°F.)	5–6
Brinell hardness	
Sintered bar 18 × 18 mm.	150–160
Forged bar 8 mm. thick	200–230
Sheet 2 mm. thick	240–250
Sheet 1 mm. thick	250–255

THERMAL PROPERTIES	
Melting point, °C. (°F.)	2620 (4750)
Boiling point, °C. (°F.) at 750 mm. Hg	About 3700 (6700)

TABLE 89 (*concluded*)

THERMAL PROPERTIES (*continued*)

Vapor pressure, mm. Hg	
1530 °C.	6.4×10^{-9}
1730 °C.	8×10^{-7}
1930 °C.	4×10^{-5}
Vapor pressure of metallic oxide, mm. Hg at 1160 °C.	760
Linear coefficient of thermal expansion, per °C.	
25–300 °C.	$5.3\text{–}5.7 \times 10^{-6}$
25–700 °C.	$5.8\text{–}6.2 \times 10^{-6}$
Heat conductivity, cal./cm./sec./ °C.	
20 °C.	About 0.35
1000 °C.	About 0.236
Specific heat, cal./g./ °C.	
20–100 °C.	6.5×10^{-2}
1000 °C.	7.5×10^{-2}
Heat of fusion, cal./g.	About 50
Heat of vaporization at normal boiling point, cal./g.	About 1600

ELECTRICAL PROPERTIES

Electrical resistivity, microhm-cm.	
20 °C. (68 °F.)	5.1
800 °C. (1470 °F.)	22
1200 °C. (2190 °F.)	33
2000 °C. (3630 °F.)	60
Electrical conductivity, megmho-cm. at 20 °C. (68 °F.)	About 0.19
Temperature coefficient of resistivity	4.5×10^{-3}
Work function, volts	4.4
Electrolytic potential against hydrogen electrode, volts	−0.25
Ionization voltage, volts	7.1
Thermionic emission, ma/cm.² at 1900 °K.	1

RADIATION PROPERTIES

Total radiation, watts/cm.²	
800 °K.	About 0.2
1400 °K.	About 3.0
2000 °K.	About 19.0
2600 °K.	About 68.0
Radiation for 5500 Å., per cent of the radiation of the black body, at 20 °C.	54
Reflectivity for 5500 Å., per cent, at 20 °C.	47
Wave length of the characteristic x-ray radiation, Å.	
K-series	About 0.7
L-series	About 5.4

ACOUSTIC PROPERTIES

Velocity of sound, m./sec.	About 5300

a This table is a composite of data from R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe*, Springer, Berlin, 1943, p. 249, Table 47; H. W. Highriter, in J. Wulff, *Powder Metallurgy*, Am. Soc. Metals, Cleveland, 1942, p. 410, Table 26; P. Schwarzkopf, *Powder Metallurgy*, Macmillan, New York, 1947, p. 178, Table 38; and "Elmet Molybdenum, Tungsten and Alloys," catalog of North American Philips Co., Inc., New York, pp. 24, 25.

TABLE 90
Chemical Behavior of Molybdenum[a]

Substance	Reaction of Molybdenum
Air or oxygen	Practically none at 20 °C. (68 °F.); slight oxidation at 400 °C. (750 °F.); rapid oxidation to MoO_3 above 500 °C. (930 °F.)
Ammonia	None
Carbon dioxide	Formation of oxide above 1200 °C. (2200 °F.)
Halogens	Fluorine: no reaction at room temperature Chlorine: reaction at dull red heat Bromine: reaction at bright red heat Iodine: no reaction at 500 °C. (930 °F.)
Hydrogen	None
Hydrogen sulfide	Formation of sulfide at 1200 °C. (2200 °F.)
Nitrogen	None up to 1500 °C. (2730 °F.)
Nitrous and nitric oxide	Oxidation to MoO_3 at red heat
Sulfur dioxide	Oxidation at red heat to MoO_2
Water	In powder form, not resistant; in compact form, not attacked
Water vapor	Formation of molybdenum oxides and hydrogen above red heat
Aqua regia	Cold: slight reaction; warm: rapid reaction
Hydrochloric acid	
Concentrated	Slow reaction
Dilute	More violent reaction at 100 °C. (212 °F.)
Hydrofluoric acid	Cold and warm: no reaction
Nitric acid	
Concentrated	Slow reaction with formation of a layer of MoO_3
Dilute	More rapid reaction with complete solution
Sulfuric acid	
Concentrated	At 20 °C. (68 °F.) slow, at 200–250 °C. (400–480 °F.) rapid reaction
Dilute	Cold: practically none; at 110 °C. (230 °F.): none
Ammonium hydroxide	Slow reaction
Potassium hydroxide	
Aqueous	Cold: none; warm: weak reaction
Molten	Complete solution
Oxidizing molten salts	KNO_2, KNO_3, Na_2O_2, K_2CO_3—violent reaction
Carbon, solid (soot, coal, graphite) and hydrocarbons	Formation of carbide (Mo_2C) at 1100 °C. (2000 °F.); complete formation of carbide at 1300–1400 °C. (2370–2550 °F.)
Mercury	No amalgamation
Phosphorus	No reaction even at high temperatures
Silicon	Formation of silicides at higher temperatures
Sulfur	No reaction up to 440 °C. (820 °F.); formation of sulfide, MoS_2 and Mo_2S_3, at higher temperatures

Mixtures of acids used to dissolve the molybdenum mandrel wire in tungsten coils:

(*a*) 50% nitric acid, 30% sulfuric acid, 20% water
(*b*) 40% nitric acid, 40% sulfuric acid, 20% water

The percentages of the mixtures are given by volume; both mixtures must be used at 90 °C. (194 °F.)

Etching agents for metallographic specimens:

1. Dilute nitric acid.
2. Basic solution of potassium ferricyanide.
3. Ammonia plus hydrogen peroxide.

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[a] "Elmet" catalog, North American Philips Company, Inc., New York, pp. 12, 13.

procedures have been described by Henschkel[30c] and by Nichols, Young, and Nolan.[30d]

In conclusion, it appears appropriate to refer to the wartime development of producing ductile molybdenum by fusion, although molybdenum powder ingots serve merely as raw material. The pioneering work by Parke and Ham[30e] is described further in Chapter XXXII, page 685. The process involves feeding of presintered expendable molybdenum electrodes to a vacuum arc; the metal is cast into water-cooled copper molds. An improved procedure employs molybdenum powder which is consolidated (hot pressed) in a sintering zone of the vacuum furnace before being fed to the A.C. arc. The economy of the process—power consumption for fusion and deoxidation is about 1 kw.-hr. per pound—enables production of castings up to 200 lbs. If the contamination by oxygen is kept below 0.0025%, the metal can be forged and has excellent physical properties. Study of the cleavage structure in fractographic patterns is reported[30f] useful in predicting the forgeability of the cast metal.

PROPERTIES OF MOLYBDENUM

Molybdenum is inferior to tungsten in various ways. Its atomic number, specific gravity, and melting point are lower while its vapor pressure is higher. In the worked condition, its strength and hardness are also lower, and its electrical conductivity is about that of tungsten. After recrystallization, however, the ultimate strength is higher, and elongation appreciably greater than for tungsten. Hence, the cold-forming characteristics of molybdenum sheet are superior and permit applications that are not possible for tungsten. Since molybdenum is usually used at lower service temperatures than tungsten, recrystallization effects are of less practical significance, and additives such as ThO_2 are not generally employed (except for the purpose of improving the thermionic emission of the metal).

Figure 314 shows the change in grain structure with rising sintering temperature, according to Kingston.[31] The effect of working and annealing on the microstructure is shown in the photomicrographs, Figure 315. Its effect on the physical properties is drastic, with the tensile strength increasing gradually from about 50,000 psi for unworked metal to about 200,000 psi for fine wire with a corresponding increase in elongation from

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[30c] J. Henschkel, *Iron Age, 162,* No. 25, 87 (1948).

[30d] H. J. Nichols, H. B. Young, and M. J. Nolan, *Welding J., 28,* No. 5, 236-s (1949).

[30e] R. M. Parke and J. L. Ham, *Trans. Am. Inst. Mining Met. Engrs., 171,* 416 (1947).

[30f] C. A. Zapffe, F. K. Landgraf, and C. O. Worden, *Trans. Am. Inst. Mining Met. Engrs., 180,* 616 (1949); *Metal Progress, 54,* 328 (1948).

[31] W. E. Kingston, *Proc. International Powder Metallurgy Conference,* Graz, July 12–17, Referate No. 62.

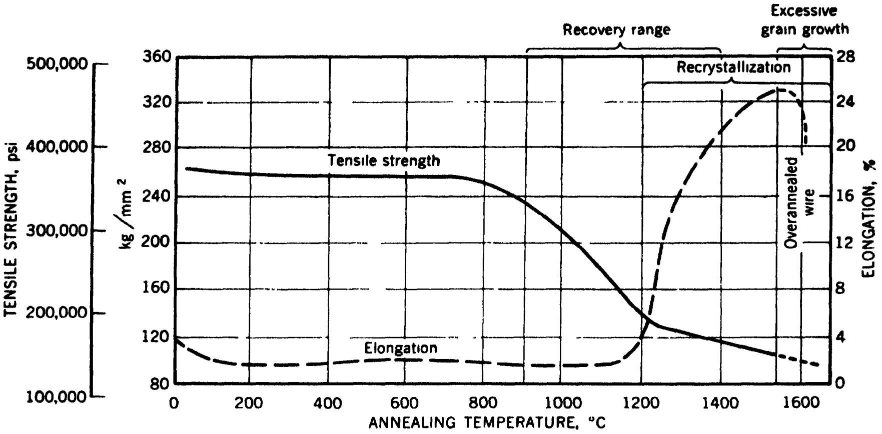
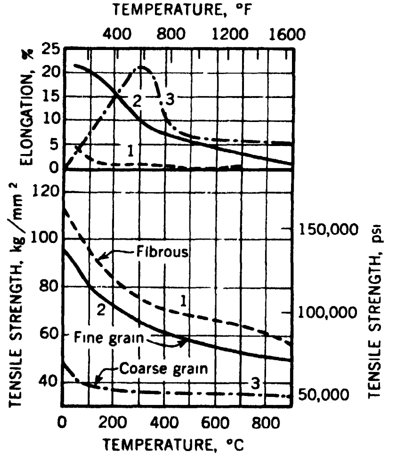


Fig. 316. Effect of annealing temperature on tensile strength and elongation of molybdenum wire of 0.1-mm. diameter (according to Kieffer and Hotop[28]).



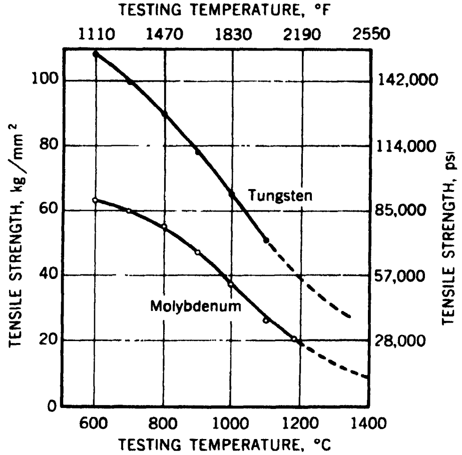


Fig. 317. Tensile properties of molybdenum wire up to 900°C. (1650°F.). According to Espe and Knoll[38b]. Curve 1 is for wire drawn 93% while at 1300° to 1000°C. (2375° to 1830°F.); not recrystallized, fibrous in structure. Curve 2 is for above, after heating for 2 seconds in hydrogen at 65% of fusion current; average grain diameter is 0.0053 mm. Curve 3 is after heating 5 seconds at 90% of fusion current; average grain diameter is 0.03 mm.

Fig. 318. Effect of temperature on tensile strength of molybdenum and tungsten rods (according to Kieffer and Hotop[34]). The solid curves represent data determined by testing in hydrogen; the broken-line curves represent extrapolated values. Testing in air at these temperatures is impossible due to the excessive rate of oxidation of the metals and the rapid volatilization of the resulting oxides.

a few per cent to 25–50%.[32] The physical properties of molybdenum are reproduced in Table 89; the chemical behavior is indicated in Table 90. The effect of annealing on tensile strength and elongation is shown in Figure 316. The tensile properties of wrought molybdenum at elevated temperatures are given in Figure 317 while in Figure 318 the change in tensile strength with rising temperature is compared with that for tungsten. The oxidation behavior of molybdenum (including that at high temperatures in vacuum), the volatility of thin oxide films, and the reduction of these films in pure hydrogen have been investigated by Gulbransen and Wysong.[33]

INDUSTRIAL APPLICATIONS

The industrial uses for molybdenum are manifold, and, as in the case of tungsten, are determined by properties of the metal.[33a] A large proportion of ductile molybdenum is used in form of hooks, eyes, and other structural forms as supports of the tungsten filaments in incandescent lamps and electronic tubes, as schematically shown in Figure 319. Another application of considerable value is for grids in electronic tubes.[33b]

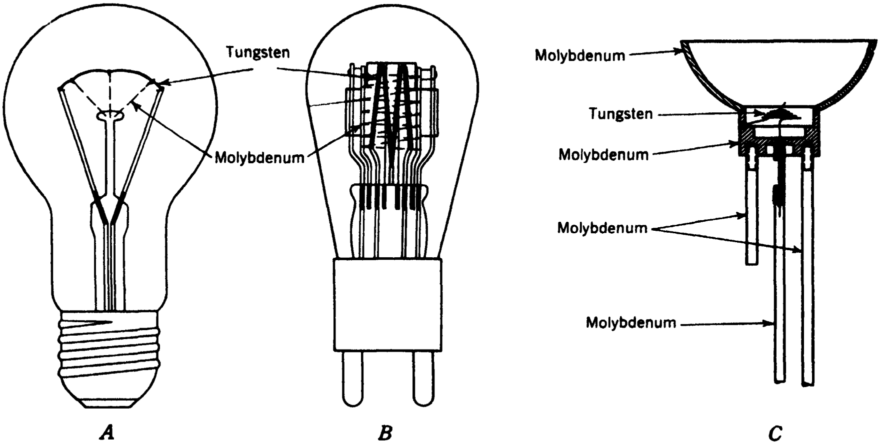


Fig. 319. Schematic presentation of tungsten and molybdenum parts in incandescent lamp bulbs (*A*), radio tubes (*B*) and in cathodes of x-ray tubes (*C*), according to Kieffer and Hotop[34].

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[32] J. W. Marden and D. M. Wroughton, *Trans. Electrochem. Soc., 89,* 217 (1946).

[33] E. A. Gulbransen and W. S. Wysong, *Trans. Am. Inst. Mining Engrs., 175,* 628 (1947).

[33a] R. Kieffer and F. Benesovsky, *Elektrotechnik und Maschinenbau, 65,* No. 9/10, 140 (1948).

[33b] W. Espe and M. Knoll, *Werkstoffkunde der Hochvakuumtechnik.* Springer, Berlin, 1936.

The metal is particularly suitable for this application because it is sufficiently elastic and resistant to deformation at the high temperatures at which electronic tubes are generally evacuated to permit a constant distance between the individual grid wires—so essential for good performance of the tube. Molybdenum sheets are widely used in electronic power tubes as anodes, and as structural parts in x-ray and radio tubes (Fig. 319*C*). Wires are used for metal-to-glass seals, and thoriated molybdenum is used in rectifiers for emission wires. Molybdenum, either as pure metal or in combination with metals of higher conductivity (see Chapter XXIII), is also used for a variety of electrical contacts and in heavy-duty switches and relays. One well-known application of molybdenum that has already been described before (Volume I, Chapters XV and XVI) is its use in resistor heating elements for high temperature electric furnaces. However, the strong tendency of the metal to oxidize at elevated temperatures requires operation of the furnace in a protective atmosphere. Its strongly positive temperature coefficient of resistance is apparent from the diagram of Figure 320, showing the specific resistance of molybdenum as a function of temperature, compared with tungsten and nickel–chromium wire. A detailed discussion of the subject of molybdenum for furnace heating elements is given by Kieffer and Hotop,[34] Kieffer and Krall,[34a] and Kieffer and Natter.[34b]

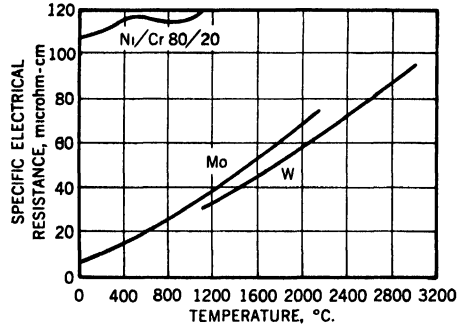

Fig. 320. Effect of temperature on specific resistance of molybdenum, tungsten and nickel–chromium heating elements (according to Kieffer and Hotop[34]).

During the war, the molybdenum production underwent a fifteenfold

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[34] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe*. Springer, Berlin, 1943, p. 253.

[34a] R. Kieffer and F. Krall, *VDE-Fachberichte, 11*, 107 (1939); *Elektrowärme, 12*, 33 (1942).

[34b] R. Kieffer and B. Natter, *Radex-Rundschau*, No. 3/4, 49 (1948).

expansion, and its products found additional applications in Signal Corps radio equipment, radar, and for the atomic bomb project.[35] Many new uses developed during the war required the manufacture of much larger pieces than had ever been attempted in the past; until that time the largest items that could be produced were restricted in size and shape due to the limited weight of the starting ingot (which did not exceed 10 lb.). By use of the above-mentioned improved manufacturing methods and techniques, [29,30] however, it was found possible to remove the previous limitations on size and shape of ingots to the extent that ingots weighing as much as 250 lb. could be produced.[36] Solid cylinders, tubes, disks, squares, and other shapes have been produced in diameters up to 7 in. and in lengths up to 30 in. Molybdenum sheets 20 in. wide and 36 in. long have been produced from these large ingots, and still larger sheets seem feasible with the installation of larger rolling and fabricating equipment.[36] In Table 91, a variety of commercial forms of ductile molybdenum are compiled.

TABLE 91
Commercial Molybdenum Shapes[a]

Applications	Sizes		Normal tolerance, %		Finish
	Inch	Mm.	Weight	Diameter	
Drawing to fine wire	0.050–0.80	1.25–20	—	±3	Swaged
Support rods.... .	0.020–0.630	0.5–16	—	±3	Cleaned and annealed
High temperature electric resistance furnaces......	0.050–0.40	1.25–10	—	±3	Swaged or smooth drawn
Glass-to-metal seals	0.100–0.630	2.54–16	—	±2	Centerless ground
Glass-to-metal seals	0.160–0.630	4–16	—	±2	Centerless ground and high polished
Hook and anchor wire for lamps ..	0.002–0.024	0.051–0.60	—	±3	
Grid wire for tubes.	0.0015–0.024	0.038–0.60	—	±3	
Mandrel wire for lamp filaments...	0.003–0.040	0.076–1.00	—	±1	
Electrode wire for glass-to-metal seals......... ...	0.040–0.10	1.00–2.54	±3	—	
Furnace resistance wire; black, smooth drawn, or soft annealed. .	0.040–0.10	1.00–2.54	±3	—	

[a] "Elmet" catalog, North American Philips Company, Inc., New York, pp. 10, 11.

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[35] M. H. McClement, *Steel, 118,* No. 9, 141 (1946).

[36] J. Gelok, *Materials and Methods, 26,* No. 3, 86 (1947).

Tantalum

Unlike tungsten and molybdenum, tantalum does not form readily reducible oxides, so that tantalum powder must be prepared differently. This fact has had its impact on the historical development of the manufacturing process for ductile tantalum. The first attempts to gain pure tantalum metal were all concerned with methods to reduce a tantalum salt or tantalum oxides. In 1824, Berzelius[37] reduced potassium tantalum fluoride, K_2TaF_7, with potassium, and later investigators[38-40] used the same salt, as well as the pentachloride, $TaCl_5$, and the pentoxide, Ta_2O_5, as raw materials, and obtained reduction with alkali or cerium–iron Through reduction of Ta_2O_5 with carbon in an electric furnace, Moissan[41] produced a brittle metal powder with 0.5% carbon (*i.e.*, 9% TaC). Ductile tantalum was first produced in 1905 by von Bolton,[41a] who dissociated tantalum tetroxide, Ta_2O_4, at very high temperatures. The reduction of double salts and halides with alkalis in the presence of alkali halides has now given way almost entirely to the fusion-electrolysis of K_2TaF_7.[42,43] It is, however, interesting to note that more recently the reduction of the pentachloride (with magnesium chips) has again been suggested as an industrially feasible process.[44] It is claimed that better control is thereby possible than in the customary fused-salt process, and that the resulting powder has a finer particle size, making it especially suitable for further processing.

MANUFACTURE OF THE DUCTILE METAL

Powder Production. The production of tantalum powder has already been described in some detail in Volume I, Chapter VI. The tantalum ore is always associated with columbium, necessitating a separation of the two metals. The principal ores contain tantalates and columbates of iron and manganese, known as tantalites or columbites, and containing up to 60% Ta_2O_5 and 15% Cb_2O_5. These ores are fused with Na_2CO_3, KOH, or $K_2S_2O_7$; from the alkali tantalates and columbates

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[37] J. J. Berzelius, *Poggendorffs Ann.*, *4*, 10 (1825).

[38] H. Rose, *Poggendorffs Ann.*, *99*, 69 (1856); *100*, 146 (1857).

[39] W. Muthmann, L. Weiss, and R. Riedelbauch, *Ann. Physik*, *355*, 58 (1907).

[40] V. Spitzin and L. Kaschtanoff, *Z. anorg. allgem. Chem.*, *182*, 207 (1929).

[41] H. Moissan, *Compt. rend. acad. sci. Paris*, *134*, 211 (1902).

[41a] W. von Bolten, *Z. Elektrochem.*, *11*, 45 (1905).

[42] C. W. Balke, *Ind. Eng. Chem., Ind. Ed.*, *21*, 1002 (1929).

[43] F. H. Driggs and W. C. Lilliendahl, *Ind. Eng. Chem., Ind. Ed.*, *22*, 516, 1302 (1930); *23*, 634 (1931).

[44] J. Prieto Isaza, A. J. Shaler, and J. Wulff, *Trans. Am. Inst .Mining Met. Engrs.*, *175*, 784 (1948).

formed, the corresponding hydroxides are separated and dissolved in concentrated hydrofluoric acid. By adding potassium fluoride to the solution, the double fluorides K_2TaF_7 and $K_2CbOF_5.H_2O$ precipitate. Commercially pure K_2TaF_7 can be obtained by fractionated crystallization, since it is but one-twelfth as soluble in water as the K_2CbOF_5.

Two methods of production of tantalum powder from Ta_2O_5 and K_2TaF_7 are in use, namely, chemical decomposition of K_2TaF_7 with alkali metals and fusion-electrolysis. In the first instance, the double fluoride is charged in layers into a nickel crucible together with potassium metal and additions of alkali chlorides or fluorides. The reaction is initiated by heating the crucible, but continues exothermic. According to Kieffer and Hotop,[45] the charges are best placed into gas-tight iron or nickel bombs that are heated to about 1000°C. (1830°F.) in order to assure reproducible results. After completion of the reaction, the product is washed with a liberal amount of water, and tantalum metal powder of various particle sizes is obtained. Since the very fine powder fractions contain traces of oxygen, these are again charged in the furnace, resulting in purification and coarsening of the powder.

The method predominantly used today in the manufacture of ductile tantalum is based on the electrolysis of fused K_2TaF_7 in graphite, cast iron, or nickel crucibles that serve as cathodes. Graphite is used for anode material; Ta_2O_5 is added to the bath at regular intervals in order to prevent polarization. Additions of alkali chlorides increase the current efficiency. The metal powder is deposited as a fine network of crystals at the walls of the crucible, with the salt gradually solidifying in the network, and also freezing at the surface and around the anode. Electrolysis proceeds until the crucible has been filled with the deposit. The anode is then withdrawn and the crucible cooled; the deposit shrinks enough to permit easy removal. It is then pulverized and the salt removed from the metal particles by air separation. After thorough washing and after alternate reactions with dilute acids and potassium hydroxide, and finally with dilute hydrofluoric acid, a very pure powder of about 99.8% Ta can be obtained. The powder usually retains a small percentage of salt, 50–150 volumes of hydrogen, 0.05–0.2% C, and up to 0.02% Fe.[46] Heating in vacuum to 1200–1600°C. (2200–2900°F.) further purifies the metal and removes the final traces of fluoride. In order to remove carbon, MgO is mixed in stoichiometric relation to it. During subsequent sintering, some of the tantalum is believed to react with the MgO, giving up magnesium in

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[45] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe*. Springer, Berlin, 1943, pp. 255, 256.

[46] C. C. Balke, *Iron Age, 147,* No. 16, 23 (1941).

vapor form (which is removed by the vacuum pump). At the same time, some tantalum particles are oxidized. Since the oxide is rather soluble in the metal, oxygen diffuses through the metal, and solid carbon is eliminated as carbon monoxide. Carbon monoxide does not carburize the tantalum, and is also removed by the vacuum pump.[46]

Heating in hydrogen at about 1200–1400°C. (2200–2550°F.) results in absorption of up to 750 volumes of the gas and renders the metal extremely brittle. This property enables the mechanical comminution of tantalum scrap. Powder thus produced can be admixed (after annealing in vacuum at about 1000°C., 1830°F.) in limited proportion to virgin tantalum powder in the manufacture of the ductile metal.

The production of tantalum powder from tantalite ore at the Fansteel Metallurgical Corporation has recently been described by Lee[46a] (the same paper also describes the production practices for tungsten powder by the same company).

Pressing. Tantalum powder is pressed into bars or ingots much like tungsten or molybdenum. In spite of its coarser particle size, the compactibility of tantalum is good. Usually, a small proportion of very finely ground tantalum is added to the regular powder to facilitate the molding operation. The sizes of the ingots are comparable with those used in the tungsten industry; the largest size reported is 30 in. long, $2^1/_2$ in. wide, and $1^1/_4$ in. thick. Most tantalum bars weigh between 8 and 12 pounds. Pressures of about 50 tsi are required to give the bar sufficient strength for handling without the need for presintering.

First Sintering. The bars are clamped firmly between molybdenum screws inside heavy water-cooled copper terminals in the vacuum furnace. The bars are then heated by their own resistance to current passing through them—analogous to the sintering of tungsten. A peak temperature of 2700°C. (4900°F.) is maintained. The operation must be conducted in high vacuum; sintering in a protective gas such as hydrogen is impossible because of the strong solubility of tantalum for all gases. Hydrogen, moreover, when dissolved in tantalum causes the metal to become markedly brittle. During the course of the heating (first sintering), hydrogen is evolved rapidly at a low temperature, and gases and moisture occluded on the surfaces are removed. As the temperature rises, the remaining salt impurities are fused, and evaporate gradually; it is therefore important that this process occurs slowly so that spontaneous gas evolution and splitting or blistering of the bar are avoided. As the temperature increases the reaction for the removal of carbon takes place, and at still higher temperature, dissolved oxides are gradually evaporated

[46a] J. A. Lee, *Chem. Eng.*, *55*, 110 (1948).

until the metal becomes very pure. It is essential for the successful removal of all these gases that the bar be porous, and remain so during the heat treatment until all impurities are removed. This is accomplished by selecting a fairly coarse powder to start with, so that no appreciable shrinkage takes place during the first sintering, and grain growth is restricted by the pattern of pores. The density of the heat-treated bar is approximately 12–13 g./cc.In spite of the limited number of contact points between the particles resulting from compression (which is only slightly enlarged during sintering) the bar, after the first heat treatment, is strong and susceptible to cold deformation.

Intermediate Forging and Second Sintering. A severe hammering operation reduces the cross section of the sintered bar 5–20%, closing the pores, analogous to the action that would be encountered during sintering of a structure having fine grains. This forging must be done cold, because heating of the metal would cause embrittlement due to absorption of all common gases. A second resistance sintering follows, in which the metal is again heated in high vacuum close to its melting point. Further removal of gases and evaporation of impurities take place, and at the higher temperatures, grain growth occurs and the remaining pores are closed; recrystallization is aided by the cold working from the hammering operation. The density after the second sintering is substantially equal to that of the solid metal: 16.6 g./cc. The finished product has the polygonal grain structure of a pure fusion metal that has been cast, worked, and annealed.

Subsequent Fabrication. The metal now has excellent susceptibility to cold working and by known methods can be fabricated into sheet or wire. Foils as thin as 10 μ can be rolled out without intermediate annealing. Sheets can also be spun, deep drawn, or fabricated into seamless tubes. Welding and other joining methods in the construction of tantalum equipment are easily possible. Butt welding, arc welding, and roller welding of the metal to itself or to other metals, such as nickel or steel, are commonly practiced.

Alternate Procedure. A processing cycle somewhat different from the aformentioned was recently described by Myers.[46b] Electrolytic tantalum powder is compacted at 56 tsi and then subjected to a three-stage sintering cycle under vacuum of 10^{-3} to 10^{-4} mm. Hg pressure. The first stage is ended when the temperature reaches 1150°C. (2100°F.) and a pause is introduced to facilitate removal of oxides and other volatile impurities. Heating is then continued during the second stage until a temperature of 2000°C. (3630°F.) is reached. At this point, again, the

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[46b] R. H. Myers, *Metallurgia, 38,* 307 (1948).

heating cycle is interrupted to allow for the removal of remaining volatile contaminants. The final stage involves heating to the maximum sintering temperature of 2600°C. (4710°F.) and keeping the bars at this temperature for 4 hours. The sintered bars are then cold swaged to 40–60% reduction in cross section, and then again reheated in vacuum to 2600°C. (4710°F.) for 1–2 hours. Shrinkage during these treatments amounts to 4–5%, and the density after the second heat treatment is about 16.5 g./cc.; the hardness measures 65–70 Vickers units. The material is then susceptible to further working (*e.g.*, swaging, rolling, or wire drawing) and to various fabricating operations (*e.g.*, spot welding) in accordance to well-defined techniques.[46c]

PROPERTIES OF TANTALUM

Tantalum possesses a variety of properties that are unique among pure metals. Its melting point is above that of molybdenum, though below that of tungsten. But its ductility in the case of the polygonal grain structure far surpasses that of molybdenum, and its workability is not, as in the case of other common ductile metals (Ag, Au), restrained by appreciable work hardening, making it unnecessary to interrupt cold-working operations by repeated annealings. Recrystallized tantalum is very ductile in contrast to molybdenum or tungsten. The capacity of the metal to absorb and retain gases at elevated temperatures has already been mentioned. These characteristics, coupled with low thermal expansion and low vapor pressure, make tantalum particularly suitable for grids in electronic power tubes, since many gases are absorbed by it at lower pressures and at higher temperatures than possible with other metals.

The most outstanding characteristic of tantalum is its great resistance to acid corrosion, in which respect it is equivalent to glass, while having the added advantage of a much higher rate of heat transfer. Tantalum also has the distinctive property of forming anodic oxide films of unusual stability.[47]

Heating in nitrogen at 600 to 900°C. (1100 to 1650°F.) results in nitrogen absorption and nitride formation. The absorption of gas generally causes embrittlement of the metal and can raise the hardness up to 600 Brinell.[48] This has been confirmed by J. N. Greenwood and R. H. Myers[49] who have studied the effect of various annealing treatments on

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[46c] R. H. Myers, *Metallurgia, 39,* 7 (1948).

[47] H. W. Highriter, in J. Wulff, *Powder Metallurgy.* Am. Soc. Metals, Cleveland, 1942, p. 416.

[48] C. W Balke, *Ind. Eng. Chem., 27,* 1166 (1935).

[49] J. N. Greenwood and R. H. Myers, *Nature, 160,* 675 (1947).

TABLE 92

Characteristics of Tantalum[a]

PHYSICAL PROPERTIES

Crystal lattice, type	Body centered, cubic
Parameter, Å	3.296
Atomic weight	180.88
Isotopes, half-life	
Ta^{180}	14–21 min.
Ta^{180}	8.2 hrs.
Ta^{181}	Not radioactive
Ta^{182}	97 days
Density, g./cc. at 20°C. (68°F.)	16.6
Tensile strength, psi.	
Sintered bar	42,000
Wire, unannealed	125,000–178,000
Sheet, annealed	45,000–65,000
Elongation, %	
Cold rolled	1–3
Annealed	25–40
Modulus of elasticity, psi	27,000,000
Compressibility per unit volume, per kg./cm.^{2} at 20°C. (68°F.)	0.52×10^{-6}
Brinell hardness	
Annealed	45–125
Worked	125–350
Gas-strained	Up to 600
Scleroscope hardness, annealed	10

THERMAL PROPERTIES

Melting point, °C. (°F.)	2996 (5425)
Boiling point, °C. (°F.)	5300 (9570)
Vapor pressure, mm. Hg	Between W and Mo, but nearer W
Linear coefficient of thermal expansion, per °C.	
0–100°C.	6.5×10^{-6}
0–500°C.	6.6×10^{-6}
20–1500°C.	8.0×10^{-6}
Heat conductivity, cal./cm./sec./°C. between 20 and 100°C.	0.13
1430°C.	0.174
1630°C.	0.186
1830°C.	0.198
Specific heat, cal./g./°C., at 0°C.	0.036
Heat of combustion, cal./g.	1379

ELECTRICAL PROPERTIES

Electrical resistivity, microhm-cm.	
20°C. (68°F.)	15
1130°C. (2070°F.)	61
1430°C. (2600°F.)	71
1730°C. (3150°F.)	80
Temperature coefficient of resistivity at 0–100°C. (32–212°F.) per °C.	3.82×10^{-3}
Magnetic susceptibility	$+0.93 \times 10^{-6}$
Electrochemical equivalent, mg. per coulomb (valency)	0.3749

Table continued

TABLE 92 (*concluded*)

ELECTRICAL PROPERTIES (*continued*)	
Work function, volts	4.10
Positive ion emission, volts	10.0
Electron emission, ma./cm.^{2}	
1273°K.	1.0×10^{-6}
1500°K.	4.7×10^{-3}
2000°K.	19.5
RADIATION PROPERTIES	
Radiation emission coefficient for 6500 Å.	0 49

a This table is a composite of data from R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe*, Springer, Berlin, 1943, p. 261, Table 52; H. W. Highriter, in J. Wulff, *Powder Metallurgy*, Am. Soc. Metals, Cleveland, 1942, p. 410, Table 26; P. Schwarzkopf, *Powder Metallurgy*, Macmillan, New York, 1947, p. 180, Table 39; and "The Metal Tantalum," Fansteel Metallurgical Company, North Chicago, Ill.

TABLE 93

Chemical Behavior of Tantalum (Kieffer and Hotop[49a])

Medium	Behavior of tantalum
Air and oxygen	At room temperature: stable At 400°C. (750°F.): blue coloring At 600°C. (1110°F.): gray coloring At higher temperature: formation of a white coat of Ta_2O_5
Water vapor	At red heat: quick oxidation
Hydrochloric or sulfuric acid	Cold, diluted, and concentrated: stable; warm, until 100°C. (212°F.), diluted and concentrated: stable
Sulfuric acid, containing free sulfur trioxide	Cold and warm: attack
Nitric acid or aqua regia	Cold, diluted, and concentrated: stable; warm, diluted, and concentrated: attack, while forming a protective coat of tantalic acid
Hydrofluoric acid	Cold and warm: attack, while absorbing hydrogen
Hydrofluoric and nitric acid	Strong attack, quick dissolution
Alkalis	Cold potassium hydroxide or caustic soda solution: light attack; warm potassium hydroxide or caustic soda solution: strong attack; potassium hydroxide or sodium carbonate: quick dissolution
Solid carbon (lamp black, carbon, graphite) and hydrocarbons	Carbide formation from about 1200°C. (2190°F.); complete carburization at about 1400°C. (2550°F.)
Carbon monoxide	Absorption at red heat
Hydrogen	Strong absorption of hydrogen at low temperatures, possible formation of hydride; slow evolution of hydrogen above 1400°C. (2550°F.) in vacuum
Nitrogen	Nitrogen absorption below 600°C. (1110°F.); nitride formation at higher temperature
Halogens	Wet and dry: stable up to 150°C. (300°F.)
Phosphoric acid	Stable up to 145°C. (290°F.)

[49a] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe*. Springer, Berlin, 1943, p. 262.

TABLE 94
Corrosion Resistance of Tantalum[a]

Substance	Time	Temperature		Per cent loss in weight per month	Depth of corrosion (inches per year $\times 10^{-5}$)	Rating
		°C.	°F.			
Hydrochloric acid, HCl conc.	4.5 mo.	19–26	66–79	None	None	Excellent
Sulfuric acid, H_2SO_4 conc.	4.5 mo.	19–26	66–79	None	None	Excellent
Nitric acid, HNO_3 conc.	4.5 mo.	19–26	66–79	None	None	Excellent
Phenol, satd. sol. H_2O, C_6H_5OH	4.5 mo.	19–26	66–79	None	None	Excellent
Aniline C.P., $C_6H_5NH_2$	4.5 mo.	19–26	66–79	None	None	Excellent
Cleaning solution, H_2SO_4, $K_2Cr_2O_7$	4.5 mo.	19–26	66–79	None	None	Excellent
Cleaning solution, H_2SO_4, $K_2Cr_2O_7$	3 mo.	150	302	0.013	0.4248	Excellent
Iodine, KI-H_2O satd. I_2	4.5 mo.	19–26	66–79	None	None	Excellent
Bromine (liq.), Br_2	4.5 mo.	19–26	66–79	None	None	Excellent
Barium hydroxide, $Ba(OH)_2$ satd.	4.5 mo.	19–26	66–79	None	None	Excellent
Ferric chloride, $FeCl_3$, conc. sol.	4.5 mo.	19–26	66–79	None	None	Excellent
Muriatic acid, HCl (commercial)	4.5 mo.	19–26	66–79	None	None	Excellent
Stannic chloride, $SnCl_4$ sol. (satd.)	4.5 mo.	19–26	66–79	None	None	Excellent
Acetic acid, $HC_2H_3O_2$ glacial	4.5 mo.	19–26	66–79	None	None	Excellent
Lactic acid, 85% sol.	4.5 mo.	19–26	66–79	None	None	Excellent
Oxalic acid, satd. sol.	4.5 mo.	19–26	66–79	None	None	Excellent
Acetone, $(CH_3)_2CO$	4.5 mo.	19–26	66–79	None	None	Excellent
Sodium chloride, NaCl satd. sol.	3 mo.	100	212	None	None	Excellent
Potassium chloride, KCl satd. sol.	3 mo.	94	201	None	None	Excellent
Sodium tungstate, Na_2WO_4–$2H_2O$ (satd.)	3 mo.	97	207	None	None	Excellent
Silver nitrate, $AgNO_3$, 50 g. per 100 cc. sol.	3 mo.	102	216	None	None	Excellent
Oxalic acid, satd. sol.	3 mo.	96	205	0.03	0.9912	Excellent
Phosphoric acid, H_3PO_4 conc.	3 mo.	145	293	0.014	0.4673	Excellent
Chromium plating sol., CrO_3 in dilute H_2SO_4	3 mo.	98	208	0.007	0.236	Excellent
Sodium sulfate, Na_2SO_4 satd. sol.	3 mo.	101	214	0.007 gain	Slight tarnish	Excellent
Sulfuric acid, H_2SO_4 conc.	3 mo.	147	297	0.013	0.4248	Excellent
Sulfuric acid, H_2SO_4 conc.	1 mo.	175	347	0.324	1.274	Good
Sulfuric acid, H_2SO_4 conc.	1 mo.	200	392	3.7	152.9	Fair
Sulfuric acid, H_2SO_4 conc.	6 hr.	250	482	71.2	2832	Poor
Sodium hydroxide, NaOH 5% sol.	2 mo.	100	212	1.13[b]	38.23	Fair
Potassium hydroxide, KOH 5% sol.	2 mo.	100	212	0.01	0.3398[c]	Good
Sodium hydroxide, NaOH 40% sol.	2 days	110	230	Completely corroded		
Potassium hydroxide, KOH 40% sol.	2 days	110	230	Completely corroded		

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[a] "The Metal Tantalum," Fansteel Metallurgical Corporation, North Chicago, Ill.

[b] Slight coating.

[c] Forms protective coating.

hardness and brittleness of the metal. The investigators established that cold-worked tantalum is slightly softened by annealing to 1100°C. (2010°F.), as shown by a drop in diamond pyramid hardness from 120 to 100. With rising annealing temperature up to 1800°C. (3270°F.) the hardness and brittleness rise sharply, and the diamond pyramid number increases from 100 to 400—and even to 500. Further increase in the annealing temperature up to 2400°C. (4350°F.) produces a gradual reduction in the hardness number. Slow cooling from the latter temperature results in a rather soft product, but rapid cooling at 7°C./min. (12.6°F./min.) produces a comparatively hard and brittle material. Gas absorption—even in minute quantities—is believed responsible for the described embrittlement effects, and possibly also for the abnormal effect observed in connection with the rate of cooling from the annealing temperature.

The physical properties of tantalum metal are assembled in Table 92, and the chemical behavior is given in Table 93. Detailed data for the corrosion resistance of tantalum are given in Table 94. From these data, it is apparent that with the exception of hot sulfuric acid, hot caustic potash, and cold or hot hydrofluoric acid of various concentrations, practically no other reagent has any significant effect. In spite of this corrosion resistance, however, tantalum cannot be considered a noble metal, since it strongly oxidizes in air above 400°C. (750°F.).

INDUSTRIAL APPLICATIONS

During the period from 1940 to 1944 the production of tantalum increased twelvefold.[50] Because of the combination of resistance to a wide variety of corrosive chemicals and the strength, ductility, and workability of steel, tantalum is employed widely and in ever-increasing amounts for such equipment as stills, agitators, containers, or pipes in the chemical industry for the processing of corrosive chemicals, dyes, or organics. Tantalum is also used in chemical equipment in combination with plastics and ceramics, the metal being utilized either as heat exchanger or for absorption, evaporation, and condensation of hydrochloric acid.

The ability of tantalum to form stable anodic oxide films, combined with passivity to acid electrolytes, make this metal useful in wet rectifiers. These films permit the flow of current from electrolytic solutions to tantalum, but not the flow in the opposite direction. If used in a porous form (*i.e.*, after the first sintering), which gives a large surface

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[50] A. I. Percy, *Steel, 118,* No. 24, 106 (1946).

in a small space, tantalum is used for self-healing electrolytic condensers and lightning arrestors. The ability of the metal to absorb and retain gases at low pressures makes it an ideal material for "getters" and grids in electronic tubes, especially for ultra-high-frequency transmission.[47] Other uses for the metal include such diverse products as blades for steam turbines, valves, nozzles, diaphragms, spinnerets for rayon spinning,

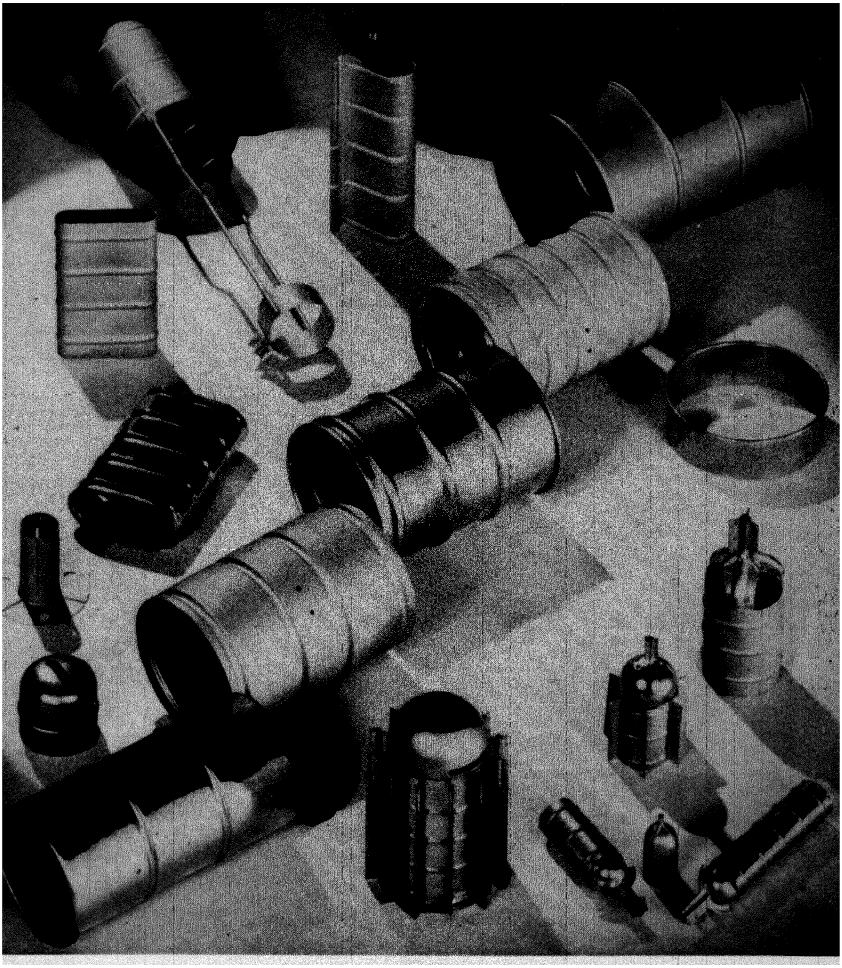

Fig. 321. Assortment of tantalum anodes in electronic power tubes, especially those used in ultra-high-frequency service (courtesy of Fansteel Metallurgical Corp.).

thermometer wells, and fountain pen points. Applications of the metal in the high-vacuum field are described in detail by Espe and Knoll.[50a]

Figure 321 shows an assortment of tantalum anodes for electronic power tubes, especially those used in ultra-high-frequency service.

One of the most interesting applications found for tantalum in recent years is in surgery for the replacement of shattered bones or destroyed tissues. Tantalum wires have been used with great success in the medical treatment of war wounded to unite fractured bones, and tantalum plates have been employed to replace lost skull tissue. Even nerves and tendons can be successfully stitched together, and the repaired nerves can be protected by tantalum foils.[51]

The use of tantalum for dental instruments is well known.

TABLE 95

Commercial Tantalum Shapes[a]

Shape	Size range, in.	Dimensional tolerance
Rods	0.3125–1.000	—
Sheet	0.001–0.020	±0.0002–±0.001
Wire	0.001–0.250	±0.0002–±0.0015
Seamless tubing	0.020–2.0 O.D.	—

[a] "The Metal Tantalum," Fansteel Metallurgical Corporation, North Chicago, Ill.

A good description of tantalum as an engineering material has recently been published by Rose[52] and some applications of tantalum in the electronics industry have also been described by Yntema and Yancey.[53] An assembly of commerical tantalum shapes is given in Table 95.

Columbium

MANUFACTURE OF THE DUCTILE METAL

The manufacture of ductile columbium follows closely that of its "sister metal" tantalum. The preparation of pure columbium powder has been described in Volume I, Chapter VI. The powder is obtained as a by-product from the iron and manganese tantalates and columbates used in the production of tantalum. Ores richer in columbium are preferred, however, since they give a greater yield. The separation of tantalum

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[50a] W. Espe and M. Knoll, *Werkstoffkunde der Hochvakuumtechnik.* Springer. Berlin, 1936.

[51] M. Z. Gross, *Hygeia, 22,* 438 (1944).

[52] K. Rose, *Materials and Methods, 26,* No. 4, 94 (1947).

[53] L. F. Yntema and R. W. Yancey, *Trans. Electrochem. Soc., 91,* 485 (1947).

from columbium is accomplished by crystallizing the less soluble tantalum salt (K_2TaF_7) from the more soluble columbium salt ($K_2CbOF_5 \cdot H_2O$). This solution is further treated to remove tantalum, tungsten, and other impurities originating from the ore.[54] However, the purification of columbium is far more difficult than that of tantalum because of its greater solubility and because residual impurities from the mineral tend to concentrate with it.

Several new processes for the separation of columbium from tantalum have been mentioned in the recent patent literature, but their practical value has not yet been established. One process given by Cuvelliez[54a] involves selective chlorination of columbium resulting in the formation of the volatile $CbCl_5$ at 800–1050°C. (1470–1920°F.). Basic addition agents, such as CaO, BaO, KOH, NaOH, or alkali carbonates, aid the separation by binding more of the initial Ta_2O_5 than Cb_2O_5. Kroll and Bacon recommend either selective nitriding[54b] or selective reduction of Cb_2O_5[54c] prior to halogenation. In the first procedure Cb_2O_5 is subjected to treatment with NH_3 at about 700°C. (1300°F.), and the resulting CbN is readily chlorinated at 400–600°C. (750–1110°F.); in the second, Cb_2O_5 is selectively reduced to Cb_2O_4 by treatment with hydrogen at temperatures ranging from 600 to 1200°C. (1110 to 2190°F.), and the tetroxide is then chlorinated at the same low temperature range.

The production of metallic columbium powder is based on fusion electrolysis. Except for a few variations, the process is the same as described for tantalum. The purified salt is fused in a nickel pot which serves as cathode together with a graphite anode. Alkali chlorides, fluorides and Cb_2O_5 are added regularly to prevent anodic polarization. It is important that the deposit remains fairly coarse, since it must be washed with dilute acids after pulverizing. If the particles are too fine they may be converted into colloidal columbic acid solutions.[55] The ready powder is molded into bars at pressures slightly below those used in pressing tantalum because columbium is somewhat softer. Sintering must be conducted in vacuum by passing a current through the bar as for tantalum. The sintering temperature, however, is considerably lower due to the lower melting point of columbium; the removal of impurities during sintering, by degassing and evaporation, is less effective for this reason. In order to close the pores, the material must be cold-worked and sub-

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[54] C. W. Balke,, *Ind. Eng. Chem.*, *27*, 1166 (1935).

[54a] U. S. Pat. 2,429,671.

[54b] U. S. Pat. 2,427,360.

[54c] U. S. Pat. 2,443,254.

[55] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe*. Springer, Berlin, 1943, p. 265.

TABLE 96

Characteristics of Columbium[a]

PHYSICAL PROPERTIES	
Crystal lattice, type	Body centered, cubic
Parameter, Å	3.294
Atomic weight	92.9
Density, g./cc. at 20°C. (68°F.)	8.57
Tensile strength, psi	
Sintered and worked	85,000
Annealed	42,500
Wire, unannealed (tentative)	96,000–130,000
Sheet, annealed (tentative)	48,000–59,000
Elongation, %	
Worked	2
Annealed	10
Brinell hardness	
Worked	200–250
Annealed	75
Scleroscope hardness, annealed	10
THERMAL PROPERTIES	
Melting point, °C. (°F.)	2415 (4380)
Boiling point, °C. (°F.)	3300 (5980)
Linear coefficient of thermal expansion, per °C., 0–100°C.	7.1×10^{-6}
Specific heat, cal./g./° C. at 0°C.	0.064
Heat of vaporization, cal./g.	1840
Heat of combustion, cal./g.	2379
ELECTRICAL PROPERTIES	
Electrical resistivity, microhm-cm. at 20°C. (68°F.)	13.2
Temperature coefficient of resistivity at 20°C. (68°F.)	3.95×10^{-3}
Magnetic susceptibility	$+2.28 \times 10^{-6}$
Electrochemical equivalent, mg. per coulomb	0.1926
Work function, volts	4.01
Positive ion emission, volts	5.52
RADIATION PROPERTIES	
Radiation emission coefficient for 6500 Å.	0.37

[a] This table is a composite of data from R. Kieffer and W. Hotop, *Kolloid Z.*, *104*, No. 2/3, 208 (1943); P. Schwarzkopf, *Powder Metallurgy*, Macmillan, New York, 1947, p. 183, Table 40; and "Fansteel Columbium," Fansteel Metallurgical Corporation, North Chicago, Ill.

jected to a second sintering in vacuum at a temperature near its melting point. After this second sintering operation, the metal—like tantalum—can be worked cold by known methods into wire, sheet, or complicated shapes.

TABLE 97

Corrosion of Columbium in Aqueous Media[a]

Solution	Temperature		Duration of test, days	Loss in weight		Condition of specimen at end of test
	°C.	°F.		g./dm.^{2}/d.	oz./ft.^{2}/yr.	
HCl, 20%	21	70	82	0.00025	0.003	No change
HCl, conc.	21	70	82	0.0006	0.072	Slight etch—not embrittled
HCl, conc.	100	212	67	0.0234	2.79	Brittle
HNO_3, conc.	100	212	67	0.0000	0.0000	No change
Aqua regia	22	72	6	0.0000	0.0000	No change
H_2SO_4, 20% by vol.	21	70	3650	0.00002	0.0025	No change, total loss 0.7%
H_2SO_4, 25% by vol.	21	70	3650	0.00003	0.0036	No change, total loss 1.0%
H_2SO_4, conc. 98%	21	70	3650	0.00056	0.067	Partial embrittlement, loss 18.3%
H_2SO_4, conc.	50	122	67	0.0048	0.57	Brittle
H_2SO_4, conc.	100	212	32	0.1131	13.5	Brittle
H_2SO_4, conc.	150	302	2	1.247	149.3	Brittle
H_2SO_4, conc.	175	347	1	8.32+	995+	Completely dissolved
H_2SO_4, conc. + CrO_3	100	212	42	0.0464	5.56	Pitted and brittle
H_3PO_4, 85%	21	70	82	0.00007	0.0084	No change
H_3PO_4, 85%	100	212	31	0.0193	2.32	Brittle
Tartaric acid, 20%	22	72	82	0.0000	0.0000	No change
Oxalic acid, 10%	21	70	82	0.0033	0.40	Brittle
NH_4OH	21	70	82	0.0000	0.0000	No change
Na_2CO_3, 20%/100 cc.	100	212	50	0.0074	0.88	Brittle
NaOH, 5%	21	70	31	0.0066	0.79	Action at surface of liquid
NaOH, 5%	100	212	5	0.1086	13.0	Brittle
KOH, 5%	21	70	31	0.0442	5.3	Action at surface of liquid
KOH, 5%	100	212	5	0.2744	32.8	Brittle
H_2O_2, 30%	21	70	61	0.0011	0.13	Oxide film—not brittle

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[a] "Fansteel Columbium," Fansteel Metallurgical Corporation. Size of specimen: sheet 0.2 mm. (0.008 in.) thick; area of surface 26 cm.^{2} (4 in.^{2}); immersion: 75% of surface in liquid, 25% in air; weighed in analytical balance to 0.0001 g.

PROPERTIES OF COLUMBIUM

Columbium has no unique properties, but rather a combination of properties that differ from other engineering materials. Cold working of the pure metal produces a pronounced springiness, toughness, and resistance to deformation which is possessed only by some special alloy steels. Like tantalum, columbium is extremely ductile in the annealed condition and becomes work-hardened at a much lower rate than most other metals. It is annealed by heating in vacuum. When subjected to deep drawing operations, it resists tearing more than most other ductile metals. Columbium is weldable and machinable, and is soft if sufficiently pure; small amounts of impurities tend to make the metal hard and brittle.

The melting point of columbium is considerably below that of tantalum, and even lower than that of molybdenum. It has close to half the atomic weight and density of tantalum, and its thermal expansion coefficient is slightly more than that of tantalum, and less than half that of copper. Its conductivity at room temperature is about one-eighth of that of copper. Its radiation coefficient (0.37 at 6500 Å.) is much lower than that of tantalum (0.49), and the thermionic emission, given by a work function of 4.01 volts, is the lowest of the pure refractory metals. The properties are summarized in Table 96. Columbium starts to oxidize in air at approximately 200°C. (400°F.), but the oxide film thus formed is strongly adherent, preventing further oxidation until the temperature is raised. Unlike tantalum, columbium does not become brittle on heating in air for short periods. The metal, however, is slightly less resistant to chemical corrosion than is tantalum. It is attacked by 5% sodium hydroxide, 5% potassium hydroxide, but not by ammonium hydroxide; it is dissolved by hydrofluoric acid and solutions of hydrofluoric and nitric acids. The chemical properties are given in Table 97.

TABLE 98

Commercial Columbium Shapes[a]

Shape	Size range, in.
Rods	0.3125–0.500
Sheet	0 001–0.020
Wire	0 001–0 250
Seamless tubing	0 060–1 0 O.D.

[a] "Fansteel Columbium," Fansteel Metallurgical Corporation.

APPLICATIONS

Commercial shapes of columbium are given in Table 98. Practical uses for columbium to date appear to be limited to permanent "getters" in electronic tubes, where the favorable thermionic mission and radiation coefficient coupled with good spot-weldability make columbium preferable to tantalum in some cases. The getter properties of absorbing gases in high vacuum tubes appear to be more pronounced, extending to lower temperatures than in tantalum, but the latter retains absorbed gases at higher temperatures than columbium.

Titanium, Zirconium, Vanadium, Thorium, and Uranium

The comparatively rare refractory metals, titanium, zirconium, vanadium, thorium, and uranium—with the possible exception of the first and the last in the not-too-distant future—have only limited production and application as metals or alloys other than with iron in the form of ferroalloys, and are therefore treated in the survey of sintered metals and alloys for potential industrial use in Chapter XXXII.

REFRACTORY METAL ALLOYS

Tungsten-Base Alloys

TUNGSTEN–MOLYBDENUM

Tungsten and molybdenum are isomorphous, and crystallize in body-centered cubic lattices with parameters of 3.16 and 3.14 Å., respectively, forming a continuous series of solid solutions.

For the production of ductile tungsten–molybdenum alloys, mixtures of either the pure metals or of their trioxides are used as starting materials. The oxide mixture is reduced at a temperature range falling within the temperatures used for the reduction of the individual component oxides. Fabrication of wire then follows the same methods used for the pure metal, namely compacting, sintering, hot swaging, and hot drawing. The rate of diffusion of tungsten and molybdenum into each other is, according to Van Liempt,[56] faster for polycrystalline than for single–

TABLE 99

Diffusion of Molybdenum in Tungsten (Van Liempt[56])

Temperature		Rate of diffusion, cm.^{2}/sec.	
°C.	°F.	Polycrystalline	Single crystal
930	1690	$1\ 3 \times 10^{-17}$	1.7×10^{-18}
1530	2770	$9\ 3 \times 10^{-13}$	1.2×10^{-13}
2130	3850	$2\ 5 \times 10^{-10}$	$3\ 2 \times 10^{-11}$
2330	4040	9.1×10^{-10}	$1\ 1 \times 10^{-10}$

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[56] J. A. Van Liempt, *Rec. trav. chim.*, *51*, 114 (1932).

crystal wires, as shown in Table 99. The sintering cycle commonly employed for refractory metals is sufficient to ensure the formation of homogeneous alloys.

TABLE 100

Physical Characteristics of Tungsten–Molybdenum Alloys[a]

Composition, per cent by weight		Melting point		Density, g./cc.	Electric resistivity at 20°C., microhm-cm	Temperature coefficient of electrical resistivity between 20 and 100°C.	Brinell hardness
Mo	W	°C.	°F.				
100	0	2600	4712	10.3	4.8×10^{-6}	4.75×10^{-3}	200
90	10	2620	4750	11.2	6.7	4.02	210
80	20	2640	4784	12.1	7.6	3.50	230
72.5	27.5	2675	4847	12.8	8.3	3.25	250
51	49	2850	5160	14.8	9.0	2.9	300
20	80	3075	5570	17.5	8.0	3.2	330
0	100	3370	6100	19.3	5.5	4.82	350

[a] This table is a composite of data from R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe*, Springer, Berlin, 1943, p. 267, Table 55; P. Schwarzkopf, *Powder Metallurgy*. Macmillan, New York, 1947, p. 184, Table 41; and "Elmet Molybdenum, Tungsten and Alloys," catalog of North American Philips Co., Inc., New York, p. 38.

The physical properties of tungsten–molybdenum alloys of various compositions are given in Table 100. As shown in Figure 322, the melting point and density decrease continually with increasing molybdenum content; the electrical resistivity reaches a maximum and the temperature coefficient a minimum at about 40% Mo. According to Fahrenwald,[57] a hardness maximum exists between 40 and 50% Mo in sintered bars that have been reduced about 60% by swaging. This result could not be duplicated by Kieffer and Hotop, who found a continuously decreasing hardness with increasing molybdenum content (Table 100).[57a] The tensile strength of tungsten is also reduced by molybdenum additions. Fine wire, for example, is reduced at room temperature from about 485,000 psi for pure tungsten, to 425,000 psi by the addition of 4% Mo.[58] Alloys containing 27 to 80% W, after swaging to 5-mm. diameter, are reported to have tensile strengths of 74,000–78,000 psi at 1000°C. (1830°F.), and 21,000–36,000 psi at 1400°C. (2550°F.).[58a]

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[57] F. A. Fahrenwald, *Trans. Am. Inst. Mining Met. Engrs.*, *54*, 570, 583 (1917); *56*, 612 (1917).

[57a] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe*. Springer, Berlin, 1943, pp. 266, 267.

[58] C. Agte and K. Becker. *Z. tech. Physik*, *11*, 107 (1930).

[58a] W. Köster and H. Bückle, see R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe*. Springer, Berlin, 1943, p. 266.

Tungsten–molybdenum alloys (sometimes called "moly-B" metals [59]) have found some industrial applications in the lamp industry for hooks and pig tails in high wattage lamps, as supports and springs in discharge tubes, and as heaters in certain radio tubes; they are also used occasionally

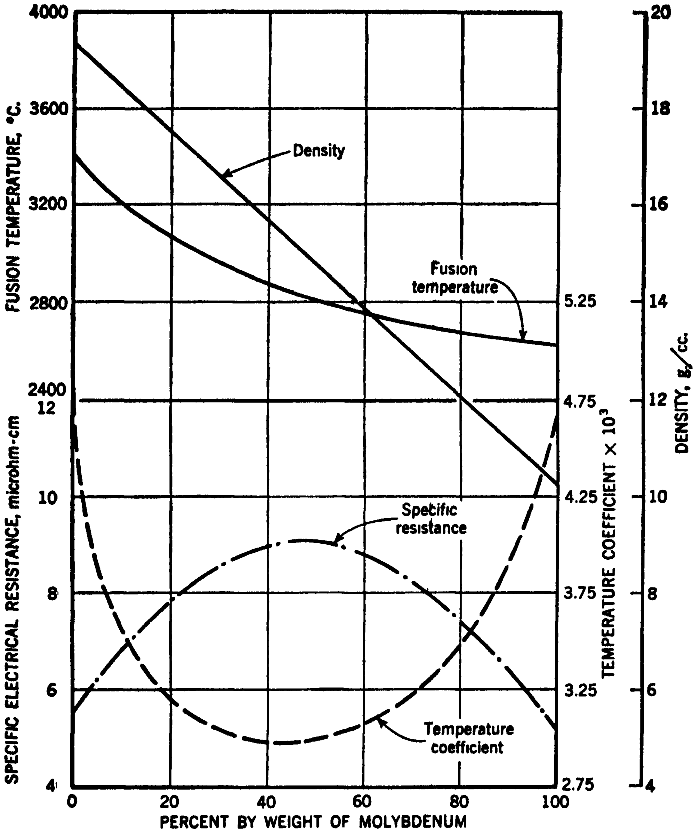

Fig. 322. Fusion temperature, density, specific electrical resistance and temperature coefficient at room temperature for the binary system: tungsten–molybdenum (according to data by Kieffer and Hotop[57a]).

as resistance wire in high temperature electric furnaces. The chief advantage in using the alloys lies in the considerable reduction in diameter in comparison with molybdenum and the better workability in comparison with tungsten.

[59] North American Philips Co., Inc., "Elmet" Catalog, p. 38.

TUNGSTEN–MOLYBDENUM–NICKEL

A tungsten-base alloy containing 5% each of molybdenum and nickel has been developed for special lead-in wires in seals to glass and ceramic materials.[60] For very close adjustment of the thermal coefficient of expansion, the nickel may be replaced in part or fully by iron or cobalt; the addition of 0.25% gold improves the ductility of the alloy, and the addition of 1–2% boron improves the sealing and bonding properties. The alloy has been suggested for use in electronic valves and spark plug center electrodes.

TUNGSTEN–TANTALUM AND TUNGSTEN–COLUMBIUM

Tungsten and tantalum or columbium are reported to form a continuous series of solid solutions.[61,62] The production of the alloys is best started with mixtures of tungsten and tantalum (or columbium) powders; the mixtures are then compacted and, like pure tantalum, are sintered in vacuum at temperatures slightly below the melting point of the respective alloy. Alternating sintering in hydrogen and in vacuum has also been suggested.[63] Alloys containing not more than 5% of either component are ductile, while all other compositions are relatively brittle and difficult to work.

Some of the properties of tungsten alloys containing tantalum, columbium, and molybdenum are apparent from Figures 323 and 324.[64] The lattice parameters of binary alloys of the four metals as shown in Fig. 323 permit the conclusion that all binary and ternary systems of tungsten, molybdenum, tantalum, and columbium form continuous series of solid solutions. Microhardness measurements (Fig. 324) show that additions of tantalum and columbium decrease the hardness of tungsten in the same manner as additions of molybdenum, *i.e.*, without formation of a hardness maximum at intermediate compositions. The resistivity of tungsten is increased considerably by additions of tantalum or columbium, an alloy containing 3.7% Ta having about 30–40% more resistivity than pure tungsten.[65] For this reason, the application of tungsten–tantalum alloys

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[60] Brit. Pat. 584,289.

[61] W. von Bolton, *Z. Elektrochem.*, *11*, 45 (1905).

[62] C. Agte and K. Becker, *Z. Physik, 32,* 65 (1931).

[63] German Pat. 635,644.

[64] W. Köster and H. Bückle, see R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe*. Springer, Berlin, 1943, p. 268.

[65] R. Kieffer and W. Hotop, *loc. cit.*, p. 267.

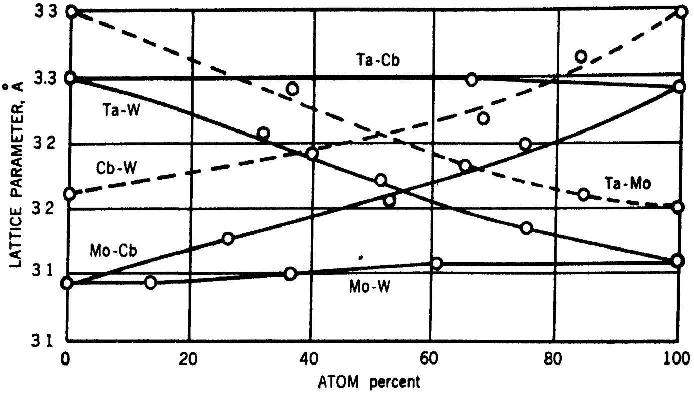

Fig. 323. Lattice parameter of binary alloys of the metals: tungsten, molybdenum, tantalum, and columbium (according to Köster and Bückle[64]).

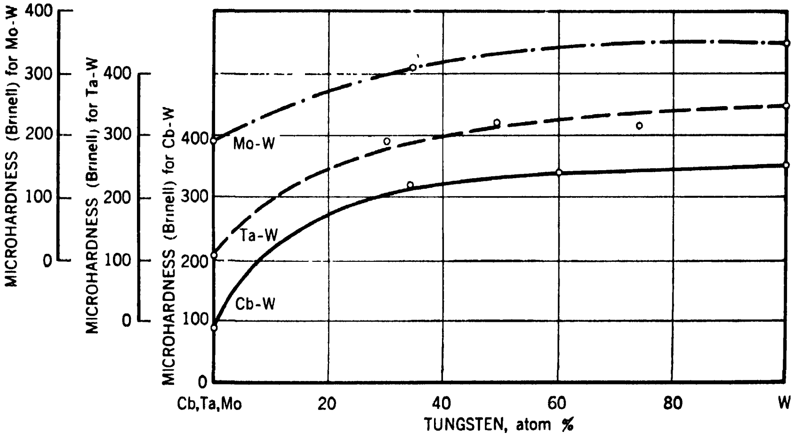

Fig. 324. Microhardness (in Brinell equivalents) of binary tungsten alloys with molybdenum, tantalum, and columbium (according to Köster and Bückle[64]).

as resistor heating elements or as high temperature thermoelements has been suggested.

TUNGSTEN—THORIUM

Alloys of tungsten and thorium are prepared either by mixing the metal powders, or from mixtures of tungsten, thoria, and carbon. In the latter instance, carbon is added in excess of the theoretical amount. If three times the stoichiometric amount of carbon is added, a complete reduction of ThO_2 is achieved during sintering.[66] Above 2350°C. (4250°F.) ThO_2 is, according to Smithells,[67] directly reduced by tungsten, but extended sintering times (about 24 hr.) make this procedure prohibitive for practical purposes, so that the addition of carbon is necessary. Alloys containing up to 5% Th are readily worked, and are used as thermionic emission cathode wires. The use of thoriated wires for straight tungsten wires in incandescent lamps has already been mentioned, but with the advent of the coiled filament, this application has lost its importance.

TUNGSTEN–IRON

Although both tungsten and α-iron crystallize into body-centered cubic lattices, they do not form a continuous series of solid solutions; instead there exist two iron tungstides, Fe_2W and Fe_3W_2.[68-70] Since the diffusion rate of tungsten in iron is slow, long sintering times are necessary to obtain solid solutions in compacts prepared from the two elemental powders. An alloy containing 10–20% W requires at least 6 hours of sintering at 1250°C. (2280°F.). Intermediate hot working between various stages of sintering can, however, accelerate diffusion, reducing the sintering period to some extent. Alloys of 10–25% W can be rolled or forged readily; sintered alloys with up to 40% W can still be rolled or forged at 1200–1300°C. (2200–2370°F.), but this is no longer possible with fused alloys of the same composition. The hardness of sintered alloys does not differ from that of the fusion products. Alloys containing up to 32% W after quenching from 1300°C. (2370°F.) show a ferritic structure and are rustproof; slow cooling produces a heterogeneous alloy which is not rustproof. The use of tungsten in steels in proportions up to 25% is well known. In the form of ferroalloys, it constitutes the chief application of the metal in industry (approx. 90% of annual production). As yet, however, there have been no important applications developed for the sintered iron-tungsten alloys.

TUNGSTEN–NICKEL

Alloys of the system tungsten–nickel were studied thoroughly by Ellinger and Sykes,[71] as well as by Vogel[72] and Grube and Schlecht.[73]

[66] P. Schwarzkopf, *Powder Metallurgy*. Macmillan, New York, 1947, p. 186.
[67] C. J. Smithells, *Trans. Chem. Soc., 131,* 2236 (1922).
[68] W. P. Sykes, *Trans. Am. Inst. Mining Met. Engrs., 73,* 968 (1926).
[69] J. L. Gregg, *The Alloys of Iron and Tungsten*. McGraw-Hill, New York, 1934.
[70] C. J. Smithells, *Tungsten,* 2nd ed. Chapman & Hall, London, 1945, p. 180.
[71] F. H. Ellinger and W. P. Sykes, *Trans. Am. Soc. Metals, 28,* 619 (1940).
[72] R. Vogel, *Z. anorg. u. allgem. Chem., 116,* 231 (1931).
[73] G. Grube and H. Schlecht, *Z. Elektrochem., 44,* 367 (1938).

The constitutional diagram shows a maximum of 1505°C. (2740°F.) in the solidus and liquidus curve at a tungsten concentration of about 35% by weight. The solubility of tungsten in the nickel-rich solid solution decreases from about 39% at 1495°C. (2725°F.), the eutectic temperature, to 38% at 970°C. (1780°F.) and to 32% at 800°C. (1470°F.). The eutectic occurs at a tungsten concentration of 45%. The solubility of nickel in tungsten is very small; it is about 0.3% at 800°C. (1470°F.).

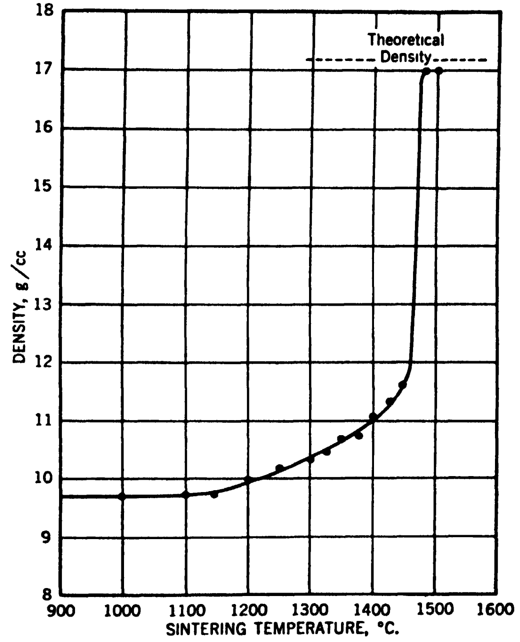

Fig. 325. Effect of sintering temperature on the density of a 90–10 tungsten–nickel alloy for a sintering time of 1 hour (according to Price, Williams, and Garrard[74]).

Tungsten–nickel alloys can be prepared by mixing the elemental powders and, after pressing, by sintering at temperatures between 1400 and 1470°C. (2550 and 2700°F.). The effect of the sintering temperature of a 90–10 W–Ni alloy for sintering periods of 1 hour is shown in Figure 325, according to the work of Price, Williams, and Garrard.[74] Densities close to the theoretical value (17.3 g./cc.) can only be obtained by sintering above 1450°C. (2640°F.)—the melting point of nickel. An alloy containing 60% Ni is supposed to be nonmagnetic when sintered only, but

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[74] G. H. S. Price, S. V. Williams, and C. J. O. Garrard, *J. Gen. Electric Co., (London)*, *11*, No. 4, 223 (1941).

magnetic when fused.[75] In the range of composition between 32 and 45% W, the alloys are susceptible to precipitation hardening, and a maximum of 490 Brinell can be developed in a 45% tungsten alloy after 100 hours' treatment at 900°C. (1650°F.).

Due to the high sintering temperatures involved, binary W–Ni alloys have found no particular commercial application, with the possible exception of certain contact alloys (W–Ni alloys with up to 10% Ni) developed in Germany [76] during the war. The use of 2 to 8% nickel additions to tungsten for the manufacture of ductile tungsten wire, involving subsequent evaporation of the nickel,[77] is now only of historical interest.

TUNGSTEN–NICKEL–COPPER

The high sintering temperatures of binary W–Ni alloys containing about 90 to 95% W that are required to obtain a density above 16.5 g./cc. can be reduced considerably by the addition of copper. Price and coworkers [78,79] and Hausner [80,81] investigated the ternary system, and

TABLE 101

Effect of Sintering Temperature on Shrinkage and Density of Heavy Alloy Containing 93% Tungsten, 5% Nickel, and 2% Copper[a] (Price, Williams, and Garrard[79])

Sintering temperature[b]		Linear shrinkage, %	Density, g./cc.
°C.	°F.		
950	1740	0	10.5
1050	1920	0.3	10.7
1150	2100	1.3	11.1
1250	2280	3.0	12.0
1300	2370	6.6	12.8
1350	2460	12.7	16.1
1400	2550	16.2	17.2

[a] Particle size distribution of the powder mixture: 0–1μ—11%, 1–2μ—29%, 2–5μ—42%, >5μ–18%; compacting pressure: 2.5 tsi.

[b] Sintering time: 1 hr.; sintering atmosphere: hydrogen.

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[75] K. Becker and F. Ebert, *Z. Physik, 16,* 168 (1923).

[76] Staatl. Forschungsinstitut für Metallchemie, Marburg, British Intelligence Objectives Subcommittee Doc. F.D. 1594/46; see also *Metal Powder Rept., 1,* 76 (Jan. 1947).

[77] German Pat. 233,885.

[78] G. H. S. Price, C. J. Smithells, and S. V. Williams, *J. Inst. Metals, 62,* 239 (1938).

[79] G. H. S. Price, S. V. Williams, and C. J. O. Garrard, *J. Gen. Electric Co. (London), 11,* No. 4, 223 (1941).

[80] H. H. Hausner, *Metals & Alloys, 18,* No. 6, 1335 (1943).

[81] H. H. Hausner and P. W. Blackburn, in J. Wulff, *Powder Metallurgy.* Am Soc. Metals, Cleveland, 1942, p. 470.

studied the effects of a variation of the nickel–copper ratio, as well as of sintering temperature and time. The manufacture of the alloys consists of compressing the mixed metal powders at 2.5 to 10 tsi, presintering at approximately 1000°C. (1830°F.) in hydrogen or dissociated ammonia, and finally sintering to a fully dense alloy at a temperature high enough to permit formation of a liquid phase above 1350°C. (2460°F.). The linear shrinkage during sintering amounts to about 20%, and densities may approach 18 g./cc. Table 101 shows the effect of sintering temperature on density and shrinkage for an alloy containing 93% W, 5% Ni, and 2% Cu.[79] Modifications of the process involve infiltration of the copper–nickel alloy into a presintered tungsten skeleton,[82] or sintering at a lower temperature (1240–1330°C.; 2265–2425°F.) and subsequent hot forging and annealing.

TABLE 102

Effect of Sintering Time on Shrinkage and Density of Heavy Alloy Containing 93% Tungsten, 5% Nickel, and 2% Copper[a] (Price, Williams, and Garrard[79])

Sintering time[b]	Linear shrinkage, %	Density, g./cc.
5 sec.	9.7	13.9
1 min.	10.0	14.1
5 min.	11.9	15.0
15 min.	14.1	16.3
30 min.	15.3	16.7
1 hr.	16.2	17.2
6 hr.	17.2	17.8

[a] Particle size distribution of the powder mixture: 0–1μ—11%, 1–2μ—29%, 2–5μ—42%, >5μ—18%; compacting pressure: 2.5 tsi.

[b] Actual time held at sintering temperature of 1400°C. (2550°F.). Sintering atmosphere: hydrogen.

The microstructure of an alloy containing 6% Ni, 4% Cu, balance W has been shown in Volume I, Chaper XIV, both for a sintering temperature below (Fig. 232*A*) and above (Fig. 232*B*) the melting point of the nickel–copper alloy. The increase of the sintering temperature above the melting point of the alloy results in a distinct change of structure. Fine tungsten grains are dissolved in the liquid phase and, upon cooling, are reprecipitated on certain nuclei to form larger, rounded tungsten grains.

The effect of sintering time on shrinkage and density is given in Table 102 for an alloy containing 93% W, 5% Ni, and 2% Cu, according to Price, Williams, and Garrard.[79] Apparently, at least 15 minutes must be allowed for sintering in the presence of the liquid phase to obtain suffi-

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[82] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe.* Springer, Berlin, 1943, p. 330.

ciently high density. The amount of tungsten that can be dissolved at the sintering temperature used can be seen from Figure 326, which shows the melting point of the ternary composition as a function of tungsten content for a 3:1 nickel–copper ratio. The necessity of using low molding pressures becomes apparent from Figure 327, where shrinkage is shown to decrease markedly with increasing pressures.

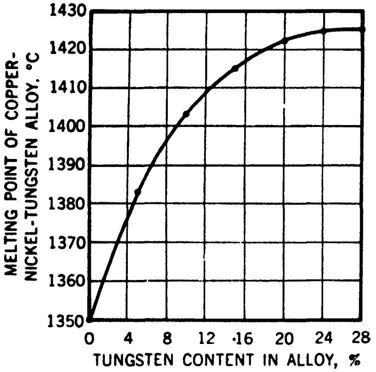

Fig. 326. Effect of tungsten in solution on the melting temperature of a 3–1 nickel–copper alloy (according to Price, Williams, and Garrard[79]).

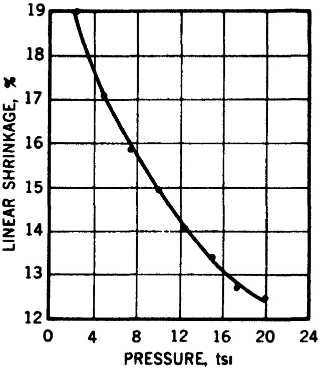

Fig. 327. Effect of the initial pressure on the shrinkage of Heavy Metal (according to Price, Williams, and Garrard[79]).

Price aptly extended his earlier work by experimenting with the sintering of loose powders and also with material that was subjected to metal working subsequent to the sintering operation.[83] In his thesis, Price has essentially confirmed the fundamentals of the sintering mechanism based on the action of the liquid phase. The effects of variables such as tungsten particle size, total tungsten content, nickel–copper ratio, and sintering temperature and time on the rate of diffusion and solubility of tungsten were studied with the aid of x-ray tests and melting point determinations. A fully dense alloy with physical properties identical to those of a pressed and sintered compact was obtained from a loose powder mixture that was sintered by retaining it in a mold during the early stages. Upon swaging a sintered tungsten–nickel–copper bar to wire size, a fibrous structure was developed. Annealing experiments at various temperatures up to the original sintering temperature indicated the existence of three distinct metallographical stages: (*1*) between 900 and 1200°C. (1650 and 2190°F.) elimination of cold work, lattice distortion,

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[83] C. H. S. Price, "The Sintering of Metal Powders in the Presence of a Liquid Phase with Particular Reference to the Tungsten–Nickel–Copper System." *Thesis.* University of London, 1946.

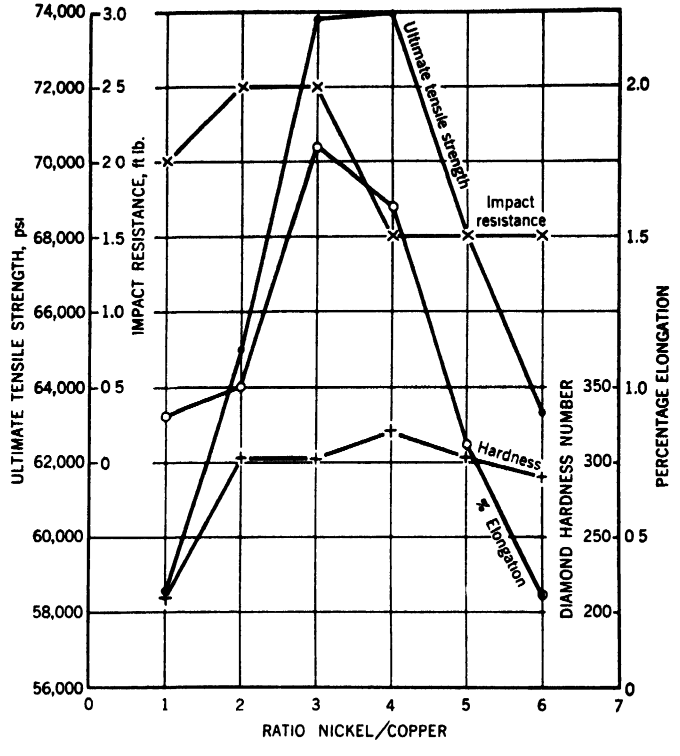

Fig. 328. Effect of nickel–copper ratio on the mechanical properties of a 90% tungsten alloy (according to Price, Williams, and Garrard[79]).

TABLE 103

Effect of Nickel–Copper Ratio on Tensile Strength of Heavy Alloy (Price, Williams, and Garrard[79])

Tungsten, %	Nickel–copper ratio	Ultimate tensile strength, psi	Density, g./cc.
90	1	58,400	15.2
90	2	64,800	16.3
90	3	73,800	16.3
90	4	74,000	16.2
90	5	68,000	16.1
90	6	63,400	16.3

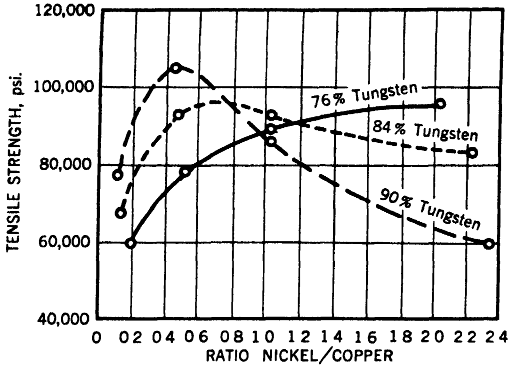

Fig. 329. Effect of nickel–copper ratio on the tensile strength of Heavy Metal compositions of different tungsten content (according to Hausner[80]).

and some recrystallization of the tungsten-saturated nickel–copper phase (*2*) between 1200 and 1400°C. (2190 and 2550°F.) onset of recrystallization of the tungsten grains, development of new very small grain (about 1 μ), but still retention of the preferred orientation induced durin the plastic deformation in the swaging operation; and (*3*) above 1400°C (2550°F.) reorientation of the tungsten grains caused by the process o dissolution and reprecipitation from the liquid phase.

The effect of the nickel–copper ratio on the mechanical properties o an alloy containing 90% W can be seen from the diagram of Figure 328 and from Table 103. For other tungsten contents, the tensile strength i shown in the diagram of Fig. 329, and also in Table 104.[80] A typica alloy containing 90% W has the following properties, according to Price Williams, and Garrard:[79]

Tensile strength, psi	80,000
Yield point, psi	76,000
Elongation in 1 in., 2%	4
Modulus of elasticity, psi	32,000,000
Brinell hardness	250–290
Specific gravity	16.3–17.0
Linear coefficient of expansion	5.6 × 10
Thermal conductivity, cal./cm./sec./°C.	0.2
Specific resistance, microhm-cm.	11.
Electrical conductivity, megmho-cm.	0.08

Lately, these data have been further improved in this country, and fo an alloy containing 90% W, 6% Ni, and 4% Cu, tensile strength value as high as 118,000 psi, elongations up to 10%, modulus of elasticit values up to 35,000,000 psi, and Rockwell hardness "C" values up to 4 have been reported[83a]; the x-ray absorption of the alloy at 2,000,000 volt was found to be 1.5 times that of lead.

[83a] Anonymous, *Inco*, 22, No. 3, 14 (1948).

TABLE 104
Compositions and Properties of Various "Heavy Metal" Alloys (Hausner[80])

Properties		Alloy No.										
	A1	A2	A3	A4	B1	B2	B3	B4	C1	C2	C3	C4
Composition, % W	90	90	90	90	84	84	84	84	76	76	76	76
Composition, % Ni	7	5	3	1	11	8	5	2	16	12	8	4
Composition, % Cu	3	5	7	9	5	8	11	14	8	12	16	20
W–Ni ratio	12.9	18	30	90	7.6	10.5	17	42	4.8	6.3	9.5	19
Ni–Cu ratio	2.33	1	0.43	0.11	2.2	1	0.45	0.14	2	1	0.5	0.2
Sintering temperature, ° C	1375	1330	1300	1240	1375	1330	1300	1240	1375	1330	1300	1240
° F	2510	2425	2375	2265	2510	2425	2375	2265	2510	2425	2375	2265
Theoretical density, g./cc	17.6	17.6	17.6	17.6	16.9	16.9	16.9	16.9	16.2	16.2	16.2	16.2
Density after sintering g./cc	13.6	13.3	14.3	13.6	13.1	12.8	14.2	13.2	12.4	11.8	13.9	13.2
Density after working and annealing, g./cc	16.6	16.5	16.7	16.6	15.5	15.4	15.6	15.6	15.0	14.4	14.6	14.5
Electrical conductivity, %, I.A.C.S.	16.5	17	17.5	19	13	14.2	15.5	17	9.8	11.5	13.3	15.4
Tensile strength, psi	60,000	86,000	105,000	78,000	84,000	93,000	93,000	68,000	96,000	90,000	78,000	60,000
Brinell hardness	213	218	238	248	208	214	214	208	170	220	185	176

Alloys of the tungsten–nickel–copper compositions are known as "Heavy Alloys," and have found commercial applications requiring high specific gravities. Since the alloys exhibit a tensile strength comparable with that of a mild steel, additional applications have been found where strength requirements are significant. In contrast to pure tungsten, the "Heavy Alloys" are easily machinable and can be readily brazed or silver-soldered to other materials. The chief uses of the materials are radium containers and screen materials for α-rays and x-rays, and balancing parts, such as balance crankshafts of aeromotors. Other applications are centrifugal clutch plates that provide the slipping mechanism for supercharger drives, rotors of gyroscopes and gyro-compasses, vibration dampers, and balancing weights for flight control surfaces and variable pitch propellers.[84] The material is also used for heavy-duty contacts where high currents (short-circuit currents) are expected and contact wear has to be kept to a minimum. Figure 330 shows a photograph of such Heavy Alloy contact tips.

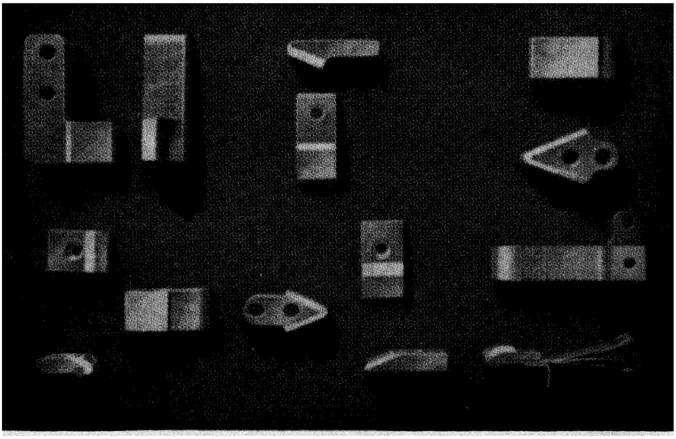

Fig. 330. Assembly of "Heavy Alloy" arcing tips brazed onto copper or steel contacts (according to Price, Williams, and Garrard[79]).

TUNGSTEN–COBALT–SILVER

A high-density alloy containing 90% W, balance Co and Ag has been described by Kurtz.[58] This material compares favorably with the

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[84] G. H. S. Price, *Iron Age, 158*, No. 12, 62 (1946).

[58] J. Kurtz, *Proc. Second Annual Spring Meeting, Metal Powder Association,* New York, June 13, 1946, p. 40.

conventional Heavy Metal (90% W, balance Ni and Cu) as far as strength and conductivity are concerned. If the alloy is produced by careful mixing of ultrafine, very pure elemental powders, and, after compaction at a pressure not exceeding 30 tsi, a presintering treatment at 800–900°C. (1470–1650°F.) is included in the process, a 99.5% dense (17.4 g./cc.) end product is obtained after sintering at 1350°C. (2460°F.). Tensile strength values of 70,000–90,000 psi, and electrical conductivity values of 14–20% I.A.C.S. compare with 60,000–80,000 psi, and 13–17% I.A.C.S., respectively, for a 90–6–4 W–Ni–Cu alloy of identical hardness (240–280 Brinell), and also of 99.5% density.

Applications of this alloy are listed as balancing weights where space is at a premium, rotors for gyroscopes, special contact materials, and containers and absorption screens for radioactive substances.

Molybdenum-Base Alloys

Only two sintered molybdenum-base alloys have so far acquired industrial significance, namely, alloys with iron and with nickel. Sintered compositions of molybdenum with other metals such as chromium, cobalt, or combinations of these metals (Vitallium) have not yet been developed on an industrial scale. Their potential use in heat-resistant construction material for turbine blading and the like is discussed elsewhere (see Chapter XXXII).

MOLYBDENUM–IRON AND MOLYBDENUM–IRON–COPPER

Molybdenum and iron form a compound (Fe_3Mo_2) that is insoluble both in molybdenum and in iron.[86–88] Alloys containing up to 25% Mo can be hot rolled after sintering at 1300°C (2370°F.) for 4 to 6 hours. According to Kurtz,[89] the addition of 1% copper improves the workability of the alloys considerably, and the sintering temperature can be reduced to 1200°C. (2200°F.). Alloys prepared by mixing 200-mesh iron, molybdenum, and copper powders, pressing at 12.5 tsi and sintering for 1 hour, have a much finer grain size and can be more easily rolled, swaged, and drawn than cast alloys of identical composition. A comparison of the properties of cast and sintered alloys containing 5, 10, 15, and 20% Mo and 1% Cu can be found in Chapter XXXI. The sintered alloys containing 10% Mo and over have a coefficient of thermal expan-

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[86] W. P. Sykes, *Trans. Am. Soc. Metals, 28,* 892 (1940).

[87] W. P. Sykes, *Trans. Am. Inst. Mining Met. Engrs., 95,* 307 (1931).

[88] J. L. Gregg, *The Alloys of Iron and Molybdenum.* McGraw-Hill, New York, 1932.

[89] J. Kurtz, in J. Wulff, *Powder Metallurgy.* Am. Soc. Metals, Cleveland, 1942, p. 497.

sion within the range that permits their sealing to soft glass (9 to 11 × 10^{-6}). They are therefore suitable for metal-to-glass seals, where the glass corresponds to the Corning G-1 type, replacing some of the nickel alloys now used in the radio tube and incandescent lamp industries.[89]

MOLYBDENUM–NICKEL

The system molybdenum–nickel has been thoroughly investigated by Ellinger,[90] and also by Baar[91] and Grube and Schlecht.[92] As in the case of the tungsten–nickel system, additions of the refractory metal up to nearly 40% by weight form a solid solution at elevated temperatures (about 1320°C.; 2410°F.). At room temperature, only about 18% of molybdenum is dissolved by nickel, and concentrations between 21 and 35% are susceptible to precipitation hardening. The addition of molybdenum to nickel causes the solidus–liquidus temperatures to be gradually lowered from the melting point of pure nickel to the eutectic temperature at 1320°C. (2410°F.), the eutectic point occurring at 46.5% Mo.

As in tungsten–nickel alloys, the preparation of molybdenum–nickel alloys is possible by pressing the mixture of the metal powders and by sintering at temperatures close to the solidus curve.[92] Sintered alloys containing up to 22% Mo can be cold-rolled, and alloys containing between 20 and 35% can be hot-rolled at 1000°C. (1830°F.). The hardness of sintered molybdenum–nickel after quenching and after slow cooling reaches a maximum of about 550 Brinell for a molybdenum content of 60% by weight, according to Grube and Schlecht.[92] The corrosion resistance of nickel can be materially improved by additions of molybdenum, as established by Guertler and Liepus[93] and confirmed by Grube and Schlecht.[92] For example, the corrosion resistance to hydrochloric acid of pure nickel can be increased twentyfold by adding 16% Mo. At higher molybdenum concentrations, the corrosion resistance decreases somewhat, but between 25 and 30% Mo, the alloys are again increasingly corrosion-proof. Small additions of chromium, cobalt, aluminum, or silicon also tend to improve the corrosion resistance of the molybdenum–nickel alloys.[93]

Sintered molybdenum–nickel alloys have reportedly found limited use as a substitute for pure nickel in chemical equipment, and in the

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[90] F. H. Ellinger, *Trans. Am. Soc. Metals, 30,* 607 (1942).
[91] N. Baar, *Z. anorg. u. allgem. Chem., 70,* 352 (1911).
[92] G. Grube and H. Schlecht, *Z. Elektrochem., 44,* 413 (1938).
[93] W. Guertler and C. Liepus, *Z. Metallkunde, 17,* 310 (1925).

lamp and radio tube industries. Their potential use in heat-resistant alloy products is discussed elsewhere (Chapter XXXII).

Summary

Ductile tungsten leads in importance as a refractory metal used for industrial purposes. The technique for its manufacture has set an example not only for the production of other refractory metals, but for the entire powder metallurgy industry. The obvious uses of tungsten wires in the lamp, x-ray, and electronics industries are well known. Second in importance is molybdenum (manufactured in a similar manner), which is used in wire and sheet form for supporting members or emission wires in lamp and x-ray industries. Tantalum excels in its remarkable corrosion resistance, which makes it extremely valuable as a container material in the chemical industries and as a supporting material in orthopedic surgery. The production of the ductile metal differs from that of tungsten principally by the necessity of sintering in vacuum, since tantalum possesses a strong capacity to absorb gases of any kind. The latter property is exploited in tantalum getters produced for the electronic tube industry.

Of the various refractory metal-base alloys, only two have gained some commercial significance. Tungsten–molybdenum alloys are produced as ductile wire for certain types of supports in lamps and x-ray tubes, where advantage is taken of the better workability of the alloy as compared with pure tungsten, and of the thinner wire diameters as compared with pure molybdenum. The other alloy of commercial value is the so-called "Heavy Metal," a tungsten–base composition containing a nickel–copper alloy of a ratio of approximately 3 to 1. The properly sintered alloy can reach a density up to 17 g./cc. and is easily machinable. Its high density permits the use of the alloy for radium containers and balance parts, and the good wear properties—coupled with a fairly good electrical conductivity—have opened a number of applications in the heavy-duty contact metal field.

CHAPTER XXII

Hard Metals and Compositions

CEMENTED CARBIDES

The production of sintered hard metals has progressed in recent years to the point where it is now possibly the most important branch of powder metallurgy. No other individual branch has contributed so much to the industrial accomplishments of this nation during the war, and it can be said without reservation that the marvelous production record of the United States has been made possible primarily by the ever-increasing output of sintered hard metals for the entire tool-employing industry. Remarkable production increases have in turn promoted a decrease in cost of the various commercial carbide grades during recent years, and so further stimulated their use. While statistics of the quantity of hard metal produced during the war years for industrial and ordnance use in the United States are not available, some figures have been reported for the German and British production[1]; and these figures are impressive, indeed. The annual German output of cemented carbide for tool tips and dies increased from about 15 tons in 1933/4 to over 500 tons in 1943/4. The parallel development of lower grades of cemented carbide for armor-piercing projectile cores and tips reached similar output figures, culminating in a peak production of 682 tons of carbide shot in 1940. This German maximum was more than doubled in Great Britain by 1944, after only two years of production. Thus, the rise in cemented carbide output in the major industrial countries of the world during the immediate prewar and war years represents one of the greatest commercial and technological developments in powder metallurgy.

Although the subject of sintered hard metals deserves the fullest attention, it is unfortunate that the topic cannot be treated in too great detail because of the physical limits of this book, and because of the need for balancing this subject with others dealing with powder metallurgy applications worthy of discussion. Moreover, certain experimental observations and conclusions which have led to the introduction of multiple carbides instead of single carbides cannot, at present, be aired,

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[1] British Intelligence Objectives Sub-committee, Final Report No. 1385 (Aug. 1947); see also *Met. Powd. Rept., 2,* No. 4, 55 (1947).

since they are still controversial and are still the object of pending patent suits. As a result, the author will confine himself to a survey of the known facts of the manufacturing techniques, the cementing process, and the properties and applications of hard metals.

Historical Development

The commercially important hard metals are sintered products consisting of a major constituent of carbides of tungsten, titanium, and/or tantalum, cemented together by a metal of the iron group, in particular, cobalt. The favorable properties of these hard metals are due to the extreme hardness of the carbides that is retained to a large extent at moderately high temperatures (red heat), and to the mechanical strength of the cementing metal—alone and in conjunction with the carbide. These factors were recognized about 40 years ago when the development of hard metals began.

At the turn of the century, alloy steels were the sole cutting materials used. Cobalt-base alloys, rich in chromium and tungsten, of the "Stellite" type were first introduced commercially in 1907. These alloys contained only up to 20% Fe, 2 to 3% C, 10 to 25% W, 25 to 35% Cr, and 40 to 55% Co; they proved to be about 50% more efficient for cutting than tungsten–chromium–cobalt high-speed steels. In contrast with this, the introduction of tungsten carbides boosted the cutting efficiency several hundred per cent, which increase was further enhanced by the introduction of the multiple-carbide tools.

The first step toward the development of these cemented carbides was the production of cast tungsten carbides which were attempted by Lohmann for drawing dies in 1914.[2] The cast carbides proved brittle and nonuniform in structure, and induced Lohmann to try to produce better materials with the aid of powder metallurgy methods. He employed a very fine tungsten carbide powder which he sintered at a temperature close to the melting point of the carbide.[3] In the absence of a lower melting binder, no liquid phase was as yet generated during sintering, and the resulting products were extremely brittle. Nevertheless, his work formed the foundation for the development of the sintered hard metals.

In 1917, Fuchs and Kopietz[4] produced alloys of tungsten, titanium, and carbon, to which iron or cobalt was added. A typical analysis was 55% W, 3.5%Ti, 3.5% C, 5% Cr, 33% Co. This material was cast or sintered under slight pressure between graphite electrodes. The micro-

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[2] German Pat. 286,184.

[3] German Pats. 289,066; 292,583; 295,656; 295,726.

[4] German Pats. 307,764; 310,041; 320,996.

structure of the cast material contained as major constituent the tungsten–titanium double carbides, distinguished by their partly spheroidized rhombic and tetrahedral shape; the structure of the sintered material contained still appreciable amounts of the unspheroidized tungsten carbide grains in addition to the double carbides precipitated from the tungsten–chromium–cobalt matrix. The material thus produced was less brittle than the plain carbide products, but its hardness was also inferior.

Another step was taken by Baumhauer in 1922,[5] by infiltrating a porous body of carbide particles with metals of the iron group. The mechanical properties of the product were considerably improved, but a residual porosity could not be avoided at the side through which the auxiliary metal had infiltrated.

The modern production of hard metals is based principally on Schröter's[6] process of mixing powdered tungsten carbide (WC) with up to 20% by weight of metals of the iron group (cobalt), followed by briquetting and sintering at a temperature close to the melting point of the metal of the iron group. The details of this development—carried out at the Osram Studiengesellschaft in Germany—are reported by Skaupy.[7-9] Materials made by this process by Krupp, and known as "Widia," had greatly improved mechanical and cutting properties and, in addition, permitted sintering at reasonably low temperatures where less specialized furnace equipment could be used. Products consisting of tungsten carbide with varying amounts of cobalt (6–20%) as the auxiliary metal have retained their usefulness to date. They exhibit high hardness, extraordinary strength, and high thermal conductivity, and have proved satisfactory for drawing dies and cutting tips for cast iron and other materials which form short chips upon machining.

The cobalt-cemented, sintered tungsten carbides proved unsuitable for machining tougher materials, forming long, coiled chips, such as steel, and it was necessary to develop new hard metals. Attempts were made to replace partly or completely the tungsten carbide by the carbides of titanium, tantalum, molybdenum, or columbium, and the cobalt by nickel and iron or by their alloys. In 1931, Fansteel Products Co.[10] began to produce a hard metal based on tantalum carbide, known as "Ramet." An alloy of nickel and cobalt amounting to between 8 and 13%

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[5] German Pat. 443,911; U. S. Pat. 1,512,191.

[6] German Pats. 420,689; 434,527; U. S. Pat. 1,549,615.

[7] F. Skaupy, *Z. Elektrochem, 33,* 487 (1927).

[8] F. Skaupy, *Metallwirtschaft, 20,* 537 (1941).

[9] F. Skaupy, *Kolloid-Z., 98,* 92 (1942).

[10] Brit. Pats. 373,708; 375,854; 376,266; French Pats. 713,086; 713,087; U. S. Pats. 1,913,100; 1,937,185.

was used for cementing either plain tantalum carbide or a multiple carbide containing up to 10% Mo and 20% W of the total composition. The carbon content was between 5 and 6% by weight.

The turning point in the history of hard metals occurred with the successful replacement of the plain tungsten carbide (WC) by combinations of tungsten carbide and titanium carbide (TiC) in single-phase solid solutions, as initiated by Schwarzkopf.[11]

The claim that superior products are obtained by synthesizing a compound $WTiC_2$[12,13] instead of solid solutions of WC and TiC has not yet been substantiated by x-ray and other evidence.[14,15]

Since 1929, hard alloys consisting of solid solutions of WC–TiC, Mo_2C–TiC, and WC–Mo_2C–TiC have been produced with metals of the iron group, especially cobalt and nickel or their alloys as auxiliary binders. WC–TiC–Co and WC–TiC–TaC–Co combinations have given outstanding performance as tool materials in the high-speed machining of steels and other materials that form long and tenacious chips. The titanium carbide content is usually 16 or 30%, but may be as low as 12 or even 5%; the cobalt is usually either 6, 9, or 13%. In special cases involving fine drilling, the titanium carbide content has been raised to 60%.[15a] Recently, the claim has been made[15b] that on the basis of research conducted in France until 1941 it was found that titanium carbide and tungsten carbide combine under optimum conditions in the stoichiometric ratio 3:1, which represents practically equal weight. This, however, could not be entirely confirmed in commercial practices.[15c]

The addition of carbides of molybdenum, tantalum, columbium, and vanadium up to 20% has also resulted in usable materials. A tungsten-free composition containing 45% TiC, 45% VC, and either 10% Ni or 7% Ni and 3% Co, and obtained by the carburization of ferroalloy powders has been employed successfully in certain cases to substitute

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[11] Austrian Pat. 138,284; German Pat. 720,502; U. S. Pats. 1,959,879; 2,122,157; 2,170,433; 2,246,287; 2,356,009 (Reissues 22,073; 22,074; 22,166; 22,207).

[12] U. S. Pat. 2,113,355.

[13] P. M. McKenna, in J. Wulff, *Powder Metallurgy*. Am. Soc. Metals, Cleveland, 1942, p. 456.

[14] G. A. Meerson, G. L. Zverev, and B. E. Osinovskaya, *Zhurnal Priklad. Khimii, 13,* No. 1, 66 (1940); *Metal Ind. London, 59,* 306 (1941).

[15] A. G. Metcalfe, *Metal Treatment, 13,* 127 (1946).

[15a] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe*. Springer, Berlin, 1943, p. 276.

[15b] M. Oswald, *Proc. International Powder Metallurgy Conference*, Graz, July 12–17, 1948, Referate No. 52.

[15c] R. Kieffer, *private communication.*

TABLE 105
Production Methods for Hard Materials (Kieffer and Hotop[15a])

Substance	Method	Temperature	
		°C.	°F.
Carbides			
W_2C; WC.....	WO_3 + lampblack	1400–1600	2550–2910
	W metal powder + lampblack		
	W metal powder + lampblack + hydrocarbon gas	1200–1400	2190–2550
Mo_2C....	MoO_3 + lampblack	1200–1400	2190–2550
	Mo metal powder + lampblack		
	Mo metal powder + lampblack + hydrocarbon gas	1100–1300	2010–2370
TiC.........	TiO_2 + lampblack	1700–1900	3090–3450
ZrC..........	ZrO_2 + lampblack	1800–2000	3270–3630
VC...	V_2O_5 or V_2O_3 + lampblack	1100–1200	2010–2190
CbC....	Cb_2O_5 or Cb metal powder + lampblack	1300–1400	2370–2550
TaC...	Ta_2O_5 + lampblack	1300–1500	2370–2730
	Ta metal powder + lampblack		
Multicarbides[a]...	Metal oxide A + metal oxide B + lampblack	1500–1700	2730–3090
	Metal powder A + metal powder B + lampblack	1500–1700	2730–3090
	Carbide powder A + carbide powder B	1700–2000	3090–3630
	Chemical isolation of highly carburized ferroalloys by acid digestion	20– 100	68– 212
Nitrides[b]...	Metal powder + nitrogen	1200–1400	2190–2550
	Metal powder + ammonia	1200–1400	2190–2550
	Metal oxide + lampblack + nitrogen or ammonia	1200–1400	2190–2550
Borides[c].....	Metal powder + boron powder in vacuum	1800–2200	3270–3990

[a] Solid solutions of two or more of the carbides above.
[b] TiN, ZrN, HfN, VN, CbN, TaN.
[c] WB, ZrB, ZrB_2.

for WC–Co and WC–TiC–Co compositions by the Germans during World War II.[15d–19] A composition containing 90% VC and 10% TiN proved to be too brittle and too difficult to manufacture for serious consideration as a substitute tool material, although some test results showed promise.[19]

[15d] German Pat. 748,933.

[16] G. J. Comstock, *Metal Progress, 46,* 117 (1946).

[17] British Intelligence Objectives Sub-committee, Final Report No. 1076, Item No. 21 (Apr. 1947); see also *Met. Powd. Rept. 1,* No. 10, 150 (1947).

[18] British Intelligence Objectives Sub-committee, Final Report No. 1385 (Aug. 1947); see also *Met. Powd. Rept., 2,* No 4, 55 (1947).

[19] G. J. Trapp, B. E. Berry, H. Burden, A. E. Oliver, and T. Raine, *Symposium on Powder Metallurgy,* The Iron and Steel Institute, Special Report No. 38, London, 1947, p. 92.

TABLE 106. Properties of the Most Important Hard Compounds (Meyer and

No.	Compound	Formula	Molecular weight	Carbon content, %	Nitrogen content, %	Lattice type
1.	Boron carbide	B_6C	76.9	15.61	—	Regular tetrahedral[b]
2.	Silicon carbide	SiC	40.1	26.97	—	Hexagonal tetrahedral[b]
3.	Titanium carbide	TiC	59.9	20.05	—	Regular NaCl type
4.	Zirconium carbide	ZrC	103.2	11.64	—	Regular NaCl type
5.	Vanadium carbide	VC	63.0	19.07	—	Regular NaCl type
6.	Columbium carbide	CbC	104.9	11.46	—	Regular NaCl type
7.	Tantalum carbide	TaC	192.9	6.22	—	Regular NaCl type
8.	Chromium carbide	Cr_3C_2	180.1	13.31	—	Orthorhombic
9.	Molybdenum carbide	Mo_2C	203.9	5.89	—	Hexagonal, most closely packed
10.	Tungsten carbide	W_2C	380.0	3.16	—	Hexagonal, most closely packed
11.	Tungsten carbide	WC	195.9	6.13	—	Hexagonal
12.	Chromium-tungsten carbide[c]	$3\ Cr_3C_2\ W_2C$	920.0	9.14	—	—
13.	Titanium nitride	TiN	61.9	—	22.10	Regular NaCl type
14.	Titanium nitrocyanide	4 TiN.TiC	307.5	3.90	18.21	Regular NaCl type
15.	Vanadium nitride	VN	65.0	—	21.57	Regular NaCl type
16.	Vanadium nitride	V_2N	115.9	—	12.07	—
17.	Chromium nitride	CrN	66.0	—	21.22	Regular NaCl type
18.	Chromium nitride	Cr_2N	118.0	—	11.87	Hexagonal, most closely packed
19.	Molybdenum nitride	Mo_2N	205.9	—	6.80	Regular NaCl type
20.	Diamond	C	12.01	100.0	—	Regular tetrahedral
21.	Corundum	Al_2O_3	101.94	—	—	Hexagonal

[a] Determined by W. Köster and W. Rauscher, *unpublished*.
[b] Diamond-type bond.
[c] 51.0% chromium.

Shortly before the end of the war, however, a tool tip material having an average composition of 40% TiC, 40% VC, 12% Fe, and 8% Al was perfected and scheduled for production[17]; the quality of this material fell between 25 and 60% of the standard 78% WC, 16% TiC, and 6% Co grade (German grade S1).

R. Kieffer and his coworkers[19a,19b] have recently completed some

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[19a] R. Kieffer and F. Kölbl, *International Powder Metallurgy Conference*, Graz, July 12–17, 1948, Referate No. 28; also *Powder Met. Bull.*, *4*, No. 1, 4 (1949).

[19b] H. Nowotny and R. Kieffer, *Metallforschung*, *2*, 257 (Sept. 1947).

Eilender,[20] Kieffer and Hotop,[15a] and Kieffer and Kölbl[19a])

No.	Fusion temperature °C.	°F.	Density, g./cc. Calcd.	Obsd.	Modulus of elasticity,[a] psi	Compressive strength, psi	Transverse rupture strength, psi	Vickers hardness, kg./mm.^{2}
1.	2550	4620	—	2.51	—	280,000[d]	30,000–40,000[d]	5000[d]
2.	Decomposable		—	3.12	—	140,000	7,000–21,000	4200
3.	3200	5800	4.23	4.25	45,800,000	430,000[d]	40,000–57,000[d]	3000[d]
4.	3250	5880	6.51	6.70	20,000,000	—	—	—
5.	2800	5070	5.25	5.36	39,000,000	—	—	—
6.	3800	6870	8.20	7.76	49,400,000	—	—	—
7.	3800	6870	13.95	14.49	41,300,000	—	—	—
8.	1750	3180	—	6.68	—	—	—	—
9	2500	4530	—	8.82	32,300,000	—	—	—
10.	2850	5160	17.15	17.2	61,000,000	—	—	—
11.	2900	5250	15.52	15.6	102,800,000	430,000[e]	70,000–85,000[e]	2200[e]
12.	1950	3540	—	8.50	—	—	—	—
13.	2950	5340	4.81	5.29	12,500,000	—	—	—
14.	—	—	5.32	5.29	—	—	—	—
15.	Decomposable		—	5.91	—	—	—	—
16.	Decomposable		—	—	—	—	—	—
17.	Decomposable		6.1	5.9	—	—	—	—
18.	Decomposable		—	—	—	—	—	—
19.	Decomposable		—	—	—	—	—	—
20.	3750	6780	—	3.51	—	280,000	30,000–70,000	8000
21.	2050	3720	—	3.9	—	430,000[e]	30,000–35,000[e]	3000[e]

[d] Hot pressed.

[e] Sintered.

postwar work with TiC–VC materials, and also with a TiC–Mo_2C type tungsten carbide-free hard metal. Under optimum conditions, *i.e.*, vacuum-sintering or, preferably, hot-pressing, a transverse rupture strength of about 75% of that of standard multicarbide grades could be attained.

Substitution of the carbides by other hard compounds such as borides, nitrides, or silicides for use as tool materials has been repeatedly suggested,[19a,20] but so far has proved unsuccessful.

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[20] O. Meyer and W. Eilender, *Arch. Eisenhüttenw.*, *11,* 545 (1937–38).

Production of Hard Metal Compounds

The principal constituents of the sintered hard metals are compounds of the elements of the 4th, 5th, and 6th groups of the periodic system: Ti and Zr (4th group); V, Cb, and Ta (5th group); and Mo and W (6th group). Only the carbides of certain of these metals have become of great technical significance, with the silicides, nitrides, and borides now merely of academic interest. For this reason, the latter will not be considered here to any length, and the reader is referred to the detailed descriptions of the hard materials by Becker[21,22] and Skaupy,[23] as well as to the publications by Van Arkel,[24] Agte and collaborators,[25,26] Sykes[27] *et al.*

Numerous investigations of more recent date are concerned with the constitution and characteristics of the carbides and related interstitial compounds. Franssen[27a] has analyzed the equilibrium diagram of the system W–C, and the construction of preliminary phase diagrams of the systems Ti–C and Ti–N on the basis of available information in the literature has been reported by Nielsen *et al.*[27b] The diffusion rates of carbon into granulated tungsten at 1535–1700°C. (2795–3090°F.) were studied by Pirani and Sandor,[27c] and Krainer and Konopicky[27d] determined the presence of W_2C in WC samples by x-ray diffraction methods (the same investigators also determined the amount of combined carbon in TiC–TiO solid solutions) and the lattice parameters of WC and VC. The lattice parameter of VC was also checked by Dawihl and Rix,[27e] together with those of VN, TiC, and TiN; Norton and Mowry[27] and Nowotny and Kieffer[27g] determined the lattice parameters of TiC, ZrC, VC, TaC, and CbC; those of WC and Mo_2C were also redetermined by

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[21] K. Becker, *Hochschmelzende Hartstoffe und ihre Technische Anwendung.* Verlag Chemie, Berlin, 1933.

[22] K. Becker, *Z. Elektrochem., 34,* 640 (1928); *Z. Metallkunde, 20,* 487 (1928).

[23] F. Skaupy, *Metallkeramik.* 2nd ed., Verlag Chemie, Berlin, 1943.

[24] A. E. Van Arkel, *Physica, 4,* 286 (1924).

[25] C. Agte and K. Moers, *Z. anorg. allgem. Chem., 198,* 233 (1931).

[26] C. Agte, H. Alterthum, K. Becker, G. Hayne, and K. Moers, *Z. anorg. allgem. Chem., 196,* 129 (1931).

[27] W. P. Sykes, *Trans. Am. Soc. Steel Treating, 18,* 968 (1930).

[27a] H. Franssen, *Arch. Eisenhüttenwesen, 19,* 79 (1948).

[27b] J. P. Nielsen, E. A. Palty, I. Cadoff, and E. J. P. Rattin, *Symposium on Titanium,* Office of Naval Research, Washington, D. C., December 16, 1948. Paper No. 17.

[27c] M. Pirani and J. Sandor, *J. Inst. Metals, 73,* 385 (1947).

[27d] H. Krainer and K. Konopicky, *Berg- u. Hüttenmann. Monatshefte, 92,* 166 (1947).

[27e] W. Dawihl and W. Rix, *Z. anorg. allgem. Chem., 244,* 191 (1940).

[27f] J. T. Norton and A. L. Mowry, *J. Metals, 1,* 133 (1949).

[27g] H. Nowotny and R. Kieffer, *Metallforschung, 2,* 257 (1947).

the latter. The thermal properties of TiC and TiN were investigated by Naylor,[27h] those of VC and VN were investigated by Shomate and Kelley[27i] and King,[27j] and the heat of formation of WC was calculated by McGraw, Seltz, and Snyder,[27k] and by Huff, Squitieri, and Snyder.[27l]

The carbides of the above-mentioned metals exhibit unique properties that render them metallic in character. Their melting point is very high, in some cases above that of tungsten; their electrical and heat conductivities is within a range encountered in metals; their hardness and strength, both at ordinary and at elevated temperatures, are extremely high; their resistivity against chemical attack is good; and finally, they are capable of forming, at least to some extent, alloys with the metals of the iron group.

TABLE 107

Characteristics of Metal Carbides (Kieffer and Kölbl[19a])

Group of periodic System	Carbide	Carbon content, %	Lattice type	Density (measured), g./cc.	Vickers hardness, kg./mm.^{2}	Rockwell hardness, "A"	Melting point	
							°C.	°F.
4	TiC	20.04	NaCl	4.7	3200	92–93.5	3250	5880
	ZrC	11.70	NaCl	6.7	2600	90–92	3250	5880
5	VC	19.00	NaCl	5.3	3000	90–91	2800	5070
	CbC	11.40	NaCl	7.7	2400	90–91	3800	6870
	TaC	6.20	NaCl	14.0	1800	87–88	3800	6870
	Cr_3C_2	13.33	Ortho rhombohedric	5.6	1300	85	2000	3630
6	Mo_2C	5.88	Hexag. close-packed	8.8	1500	88–90	2500	4530
	WC	6.12	Hexag.	15.6	2200	92	2900	5250
	W_2C	3.16	Rhombohedric	16.5	3000	93	2700	4890

A number of production methods for different hard metal compounds are summarized in Table 105, according to Kieffer and Hotop;[28] the properties of the most important compounds are reproduced in Table 106, according to data by Meyer and Eilender,[20] Kieffer and Hotop,[28] and Kieffer and Kölbl,[19a] and those of a number of different carbides in Table 107, also according to Kieffer and Kölbl.[19a]

[27h] B. F. Naylor, *J. Am. Chem. Soc., 68,* 370 (1946).

[27i] C. H. Shomate and K. K. Kelley, *J. Am. Chem. Soc., 71,* 314 (1949).

[27j] E. G. King, *J. Am. Chem. Soc., 71,* 316 (1949).

[27k] L. D. McGraw, H. Seltz, and P. E. Snyder, *J. Am. Chem. Soc., 69,* 329 (1947).

[27l] G. Huff, E. Squitieri, and P. E. Snyder, *J. Am. Chem. Soc., 70,* 3380 (1948).

[28] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe.* Springer, Berlin, 1943, pp. 281, 282.

CARBIDES

The following methods of producing carbides can be distinguished: (*1*) production by fusion; (*2*) carburization of pulverized metals or metal oxides by means of solid carbon; (*3*) carburization of pulverized metals or metal oxides by means of carbonaceous gases, if necessary with the addition of solid carbon; (*4*) precipitation from a gaseous phase; (*5*) chemical separation from carburized ferroalloys; and (*6*) precipitation in an inert molten menstruum.

The methods (*1*) and (*4*) are no longer in use; (*5*) is not used much; and (*6*) is used only in the production of titanium and tungsten–titanium carbides. The method most commonly used is (*2*) whereby powdered carbides are produced by carburizing the refractory metals or their oxides with solid carbon below the melting point of the carbide. Lampblack is most suitable for the purpose. If the pure metal powder is used, about 5 to 10% excess carbon is added to the composition for reaction with residual oxygen; in the case of metal oxide as raw material, 70 to 90% above the theoretically necessary amount of carbon is added, and the carbon monoxide aids in the reduction of the oxide by the reducing atmosphere. Mixing is conducted in ball mills, and carburizing is carried out in one or several stages either in continuous muffle furnaces or in batch-type high frequency furnaces. Hydrogen, as well as natural gas and dissociated ammonia, can be used as reducing gas. Carburization takes place between 1200 and 1900°C. (2200 and 3450°F.). Although carbide formation proceeds more rapidly at higher temperatures, a limit is set by increasing grain growth. Hence, the lowest possible temperature still economically feasible is usually selected for the treatment.

The effect of variations of production techniques on the constitution of the principal carbide and binder metal powders employed in the manufacture of hard metal alloys has recently been discussed by Krainer.[28a] Determination of the desired as well as the undesired phases (*e.g.*, the brittle compounds W_2C and Co_3W_3C) in the hard alloys was accomplished with the aid of such special physical testing methods as x-ray analysis work and magnetic testing.

Tungsten Carbide Powder. This carbide is usually produced by mixing ~~pure~~ tungsten powder of a similar quality to that used in the production of ductile tungsten products with between 6.9 and 7.2% lampblack. Insufficient quantities of carbon causes the formation of the

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[28a] H. Krainer, *Proc. International Powder Metallurgy Conference*, Graz, July 12–17, 1948, Referate No. 31.

undesirable compound Co_3W_3C during sintering of the hard metal. Heating of the mixture is generally performed for about two hours at 1400 to 1500°C. (2550 and 2750°F.) Heating at lower temperatures or for insufficient time results in the formation of the extremely brittle compound W_2C. On the other hand, overcarburization takes place at excessively high temperatures or over prolonged heating times, and results in free carbon, which causes porosity in the end product. The treatment is performed under hydrogen in a carbon resistor furnace or inside a graphite crucible in a high-frequency furnace. The sintered cake is pulverized by dry milling and should contain at least 5.9–6.0% combined carbon, and not more than 0.2% free carbon (the stoichiometric value of C in WC is 6.12%). In case of a deficiency in combined carbon, a repeat treatment with additional lampblack is possible; if too much free carbon is analyzed, reheating with the addition of metal or metal oxide is also feasible.

Details of the up-to-date practices employed in preparing high-grade tungsten carbide powder, dealing specifically with the type and proper allotments of the raw materials and with the carburization and subsequent pulverizing operations, are given by Brownlee, Geach, and Raine[28b]; the reader interested in this particular phase is urged to study the reference closely. The authors recommend as raw materials a tungsten powder with not more than 0.2% total impurities (average analysis of impurities: alkalis, 0.05%; iron, 0.05%; silicon, 0.04%) and a carbon powder having low ash, volatile matter and moisture contents (typical carbon black or lampblack analysis: volatile matter, 0.50%; ash, 0.1%; moisture, 0.20%; carbon, 99.20%). The mixture used in the carburization contains a slight excess over the theoretical requirements (*e.g.*, 6.25% carbon black) in order to allow for reduction of oxide during the early stages of heating. Special emphasis should be placed on the charging of the carburizing furnace. The charge must be porous enough to permit the escape of evolved gases, and the texture of the mixture is therefore of considerable importance. The mixture is either pressed into small blocks or cylinders, or is filled loosely into the crucible and then tamped to a packing in which air pockets are avoided (without seriously reducing the permeability). Either method has its advantages and disadvantages: some types of carbon powders give mixtures that cannot be pressed to satisfactory coherence for handling; furthermore, pressed pieces are more difficult to crush and mill after carburizing. On the other hand, loose powder with its larger mass frits into a single block that can be removed intact from the

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[28b] L. D. Brownlee, G. A. Geach, and T. Raine, *Symposium on Powder Metallurgy,* The Iron and Steel Institute, Special Report No. 38, London, 1947, p. 73.

furnace; however, the severe work necessary for breaking the cake loose may result in damage to the crucible. During carburizing in the high-frequency furnace, reduction of traces of oxide becomes apparent at about 700°C. (1300°F.), and hydrogen is introduced into the crucible only after the flames at the vents—resulting from a burning of the evolved gases—have died down. The furnace is then heated to the required carburizing temperature and held there for 2 hours, after which it is allowed to cool slowly (*i.e.*, for at least 10 hours), the charge being protected by hydrogen at all times. The resulting cake should possess a perfectly even, grey color (light and dark bands would indicate previous segregation in the mixture; black spots would be a sign of free carbon agglomerations in a poor mixture). The cake is pulverized in a jaw crusher and a carbide-lined ball mill; the time of mixing depends on the carburizing temperature and is at least 2 hours. Grading by passing through a 200-mesh sieve concludes the process. The resulting powder should have a total carbon content of 6.10 to 6.15%, and a combined carbon content of not less than 6.05%.

Of special significance is the reactivity of the carbon in the mixture with the protective atmosphere. According to Brownlee, Geach, and Raine,[28b] production of tungsten carbide (WC) of theoretical carbon content is impractical in vacuum furnaces, since the reaction between W and C is very slow under vacuum. Skaupy,[28c] however, has recently suggested the use of a mercury vapor atmosphere for the preparation of carbides, since no volatile compounds of carbon and mercury are known to exist, and, therefore, loss of carbon by reaction with the atmosphere could be prevented. (In the same publication, Skaupy also suggests the preparation of carbides by direct resistance heating, *i.e.*, by passing a high-amperage current through the powder mixture contained in a carbonaceous atmosphere).

In specific instances, tungsten carbide obtained by recovering hard metal scrap is used either as addition to virgin carbide powder, or as exclusive hard metal constituent. One procedure, suggested by Trent,[28d] involves the removal of the binder metal in the form of an alloy with zinc by dissolution in dilute sulfuric acid.

Titanium Carbide Powder. This carbide is produced by heating the oxide with carbon. Commercially pure titanium oxide containing not more than 0.2% SiO_2 is mixed with lampblack. To avoid separation, it is best to mix in the presence of water. The wet mixture is dried and

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[28c] F. Skaupy, *Proc. International Powder Metallurgy Conference,* Graz, July 12–17, 1948. Referate No. 8*a*.

[28d] U. S. Pat. 2,407,752.

preheated to 1700°C. (3100°F.) under hydrogen in a high-frequency furnace. As a precaution against decarburization by the hydrogen, the charge is heated in a graphite crucible closed by a graphite cover, and a protective layer of carbon gravel is usually placed on top of the charge. (A photograph of such a setup is shown in Fig. 238 in Vol. I, Chapter XV.) After the treatment, the gravel is removed by screening and the mixture is dry milled. Depending upon the analysis, either lampblack or titanium oxide is added to adjust the carbon content to approximately 19.5% combined carbon and 1% free carbon.[29] After milling for about a half-hour, the mixture is reheated under the above-mentioned conditions, except that the temperature is now raised to 1800–1900°C. (3300–3450°F.) and the treatment extended to 2 to 3 hours. The sintered cake is pulverized by crushing and grinding in the ball mill.

The method described by Brownlee, Geach, and Raine[28b] provides for thorough (4 hours) wet mixing of titanium dioxide and carbon black in proportions of 68.5 to 31.5%. The water of the pasty mixture is removed by carefully drying the powder for 3 hours at 180°C. (360°F.) in order to avoid the liberation of water vapor during the subsequent carburization cycle, which would lead to partial decarburization of the mixture. The dried powder mixture is pressed at 10 tsi into 6 × $2^1/_2$ × 1-in. briquettes to facilitate loading of the crucible of the carburizing furnace. The latter is a vacuum–high-frequency type construction which is reproduced in the diagrammatic sketch of Figure 331 (a similar furnace design is given in Figure 252 in Volume I, Chapter XVI) and which permits 20-kg. charges. A vacuum of 0.1 mm. Hg at room temperature is rapidly depreciated during heating due to the evolution of gases during the initial reduction of the oxide, which begins at about 800°C. (1470°F.) and proceeds rapidly at 1200–1400°C. (2200–2550°F.). The pressure reaches a peak of 40 mm. Hg at about 1300°C. (2370°F.). Under the prevailing conditions the reaction is usually complete at 1600–1650°C. (2900–3000°F.), but, for the sake of ensuring removal of the last traces of oxygen and obtaining as nearly complete carburization as possible, the charge is heated to 1900–1950°C. (3450–3550°F.) for 30 minutes, the pressure in the furnace being 4 mm. Hg. Subsequent pulverization of the cooled cake in a jaw crusher and carbide-lined ball mill is aided by initial pressing laminations in the briquettes, which were widened during the heating operation by the escaping gases. The yield is 52% of the furnace load; typical analysis figures are 19.5–20.3% total carbon, 0.1–0.8% free carbon, and 79.5–80.2% titanium.

Other methods of producing titanium carbide include vacuum car-

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[29] G. A. Meerson *et al., Zhurnal Priklad. Khimii, 13,* No. 1, 66 (1940).

burization to permit a closer approach to the theoretical combined carbon content of 20%[29]; and carburization with hydrocarbon gases.

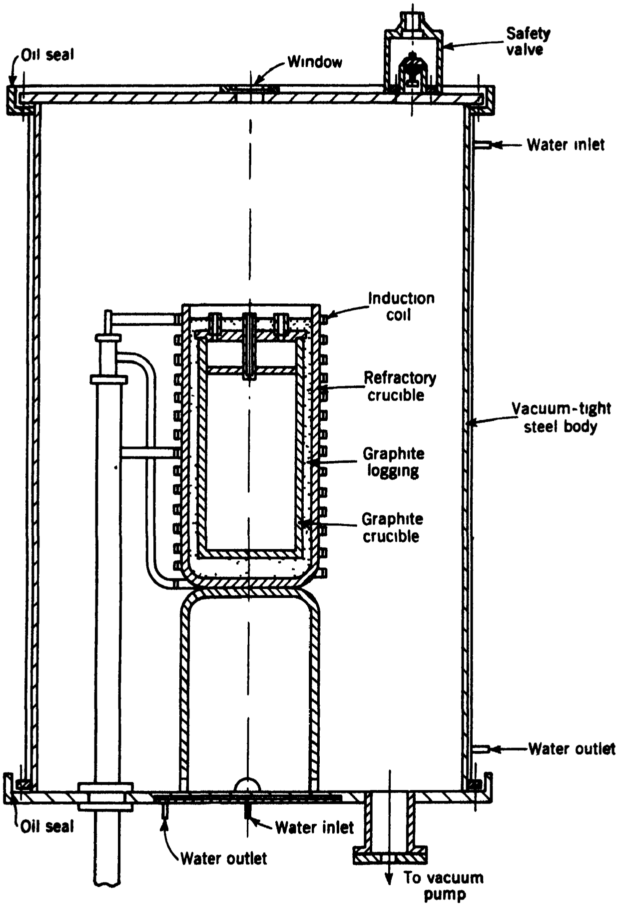

Fig. 331. Diagrammatic cross section through vacuum-carburizing furnace for the production of titanium carbide (according to Brownlee, Geach, and Raine[28b]).

Very recently, an entirely new and apparently quite effective method of producing titanium carbide powder of nearly theoretical combined carbon content was reported.[29a] Powder, virtually free of uncombined

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[29a] V. Fattinger, communication on "Experiments with a View of Producing Pure Titanium Carbide Powder by Means of Carbonizing Gases Favorable to the Reaction," *Symposium on the Physics of Powder Metallurgy,* sponsored by Sylvania Electric Products, Inc., Bayside, L. I., N. Y., August 24–26, 1949.

carbon, is obtained by means of chlorine-containing carburizing gases favorable to the reaction; in the case of carburization of titanium metal or titanium dioxide (rutile) powder with solid carbon (lampblack) under hydrogen, titanium tetrachloride, carbon tetrachloride, or chloroform vapors are added. These gaseous additions have the dual purpose of functioning catalytically, and also aiding the carburization directly by contributing carbon. It was found to be advantageous, to limit the amount of solid carbon in the mixture to below the stoichiometrical quantity required for the formation of the carbide, and to complete the reaction with the aid of the carburizing gas phase. Additional raw materials used in connection with this work[29b] were titanium hydride and anatas. The latter is a comparatively unstable type of titanium dioxide which must be produced synthetically; it is transformed to the stable rutile spontaneously at about 1300°C. (2370°F.). At the point of transformation, the rutile in *statu nascendi* is highly susceptible to the action of the carburizing gases. As a result, a titanium carbide product with a combined carbon content corresponding to the theoretical value, and without even traces of free carbon, is obtainable in a comparatively short time.

Tantalum Carbide Powder. Tantalum carbide is prepared in about the same manner as titanium carbide. It can be produced either from the oxide or more suitably from the pure metal. Although the carbide has a much higher melting point than the metal itself, a carburization temperature of 1400 to 1600°C. (2550 to 2900°F.) is sufficient for the reaction For further details of tantalum carbide powder production, the reader is again referred to the paper by Brownlee, Geach, and Raine.[28b]

Other Single Carbide Powders. Making zirconium carbide involves heating of a mixture of zirconium oxide with lampblack to temperatures between 1900 and 2000°C. (3450 and 3650°F.). Columbium and vanadium carbides can be obtained by carburization of the trioxide or pentoxide—the high price of the pure metals making their use prohibitive. The preparation of uranium carbides by heating mixtures o uranium oxide and carbon is described in Chapter XXXII.

Multicarbide Powders. X-ray studies[30] dealing with determining the lattice constants of TiC, ZrC, VC, CbC, TaC, Mo_2C, and WC, and binary combinations thereof, have shown that carbides of the 4th, 5th, and 6th group metals of the periodic system apparently form, in all instances, complete solid solutions with the equivalent carbides of their

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[29b] G. F. Hüttig, discussion of V. Fattinger, *loc. cit.*

[30] H. Nowotny and R. Kieffer, *Metallforschung, 2,* 257 (Sept. 1947).

own group, as for example in the case of Mo_2C–WC and TaC–CbC[31]; or TaC–VC, CbC–VC, (TaCb)C–VC, and probably also TiC–ZrC.[31a] Similarly, most of the carbides of the metals of the 4th group apparently form complete solid solutions with the carbides of metals of the 5th group, as in the systems ZrC–TaC,[31] or ZrC–CbC, TiC–CbC, TiC–TaC, and TiC–VC, while VC and ZrC have only a very limited mutual solubility.[30,31a] (The complete solid solubility between TiC and TaC has recently been disputed by Brownlee, Geach, and Raine.[28b]) The solubility is also limited where carbides of metals of the 4th or 5th group are to be mixed with carbides of the 6th group, on account of a difference in crystal structure. Combinations of any one of these carbides with WC or Mo_2C indicate that the latter are always quite soluble in the other carbide, but never dissolve the other carbide, with the exception of combinations with TiC. Thus, it has been found that in the system TiC–Mo_2C, for example, the range of solid solution extends from 0 to 50% Mo_2C and again from 80 to 100% Mo_2C.[31] In the case of the system TiC–WC, the solubilities were determined as 70% WC in titanium carbide, and 5–10% TiC in tungsten carbide.[32]

The production of multicarbide powders constitutes a major part of the modern cemented carbide manufacture. There are several ways by which such powders can be obtained satisfatcorily: (*1*) carburizing of intimate mixtures of the metal oxides with lampblack; (*2*) carburizing of intimate mixtures of the refractory metals with lampblack; (*3*) diffusion heat treatment of intimate mixtures of individual carbides; (*4*) chemical separation of carbide solid solution ("mix"-) crystals from carburized complex ferroalloys; and (*5*) formation of multicarbides by solution of the metals and carbon in a menstruum of molten metal followed by chemical separation.

The first three methods are generally applicable for the formation of multicarbides of the systems WC–Mo_2C, WC–TiC, Mo_2C–TiC, WC–TaC, WC–Mo_2C–TiC and WC–TiC–TaC. The fourth method has been claimed to give good results in the case of TaC–CbC and WC–TiC.[33] The fifth process has been described by McKenna[34] in connection with the production of TaC, CbC, and multicarbides of WC with TiC. The carbide is formed above 2100°C. (3800°F.) in a menstruum of a molten metal, such as aluminum or nickel, which does not form stable carbides;

[31] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe.* Springer, Berlin, 1943, p. 281.

[31a] J. T. Norton and A. L. Mowry, *J. Metals, 1,* 133 (1949).

[32] H. Nowotny and G. Glenk, *Metallforschung, 2,* 265 (Sept. 1947).

[33] French Pats. 828,551; 846,617.

[34] P. M. McKenna, in J. Wulff, *Powder Metallurgy.* Am. Soc. Metals, Cleveland, 1942, p. 456.

the multicarbide powder is obtained by slow cooling in the menstruum followed by chemical separation.

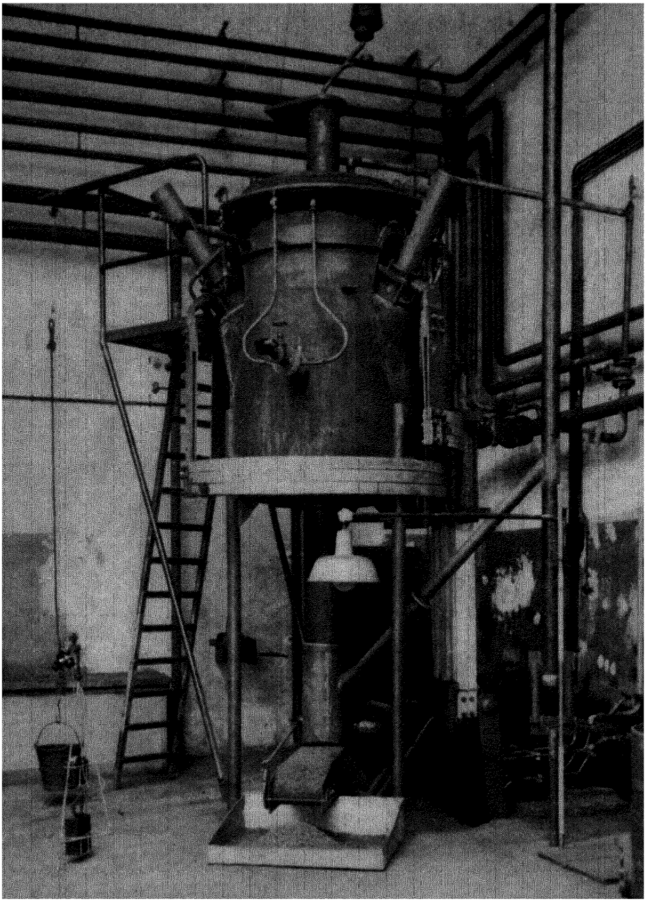

Fig. 332. Vertical three-phase 300-kw. electrode furnace for the continuous production of carbides and solid solution of carbides at temperatures up to 2500°C. (4520°F.) (according to Kieffer and Kölbl[34b]).

The high affinity of titanium carbide to gaseous impurities, especially oxygen and nitrogen, constitutes a major problem and requires careful

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[34a] M. Oswald, *Proc. International Powder Metallurgy Conference*, Graz, July 12–17, 1948. Referate No. 52.

[34b] R. Kieffer and F. Kölbl, *Proc. International Powder Metallurgy Conference*, Graz, July 12–17, 1948. Referate No. 28; *Powder Met. Bull.*, *4*, No. 1, 4 (1949).

control of the carbide powder manufacturing process (according to Oswald[34a] these impurities in the TiC lead to the development of CO and N during subsequent sintering with detrimental effects on the quality of the cemented WC–TiC products). Oswald therefore suggests elimination of these gases by treating the WC–TiC powder mixtures in vacuum at 2000°C. (3630°F.).

Brownlee, Geach, and Raine[28b] report that, in the manufacture of the tungsten carbide–titanium carbide solid solution (mix-crystal) powders, it is usual to make 50–50 to 65–35 WC–TiC compositions (the 50–50 mixture is generally preferred for reasons of economy). Tungsten carbide and titanium carbide powders are mixed together by ball milling for 4 hours. The mixture is loaded directly into the graphite crucible in the type of high-frequency vacuum furnace used in the manufacture of pure titanium carbide. The powder mixture is tamped down and heated for 2 hours at 1800°C. (3270°F.) to obtain complete solid solution. Cooling is performed under hydrogen at a pressure of a few centimeters Hg; the sintered cake is pulverized and graded by conventional means. The 50–50 "prealloyed" solid solution powder contains 13.0–13.2% total carbon, and 12.7–12.8% combined carbon. In order to arrive at the desired fiinal proportion of titanium carbide (*e.g.*, 16, 12, or 5%), cobalt powder, titanium carbide–tungsten carbide mix-crystals and excess tungsten carbide (with tantalum carbide added where required) are milled together in ball mills.

Kieffer and Kölbl[34b] have recently disclosed a continuous production method for multicarbide powders, employing a 300-kw., 3-phase vertical furnace of the type known as "Cryptal"–furnace, and reproduced in Figure 332 (for further details see Volume I, page 618).

NITRIDES

The production of nitrides of the metals titanium, zirconium, tantalum, columbium, vanadium, and hafnium is easily accomplished by heating the pure metals to 1100–1200°C. (2000–2200°F.), in nitrogen atmosphere. But inasmuch as these metals, with the exception of tantalum and columbium, are rather difficult to obtain in pure form, it is more practical to obtain the nitrides by heating metal oxide–carbon mixtures under nitrogen or dissociated ammonia gas above 1200–1300°C. (2200–2350°F.).[35] The nitrides thus obtained, however, are usually contaminated by carbides. With the stability of the nitrides and carbides of the metals of the 6th group of the periodic system apparently being inversely proportional, chromium nitride is still producible, with some technical importance ascribed to it,[34b] whereas molybdenum or tungsten nitrides are

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[35] K. Becker, *Z. Elektrochem.*, *34*, 640 (1928); *Z. Metallkunde*, *20*, 487 (1928).

definitely unstable.[35a] Generally speaking, however, the nitrides are not very suitable for the production of hard alloys for a number of reasons, including their insufficient hardness, a high partial pressure of nitrogen at the required sintering temperatures, and a tendency to form carbides under customary sintering conditions.[34b]

CARBO-NITRIDES

Certain carbides and nitrides form complex compounds, frequently called "carbo-nitrides." Of special interest have been the systems TiC–TiN and TaC–TaN—which appear to be of greater stability than other compounds of this general type—and Becker[35b] and Agte and Moers[35c] have studied these systems microscopically and by x-ray analysis. The double compounds were produced by first mixing the individual carbides and nitrides in different molecular ratios, and then heating the mixtures in the compacted state to near the fusion temperature under technical argon atmosphere (containing 12–15% nitrogen). While the system TaC–TaN apparently has only a limited solubility, if any,[35b] the system TiC–TiN has a continuous series of solid solutions, and titanium carbonitrides are readily formed. In fact, it is because titanium nitride is isomorphous with titanium carbide that from 1 to 3% TiN is found in many high titanium carbide products.[34b]

BORIDES

The borides of the metals of the 4th, 5th, and 6th groups of the periodic system display extreme hardness and good electrical conductivity. They can be produced by heating mixtures of the metal powder and boron powder in a high-frequency vacuum furnace to between 1800 and 2200°C. (3300 and 4000°F.), or by precipitation from the gaseous phase produced by an electric arc.[36] Other production methods are the aluminothermic reduction of mixtures of metal and boron oxides, and fusion electrolysis of mixtures of borax, metal oxides, and fluxes (such as calcium fluoride).

Manufacture of Cemented Carbides

While the manufacturing techniques for cemented carbides in their essential steps fall well within the framework of powder metallurgy

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[35a] K. Becker, *Hochschmelzende Hartstoffe und ihre technische Anwendung.* Verlag Chemie, Berlin, 1933, p. 30.

[35b] K. Becker, *loc. cit.*, pp. 86 ff.

[35c] C. Agte and K. Moers, *Z. anorg. allgem. Chem.*, *198*, 233 (1931).

[36] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe.* Springer, Berlin, 1943, pp. 281 ff.

operations in general, it has been due to the two decades of accumulated specialized experience in the production departments of the carbide manufacturers the world over that this phase of powder metallurgy has gained its mastery in the art. It is therefore not surprising that the high quality of many of the industrial cemented carbide products is based chiefly on the individual know-how of the manufacturers, and that the publicly known procedures only serve as a broad guide. Nevertheless, the available literature on the manufacture, properties, and uses of the industrially important cemented carbide compositions is by now very sizable, and much information of basic value can be obtained.

The manipulation and sintering of hard metals has been described in a recent paper by Burden,[37] which presents excellent advice on the proper choice of manufacturing equipment. Manufacturing details have been treated together with a survey of the properties and applications by Hull and Schwartz.[37a] Rose[37b] has presented an excellent review of the subject, with particular emphasis on conditions prevailing in the domestic industry; and T. A. Hood[37c] has published a comprehensive literature survey of American, British, and German manufacturing practices (the last from reports from Allied field investigators) with a view to encouraging the development of a cemented carbide industry in Australia.

PREPARATION OF POWDERS

The carbide powders are mixed with the auxiliary metal powders, cobalt or nickel, in a procedure requiring great skill and close control, especially with regard to particle size. Particle size measurements of carbide and binder are made regularly, and are used to control the milling and sintering operations.

The cobalt powder is of commercial grade, *i.e.*, 98 to 99% pure and all passing through a 200-mesh screen. It is obtained by the reduction with solid carbon or hydrogen of cobalt oxide or oxalate. The nickel powders suitable for cementing tantalum carbide containing hard metals are also of commercial grade, *i.e.*, 99% pure and 150 mesh and finer. The powder can be obtained either by reduction of the oxide or by comminution of shotted electrolytic nickel. Carbonyl nickel powder is

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[37] H. Burden, *Symposium on Powder Metallurgy,* The Iron and Steel Institute, Special Report No. 38, London, 1947, p. 78.

[37a] L. J. Hull and D. L. Schwartz, *Metals Handbook.* Am. Soc. Metals, Cleveland, 1948, p. 59.

[37b] K. Rose, *Materials & Methods, 29,* No. 2, 73 (1949).

[37c] T. A. Hood, *Information Circ. No. 12,* Commonwealth of Australia, Defense Research Laboratories, Canberra, November, 1947.

also suitable and has been used extensively in German hard metal manufacturing practices.

The carbide powders are milled with hard metal balls in wear-resistant mills (*e.g.*, with liners of stainless steel, Stellite, or tungsten carbide) or in other grinding equipment for the two-fold purpose of (*a*) reducing the powder to the desired particle size, and (*b*) facilitating the coating of each carbide particle with a more-or-less continuous layer of the softer binder metal. (A typical milling and screening installation has been shown in Figure 64 in Chapter VII, Volume I.) The milling operation may be carried out in two steps: preliminary grinding of the carbide alone, followed by milling of the carbide and binder metal together. If the carbide powders are produced to the desired size, no grinding is required, and milling of carbide and binder can take place at once.

The dry powders may be milled in air or a protective atmosphere (*e.g.*, hydrogen, cracked propane, nitrogen) or the powders may be milled in the presence of a liquid, such as water, benzene, or other organic solvents. Naturally, the powders will be subjected to some mechanical contamination from the mill, the balls, and the fluid medium. Contamination from the mill and oxidation of the powder are most pronounced in the presence of air, and least pronounced if milling is done in a hydrogen atmosphere,[38] or a special liquid protection. Iron and oxygen are the most important impurities encountered.

The time of milling varies between several hours and several days,[39] and is considered satisfactory only if the binder metal film can no longer be separated magnetically from the carbide particles.[40] If wet milling has been employed it is desirable to subject the powder to a subsequent reduction treatment in dry hydrogen at temperature between 600 and 700°C. (1100 and 1300°F.). It is important, however, that the reduction cycle is adjusted according to the particle size of the powder, since for increasingly fine sizes, decarburization of the tungsten carbide particles proceeds with rising temperature and increasing time at temperature.

Powders to be processed by the cold-pressing (and sintering) method are usually mixed with a lubricant such as paraffin, stearic acid, or camphor; 0.5 to 2% by weight is generally sufficient to make the powder easily moldable. The lubricant is added to the powder as a solution in a commercial solvent such as carbon tetrachloride, and intensive mixing produces surface films around the individual particles.

Of particular interest is the method of preparing carbide powder

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[38] O. Meyer and W. Eilender, *Arch. Eisenhüttenw.*, *11*, 545 (1937–38).

[39] E. W. Engle, in J. Wulff, *Powder Metallurgy*. Am. Soc. Metals, Cleveland, 1942, p. 437.

[40] S. L. Hoyt, *Trans. Am. Inst. Mining Met. Engrs.*, *89*, 9 (1930).

used in Germany during the war, and reported by Comstock in considerable detail.[41] The tungsten carbide powder was prepared by milling and grinding batches of 250 kg. tungsten and sugar carbon powders in vibrating steel ball mills, the carbon having been ground previously in the same type of vibratory mills with porcelain balls.[42] The vibratory-type mill reduced the milling time to about one-sixth of that necessary in ordinary rotating ball mills. The mixtures were pressed into briquettes in hydraulic presses; the briquettes were inserted into graphite containers and very effectively carburized in carbon-tube resistance furnaces. The resulting sinter cakes were broken down in jaw crushers and reduced to fine powder in impact mills. The binder metal powder was added and the mixtures made by wet-grinding 250-kg. batches in the vibratory mill. Hot-pressed cemented carbide balls were used for grinding. The wet mixtures were then vacuum-dried at 80°C. (175°F.) and subsequently reduced in vessels at 600°C. (1100°F.) in hydrogen atmosphere by rapidly stoking through multiple-tube hydrogen furnaces. Before pressing, the mixture was moistened with glycol, acetone, or methyl alcohol, or the usual camphor solution in benzene (70 g. camphor to 1 liter benzene; 350 mm.^{3} of this solution per 10 kg. of the powder mixture).

COLD-PRESS METHOD

Details of the cold-press method can be found in the papers by Engle[39] and Burden[37] and in the texts by Jones[43] and Kieffer and Hotop.[43a]

Molding. The carbide powder mixtures are generally cold pressed at pressures of 5 to 30 tsi in molds of hardened steel or cemented carbides. Depending on the size of the compact and the shape of the end product, high-tonnage hydraulic presses as well as quick-acting mechanical tableting presses are suitable equipment. Agglomeration of the ultrafine powder by briquetting and crushing may be necessary to assure flow into the die. Figure 333*A* shows the molding of a round blank in a hydraulic press, and Figure 333*B* illustrates the molding of small standard blanks in an automatic tableting press. Extreme care is also necessary in ensuring a *uniform* filling of the die cavity because of the poor flow characteristics of the powder under compression. The compression ratio of the powders is about 3:1, and multiple-level parts require split punches that are

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[41] G. J. Comstock, *Iron Age, 156,* No. 9, 36A (1945).

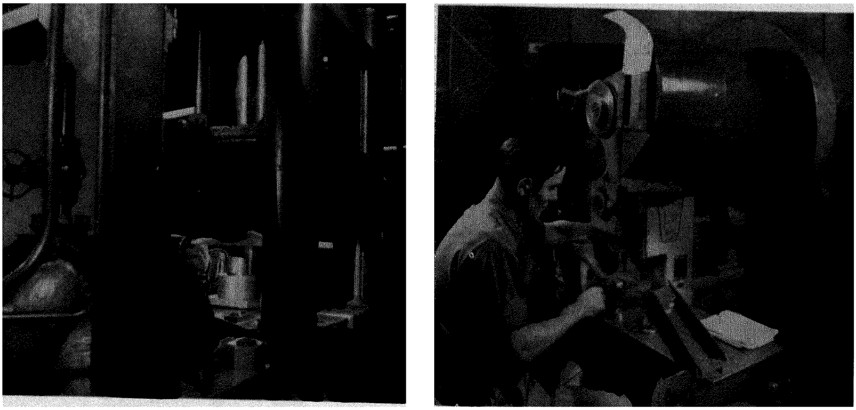
[42] British Intelligence Objectives Sub-committee, F.I.A.T. Final Report Nos. 617 and 754 (Nov. 1946 and Apr. 1947); see also *Met. Powd. Rept. 1,* No. 5, 78 (1947); No. 10, 146 (1947).

[43] W. D. Jones, *Principles of Powder Metallurgy.* Arnold, London, 1937, p. 161.

[43a] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe.* Springer, Berlin 1943, pp. 284 ff.

individually activated to permit the correct compression for each cross section. (For a description of the mechanics of molding with split punches see Volume I, Chapter IX.)

The direct molding of hard metal shapes is confined to fairly symmetrical forms. The process consists then of only three operations, namely, pressing, drying to evaporate the lubricant, and final sintering. More complicated shapes are obtained by pressing briquettes of a simple form and machining them to the desired contours. The photographs of Figure 334 *A–D* show a sequence of operations connected with the molding of a bar-shaped ingot in a heavy hydraulic press.

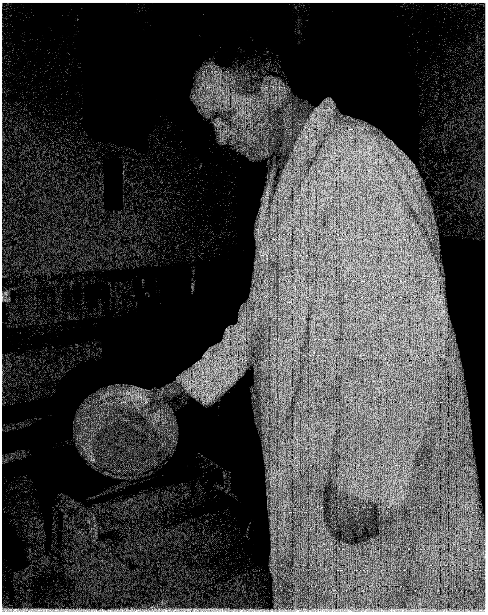


A *B*

Fig. 333. Molding of shapes from hard metal powder mixtures: *A*, forming of round ingot in large hydraulic press; *B*, forming of standard blanks in automatic tableting press (courtesy of Carboloy Co., Inc.).

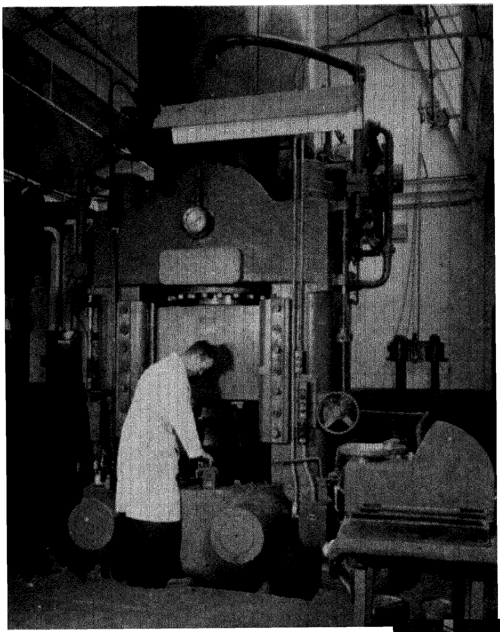
Presintering. In order to give the compacts sufficient strength for handling and shaping they are first heated to a temperature low enough so that only the binder metal produces sintering effects. Figure 335*A* illustrates the charging of the molded, standard blanks, and Figure 335*B*, of ingot bars in metal boats into the presintering furnace. Depending on the amount of cobalt present in hard metals containing tungsten carbide, the presintering temperature varies between 900 and 1000°C. (1650 and 1850°F.); the compacts that contain a larger proportion of cobalt permit a lower temperature. During this treatment the lubricant evaporates, but no important volume changes occur. The presintered compacts have a cohesive strength similar to that of chalk, which is sufficient for further handling.

A, accurate weighing of the carbide powder for each briquette; molded bars are in foreground.

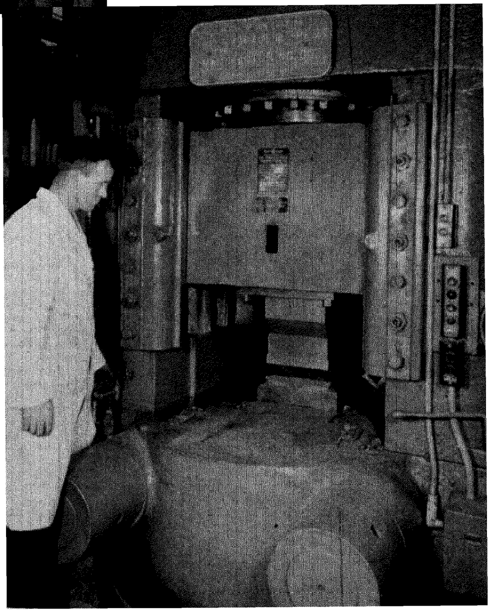


B, pouring of powder allotment into steel mold; the mold has several sections to permit ready extraction of the molded bar; it is held together by temporary clamps.

Fig. 334. Series of operations connected with the molding of a bar-shaped hard metal ingot in a 750-ton hydraulic press.



C, positioning of the mold assembly into the press.



D, **lowering of mold into opening of press bed prior to power-clamping it during the briquetting operation by means of a horizontally acting hydraulic ram.**

(Courtesy of A. C. Wickman, Ltd. and The Hydraulic Press Manufacturing Co.)

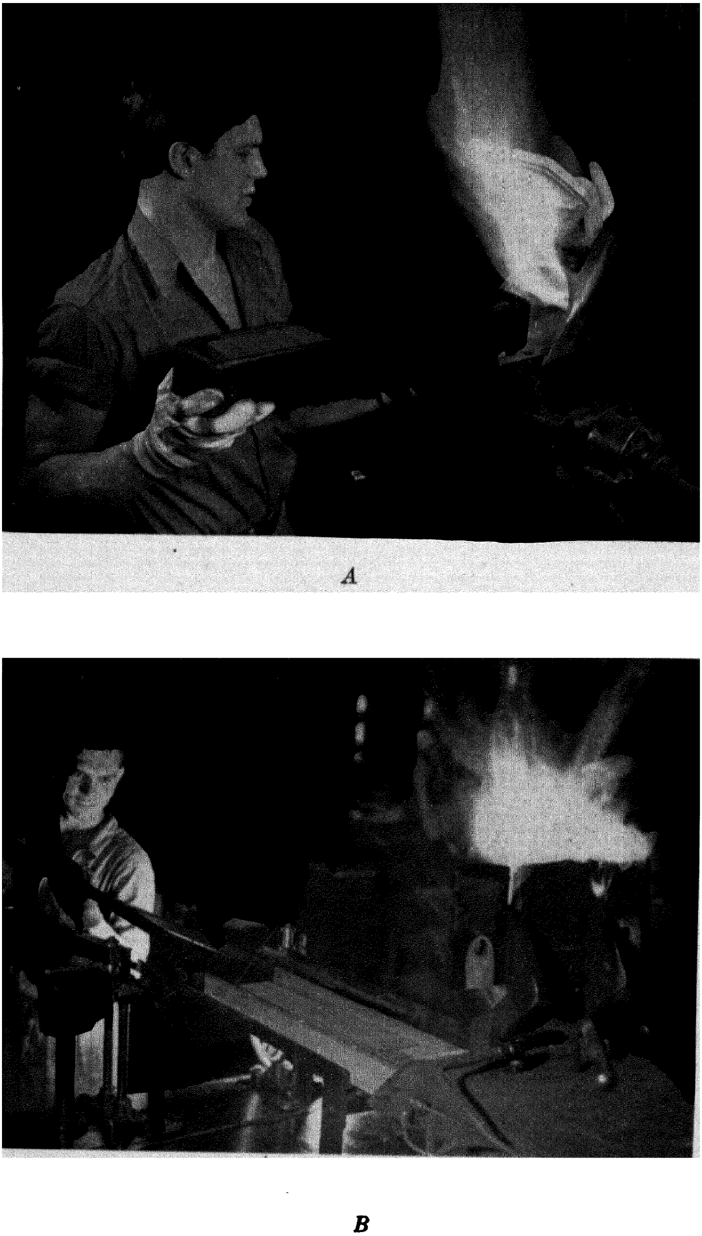
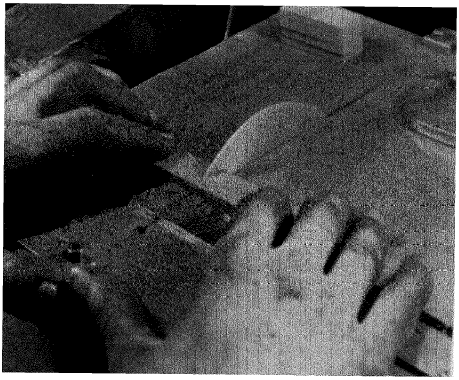
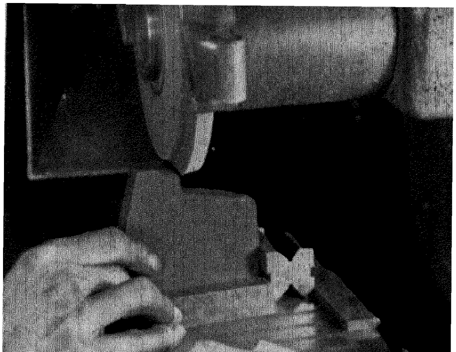


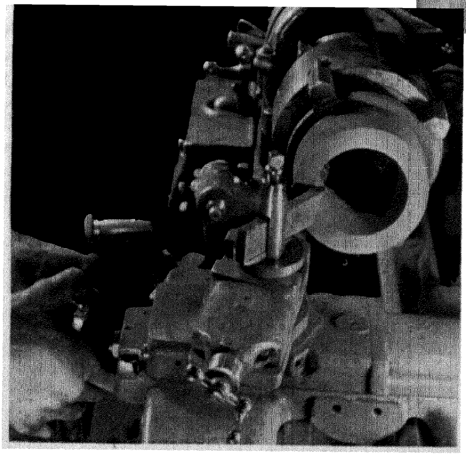
Fig. 335. Charging of the molded hard metal shapes in metal trays into presintering furnaces, equipped with protective flame curtains to prevent formation of explosive gas mixtures of air with the hydrogen in the furnaces: *A*, charging of standard blanks; *B*, charging of ingot bars (courtesy of Carboloy Co., Inc.).



A, cutting into smaller slabs with an abrasive or diamond cutoff wheel or saw.



B, grinding of profiles with an abrasive wheel.



C, turning or boring of annular shapes in a lathe.

Fig. 336. Forming of presintered hard metal blanks and ingots (courtesy of Carboloy Co., Inc.).

One procedure adopted in Germany during the war[43b] succeeded in eliminating presintering in favor of an addition of a 2.5% aqueous solution of polyvinyl alcohol to the hard metal powder mixture (12 drops per 100 grams); however, immediate pressing of the mixture was necessary because of rapid hardening.

Fig. 337. Forming of presintered tungsten carbide slabs into the shape of small tool tips by means of a diamond saw (courtesy of A. C. Wickman, Ltd. and The Hydraulic Press Manufacturing Co.).

Forming. The presintered hard metal compacts are formed into the desired shapes by cutting and grinding operations as shown in Figures 336 and 337. Silicon carbide cut-off wheels or diamond saws cut the briquettes into smaller slabs (Fig. 336*A*) and finally into small plates and blocks (Fig. 337), out of which profiled shapes such as tool tips and

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[43b] British Intelligence Objectives Sub-committee, Document F. D. 1179/46; see also *Met. Powd. Rept.*, *1*, No. 5, 75 (1947).

drill bits, etc., are obtained by cylindrical or profile grinding (Fig. 336*B*). Annular shapes are obtained by turning or boring in a lathe (Fig. 336 *C*). All shapes must be considerably overdimensioned (15 to 25% linearly) in order to allow for the appreciable shrinkage of the hard metal during sintering.

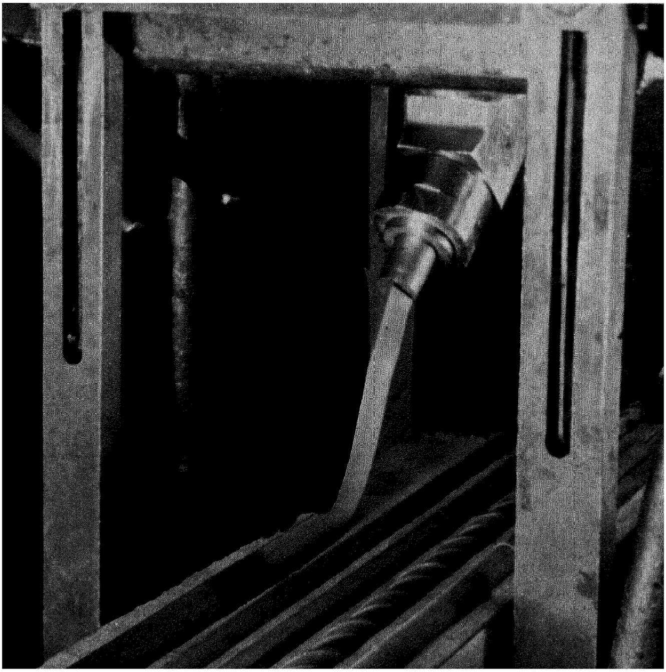

Fig. 338. Extrusion of hard metal powder paste through shaped nozzles into triangular cross section. For comparison, half-round, square, twist-drill, and tubular cross sections are placed next to the extruded rod. (Courtesy of Carboloy Co., Inc.)

Extrusion Forming. A deviation from the regular cold-press method of molding is the direct production of profiled shapes by extrusion.[39,44] The production method is similar to the paste process originally developed for the plain refractory metals, the hard metal powder mixture being extruded with the aid of organic binders that are volatilized during sintering. This method enables the production of pieces of greater length and better uniformity in section throughout their length. Shapes thus produced include rods, tubes, flats, angles, half-rounds,

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[44] U. S. Pat. 2,414,029.

Fig. 339. Loading of presintered hard metal shapes into graphite boats. Careful spacing prevents sticking together during subsequent sintering. (Courtesy of Carboloy Co., Inc.)

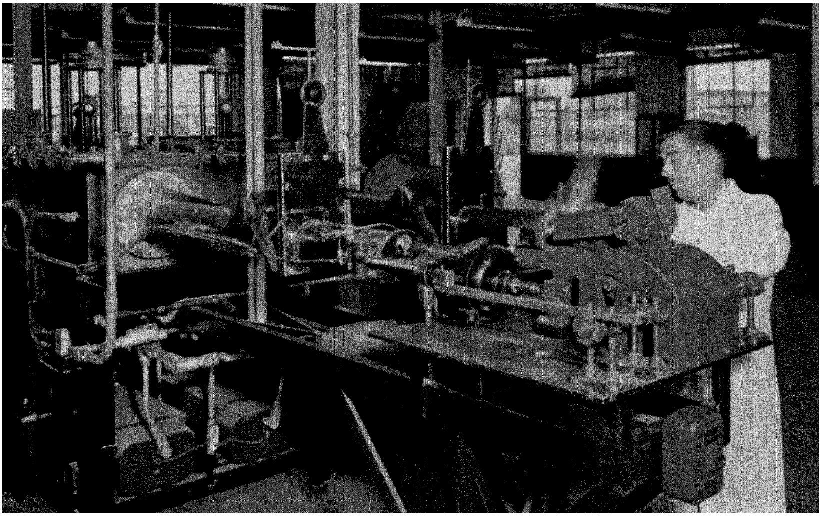

Fig. 340. Charging of a graphite boat containing carbide tips into a pusher-type continuous sintering furnace (courtesy of A. C. Wickman, Ltd. and The Hydraulic Press Manufacturing Co.).

and even twist-drill forms. Figure 338 illustrates the extrusion operation by which the hard metal powder paste is formed into a triangular shape.

Sintering. The sintering operation imparts to the hard metal compacts their final physical characteristics, the mechanism of the process involving partial fusion, solution, and reprecipitation. The sintering temperatures vary between 1350 and 1550°C. (2450 and 2800°F.); the time at temperature is usually held between 1 and 2 hours. Both batch and continuous sintering methods are used; in the former, the charge is placed in the cool furnace, heated to temperature, kept for a specified time, and allowed to cool; in the latter, the material is placed in trays which are transported slowly by stoking along zones of gradually increasing temperature until final sintering is attained, after which the charge is pushed into a cooling chamber. In Figure 339 the loading of a graphite boat is shown, and in Figure 340, the charging of a boat into the sintering furnace. During the entire sintering operation the charge must be protected against oxidation and decarburization by surrounding it with a neutral or reducing atmosphere. Usually, hydrogen is used in the presence of carbon. The three types of furnaces are (*1*) Alundum-tube muffle furnaces with molybdenum resistor elements; (*2*) carbon-tube short-circuiting furnaces, and (*3*) high-frequency induction furnaces. In the first instance, the preformed compacts are placed in Alundum or graphite boats and covered with a mixture of Alundum and graphite powder; in the second, they are simply placed on graphite slabs. During induction sintering the carbide pieces are placed on graphite disks that are properly spaced and supported by a central trunk; the pieces are arranged so that they are always equidistant from the crucible walls and trunk, thus ensuring uniform heating by radiation from the heated crucible. Radiation shields above and below prevent an undue temperature gradient in the longitudinal direction, and a tightly fitting graphite cover retains the hydrogen atmosphere in the crucible.

Figure 341 gives a view of the sintering furnace department in a large hard metal manufacturing company.

During the sintering operation, marked shrinkage occurs which usually amounts to between 12 and 25% of the linear dimensions. A sound material is characterized by a uniform shrinkage, so that the initial forming can compensate effectively for these dimensional changes. But even if the dimensions and the density remain fairly uniform, the presence of objectionable impurities may cause defects such as porous areas, large voids, pits, or cracks. Minute porosity is generally encountered in hard metal obtained by the cold-press method, and may be caused by solid or gaseous impurities in the powder, unsatisfactory mixing and milling practices, limitations of the molding technique, or improper heating and improper furnace conditions. However, for many commercial applications this slight porosity is not objectionable. (For the microstructure of sintered carbide materials the reader is referred to Figure 231, Volume I, Chapter XIV and to Figure 343, page 116, this volume.)

HOT-PRESS METHOD

In producing low-porosity, uniformly dense and very hard alloys, the hot-press method is preferable. Hot pressing of cemented carbides has already been broached in Chapter XIII, Volume I. In this method, which is also described in detail by Engle,[45] Jones,[43] and Kieffer and Hotop,[46] the pressing and sintering operations are carried out simultaneously. Two methods of applying pressure are practicable: either the pressure is gradually increased during heating of the compact until it reaches a maximum at sintering temperature; or the full pressure is practically instantaneously applied *after* the powder in the mold has been heated to the peak temperature. Heat is generated by direct passage

Fig. 341. View of sintering furnace department for the manufacture of cemented carbides (courtesy of Carboloy Co., Inc.).

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[45] E. W. Engle, in J. Wulff, *Powder Metallurgy*. Am. Soc. Metals, Cleveland, 1942, p. 436.

[46] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe*. Springer, Berlin, 1943, pp. 140 ff., 288.

of the current through the slightly compacted powder between graphite electrodes, by heating the hot-press mold by its resistance, or by heating the mold externally in a resistance or induction furnace. The temperatures are similar to those used for sintering after cold pressing. The pressures are only a fraction of those used for cold pressing, usually ranging from about 500 to 2500 psi. The upper pressure limit is given by the strength and wear of the graphite mold and by the tendency of the binder metal to squeeze out and extrude between mold and plungers. On the other side, the pressure must be high enough to prevent deformation of the compact through shrinkage, and to ensure a material entirely free from pores. The hardness of such products may then exceed that of cold-pressed and sintered carbides by 1 to 3 Rockwell A units. The microstructure of hot-pressed cemented carbide has already been shown in Figure 171, Volume I, Chapter XII.

TABLE 108

Characteristics of Hot-Pressed Cemented Carbides (Kieffer and Kölbl[34b])

Group of periodic system	Composition	Rockwell hardness "A"	Transverse rupture strength, psi	Density, g./cc.	Color of fracture
4	90% TiC, 10% Co	92	114,000	4.9	Mouse-gray
	90% ZrC, 10% Fe	91 –	114,000	6.8	Light gray
5	90% VC, 10% Co	89	100,000	5.4	Silvery
	90% CbC, 10% Co	88	142,000	7.7	Brownish violet
	90% TaC, 10% Co	85	107,000	13.0	Golden-yellow
6	90% Cr_3C_2, 10% Ni	84–85	71,000	5.7	Silvery
	90% Mo_2C, 10% Co	87	85,000	8.6	Light silvery
	90% WC, 10% Co	91+	260,000	14.4	Bluish gray

During the war the hot-press method was developed to a high state of perfection in Germany.[47,48] The equipment used was of the graphite resistance type, the spring-clamped mold being the resistor; a separate mechanical or hydraulic system applied the pressure for the top and bottom punches; the pressures varied between 1150 and 1700 psi. By controlling the final volume of carefully weighed prepressed charges having a constant apparent density, the loss in binder was greatly reduced, though not entirely eliminated. In hot pressing a mixture with an original binder content of 13%, the binder loss could be controlled consistently within 2%. The excessive wear of the graphite dies and plungers could

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[47] G. J. Comstock, *Iron Age, 156,* No. 9, 36A (1945).

[48] G. J. Trapp, B. E. Berry, H. Burden, A. E. Oliver, and T. Raine, *Symposium on Powder Metallurgy,* The Iron and Steel Institute, Special Report No. 38, London 1947, p. 92.

be effectively reduced by employing thin-walled cylinders or other tube forms broached from graphite, which were pressed into heavier graphite mold containers. These units were replaced after use with a minimum discard of reclaimable graphite. In order to minimize plunger movement during pressing, the powder mixture was pressed into the temporarily reinforced graphite molds under heavy hydraulic pressure before hot pressing. The production cycle was so accelerated that finished, hot-pressed mold charges could be produced in about 3–7 minutes for pieces from 50 to 1000 g. in weight.

The characteristics of a variety of hot-pressed cemented carbides is reproduced in Table 108, according to Kieffer and Kölbl.[34b]

A critical analysis of the properties obtained with this procedure, however, has disclosed that the German grades have been inferior in strength and cutting properties to the American products developed during the war.[49]

Mechanism of Cementing

SINGLE CARBIDE SYSTEMS

Cobalt–Cemented Tungsten Carbide. During the last two decades a comprehensive study has been made of the physico-chemical phenomena that occur during the sintering of cemented carbides. With testing methods, such as metallography, x-ray investigations, chemical analyses, and thermal analyses, the equilibrium conditions of the main components of the hard metals (*e.g.*, the ternary system of tungsten, cobalt, and carbon) have been clarified, and the temperature established at which a liquid phase exists. The analytical work has been aided by squeezing out the binder at peak hot-press temperatures and analyzing the limits of solubility of the carbides in the binder metal. Debye-Scherrer investigations have helped in determining the structure of the carbide phases (*e.g.*, double carbides, solid solutions, etc.).

Before going into more details of the cementing process, it should be understood that the equilibrium conditions in a hard metal obtained during the process of cementing minute carbide particles with a liquid metal binder are different from those that occur during cooling of the completely fused alloy. In the latter case the carbides are partially destroyed through precipitation of free graphite. If, for example, a mixture of 95% WC and 5% Co is fused, a heterogeneous alloy solidifies, whose constituents include free graphite, a solid solution of tungsten and cobalt, and a mixture of the carbides W_2C and WC, with the latter con-

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[49] P. M. McKenna, *Iron Age, 157,* No. 6, 64 (1946).

taining small amounts of cobalt in solid solution.[50] The free graphite and metallic tungsten–cobalt alloy constituents materially deteriorate the physical properties of the hard metal, whose excellent cutting and wear properties depend entirely on the complete preservation of the tungsten carbide within the cementing mass of the binder metal. Only heat treatment of the alloy below the melting point of the carbides can prevent their decomposition, and, hence, only those equilibrium conditions are of interest that exist at temperatures at which either the entire alloy is solid or only a limited liquid phase exists.

The sintering mechanism of cemented carbides was first investigated by Hoyt,[51,52] and by Wyman and Kelley.[53] Hoyt established by thermal analysis that during sintering of tungsten carbide–cobalt compacts, a liquid (eutectic) phase is formed at approximately 1350°C. (2450°F.), *i.e.*, below the melting point of pure cobalt (1495°C.; 2723°F.). This observation was confirmed by Wyman and Kelley, who demonstrated that the depression in melting point is caused by a partial solution of tungsten carbide in cobalt. The binder metal was extracted by squeezing during a hot-press experiment at about 1500°C. (2750°F.), and analyzed 27.5% WC. After regular cooling of the compact, most of the dissolved tungsten carbide is precipitated and deposited on the undissolved particles, the tungsten carbide content in the binder being reduced to about 4% at the solidification temperature of about 1275°C. (2325°F.), and to less than 1% at room temperature. Even after very rapid cooling of sintered cobalt–tungsten carbide compacts, the segregation of tungsten carbide from the cementing phase takes place so suddenly that neither a eutectic structure nor very fine tungsten carbide deposits in the cobalt are detectable with a microscope (see Figure 231*A* and *B*, Chapter XIV, Volume I and Figure 343*A*, page 116, this volume).

The results of Wyman and Kelley were substantiated several years later by Takeda,[54] who investigated the equilibrium conditions of the systems W–Co–C, W–Ni–C, and W–Fe–C. In sintering tungsten carbide–cobalt containing 6% Co, the latter commences to liquefy at 1400°C. (2550°F.) after 1.5% WC has been dissolved in the metal. At this temperature complete liquefaction of the cobalt is obtained after

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[50] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe.* Springer, Berlin, 1943, p. 289.

[51] S. L. Hoyt, *Trans. Am. Soc. Steel Treating, 14,* 695 (1928); *17,* 54 (1930); *18,* 1 (1931).

[52] S. L. Hoyt, *Trans. Am. Inst. Mining Met. Engrs., 89,* 9 (1930).

[53] L. L. Wyman and F. C. Kelley, *Trans. Am. Inst. Mining Met. Engrs., 93,* 208 (1931).

[54] S. Takeda, *Science Report Tôhoku Imp. Univ.,* First Ser., Honda Anniv. Vol., 864 (1936).

the tungsten carbide concentration has increased to about 20%. During prolonged sintering at the same temperature, the liquid phase continues to dissolve the tungsten carbide until a saturation value of 38% is reached. Under these conditions, the liquid phase amounts to about 10% by weight of the compact, *i.e.*, about twice the initial amount of the auxiliary metal.

Aside from the desirability of having the greatest possible ductility imparted by the binder metal, the cementing mechanism in the tungsten carbide–cobalt system promotes a controlled grain growth through the solution of the smallest tungsten carbide particles followed by a redeposition on the larger particles, which transform mostly into rectangular or triangular shapes. This redeposition tends to take place preferentially at the contact points between the particles, increasing the area of contact and also the cohesive strength of the compact. The carbide skeleton may also be strengthened by preferential dissolution of very small tungsten carbide particles, minute projections, or needlelike surface irregularities which normally would interfere with the formation of large contact areas between the carbide particles. Thus, it may be assumed that the strength of the sintered hard metals does not depend so much on the cementing action of the binder material that holds the carbide particles in place, but rather on the formation of a strong carbide skeleton during the sintering and especially during the cooling process. By dissolving the cobalt in hydrochloric acid, Dawihl[55] has shown that a sintered tungsten carbide skeleton retains a large share of the strength of the original cemented carbide alloy (see also page 112).

The mechanism of sintering, initially established by Wyman and Kelley, has been essentially corroborated by Sandford and Trent[56] in their discourse on the physical metallurgy of sintered carbides. With cobalt contents of 3 to 25% the final sintering temperature ranges from 1500–1350°C. (2730–2460°F.) and is always above the WC–Co eutectic. Figure 342 shows the approximate pseudo-binary tungsten carbide–cobalt system, according to Sandford and Trent. With rising sintering temperature, marked changes begin to take place above 1150°C. (2100°F.) and considerable solubility of tungsten carbide in cobalt accompanied by shrinkage takes place before the eutectic temperature (1320°C.; 2408°F.) is reached. However, shrinkage proceeds irregularly, and cobalt and porosity remain unevenly distributed. At the eutectic temperature a liquid phase is formed containing about 35% WC, and shrinkage continues at an accelerated rate by the action of surface

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[55] W. Dawihl, *Z. Metallkunde, 32,* 320 (1940); also *Z. Tech. Physik, 21,* 44, 336 (1940); *Stahl u. Eisen, 61,* 210 (1941).

[56] E. J. Sandford and E. M. Trent, *Symposium on Powder Metallurgy,* The Iron and Steel Institute, Special Report No. 38, London, 1947, p. 84.

tension forces. During subsequent cooling, tungsten carbide is deposited on to the existing carbide crystals without eutectic formation. Both the carbide and the cobalt tend to form continuous interwoven networks, with cobalt in the form of large grains up to 1 mm. In case of excess carbon content, graphite may be precipitated in harmful proportion. If the carbon content is too low, a double carbide of tungsten and cobalt appears (η phase) and causes a reduction of the transverse rupture strength of the material.

The complete ternary equilibrium diagram of the W–C–Co system is not yet known with accuracy, and a number of complex phases appear probable. Brownlee[56a] has recently made an attempt to establish the form of the ternary system tungsten–carbon–cobalt by examining a series of sintered alloys by x-ray diffraction. Since the alloys examined were necessarily at room temperature, it cannot be taken for granted that the results obtained are truly representative of the constitution of the alloys at the sintering temperature of 1350°C. (2460°F.) chosen for the investigation. A close approximation to the true state of equilibrium at this temperature permitting the construction of a ternary diagram is, however, indicated by the fact that sintering was performed for various times to reach equilibrium and cooling was done rapidly—in some instances by quenching—in order to retain the state of equilibrium as much as possible. The

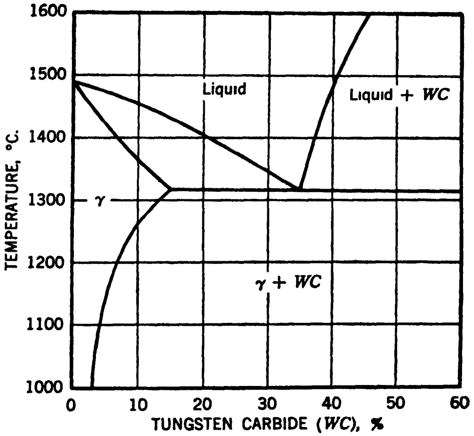

Fig 342. Approximate pseudo-binary tungsten carbide–cobalt equilibrium diagram (according to Sandford and Trent[56]).

[56a] L. D. Brownlee, *Proc. International Powder Metallurgy Conference,* Graz, July 12–17, 1948, Referate No. 15.

diagram shows a large area that is liquid at 1350°C. (2460°F.), a very large three-phase region WC + C + liquid, and a series of phase fields in the tungsten-rich corner of the system. The tungsten–cobalt double carbide (Co_3W_3C) single-phase region, η, with its complex crystal structure, is shown in its proper location, but the diagram does not include the W_2C phase. The existence of the two compounds, Co_2W_4C and Co_6W_6C, reported by Kislyakova[56b] on the basis of x-ray data could not be confirmed in more recent x-ray investigations by Metcalfe[56c] that indicate the existence of only the single phase corresponding to the compound Co_3W_3C.

Lately, however, some doubt has been cast on the original concepts of the carbide sintering process. Dawihl[57] disagrees with the theories of Takeda insofar as the function of the cobalt is concerned. Although experimental evidence is still incomplete, Dawihl holds that cobalt acts (*a*) as a pressing lubricant (*b*) as a binder during sintering, in which instance it facilitates the exertion of *adhesive* forces that are stronger than the cobalt itself, rather than functioning as a brazing or cementing material.

Dawihl and Hinnüber[58] have advanced the theory that the extreme hardness and wear resistance of the hard metals are caused primarily by a network or skeleton structure of tungsten carbide; this strength can be ascertained by dissolving and removing the binder metal.[55] Additional support for this theory was sought in expansion, rupture, and metallographic tests.

Mantle[59] has suggested that the formation of a special structure in the cobalt matrix (in which tungsten carbide grains are accommodated) is responsible for a change in the "optimum" sintering temperature with the cobalt content. This optimum sintering temperature at which maximum physical properties for each cobalt content were recorded, was found to decrease regularly with increasing cobalt content, reaching a minimum of 1305°C. (2380°F.) with 25% Co, followed by an increase up to 1325°C. (2420°F.) for 35% Co. Density and transverse rupture strength increase directly to peak values for 25% Co, and decrease again for higher cobalt contents. These findings are neither consistent with those

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[56b] E. N. Kislyakova, *Zhurnal Fizicheskoy Khimii, 17,* No. 2, 108 (1943).

[56c] A. G. Metcalfe, *unpublished work,* quoted by E. J. Sandford and E. M. Trent, *Symposium on Powder Metallurgy,* The Iron and Steel Institute, Special Report No. 38, London, 1947, p. 84.

[57] British Intelligence Objectives Sub-committee, Final Report No. 925 (Sept. 1947).

[58] W. Dawihl and J. Hinnüber, *Kolloid-Z., 104,* 233 (1943).

[59] E. C. Mantle, *Metal Treatment, 14,* 141 (1947).

of Takeda nor with those of Dawihl and Hinnüber. The eutectic temperature noted by Takeda is very close to the minimum sintering temperature for 25% Co, but no eutectic was observed and, according to Wyman and Kelley, would not be found with cobalt contents below 55%. On the other hand, the carbide network concept of Dawihl and Hinnüber does not account for the increase in transverse rupture strength with rising cobalt content as found in Mantle's experiments. Also, sintering up to 90 minutes failed to produce the network structure.

Sandford[60] takes issue with the Wyman-Kelley theory of grain growth, supported by Mantle, and maintains that it is inadequate to explain the magnitude of crystal growth that may occur under certain conditions. Instead, it is held that crystals similarly oriented are capable of coalescing into grains of considerably larger size. Sandford also comments on the formation of cobalt pools that can be observed in the alloys during the initial stages of sintering and on their subsequent dispersion with progressive sintering.

Recent reports from Germany have discussed the sintering mechanism of a 94–6 tungsten carbide–cobalt alloy by correlating the extent of recrystallization with changes in the cobalt content dissolved in the tungsten carbide grains,[61] and with changes in the magnetic saturation of the alloy after various stages of manufacture.[62] The degree of fineness of the carbide powder was found to have a profound influence on the recrystallization—as determined by metallographic means—and the magnetic saturation of the material—as measured on cooled specimens after presintering at 900°C. (1650°F.) and after final sintering at 1200, 1300, 1400, and 1500°C. (2190, 2370, 2550, and 2730°F.). In the coarser grade (made from powder of conventional particle size) recrystallization during sintering takes place to a markedly greater extent than in material prepared from especially fine tungsten powder. Also, the normal-size powder grade shows a marked decrease in the magnetic saturation values in the range from 900–1200°C. (1650–2190°F.), but recoups the loss at higher sintering temperatures. No such decrease of saturation at low sintering temperatures occurs with ultrafine material. These results can only be interpreted as a confirmation of the prevailing concepts that the recrystallization of tungsten carbide takes place by way of dissolution in the binder metal and subsequent reprecipitation, and that this sequence

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[60] E. J. Sandford, *Metal Treatment, 14,* 239 (1947).

[61] U. S. Department of Commerce, Office of Technical Services, P.B. 70489, Report No. 133 (F.I.A.T. Microfilm Reel No. 56, frames 2198–2200).

[62] U. S. Department of Commerce, Office of Technical Services, P.B. 70489, Report No. 132 (F.I.A.T. Microfilm Reel No. 56, frames 2201–2203).

of dissolution and reprecipitation is mainly responsible for the cementing mechanism.

Of certain interest in this connection is the fact that the precipitated tungsten carbide crystals may become saturated with cobalt during this sintering process. While tungsten carbide crystals which are not recrystallized can be assumed to contain no dissolved cobalt, the magnetic measurements indicated that recrystallized tungsten carbide may be saturated with cobalt. The solubility limits for cobalt in tungsten carbide—as determined by extrapolation of the magnetic saturation–cobalt concentration curves—were established as 0.1–0.15% at 1400°C. (2550°F.) and approximately 0.2% at 1500°C. (2730°F.). The determination of the cobalt solubility limit was believed of practical significance in that substantial solubility would have interfered with the magnetic analysis of the compound Co_4W_2C (referred to as *delta* phase[63]); the determined maximum solubility of 0.2%, however, lies well within the accuracy limit of the magnetic method, thus eliminating the possibility of an interference.

Taking these comparatively recent observations as a basis, Kieffer[63a] has advanced a modified and, in some respects, novel mechanism for sintering cobalt-cemented tungsten carbide. Upon heating above the liquefaction point of the ternary W–Co–C and the binary Co–C eutectics (1280 and 1315°C.; 2335 and 2400°F., respectively) the liquid phase wets the carbides and penetrates into the pores and capillaries of the carbide crystal agglomerates. At first, this process may be considered a soldering action of the cobalt on the primary carbide crystals; at higher temperatures, however, the cobalt is built into the lattice of the recrystallized WC particles. Kieffer terms this approach to the structure of the ideal crystal as a "healing" of the highly active WC primary crystals, maintaining that it is responsible for the unusually pronounced strength increase effected by the binder. The liquid phase dissolves the bridgelike bonds between the original WC crystals that were formed during presintering. Under the influence of surface tension forces, the WC agglomerates wetted by the cobalt assume the densest possible packing, resulting in gross shrinkage phenomena. At this stage the original WC particles (α) have been transformed into rounded, slightly recrystallized crystals (α_1). The formation of a solid solution permits bonding at the contact points of the densely packed α_1 crystals, resulting in a

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[63] U. S. Department of Commerce, Office of Technical Services, P.B. 70489, Report No. 131 (F.I.A.T. Microfilm Reel No. 56, frames 2205–2213).

[63a] R. Kieffer, communication on "Theoretical Aspects of Sintering of Carbides," *Symposium on the Physics of Powder Metallurgy,* sponsored by Sylvania Electric Products, Inc., Bayside, L. I., N. Y., August 24–26, 1949.

skeleton of WC which increases in strength with time of sintering. Recrystallization and grain growth caused by this increase in time, and also by a rise in temperature to the conventional level of 1375–1550°C. (2500–2820°F.), changes the rounded α_1 crystals into well-recrystallized, angular α_2 crystals. Upon cooling, WC is separated from the ternary eutectic of the liquid phase, and is precipitated at the surface of the WC (α_1 and α_2) crystals or at the WC bridges, which act as traps. Finally, the cobalt-rich solid solution solidifies. In accordance with this mechanism, Kieffer characterizes the structure of cobalt-cemented tungsten carbide as a more or less developed skeleton of α_1 and α_2 solid solutions of WC which have formed from α crystals, and the interstices of which are filled with the cobalt-rich solid solution.

Nickel– and Iron–Cemented Tungsten Carbide. In contrast to the cobalt–cemented tungsten carbide alloys, the systems containing nickel or iron behave somewhat differently. Takeda[54] found that in these systems the cementing metal dissolves tungsten carbide during sintering analogously to the cobalt-containing alloys. Upon cooling, however, the dissolved carbide is precipitated only to a negligible extent. Consequently, sintered tungsten carbide alloys with nickel or iron contain as binder metal a solid solution of tungsten carbide in nickel or iron, respectively, which is considerably more brittle than the practically pure cobalt in the WC–Co alloy.

Nickel–Cemented Tantalum Carbide. Nickel has been found most satisfactory in connection with tantalum carbide. No definite explanation has yet been advanced for this fact, since no equilibrium diagram has yet been established for the system Ta–Ni–C, but it has been suggested[64] that the type of precipitation from the liquid phase (*i.e.*, the deposition of carbides instead of free graphite and metal) may be chiefly responsible for the better performance of nickel in the case of tantalum carbide.

Cobalt– and Nickel–Cemented Titanium Carbide. Kieffer and Kölbl[64a] have investigated both nickel and cobalt as binder material for binary and ternary titanium carbide-base alloys free of tungsten carbide. From the available data it appears that nickel effects better bonding and therefore results in superior transverse rupture strength in most instances (for some of the physical properties obtained, see Table 123, page 142) and is therefore preferable for tool materials (see also page 78). Good cementing properties have also been reported from Germany with a

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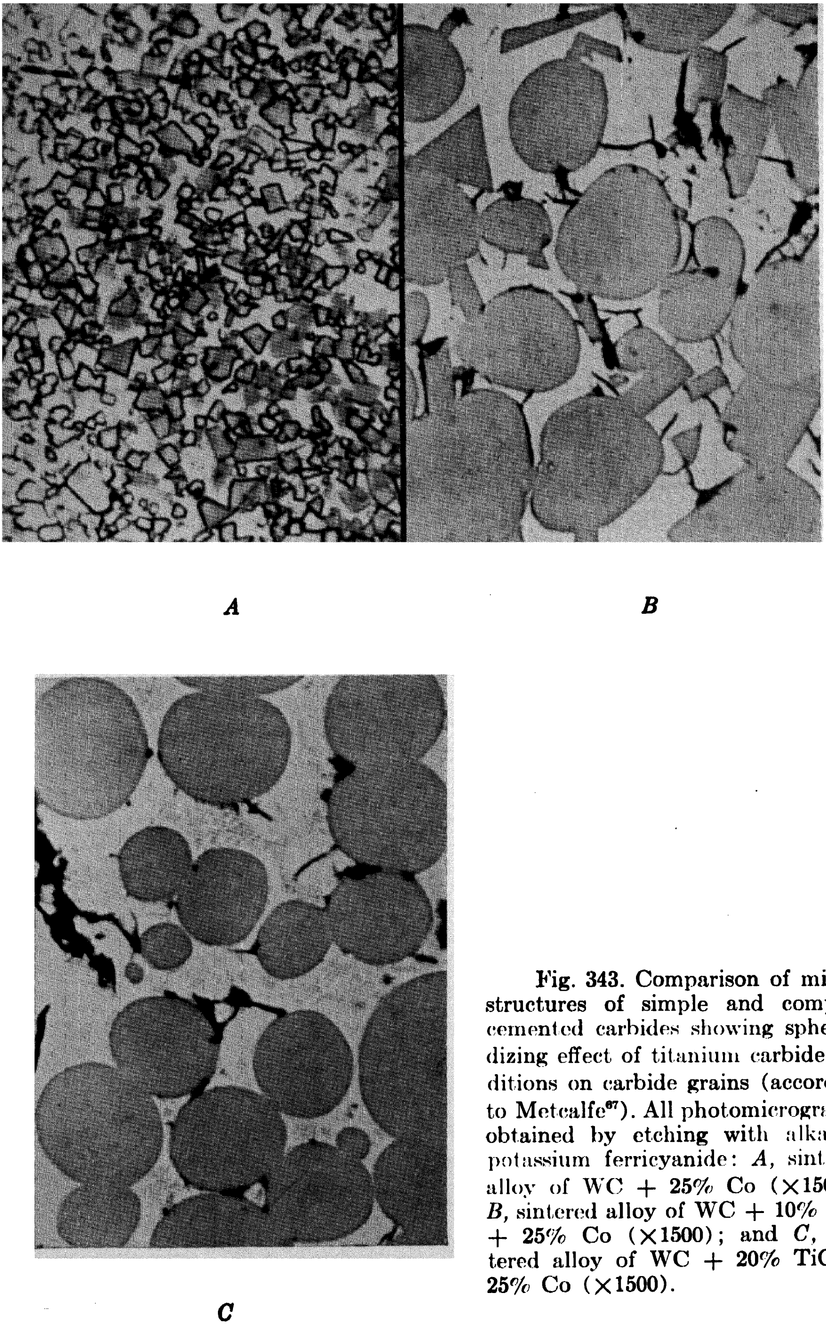
[64] F. Skaupy, *Kolloid-Z.*, *98*, 29 (1942); *102*, 269 (1943).

[64a] R. Kieffer and F. Kölbl, *Proc. International Powder Metallurgy Conference*, Graz, July 12–17, 1948, Referate No. 28; *Powder Met. Bull.*, *4*, No. 1, 4 (1949).



A *B*

C

Fig. 343. Comparison of microstructures of simple and complex cemented carbides showing spheroidizing effect of titanium carbide additions on carbide grains (according to Metcalfe[67]). All photomicrographs obtained by etching with alkaline potassium ferricyanide: *A*, sintered alloy of WC + 25% Co (×1500); *B*, sintered alloy of WC + 10% TiC + 25% Co (×1500); and *C*, sintered alloy of WC + 20% TiC + 25% Co (×1500).

70–30 Ni–Co alloy for titanium carbide–vanadium carbide compositions.[64b] Similar development work in this country has shown that cobalt as cementing agent results in surprisingly strong binary titanium carbide alloys, especially at elevated temperatures,[64c] and, according to Bobrowsky,[64d] the cementing action of cobalt is considerably more effective over that of other metals, such as tungsten or molybdenum.

MULTIPLE-CARBIDE SYSTEMS

The conditions prevailing during sintering of multiple-carbide systems are not basically different from those discussed for the single-carbide alloys. Cobalt is the only satisfactory binder metal for combinations that include tungsten carbide, *i.e.*, most multiple-carbide compositions of commercial importance (*e.g.*, WC–TiC–Co).

The sintering mechanisms of the industrially important WC–TiC–Co hard metals is of a more complex nature than that described for the WC–Co alloys. According to Meerson and coworkers,[65] tungsten carbide and titanium carbide are dissolved by the cobalt, and upon cooling are precipitated as a solid solution. At the points at which this WC–TiC solid solution is deposited on titanium carbide particles, diffusion causes a transformation of the entire particle into a uniform phase consisting of a solid solution of tungsten carbide and titanium carbide, but where this solid solution is deposited on tungsten carbide particles, tungsten carbide is dissolved only in part in the newly precipitated layer of solid solution. The extent of this partial solution depends on the solubility of tungsten carbide in titanium carbide under the prevailing conditions, but the solution is not complete. Metcalfe,[66] on the basis of x-ray diffraction data (more recently supported by electrical resistance measurements[66a]), found that this solubility was 74% by weight at 1400°C. (2550°F.), 79% at 1500°C. (2730°F.), and 82% at 1600°C. (2910°F.). In Figure 343*A–C*, photomicrographs of several different multicarbide compositions are reproduced from another recent study by Metcalfe.[67]

The structure of sintered WC–TiC–Co alloys has also been studied

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[64b] G. J. Comstock, *Metal Progress, 46,* 117 (1946).

[64c] J. C. Redmond and E. N. Smith, *J. Metals, 1,* 987 (1949).

[64d] A. R. Bobrowsky, *Trans. Am. Soc. Mech. Engrs., 71,* No. 6, 621 (1949).

[65] G. A. Meerson, G. L. Zverev, and B. E. Osinovskaya, *Zhurnal Priklad. Khimii, 13,* No. 1, 66 (1940); *Metal Ind., London, 59,* 306 (1941).

[66] A. G. Metcalfe, *Metal Treatment, 13,* 127 (1946).

[66a] A. G. Metcalfe, *Proc. International Powder Metallurgy Conference,* Graz, July 12–17, 1948, Referate No. 14.

[67] A. G. Metcalfe, *J. Inst. Met., 73,* 591 (1947).

extensively by Kieffer,[68,69] who developed a new metallographic method for this purpose. The procedure employed by Kieffer involves the production of a coarse grain structure of the carbide phase by fostering recrystallization and pronounced grain growth. This is followed by a special selective etching treatment which permits the distinction of the different carbide phases that might be present. (After etching with a mixture of hydrofluoric and nitric acids, the specimens are treated first with an alkaline ferricyanide solution and then for a half-hour with a hydrogen peroxide solution of phosphoric acid, followed by a brief immersion in a dilute ammonium sulfide solution.) The metallographic evidence thus obtained is in agreement with the x-ray diffraction data on the mutual solid solubility of carbide systems and confirms that at room temperature tungsten carbide is capable of dissolving up to 5% TiC, while titanium carbide can dissolve up to 70% WC.

A novel method of microexamination of the structure of titanium carbide containing hard metals—involving heat tinting—has recently been reported by Burden.[69a] The specimen with the polished side on top either was immersed in molten white metal at 400°C. (750°F.) for 15 minutes or was heated in an electric muffle furnace which permitted direct observation. The method apparently does not enable distinction of the actual grain boundaries, but contrasts the cobalt phase from the carbide grain structure.

According to Dawihl,[70] four basic crystal forms of carbides can be distinguished metallographically: (*1*) the rectangular prism of tungsten carbide; (*2*) the rounded prisms of titanium, vanadium, and molybdenum carbides; (*3*) the rectangular prism with rounded edges of tantalum carbide; and (*4*) the meniscus-shaped crystals into which rounded crystals are formed during hot pressing. The formation of rounded crystals is believed to be aided by impurities in the space lattice which would tend to diminish the interatomic forces to such an extent that they become smaller than the surface tension forces. The German nomenclature of phases of the W–TiC–Co system includes the following:

α: This represents normal tungsten carbide crystals; it may be either in a very finely divided form which has not recrystallized (α_1) or in a recrystallized form with well-developed angular crystals (α_2). The mechanical properties of these two

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[68] R. Kieffer, *Z. Metallkunde, 36,* No. 9 (1944); see also *Powder Met. Bull., 2,* No. 5, 104 (1947).

[69] R. Kieffer, *Metallforschung, 2,* 236 (1947).

[69a] H. Burden, *Proc. International Powder Metallurgy Conference,* Graz, July 12–17, 1948, Referate No. 12.

[70] British Intelligence Objectives Sub-committee, Final Report, No. 925 (Sept. 1947); see also *Met. Powd. Rept., 2,* No. 4, 61 (1947).

varieties are quite different, corresponding to the grades **H-1** and **H-2** of Table 121 (page 139). The α_1 variety can only be made from a fine and uniformly sized fraction of WO_3 plus 0.2% VC.

β: This represents the cobalt binder with 10% dissolved WC.

γ: This represents titanium carbide crystals with tungsten carbide dissolved in the surface layers (WC–TiC mix-crystals). With excessively long sintering, the elongated "chain" crystals break up into aggregates of small globular crystals (γ_1).

δ: This represents complex carbides of the form Co_3W_3C or Co_4W_2C; they may include chromium (δ_1) picked up from chromium steel or stainless steel balls or mills used for the powder preparation.

ϵ: This represents a white network which is present when WC crystals group into large crystals as revealed by electrolytic etching in caustic potash solution.[58]

Kieffer,[63a] in his recent analysis of the mechanism of sintering of carbides in the presence of a liquid binder (cobalt) alloy, distinguishes similar phases; he chooses, however, to designate the cobalt solid solution as γ phase, the titanium carbide-base mix-crystals as β phase, and the complex cobalt–tungsten double carbides as η phase.

A factor of considerable importance in the sintering of the complex WC–TiC–Co hard metals is the oxide content of the industrial grades of titanium carbide powders. This oxide impedes the surface contact ("wetting") between the liquid binder and the titanium carbide particles, and requires generally higher sintering temperatures. Furthermore, a considerable amount of carbon monoxide is evolved which results in a somewhat porous product. Only if the powder is produced from TiO_2 and lampblack in a vacuum furnace can a completely oxygen-free powder be obtained. WC–TiC–Co alloys prepared from such oxygen-free titanium carbide have been found flawless and completely dense; they can be sintered at temperatures as low as 1350°C. (2450°F.) *i.e.*, near the lowest sintering temperature possible for the cementing of plain tungsten carbides.[65,71]

Properties of Sintered Carbides

EFFECTS OF COMPOSITION AND PROCESSING CONDITIONS ON PHYSICAL PROPERTIES

Methods of Testing. The physical properties of cemented carbides depend entirely on their composition and production conditions. Whether produced by the hot-press method or by cold pressing and sintering, the material assumes its final physical characteristics at the conclusion of the last treatment. The properties of the material must then conform to the standards adopted by the industry for various grades. Chemical

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[71] P. Schwarzkopf, *Powder Metallurgy*. Macmillan, New York, 1947, p. 198.

composition, cutting properties, and physical properties (density, hardness, and transverse rupture strength) must be controlled carefully to assure a high quality product.

Constant and careful surveillance of the powdered carbide products and mixtures containing the binder metals is a prerequisite for the manufacture of a satisfactory end product; hence, physical testing of particle (grain) size and chemical analysis of combined and free carbon in the carbide powder, and of binder metal in the mixture ready for pressing, are routine control tests. Methods and results of grain size measurements on tungsten and tungsten carbide powders were recently reported by Burden and Barker.[71a]

Control of composition requires continuous analytical work. Loss of binder metal is as objectionable as undue increases in the ratio of free to combined carbon, since these elements are chiefly responsible for deterioration in hardness, strength, and cutting properties. Full details of the methods employed in the analyses of simple and complex tungsten carbides and cemented carbide compositions were published by Furey and Cunningham, [71b] and Touhey and Redmond,[71c] respectively. A chlorine method for the determination of nitrogen in titanium carbide and cemented carbide composition was developed in Germany.[71d]

A first indication of possible change in composition may be obtained by density determinations, for the density of sintered carbides almost coincides with the theoretical value obtained by the rule of mixed proportions. In many compositions, a value above the theoretical indicates loss of binder metal, because metals of the iron group have a lower specific gravity than the carbides of tungsten or tantalum; only where titanium carbide is involved, is this conclusion invalid, because titanium carbide is much lighter than either the other carbides or the binder metals. Density determinations also serve as a measure of the completeness of the sintering operation and of the attainment of the necessary degree of shrinkage.[71e]

For close examination of the extent of porosity, the density measurements are too crude, and a microscopic study of a ground and polished face of a fractured hard metal piece becomes necessary. Diamond cut-off wheels and diamond polishing powder are used in the preparation of the

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[71a] H. Burden and A. Barker, *J. Inst. Metals, 75,* Pt. 2, 51 (1948).

[71b] J. J. Furey and T. R. Cunningham, *Anal. Chem., 20,* 563 (1948).

[71c] W. O. Touhey and J. C. Redmond, *Anal. Chem., 20,* 202 (1948).

[71d] Studiengesellschaft Hartmetall, B. O. T. German Div. (Documents Unit), F. D. 3745/47; see also *Met. Powd. Rept., 2,* No. 9, 136 (1948).

[71e] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe.* Springer, Berlin, 1943, p. 294.

metallographic specimens. The microstructure at high magnification is best revealed after etching in an alkaline solution containing potassium ferricyanide (5% KOH, 5% $K_3Fe(CN)_6$).[72] Etching first with a mixture of HF and HNO_3 then with $K_3Fe(CN)_6$, and finally for 30 minutes with a H_2O_2 solution acidified by H_3PO_4 has been recommended by Kieffer[72a] for tungsten–titanium double carbide materials (see also page 118). Zarubin[72b] has recently investigated the effect on WC–Co, Mo_2C–Co, and TaC–Co of various etching reagents, including 1:1 of 10% $K_3Fe(CN)_6$ and 10% NaOH solution, 2:1 of concentrated HF and concentrated HNO_3, 10% ethyl alcohol solution of HNO_3, 1:1 of concentrated HNO_3 and glacial acetic acid, 8% ammoniacal solution of $CuCl_2$, and aqua regia. Electrolytic etching as well as heat tinting have been reported successfully employed by the Krupp-Widia works in Germany [72c]; the last mentioned procedure, which involves production of superficial oxide layers by heating in air at about 400°C. (750°F.) for 30–60 minutes has been described in detail by Burden[72d] and Franssen.[72e] Prolonged heating (e.g., 120 hours) at 1500°C. (2730°F). has been recommended by Kieffer[72f] as a means of producing pronounced grain growth of the carbide phase, which facilitates etching and microscopic examination.

The hardness of the cemented carbide material is one of the most important measures of its quality—a very high hardness being extremely desirable. Rockwell hardness testers with diamond indentors are generally favored for simplicity, in spite of the fact that a decrease in accuracy of the Rockwell test for increasing hardnesses makes the use of the diamond pyramid hardness test more advisable.[73] (See also Chapter XXXIV.)

Most commercial grades of cemented carbides are tested on the Rockwell "A" scale (60-kg. load) to avoid danger of fracturing by an excessive test load; the hardness values usually vary from 85 to 93 for this scale. For extremely hard compositions, a still lower test load may

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[72] E. W. Engle, in J. Wulff, *Powder Metallurgy.* Am. Soc. Metals, Cleveland, 1942, p. 436.

[72a] R. Kieffer, *Z. Metallkunde, 36,* No. 9 (1944); see also *Powder Met. Bull., 2,* No. 5, 104 (1947).

[72b] N. B. Zarubin, *Zavod. Lab., 14,* 1434 (1948).

[72c] British Intelligence Objectives Sub-committee, Final Report No. 1694 (April 1948); see also *Met. Powd. Rept., 2,* No. 10, 153 (1948).

[72d] H. Burden, *Proc. International Powder Metallurgy Conference,* Graz, July 12–17, 1948, Referate No. 12.

[72e] H. Franssen, *Arch. Eisenhüttenwesen, 19,* 79 (1948).

[72f] R. Kieffer, *Z. Metallkunde, 36,* No. 9 (1944); *Powder Met. Bull., 2,* No. 5, 104 (1947).

[73] W. Dawihl, *Z. tech. Physik, 21,* 336 (1940).

be preferable, and the Rockwell Superficial tester would have to replace the regular machine. A hardness conversion chart published by Scott and Gray[74] is reproduced in Table 284 in Chapter XXXIV.

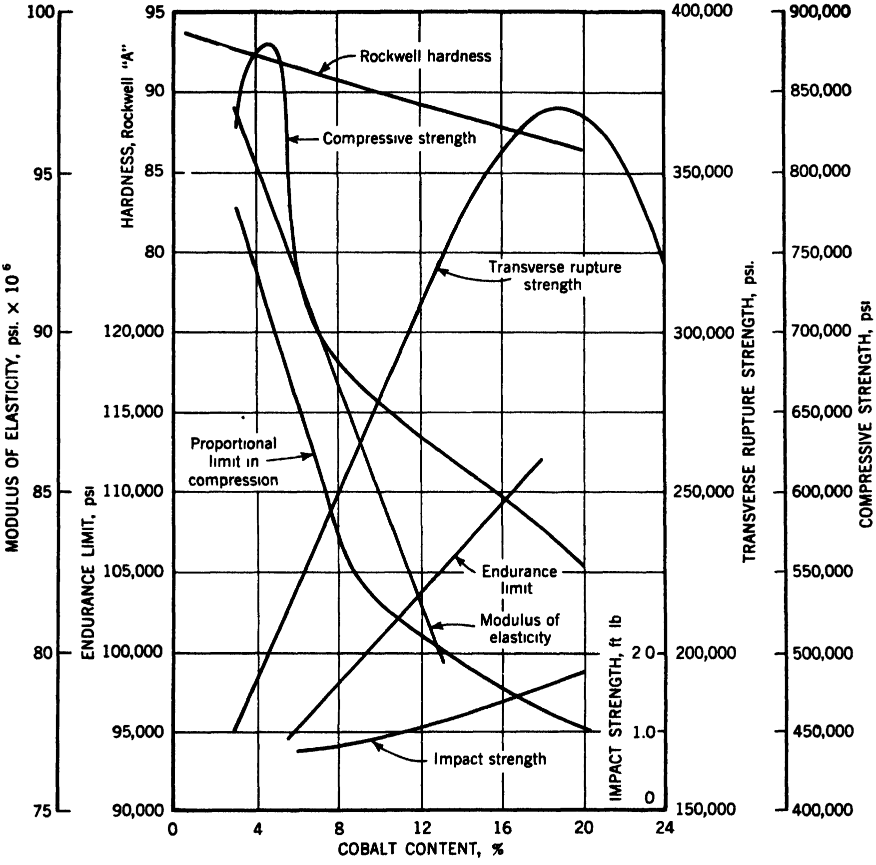

Fig. 344. Variation in physical properties of tungsten carbide with increasing relative amount of cobalt binder (according to Engle[72]).

The strength and toughness of the hard metal are generally tested by transverse rupture, a breaking load being applied to the specimen halfway between two supports. Special test specimens must be prepared for this test, and the size adjusted to avoid shear failures. Rectangular bars with a $^1/_4$-in.-square cross section or a $^1/_4 \times {}^3/_{16}$-in. rectangular cross section are commonly used[72]; the length of the specimen is in the

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[74] H. Scott and T. H. Gray, *Trans. Am. Soc. Metals*, *28*, 399 (1940).

order of 2 to $2^1/_2$ in., and the supports are spaced $1^1/_2$ to 2 in. apart. A smaller specimen, 0.200 by 0.375 in. in cross section, supported between line centers $^9/_{16}$ in. apart, has also been suggested.[75]

Changes in the constitution of the ingredient carbide powders and the cemented carbide products, such as caused by varying the type or allotment of the raw materials, adding other refractory metals or compounds, or changing pertinent factors of the sintering cycle, are determined effectively by such sensitive physical testing methods as x-ray diffraction work,[67,75a,75b] magnetic testing,[62,75c,75d] and measurements of electrical resistance.[66a] These testing methods, however, are strictly for research purposes, and not suitable for routine production control work.

Cemented Tungsten Carbides. The physical properties of the tungsten carbide–cobalt hard metals are decidedly influenced by the binder metal content. This becomes apparent from Figure 344, where Engle's findings[72] have been entered in the form of a diagram, and also from Table 109, where the physical properties of compositions containing 3, 4.5, 6, 8, 9, 11, 13, and 20% Co are compared with those of pure tungsten carbide and cobalt, respectively. Hardness decreases steadily from Rockwell A 91–93 for compositions up to 6% Co to about A 88 for 13% Co and about A 85 for 20% Co, while the transverse rupture strength increases steadily with rising cobalt content until a maximum of nearly 400,000 psi is reached for the composition containing 20% Co. Other noteworthy physical properties include an extremely high modulus of elasticity (reaching nearly 100,000,000 psi) and high compressive strength (approaching 1,000,000 psi). Although some grades of sintered carbides indicate slight ductility under compression, permanent distortion before fracture is very slight. The fatigue strength is comparable with that of hardened tool steel (85,000–105,000 psi). The impact strength of the WC–Co compositions is extremely low for grades with low cobalt content, but increases somewhat with increasing percentage of binder metal. Unnotched specimens of $^1/_4$-in. square cross section containing 94% WC and 6% Co have a Charpy impact strength of only 0.73 ft. lb., but this value increases to 1.10 ft. lb. for a composition

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[75] P. M. McKenna, in J. Wulff, *Powder Metallurgy*. Am. Soc. Metals, Cleveland, 1942, p. 454.

[75a] L. D. Brownlee, *Proc. International Powder Metallurgy Conference*, Graz, July 12–17, 1948, Referate No. 15.

[75b] P. W. Penrice, *Proc. International Powder Metallurgy Conference*, Graz, July 12–17, 1948, Referate No. 73.

[75c] H. Krainer, *Proc. International Powder Metallurgy Conference*, Graz, July 12–17, 1948, Referate No. 31.

[75d] British Intelligence Objectives Sub-Committee, Document F. D. 1179/46; see also *Met. Powd. Rept.*, *1*, No. 5, 75 (1947).

TABLE 109. Physical Properties of Sintered Tungsten Carbide–Cobalt Hard Alloy Compositions

Co content, %	Density, g./cc.	Hardness, Rockwell "A"	Transverse rupture strength, psi	Com-pressive strength, psi	Charpy impact strength, ft.-lb.	Young's modulus of elasticity, psi × 10^6	Thermal conductivity, cal./cm./sec./°C.	Coeff. of thermal expansion × 10^{-6}	Specific electrical resistance, microhm-cm. at 20°C.	Reference
0	15.60 15.52^a	91.0–94.0	42,500–64,000	—	—	102.8	—	—	—	*m, n*
3	15.25	91.0–93.0	125,000	—	—	97.5	0.19	—	—	*e, f, g*
	15.04	—	170,000	815,000	—	—	—	—	21.3	*k*
	15.15 15.32^a	89.0–91.0	130,000–170,000	—	—	—	—	—	21.0	*m*
4.5	15.05	92.3	200,000	890,000	—	90.5	—	—	—	*e, g*
6	14.7	90.0–92.0	205,000	680,000	0.73	88	0.9	5.0^b	21.1	*e, f, g*
	14.85	—	234,700	730,000	—	89	0.21	—	20	*h, k*
	14.82	—	225,000	604,000	—	—	—	—	21	
			227,500	750,000	—	—	—	—	—	
	14.80 15.13^a	90.0–91.0	185,000–242,000	—	—	78.5	0.19	5.0^c	20.0	*m, n*
8	—	85–89	—	—	—	—	0.21	5.0^b	20–25	*j*
9	14.56 14.60	88.5–91.0	—	685,000	—	—	—	—	22.3	*e, g, k*
	14.56 15.02^a	89.0–90.0	215,000–256,000	—	—	—	—	—	19.0	*m*
11	14.0	—	263,000	540,000	—	82	0.16 (12% Co)	5.5^b	18	*f, i*
	14.30 14.62^a	88.0–89.0	230,000–270,000	—	—	75.0 (10% Co)	0.16	5.5^c	18.0	*m, n*

Co content, %	Density, g./cc.	Hardness, Rockwell "A"	Transverse rupture strength, psi	Compressive strength, psi	Charpy impact strength, ft.-lb.	Young's modulus of elasticity, psi × 10^6	Thermal conductivity, cal./cm./sec./°C.	Coeff. of thermal expansion × 10^{-6}	Specific electrical resistance, microhm-cm. at 20°C.	Reference
13	14.10	87.0–89.5	300,000	540,000	1.10	80	0.652	5.9^b	19 6	*e, f, g*
	14.15	—	—	625,000	—	—	—	—	16 (12% Co)	*k, l*
	14.20 14.62^a	87.0–88.0	248,000 (20°C., 68°F.) 195,000 (800°C., 1470°F.) 180,000 (850°C., 1560°F.) 150,000 (900°C., 1650°F.)	—	—	—	—	$6\ 0^d$	20.0	*m*
20	12.54 13.55	85.0–87	350,000	550,000	1.75	—	—	—	—	*e, g, k*
	12.54 14.14^a	83.0–84.0	—	—	—	61.0	—	—	30 0	*m, n*
100	8.62 8.62^a	60.0–63.0	100,000–115,000	—	—	—	0.13–0.16	—	6 0	*m*

[a] Calculated value.

[b] Average between range of 20–700°C. (68–1290°F.).

[c] Average between range of 20–800°C. (68–1470°F.).

[d] Average between range of 20–400°C. (68–750°F.).

[e] A. McKenzie, *Metals Handbook*, 1939, pp. 909–917.

[f] F. W. Leier, *Hartmetalle in der Werkstatt.* Springer, Berlin, 1937, p. 6.

[g] E. W. Engle, in J. Wulff, *Powder Metallurgy.* Am. Soc. Metals, Cleveland, 1942, p. 446.

[h] W. Dawihl, *Z. Metallkunde*, *32*, 320–325 (1940).

[i] J. Hinnüber, *Stahl u. Eisen*, *62*, 1086 (1942).

[j] O. Meyer and W. Eilender, *Arch. Eisenhüttenw.*, *11*, 545 (1938).

[k] K. Becker, *Hochschmelzende Hartstoffe.* Verlag Chemie, Berlin, 1933, pp. 106, 112.

[l] S. L. Hoyt, *Gen. Elec. Co., Res. Lab., No. 535* (1930).

[m] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe.* Springer, Berlin, 1943, p. 296.

[n] Determined by W. Köster and W. Rauscher, *unpublished.*

containing 87% WC and 13% Co, and to 1.75 ft. lb. for a composition containing 20% Co.

The effect of impurities and particle size of WC–Co mixtures milled under various conditions upon the hardness of sintered carbides was determined by Meyer and Eilender[76] and their results are reproduced in Table 110. A study of the effect of molding pressure on the ultimate hardness was carried out on some powders (Nos. 4, 6, and 7 of Table

TABLE 110
Relation Between Powder Characteristics and Hardness of Cemented Tungsten Carbide Sintered at 1500°C. (2730°F.) (Meyer and Eilender[76])

Powder No.	Composition, % C	Co	Fe	Si	Cr	Particle size, μ	Type of comminution	Pressure, tsi	Hardness, Rockwell "A"
1	5.5	7.95	0.18	—	—	200–60	Mortar-ground and sieved	57.0	—
2	5.5	7.95	0.18	—	—	60–25		57.0	68.0
3	5.5	7.95	0.18	—	—	25–15		57.0	70.5
4	5.5	7.95	0.18	—	—	15–0		57.0	78.5
5	5.4	8.05	0.44	—	—	75% smaller than 6 μ	Milled 12 hr. under H_2	5.7	83.5
6	5.34	8.15	0.60	0.04	—	75% smaller than 4 μ	Milled 30 hr. under H_2	5.7	89.0
7	5.25	7.56	3.86	0.10	1.09	75% smaller than 3 μ	Milled 30 hr. under H_2 and 48 hr. under H_2O	1.4	92.0

TABLE 111
Effect of Pressure on Hardness of Cemented Tungsten Carbide (Meyer and Eilender[76])

Powder No. 4[a]		Powder No. 6[a]		Powder No. 7[b]	
Pressure, tsi	Hardness, Rockwell "A"	Pressure, tsi	Hardness, Rockwell "A"	Pressure, tsi	Hardness, Rockwell "A"
21.5	71.0	0.7	87.0	0.15	89.0
28.5	72.0	1.4	87.0	0.3	92.0
35.5	75.0	2.8	87.5	0.5	90.5
42.5	77.0	4.3	87.5	0.7	91.0
57.0	76.5	5.0	88.0	1.4	91.5
71.0	76.5	5.7	89.0	14.2	89.5
106.5	75.0	6.4	88.0		
		7.1	87.5		
		14.2	87.5		
		21.3	86.0		
		35.5	85.0		

[a] Sintered at 1500°C. (2730°F.).
[b] Sintered at 1400°C. (2550°F.).

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[76] O. Meyer and W. Eilender, *Arch. Eisenhüttenw.*, *11*, 545 (1938).

110), with the results noted in Table 111. A definite hardness maximum was found for each powder. When plotting hardness against sintering temperature, similar maximum values could also be detected at a temperature range from 1400–1500°C. (2550–2730°F.), and for about a half-hour sintering time, as shown in the diagrams of Figure 345.

Meyer and Eilender have also confirmed the improvement of the hardness with the hot-press method as established earlier by Hoyt.[77] The Rockwell "A" hardness of a compact prepared from the powder No. 7 (see Table 110) by hot-pressing at about 1300–1350°C. (2350–2450°F.) and at pressures of about 500 psi reached a value of 95.6, while the hardness of the same powder after cold pressing and sintering did not exceed 92.

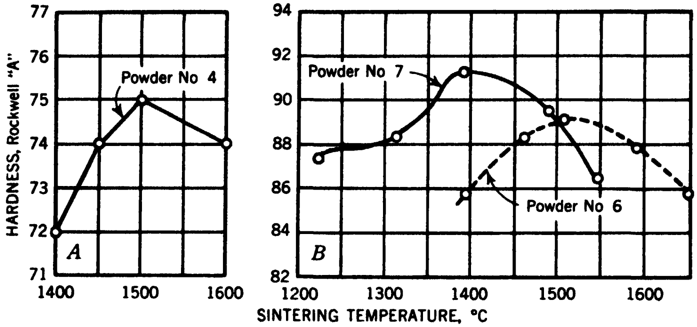

Fig. 345. Effect of sintering temperature on the Rockwell "A" hardness (according to Meyer and Eilender[76]): *A*, diagram for powder No. 4 as specified in Table 110; and *B*, diagram for powders Nos. 6 and 7 as specified in Table 110.

In a detailed study of the effect of optimum conditions during sintering on the physical properties of WC–Co compositions, Meerson and Shabalin[78] confirmed the superiority of hot-pressed material, although the actual hardness and density values obtained are below those reported by Hoyt. The results for specimens obtained by hot pressing are given in Table 112. The hardness and density of the specimens were taken after holding the compacts at the hot-pressing (sintering) temperature for 3 minutes, and also after resintering at 1400°C. (2550°F.) for 90 minutes. Meerson and Shabalin concluded that the values for maximum hardness and transverse rupture strength are obtained together with optimum cutting properties at 1450°C. (2640°F.) for WC–Co hard alloys whose

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[77] S. L. Hoyt, *Trans. Am. Inst. Mining Met. Engrs.*, *89*, 9 (1930).

[78] G. A. Meerson and V. I. Shabalin, *Tsvetnye Metally*, *3*, 77 (1940); *Metal Ind., London*, *59*, 50 (1941).

TABLE 112

Physical Properties of Hot-Pressed Tungsten Carbide – Cobalt Alloys (Meerson and Shabalin[78])

Composition, %		Hot-pressing temperature		Hot-pressing time,[a] min.	Annealing temperature,		Annealing time, min.	Hardness, Rockwell "A"	Specific gravity	
WC	Co	°C.	°F.		°C.	°F.			Actual	Calculated[b]
96	4	1450	2640	3	—	—	—	90–90.5	14.98	15.03
		1450	2640	3	1400	2550	90	91–91.5	14.99	15.03
94	6	1450	2640	3	—	—	—	89.5–90	14.80	14.81
		1450	2640	3	1400	2550	90	90–90.5	14.81	14.81
92	8	1425	2600	3	—	—	—	87.5–88	14.61	14.59
		1425	2600	3	1400	2550	90	88.5–89.5	14.60	14.59
90	10	1425	2600	3	—	—	—	83–84	[c]	14.37
		1425	2600	3	1400	2550	90	85–86.5	[d]	14.37
87	13	1400	2550	3	—	—	—	80–81	[e]	14.07
		1400	2550	3	1400	2550	90	82–83	[f]	14.07

[a] Temperature reached in 1.5–2 min.; cooled in carbon granules.

[b] Specific gravity calculated additively for WC + Co; numerical values taken as basis were: WC, 15.5 g./cc.; and Co, 8.9 g./cc.

[c] Density not determined because of porous fracture.

[d] Density not determined because of very porous fracture.

[e] Density not determined because of many pores in the material.

[f] Density not determined because of pores and laminations in the material.

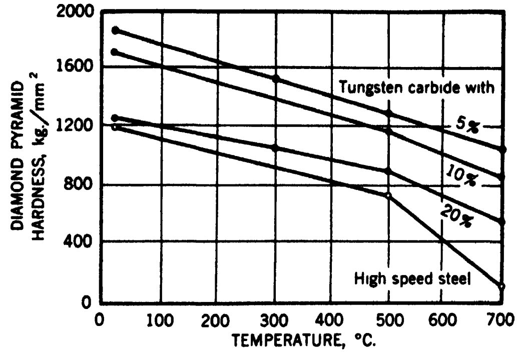

Fig. 346. Effect of temperature on the diamond pyramid hardness of tungsten carbide hard alloys containing different amounts of cobalt as compared with high-speed steel (according to Dawihl[79a]).

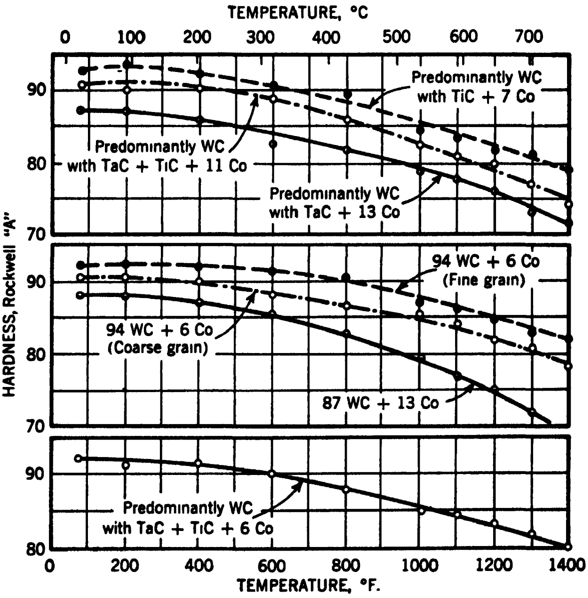

Fig. 347. Rockwell "A" hardness for commercial cemented carbide compositions at elevated temperatures (according to Engle[80]).

cobalt contents range from 4 to 13%. At this temperature a sintering time of 45 minutes is sufficient. Raising the temperature causes deterioration of physical properties and coarsening of the grain structure. The best cutting properties in conjunction with the physical properties were obtained in alloys with 4 and 6% Co, whose transverse rupture strength was found to be only about 10–15% less than that of alloys with 10 or 13% Co.

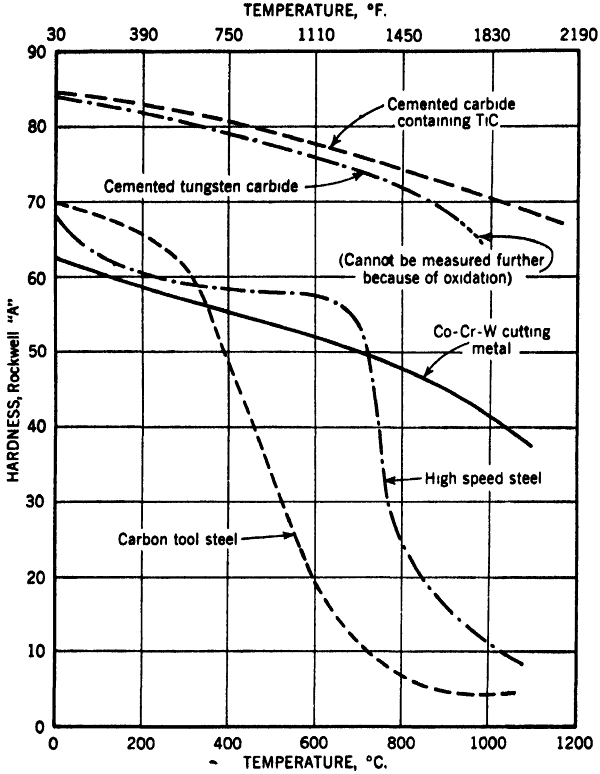

Fig. 348. Effect of temperature on the Rockwell "A" hardness of different hard metal and tool alloys (courtesy of P. Schwarzkopf and the American Electro Metal Corp.).

A comparison of some of the physical properties of hot-pressed, and sintered and fused cobalt–tungsten carbide alloys has been made by Kieffer and Hotop,[79] and is reproduced in tabular form elsewhere (Table

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[79] R. Kieffer and W. Hotop, *Kolloid-Z.*, *104*, 208 (1943).

240, Chapter XXXI). Particularly impressive is the inferiority in strength of the fused material as compared with the materials prepared by powder metallurgy methods. An explanation for these results may be seen in the heterogeneity of the structure and the decomposition of the carbide WC into graphite and the carbide W_2C (see also page 108).

The extremely high hardness of the cemented carbides, which corresponds to a value of about 9 on Mohs' scale (see also Fig. 621, Chapter XXXIV), is little impaired with rising temperature until a point is reached where rapid oxidation occurs. This is evident from the diagrams of Figures 346 to 348 in which hardness of various compositions is plotted against temperature, according to Dawihl,[79a] Engle,[80] and Schwarzkopf,[81] respectively. A Rockwell hardness of A 80–85 may be retained beyond 650°C. (1200°F.) (Fig. 347), and the hardness of a composition containing 5% Co is equivalent at 700°C. (1290°F.) to that of high-speed steel at room temperature. This property, coupled with the high abrasion resistance of the alloy, constitutes the basis for its most valuable performance as a tool material. As shown in Figure 348, the hardness of the hard metal is still in the order of Rockwell A 65 at the temperature of rapid ("catastrophic") oxidation, which is about 950°C. (1740°F.) for tungsten carbide, and about 1100°C. (2000°F.) for compositions containing titanium carbide.

Cemented Multiple Carbides. A comparison between the physical properties of simple tungsten carbide–cobalt compositions and some of the more complex multiple carbide hard metals is indicated in Table 113, according to Engle.[82] It is evident from these figures that the more complex compositions do not show an advantage in hardness or strength over the straight WC–Co alloys, with the exception of the hardness of alloys containing WC, TiC, and 6–9% Co. These results are reaffirmed by Kieffer and Hotop,[83] whose detailed data for the effects of composition on hardness, density, and transverse rupture strength are given for WC–TiC–Co alloys in Table 114; for WC–TaC–Co and WC–TaC–CbC–Co in Table 115; for WC–TiC–TaC–Co and WC–TiC–TaC–CbC–Co in Table 116. The increase in transverse rupture strength with increasing cobalt concentrations is less marked for the higher titanium carbide contents. Alloys containing 10–30% TaC or TaC–CbC that are suitable

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[79a] W. Dawihl, *Z. tech. Physik, 21,* 336 (1940).

[80] E. W. Engle, in J. Wulff, *Powder Metallurgy.* Am. Soc. Metals, Cleveland, 1942, p. 436.

[81] P. Schwarzkopf, *private communication.*

[82] E. W. Engle, in J. Wulff, *Powder Metallurgy.* Am. Soc. Metals, Cleveland, 1942, p. 446.

[83] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe.* Springer, Berlin, 1943, p. 303.

TABLE 113

Physical Properties of Some Commercial Cemented Carbide Compositions (Engle[82])

Composition	Density, g./cc.	Hardness, Rockwell "A"	Transverse rupture strength, psi	Young's modulus, psi × 10^6	Compressive strength,[c] psi	Proportional limit in compression,[d] psi	Impact strength,[e] ft.-lb.	Endurance limit,[f] psi	Coefficient of thermal expansion[g]
97% WC, 3% Co.	15.25	92.7	170,000	97.5	815,000	780,000	—	—	—
95.5% WC, 4.5% Co. . . .	15.05	92.3	200,000	90.5	890,000	740,000	—	—	—
94% WC, 6% Co.	14.85	90–92	225,000	88	750,000	600,000	0.73	95,000	5.0 × 10^{-6}
91% WC, 9% Co.	14.60	89.5–91.5	275,000	—	685,000	540,000	—	—	—
87% WC, 13% Co.	14.15	87.5–90	300,000	80	625,000	525,000	1.10	105,000	5.9 × 10^{-6}
80% WC, 20% Co.	13.55	85–87	350,000	—	550,000	425,000	1.75	—	—
Predominantly WC, with TaC and 13% Co . . .	13.90	87–88	275,000	—	610,000	475,000	—	—	7.25 × 10^{-6}
Predominantly WC, with TaC and 6% Co.	14.70	91–92	220,000	—	752,000	670,000	0.65	85,000	—
Predominantly WC, with TiC and 6% Co	11.20	92–93	160,000	—	700,000	—	0.40	90,000	6.8 × 10^{-6}
Predominantly WC, with less TiC than above, 8% Co.	12.80	91.5–92.5	250,000	—	570,000	560,000	0.60	90,000	—
Predominantly WC, larger amount of TiC, 7% Co	9.00	92–93	150,000	—	725,000	—	—	—	7.0 × 10^{-6}
Predominantly WC, with TaC and TiC, 8% Co.	11.7	91.5–92.5	165,000	72	720,000	—	—	—	6.75 × 10^{-6}
Predominantly WC, with TaC and TiC, 11% Co.	11.6	90.5–91.5	175,000	—	680,000	—	0.60	85,000	6.0 × 10^{-6}
Predominantly WC, with TaC and TiC, 15% Co.	11.4	89.5–90.5	190,000	67	670,000	—	0.92	—	7.5 × 10^{-6}

[a] The values given in this table are representative of properties obtained in good production practice. They are not necessarily the highest obtainable, nor do they represent the lowest which are of practical use.

[b] Most values for Young's modulus were obtained by W. H. Davenport of the Norton Co. by the musical pitch method.

[c] Most of the values for compressive strengths are given through the courtesy of P. W. Bridgman of Harvard University.

[d] Proportional limit in compression is the load per unit area at which the increase in strain ceases to be directly proportional to the increase in stress.

[e] Impact values are from unnotched specimens approximately 1/4-in. square section; Charpy machine was used.

[f] Values for endurance limits are based on 20,000,000 cycles, for specimens of R. R. Moore rotating-beam type.

[g] Average coefficient of expansion per °C. for the range 20–700°C (68–1290°F.).

TABLE 114
Composition and Properties of Various WC–TiC–Co Alloys (Kieffer and Hotop[83])

Composition			Hardness, Rockwell "A"	Transverse rupture strength, psi	Density, g./cc.
Co, %	TiC, %	WC, %			
5	1	94	90.5	213,000	14.6
5	2.5	92.5	90.5	200,000	14.2
6	2.5	91.5	90.5	213,000	—
10	2.5	87.5	89.5	256,000	14.0
13	2.5	84.5	87.5–88	284,500	13.9
15	2.5	82.5	86.5–87	298,500	—
5	4.5	90.5	91	185,000	13.5
10	4.5	85.5	89.5	227,500	13.4
13	4.5	82.5	89	242,000	—
15	4.5	80.5	87.5	256,000	—
7	8	85	90	200,000	12.9
13	8	79	89	227,500	—
6	12	82	90.5	163,500	12.2
8	12	80	90	185,000	—
10	12	78	89.5	200,000	12.0
15	12	73	88.5	213,000	—
5	16	79	91	142,000	11.2
6	16	78	91	153,500	11.2
7	16	77	90.5	156,500	11.1
8	16	76	90.5	171,000	—
9	16	75	90	171,000	10.9
10	16	74	89.5	176,000	—
13	16	71	89.5	192,000	—
6	25	69	92–92.5	114,000	9.9
13	25	62	91	121,000	—
10	45	45	92	121,000	7.9

TABLE 115
Composition and Properties of Various WC–TaC–Co and WC–TaC–CbC–Co Alloys (Kieffer and Hotop[83])

Composition, %				Hardness, Rockwell "A"	Transverse rupture strength, psi	Density, g./cc.
Co	TaC	TaC–CbC)[a]	WC			
5	—	1	94	90.5	227,500	14.6
6.5	—	2	91.5	90.5	256,000	14.4
5	—	3	92	90.5	227,500	14.2
6	10	—	84	89.5	227,500	14.5
8	—	11	81	90	206,000	13.7
6	15	—	79	90	213,000	14.4
6	—	20	74	90	142,000	13.2
8	25	—	67	89	126,500	14.3
13	—	25	62	88	185,000	13.0
6	30	—	64	89.5	171,000	14.3
6	—	40	54	89	156,000	11.9
6	—	75	19	88	114,000	10.3
6	94	—	0	82.5	128,000	13.8
6	—	—	94	91	256,000	14.9

[a] Ratio 3:2 (solid solution.)

TABLE 116

Composition and Properties of Various WC–TiC–TaC–Co and WC–TiC–TaC–CbC–Co Alloys (Kieffer and Hotop[83])

Composition, %					Hardness, Rockwell "A"	Transverse rupture strength, psi	Density, g./cc.
Co	TiC	TaC	TaC CbC[a]	WC			
6	5	—	5	84	89.5	185,000	13.0
6	5	—	10	79	90	171,000	12.63
6	5	—	20	69	90	156,500	12.25
6	5	—	40	49	89.5	128,000	11.26
6	5	—	65	24	88.5	100,000	12.29
6.5	7.5	10	—	76	89.5	171,000	—
6	9.5	—	5	79.5	89.5	135,000	11.8
6	9.5	—	10	74.5	90	163,500	11.5
6	9.5	—	20	64.5	90	142,000	11.0
6	9.5	—	40	44.5	90	128,000	10.6
6	9.5	—	60	24.5	89.5	92,500	9.7
6	15	15	—	64	90.5	150,000	—
6	15	—	5	74	90.5	142,000	10.98
6	15	—	10	69	90.5	156,500	10.75
6	15	—	15	64	90.5	142,000	10.59
6	15	—	20	59	90.5	135,000	10.03
6	15	—	25	54	90	135,000	9.80
6	15	—	55	24	89.5	100,000	8.96

[a] Ratio 3:2 (solid solution).

TABLE 117

Properties of WC-TiC Compositions with Cobalt Additions (Schwarzkopf[85])

	Composition type					
	1	2	3	4	5	6
	Carbide grade					
Properties	Predominantly WC + TiC	Predominantly WC + TiC	Predominantly WC + more TiC than (2)	Predominantly WC + more TiC than (1)	Predominantly WC + more TiC than (3)	Predominantly WC + more TiC than (4)
Cobalt content, %	8	13	13	6	13	7
Density, g./cc.....	12.80	12.80	11.95	11.20	10.10	9.0
Hardness, Rockwell "A"......	91.5–92.5	89.8	90.0	92.0–93.0	90.0	92.0–93.0
Transverse rupture strength, psi....	250,000	250,000	240,000	160,000	180,000	150,000
Compressive strength, psi....	720,000	—	—	700,000	—	725,000
Impact strength, ft. lb...........	0.6	—	—	0.4	—	—
Thermal expansion coefficient × 10⁶, per °C.[a]........	—	—	—	6.8	—	7.0

[a] Average range 20–700° C. (68–1290° F.).

for the machining of steel are generally inferior in hardness and strength to the cemented carbides containing WC–TiC alloys. But the hardness of the compositions containing tantalum carbide either alone or with columbium carbide can be increased by the addition of 5–10% TiC, and the cutting properties can thereby be improved to a corresponding degree. However, only the WC–TiC–TaC–Co alloys approach the machining qualities of the WC–TiC–Co alloys.[84] Additional data for WC–TiC–Co and WC–TaC–TiC–Co alloys are given in Tables 117 and 118, respectively, according to Schwarzkopf.[85] The properties of other cemented carbide hard metals are given in Table 119, according to Kieffer and Hotop.[86]

TABLE 118

Properties of WC–TaC–TiC–Co Compositions (Schwarzkopf[85])

	Composition type					
	1	2	3	4	5	6
	Carbide grade					
Properties	Predominantly WC, with TaC, TiC	Predominantly WC, with TaC, TiC	Predominantly WC, with TaC, TiC			
Refractory metal content						
% W.	—		—	62.9	55.5	62.2
% Ta.	—	—	—	9.0	13.6	14.3
% Ti.	—		—	9.4	10.2	4.0
Cobalt content, %	8	11	15	10.1	10.7	10.8
Density, g./cc.	11.7	11.6	11.4	—	—	—
Hardness, Rockwell "A".	91.5–92.5	90.5–91.5	89.5–90.5	91	90.3	89.9
Transverse rupture strength, psi.	165,000	175,000	190,000	224,000–280,000	275,000–350,000	310,000–373,000
Compressive strength, psi.	720,000	680,000	670,000	690,000	—	—
Charpy impact strength, ft. lb.	—	0.6	0.92	—	—	—
Modulus of elasticity × 10^{-6}, psi.	72	—	67	—	58	—
Thermal expansion coefficient × 10^6, per °C.[a]	6.75	6.0	7.5	—	—	—
Thermal conductivity cal./cm./sec./°C.	—	—	—	0.075	0.110	0.120

[a] Average range 20–700° C. (68–1290° F.).

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[84] P. Schwarzkopf, *Powder Metallurgy*. Macmillan, New York, 1947, p. 209.

[85] P. Schwarzkopf, *Product Eng.*, *17*, 268 (1946).

[86] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe*. Springer, Berlin, 1943, p. 305.

Meerson and coworkers[87] have studied the effect of the sintering temperature on shrinkage and hardness for WC–TiC–Co hard metals prepared from different powders that were produced either by commercial methods or in vacuum. Titanium carbide powder with the theoretical carbon content of 20% could only be produced by vacuum heating. The cobalt content was 6%, and the compacts pressed at 10 tsi were sintered in hydrogen atmosphere for 1 and 4 hours, respectively. In Figure 349 the shrinkage of the compacts during sintering is shown as a function of the temperature; in Figure 350 the hardness of the sintered products is shown.

TABLE 119

Composition and Properties of Some Hard Alloys Based on Multicarbides[a] with Different Cementing Metals (Kieffer and Hotop[86])

Composition, %							Hardness, Rockwell "A"	Transverse rupture strength, psi
WC	Mo_2C	TiC	TaC	CbC	Ni	Co		
76	2	16	—	—	—	6	91	142,000
73	5	16	—	—	3	3	91	135,000
60	16	16	—	—	8	—	91	128,000
60	16	16	—	—	—	8	91.5	114,000
30	30	25	—	—	15	—	91	114,000
15	30	45	—	—	5	5	91	121,000
15	30	40	—	—	10	5	91	135,000
15	15	55	—	—	10	5	91	135,000
20	10	65	—	—	2	3	92	128,000
—	—	42.5	42.5	—	15	—	89	121,000
—	42.5	—	42.5	—	15	—	87	128,000
—	30	25	30	—	15	—	89	135,000
93	0.5	—	—	1.5	—	5	91.5	213,000
92.5	—	0.5	0.6[b]	0.4[b]	—	6	91.5	213,000

[a] WC, Mo_2C, TiC, TaC, CbC.
[b] Solid solution of TaC–CbC of approximate ratio 3:2.

Further information regarding composition and physical properties of multiple carbide alloys has been compiled in tabular form by Schwarzkopf.[85] The values for WC–TiC–Co compositions are reproduced in Tables 117 (American data) and 120 (German data); those for WC–TaC–TiC–Co in Table 118. Information concerning the composition, chemical analysis, and properties of German wartime products are reproduced from Comstock's[88,89] reports in Table 121. The "S" grade and "F" grade designate steel cutting materials; the "G" and "H" grades cutting alloys for cast iron and nonferrous metals. The increasing nu-

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[87] G. A. Meerson, G. L. Zverev, and B. E. Osinovskaya, *Zhurnal Priklad. Khimii, 13*, No. 1, 66 (1940); *Metal Ind. London, 59*, 306 (1941).
[88] G. J. Comstock, *Iron Age, 156*, No. 9, 36A (1945).
[89] G. J. Comstock, *Metal Progress, 46*, 117 (1946).

merals indicate materials of progressively increasing strength and decreasing hardness.

The data given in these reports have been used by McKenna[90] for a comparison of German with American products. The results summarized in Table 122 indicate that the American products have a 30 to 50% higher transverse rupture strength, thus permitting feeding speeds per revolution that are three to four times higher than possible with the German grades. McKenna holds that samples of German tools also indicate careless handling of mixes and grinding of tools, and concludes that

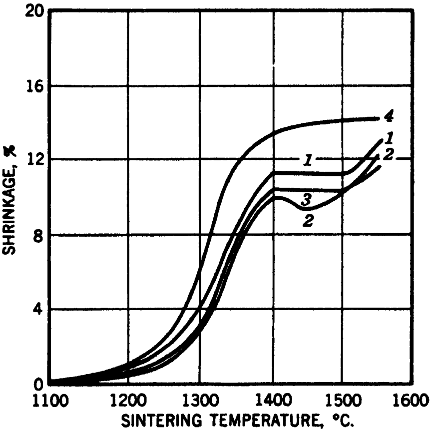

Fig 349. Effect of sintering temperature on shrinkage of tungsten carbide–titanium carbide–cobalt alloys (according to Meerson, Zverev, and Osinovskaya[87]): curve 1 is a commercial TiC powder with 46% of its particles smaller than 1 μ, analyzing 17.85% total C, 16.86% combined C, 3.05% O; curve 2 designates a commercial powder with 73% of its particles smaller than 1 μ, analyzing 18.25% total C, 17.23% combined C, 3.25% O; curve 3 designates a powder produced by commercial methods in the presence of air with 78% of its particles smaller than 1 μ, analyzing 19.11% total C, 16.85% combined C, 2.13% O; curve 4 designates a special powder produced in vacuum with 85% of its particles smaller than 1 μ; analyzing 19.65% total C, 19.15% combined C, 1.0% O.

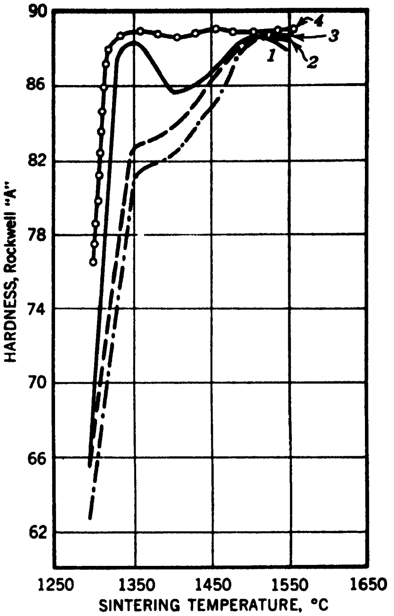

Fig. 350. Effect of sintering temperature on the Rockwell "A" hardness of tungsten carbide–titanium carbide–cobalt alloys (according to Meerson, Zverev and Osinovskaya[87]). The curves represent the same titanium carbide powder ingredients described for Figure 349.

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[90] P. M. McKenna, *Iron Age*, *157*, No. 6, 64 (1946).

TABLE 120
Composition and Properties of WC–TiC–Co Alloys—German Data

Grades (carbide composition)	Co, %	Atom ratio, Ti/W	Ti + W, %	Density, g./cc.	Hardness	Transverse rupture strength, psi	Modulus of elasticity, psi × 10^6	Thermal conductivity cal./cm./sec./°C.	Coefficient of thermal expansion, av. between range of 20–700°C. (68–1290° F.)	Electrical resistivity microhm-cm., at 20°C.	Reference
S3 (89% WC + 5% TiC)	6	18/100	87.6	13.3	1600, Vickers	213,300	—	0.15	5.5×10^{-6}	—	*a, c*
Widia X (80.5% W + 7% Ti)	5.5	33/100	87.5	12.3	1800, Brinell	—	—	0.14	6×10^{-6}	0.29	*b*
Widia XX (74.5% W + 12% Ti)	5.5	50/100	86.5	11.1	1800, Brinell	—	—	0.09	6×10^{-6}	0.43	*b*
S1 (79% WC + 15% TiC)	6	62/100	86.4	—	—	177,800 156,400	77	0.09	—	0.43	*c, d, f*
S2 (76% WC + 16% TiC)	8	69/100	84.2	—	—	—	—	—	—	—	*d, e*
F1 (69% WC + 25% TiC)	6	118/100	84.9	—	—	—	—	—	—	—	*c*

[a] J. Hinnüber, *Stahl u. Eisen*, *62*, 1086 (1942).

[b] F. W. Leier, *Hartmetalle in der Werkstatt*, Springer, Berlin, 1937, p. 6.

[c] F. Skaupy, *Kolloid Z.*, *102*, 270 (1943); *98*, 92 (1942).

[d] W. Dawihl and J. Hinnüber, *Kolloid Z.*, *104*, 233 (1943).

[e] E. Dinglinger, *Werkstattechnik u. Werksleiter*, *35*, No. 10, 173–174 (1941).

[f] W. Dawihl, *Z. Metallkunde*, *32*, 320 (1940); *Z. tech. Physik*, *21* 44, 336 (1940); *Stahl u. Eisen*, *61*, 210 (1941).

TABLE 121. Composition and Physical Properties of Standard German Cemented Carbides (Comstock[88,89])

PHYSICAL PROPERTIES

Grade	Composition	Sintering temperature °C.	Sintering temperature °F.	Minutes at sinter. temp. for thickness of tips of 2 mm.	Minutes at sinter. temp. for thickness of tips of 15 mm.	Transverse rupture strength, psi	Modulus of elasticity, psi × 10^6	Coeff of thermal expansion × 10^{-6}/°C.	Heat conductivity, cal./cm./sec./°C.	Specific heat	Specific electric resistance, microhm-cm
S1	78 WC, 16 TiC, 6 Co	1600	2910	20	100	178,000	77	6	0.09	0.06	43
S2	78 WC, 14 TiC, 8 Co	1550	2820	20	100	200,000	—	6.2	0.08	—	44
S3	88 WC, 5 TiC, 7 Co	1500	2730	20	100	214,000	84	5.5	0.15	0.05	25
G1	94 WC, 6 Co	1420	2590	20	100	228,000	88	5	0.19	0.05	2
G2	89 WC, 11 Co	1400	2550	20	100	256,000	83	5.5	0.16	0.05	18
G3	85 WC, 15 Co	1380	2520	17	60	292,000	—	—	—	—	—
H1	94 WC, 6 Co	1420	2590	17	60	228,000	91	5	0.19	0.05	21
H2	91.5 WC, 0.5 VC, 1 TaC, 7 Co	1500	2730	66	220	164,000	—	5	—	—	25
F1	69 WC, 25 TiC, 6 Co	1550	2820	66	220	156,000	74	7	0.05	—	65
F2	34.5 WC, 60 TiC, 5.5 Co	1700	3040	66	200	114,000	—	—	—	—	77

REPRESENTATIVE ANALYSES

Constituent	Grade S1	S2	S3	H1	H2	G1	G2	G3	F1	F2
C combined	7.57	7.30	6.17	5.83	5.83	5.90	5.65	5.50	8.10	12.8
free	(0.21)	(0.22)	(0.16)	(0.12)	(0.16)	(0.15)	(0.18)	(0.32)	(0.06)	(0.05)
W	73.33	73.06	82.55	87.82	85.14	87.75	83.22	79.32	66.86	32.40
Co	5.48	7.64	6.63	5.66	6.80	5.68	10.46	14.46	5.48	5.25
Ti	12.76	11.13	3.77	—	—	—	—	—	18.30	46.60
Fe	0.31	0.23	0.25	0.30	0.28	0.34	0.38	0.40	0.40	0.71
Cr	0.03	0.05	0.05	0.05	0.06	0.09	0.05	0.06	0.13	0.10
Ni	0.10	0.11	0.09	0.11	0.11	0.10	0.12	0.10	0.15	0.14
N_2	0.26	0.29	0.15	0.03	0.03	0.06	0.03	0.03	0.42	1.14
Ta	—	—	—	—	0.77	—	—	—	—	—
V	—	—	—	—	0.5	—	—	—	—	—
Cb	—	—	—	—	0.20	—	—	—	—	—
Specific gravity	11.15	11.25	13.30	14.75	14.40	14.70	14.20	13.70	9.90	6.8
Hardness, Rockwell "A"	91.0	90.5	90.0	91.0	91.5	90.0	88.5	87.0	91.5	92.5

progress in the cemented carbide field has stopped in Germany at a stage corresponding to that reached by the American industry about 10 years ago. Certain reports from Germany that deal with problems of heterogeneities encountered in the steel cutting carbide grades[90a] seem to support McKenna's opinion. Every carbide grade containing TiC, but

TABLE 122

Comparison of German and American Grades of Cemented Carbides (McKenna[90])

Grade designation	Transverse rupture strength kg./mm.²	Transverse rupture strength psi	Equivalent on standard blanks (to break), kg.	R_a, Hardness, Rockwell "A"	Computed tool value[a]	Notes on composition
GERMAN STEEL CUTTING GRADES						
S1	125	177,900	1430	91.0	92	78% WC, 16% TiC, 6% Co
S2	140	199,220	1526	90.5	94	78% WC, 14% TiC, 8% Co
S3	150	213,500	1720	90.0	101	88% WC, 5% TiC, 7% Co
STEEL CUTTING GRADES OF ONE AMERICAN MANUFACTURER						
K4H	157	225,000	1720	92.3	122	Having $WTiC_2$ as an ingredient[b]
K3H	183	260,000	2090	92.0	179	Greatest percentage of $WTiC_2$
KM	214	305,000	2460	91.0	159	Having medium content of $WTiC_2$
K2S	214	305,000	2460	91.5	164	Having $WTiC_2$ as an ingredient
GERMAN CAST IRON CUTTING GRADES						
G1	160	227,680	1830	90.0	108	94% WC, 6% Co
G2	180	256,000	2060	88.5	101	89% WC, 11% Co
G3	205	291,715	2350	87.0	96	85% WC, 15% Co
H1	160	227,680	1840	91.0	118	94% WC, 6% Co (doubtless selected grain size)
CAST IRON CUTTING GRADES OF ONE AMERICAN MANUFACTURER						
K6	157	225,000	1800	92.2	125	WC and Co with grain size control
K12	246	350,000	2800	89.0	147	WC and Co with grain size control

[a] McKenna's "tool value" is computed according to the formula:

$$\frac{10 \times \text{break strength (kg.)}}{5(93 - R_a)(47 - 0.5\,R_a) + 140}$$

[b] The existence of the compound $WTiC_2$ has not been proved.

[90a] Studiengesellschaft Hartmetall, *B. O. T., German Div.*, Documents Unit, F. D. 3930/47; see also *Met. Powd. Rept.*, *3*, No. 2, 28 (1948).

especially the S1 grade (78% WC, 16% TiC, 6% Co), was found to possess a TiC-free coating 10–100 μ thick, which coincided with different cobalt concentrations on the surface and in the interior, and with zones of different hardness. This effect was found to be the more pronounced the greater the cobalt content; inversely, with decreasing cobalt content the TiC-free coating becomes thinner, and at 2.5% Co the difference between surface and interior is practically unnoticeable. (A similar frank discussion of the causes and effects of holes, cracks, segregation of cobalt, and other defects experienced in the British commercial cemented carbide production has been published by Oliver.[90b])

The repeatedly cited investigation by Kieffer and Kölbl[90c] gives an impressive series of test results on tungsten-free cemented carbides and shows that, generally speaking, tungsten carbide can be replaced successfully by carbide combinations of metals of the 4th, 5th, and 6th groups of the periodic system. The inexpensive titanium carbide seems to be best suited as main constituent, while the carbides of vanadium, columbium, and molybdenum appear to be good prospects as additional constituents. The production of these materials by hot pressing was found to give better results than by cold pressing and subsequent sintering in hydrogen or—what would be preferable—in vacuum. Table 123 summarizes some of the physical properties of tunsten-free binary and ternary titanium carbide-base hard alloys.[90c] It may be noted that compositions containing TiC with VC or with Mo_2C give very good combinations of hardness, transverse rupture strength, and specific gravity, which indicates their possible suitability for moving components in power engines operating at elevated temperatures (see also page 168), especially since some of these compositions display good resistance to oxidation or other corrosion at high temperatures.[90d] Cobalt-cemented titanium carbide has recently been investigated by Bobrowsky[90e] for its applicability as jet turbine blade material; a binary composition containing 20% Co was found to possess the best combination of properties at test temperatures (up to 1200°C.; 2200°F.). For applications as tool materials, minimum requirements for hardness and transverse rupture strength of 88–90 Rockwell "A" and 105,000–135,000 psi, respectively, were modeled

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[90b] A. E. Oliver, *Proc. International Powder Metallurgy Conference*, Graz, July 12–17, 1948, Referate No. 11.

[90c] R. Kieffer and F. Kölbl, *Proc. International Powder Metallurgy Conference*, Graz, July 12–17, 1948, Referate No. 28; *Powder Met. Bull.*, *4*, No. 1, 4 (1949).

[90d] R. Kieffer, Communication to New York Regional Group, Powder Metallurgy Committee, *Inst. Metals Div., Am. Inst. Mining Met. Engrs.*, Dec. 15, 1948.

[90e] A. R. Bobrowsky, *Trans Am. Soc. Mech. Engrs.*, *71*, No. 6, 621 (1949).

in accordance with practical experience in Germany during the war in machining different materials under different conditions.[90c] While materials of lesser strength apparently can be used for certain wear resistant applications, the tungsten carbide-free hard metals are insufficiently strong and hard for machining of cast iron or for rock drilling.

TABLE 123

Characteristics of Binary and Ternary Titanium Carbide-Base Alloys with Different Binder Metals (Kieffer and Kolbl[90c])

TiC	VC	CbC	TaC	Mo_2C	Co	Ni	Cr	Hardness, Rockwell, "A"	Transverse rupture strength, psi	Density, g./cc
90	—	—	—	—	10	—	—	—[a]	100,000–115,000[b]	—
90	—	—	—	—	—	10	—	92.5	100,000–115,000	4.8
—	90	—	—	—	—	10	—	89	85,000–100,000	5.45
65	25	—	—	—	—	10	—	93.5	128,000–157,000	5.05
45	45	—	—			10	—	92.5	128,000–157,000	5.15
25	65	—	—			10	—	92	100,000–115,000	5.25
—	—	—	—	85		15	—	82.5	85,000	8.8
15	—	—	—	85	—	—		91.5	100,000	5.5
42.5	—	—	—	42.5	—	15	—	91	128,000	6.9
55	—	—	—	30	—	15	—	91.5	121,000	6.4
65	—	—		20	—	15	—	92	114,000	6.2
73	—		—	12	—	15	—	92	100,000	6.1
77	—	—		8	—	15	—	92.5	100,000	6.0
82	—	—		3	—	15	—	92	100,000	5.2
35	—	—	—	35	—	28	2	87	157,000	7.1
58	—	—	—	15	—	25	2	87.5	142,000	6.1
63	—	—	—	15	—	20	2	88.5	142,000	5.9
72	—	18	—	—	10	—	—	91	—	5.59
36	—	54	—	—	10	—	—	90	—	6.14
18	—	72	—	—	10	—	—	89		7.24
42.5	—	—	42.5	—	—	15	—	89	—	8.7
—	—	—	42.5	42.5	—	15	—	87	—	10.6
72	—	6	12	—	10	—	—	91.5	—	5.67
45	—	15	30	—	10	—	—	90.5	—	6.63
10	—	24	48	—	10	—	—	90	—	7.77

[a] Vickers hardness, 1800–1900.

[b] Compressive strength, 500,000 psi.

EFFECT OF COMPOSITION ON CUTTING PROPERTIES

Methods of Testing. The quality control of the hard metal products is not complete without a test of the cutting properties, which, like the physical characteristics, are governed by composition and manufacturing procedure. The cutting quality is usually established in a simple lathe test on cast iron or steel of known hardness and tensile strength. In this test the cut taken may be either continuous or intermittent. A standard procedure for cast iron of a Brinell hardness between 200 and 300 is to turn a specimen with a feed of approximately $^{1}/_{64}$ in. at a turning speed of from 130 to 200 ft./min.; in the case of steels from 110,000 to 130,000 psi tensile strength the same feed is used but the turning speed is raised to 300 to 450 ft./min.[91] The behavior of the hard metal may thus be tested either in a short test or in a test of long duration. The blunting and formation of a "built-up" edge or "crater" at the cutting edge of the tool tip as well as the formation of "craters" by the passage of the chip over the back of the tool, serve as measure for the suitability of the particular hard metal for the cutting purpose in question. Figure 351 shows the continuous chips formed in an extended test run with chrome–nickel steel as used for railroad car axles.

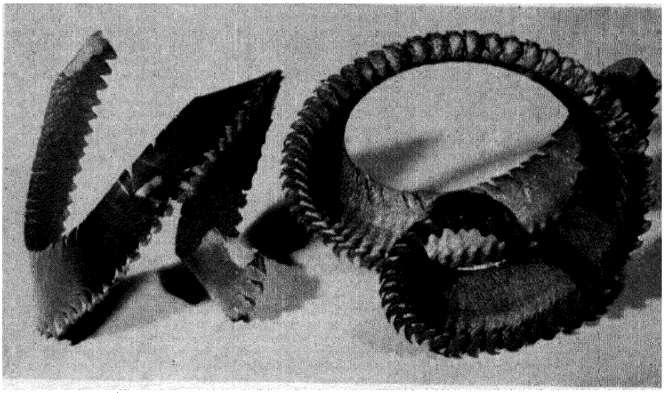

Fig. 351. Continuous chip formation in cutting test on nickel–chrome steel as used for railroad car axles (courtesy of A. C. Wickman Ltd.).

Material, nickel–chrome steel; *component,* railroad car axles; *machine,* double end center drive Bertram axle lathe; *r.p.m.,* 30; *s.f.,* 70.6 per minute; *feed per rev.,* 0.125 in.; *depth of cut,* $^{5}/_{8}$–$^{7}/_{8}$ in.; *life of tool,* 65 components per grind; *floor to floor,* 4 per hour; *tool section,* $1^{1}/_{4} \times 3^{1}/_{4} \times 16$ in.; *tip size,* $^{1}/_{2} \times 1^{1}/_{4} \times 2$ in.; *grade,* X-7; *top back rake and top side rake,* 0°; *clearance,* 4° on carbide, 6° on shank, $^{5}/_{8}$ radius full width of tool.

Cutting Characteristics. The factors that influence the cutting performance of a hard metal, and the mechanics of tool wear and tear involved are rather complex in nature, and hence not easily explained.

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[91] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe.* Springer, Berlin, 1943, p. 295.

An interesting analysis of the problem has been given by Schwarzkopf[92] in his recent book. The complexity of the cutting behavior of cemented carbide tools really is best seen when analyzing the properties of the hard metals and the stresses that are produced by cutting materials that machine differently. Pure tungsten carbide particles are more easily bonded by cobalt than WC–TiC solid solutions and plain WC–Co hard metals are stronger and more ductile than compositions of the WC–TiC–Co type; furthermore, the thermal conductivity of the former is superior to that of the latter. When machining materials that form small and crumbly chips, the number of penetrations of the cutting tool into the work is greater than in the case of materials forming long and tenacious turnings, and hence the mechanical stresses produced are more complex. This probably constitutes one of the chief reasons why the stronger and more ductile straight WC–Co compositions have given the best tool performance when machining materials of short chip formation such as cast iron. However, on the basis of such simple concepts as strength and resistance to abrasion, it is less clearly understandable why the single carbide compositions fail when the stresses encountered are lower, as is the case in the machining of steels and similar materials that form long and ribbonlike turnings. An explanation as to why, for these materials, the more complex WC–TiC–Co compositions alone give satisfactory tool performance in spite of inferior strength and inferior heat conductivity, must rather be sought in other factors, particularly friction and oxidation effects.

Oxidation Effects. One particular type of tool wear that expresses itself in the formation of craterlike abrasion effects at the tool flanks is generally attributed to a higher rate of oxidation. Caused through contact of the hard metal with the hot chips, the abrasion results in constant removal of tool material and eventual destruction of the tool tip. WC–TiC–Co and other multiple carbide tool materials are more resistant to this kind of failure than plain WC–Co compositions because the former are known to be more oxidation-proof at elevated temperatures[92] (which fact may be attributed to the different types of oxides involved: for example, WO_3 volatilizes in air even at low temperatures (500–600°C.; 930–1110°F.), but TiO_2 is a stable refractory oxide up to very high temperatures).

Another concept of the role that oxidation plays during the cutting operation is that oxide films may be instrumental in reducing wear, par-

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[92] P. Schwarzkopf, *Powder Metallurgy*. Macmillan, New York, 1947, pp. 198 ff.

ticularly at the cutting edge. Experiments by Dies[93] and by Schallbroch and Wallichs[94] indicate that, under certain conditions, oxide films tend to prevent welding or alloy formation between the hard metal tool and the work. Skaupy[95] contends that the favorable influence of titanium additions to the WC–Co alloys is based solely on the presence of oxide films.

In a discussion of the structure and steel-cutting performance of cemented multicarbide tools containing titanium carbide, Metcalfe,[96] too, has paid special attention to the role of oxygen. He attributes the superior steel-cutting performance of the multicarbide materials to the formation of a titanium oxide film at cutting temperature. The oxide layer formed is adherent, tenacious, and nonporous, since, as indicated by x-ray diffraction data, change of titanium carbide to the oxide does not involve disruptive movements of the titanium atoms. The lattice of the oxide film produced is practically identical with the titanium carbide lattice, the titanium atoms having the same positions and carbon being replaced by oxygen. While titanium carbide is oxidized at a lower temperature than tungsten carbide, the resulting oxide film protects the material against further oxidation at higher temperatures. Such a protection is not provided by the bulky and porous tungsten oxide.

In agreement with Dawihl,[97] welding together of chip and tool is held by Metcalfe to be primarily responsible for wear, and the titanium oxide film prevents contact between the carbides and the steel. Wear, therefore, takes place only when the film has been destroyed and the steel chip welds on before a new oxide surface has formed. The irreversible oxidation of titanium carbide raises the welding-on temperature by several hundred degrees Centigrade.

According to Metcalfe, additional benefits derived from the formation of oxide films are the prevention of rapid removal of the hot tool tip as oxide, and a reduction of the coefficient of friction.

It may be stated in closing this discussion, however, that the recognized superiority in resistance to oxidation of the WC–TiC–Co compositions appears to be in contradiction to the conception that oxide layers are primarily responsible for the lesser degree of welding that is experienced with these more complex compositions. Hence, an interfering oxide

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[93] K. Dies, *Z. Ver. deut. Ing.*, *83*, 307 (1939).

[94] H. Schallbroch and R. Wallichs, *Werkzeugverschleiss*, Ver. deut. Ing., Berlin (1938).

[95] F. Skaupy, *Kolloid-Z.*, *98*, 92 (1942); *102*, 269 (1943).

[96] A. G. Metcalfe, *Metal Treatment*, *13*, 127 (1946).

[97] W. Dawihl, *Z. Metallkunde*, *32*, 320 (1940); *Z. tech. Physik*, *21*, 44, 336 (1940); *Stahl u. Eisen*, *61*, 210 (1941).

phase is not wholly acceptable as an explanation, and the true reason for the lessening of the welding tendency should rather be sought in the particular crystal structure of these alloys and in a possible lower diffusion coefficient for steel into the multiple carbides.

The failure of WC–TiC–Co alloys in machining of cast iron and similar short-chipping materials may be explained by their inferior thermal conductivity when compared to ordinary WC–Co compositions. When steel is cut the long turnings conduct a large part of the heat away from the tool; thus, the hard metal tip is kept quite cool, even if its own heat conductivity is relatively poor. In the case of a short-chipping material like cast iron, however, little heat can be carried away by the chips. Moreover, cast iron itself is a poor heat conductor, and as a consequence, very high temperatures are generated in the tool tip. Whereas the more efficient heat-conducting WC–Co alloys can still withstand this severe thermal effect, the less efficient conductors such as WC–TiC–Co compositions overheat greatly and fail because of excessive oxidation and cratering.

Friction Effects. The influence of frictional effects on the cutting properties of various hard metal compositions has been studied by various investigators, including Sykes,[98] Ballhausen,[99] and Dawihl.[100] The experimental data indicate that compositions containing titanium carbide have a lower coefficient of friction, but that this in itself cannot be entirely responsible for the superiority of the WC–TiC–Co alloys for machining steel. Dawihl bases certain conclusions on observations of wear phenomena with WC–Co and WC–TiC–Co tools. Apparently, one of the most important factors in tool wear is the tendency of the tool tip to weld onto the work, followed by tearing apart of the weld as the cutting operation progresses. The welding or alloying temperature[101] appears to be of considerable importance. Dawihl[100] determined this "welding-on" temperature for various cemented carbides and their individual components in static contact either with steel or with the cemented carbides themselves; his data are reproduced in Table 124. The high "welding-on" temperatures of all cemented carbides are chiefly responsible for the suitability of the hard metals for tool applications. If cemented carbides work against other cemented carbides, particularly of different composition, very high welding-on temperatures can be observed. The WC–TiC–Co tool compositions show higher "welding-on" temperatures than compositions without titanium carbide. Of course, the low welding-on tem-

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[98] W. P. Sykes, *Trans. Am. Inst. Mining Met. Engrs.*, *128*, 76 (1938).

[99] C. Ballhausen, *Z. Metallkunde*, *32*, 326 (1940).

[100] W. Dawihl, *Metal Treatment*, *13*, 127 (1946).

[101] W. Baukloh and G. Henke, *Metallwirtschaft*, *18*, 59 (1939).

perature of the cobalt results in a reduction of this temperature for any cemented carbides as compared with pure carbides. The value of Dawihl's experiments is somewhat questionable, however, since the actual temperature at the tool tip during cutting is not known and may be different for the different cutting materials.

The actual wear of the tool tip materials, especially in machining steels that form long chips, cannot be fully explained by the welding and alloying phenomena caused by friction. If the weld would be properly separated, no wear effects would result; only if this separation is accomplished by ripping out of particles of the hard metal do wear and tear come into play. The circumstances under which the tearing-out takes place depend much on the strengths of the hard metal, the work, and the weld, and their relation to each other. According to Dawihl,[100] the strength of the weld is lower for hard metals containing titanium carbide than for those without it. This decrease in the strength of the weld, together with the more favorable welding-on temperature, helps to explain the improved performance of the WC–TiC–Co tool materials for the machining of steel. The tendency of these materials to adhere to a lesser degree to the chip coincides with the lower coefficients of friction as observed by Dawihl,[100] as well as by Sykes[98] and Ballhausen.[99]

TABLE 124

"Welding-On" Temperatures of Cemented Carbides and Their Components (Dawihl[100])

	Steel A[a]		Steel B[b]		WC–Co		WC–TiC–Co[c]	
Constituents	°C.	°F.	°C.	°F	°C.	°F.	°C.	°F.
Co	500	930	750	1380	—	—	—	—
WC	925	1700	1000	1830	—	—	—	—
TiC	1125	2060	1175	2150	—	—	—	—
WC + 6% Co	650–675	1200–1250	750	1380	925	1700	1025	1880
WC + 16% TiC (solid solution) + 6% Co	700–875	1290–1610	800–900	1470–1650	—	—	1000	1830

[a] Tensile strength, 85,000 psi.
[b] Tensile strength, 200,000 psi.
[c] Solid solution double carbide.

Applications of Cemented Carbides

Cemented carbides are used on a commercial scale for (*1*) cutting tool materials; (*2*) die materials, and (*3*) wear and corrosion-resistant materials. The first of these is predominant, with an estimated 80% of

Grade	Hardness, Rockwell "A"	Trans. rupt. strength, psi	Materials machined	Suggested operations	Types of cuts	Suggested speed range,[a]	General observations
TUNGSTEN CARBIDE GROUP							
55A	87.5 Best grade for below average conditions. Best grade for withstanding shock and vibration. Toughest grade. Minimum chipping. Dulls by wear.	295,000	Cast iron. Steel castings when tantalum grades fail from too rapid wear. Pressed steel and welded parts. Centrifugally cast bronze when speed is limited but heavy feed can be employed.	Turning. Boring. Facing. Bar, wire, and tube-drawing dies. Sheet metal drawing and forming dies.	Heavy hogging. Continuous and interrupted cuts.	100–150. Especially good where speed is limited but large range of feed is available.	Use for heavy cutting on large machines using tools up to 2″ × 2″. Use when other grades fail because of poor machine conditions. Can be used on steel castings when chips do not crater or weld to tip. Easily ground, brazed. Takes keen edge.
906	89.5 Not as tough as 55A. Requires slightly better conditions. Resists abrasion better than 55A. Is more dense than 55A and is capable of higher speeds.	275,000	Cast iron. Nonferrous metals. Steel castings with light cuts. Brass and bronze on old machines.—Cuts are usually over very rough surfaces and there is hazard of pieces loosening in chuck.	Turning, facing, boring, and milling.	Roughing. Continuous and light interrupted.	150–175. Used where speed is of secondary importance but where tools must stand up for a full shift without change.	Excellent for roughing cuts with face mills on C.I. Good for heavy work with counterbores and spot facers; rough boring with heavy feeds. Used on small diameters when harder grades are used on large diameters. Easily brazed. Easily ground.
44A	90.06 Can be used under conditions below average. The most nearly universal grade. An excellent grade with which to start.	205,000	Cast iron, nonferrous metals and nonmetallic materials.	Turning, boring, facing, and milling. Finish boring over port holes in large cylinders.	Roughing and finishing. Continuous or light interrupted.	175–225	Shanks must be adequate when interrupted cuts are taken. When rigid bars and heads are used finish cuts may be taken on brass and bronze where harder grades tend to chip—example, sand castings having irregular surfaces requiring interrupted cutting, or on parts difficult to hold in chuck. Not for roughing on old equipment having excessive vibration. Easily brazed and ground.

883	91 8	190,000	Cast iron, nonferrous metals and nonmetallic materials. Light cuts on tough steel.	Turning, boring, and facing. Finish milling. Reaming. Wear-resisting applications.	Finishing and roughing.	200–300	Where conditions are average or better use on all roughing and finishing operations on nonferrous and nonmetallic materials. Especially valuable for reaming nonferrous metals and alloy irons, rough and finish boring, rough boring on precision operations and for finish milling. Easily brazed and ground.
	Use under good average conditions. Denser than 44A hence better resists abarasive action. Not as tough as 44A.						
905	92.0	170,000	Alloy irons, nonferrous metals. Nonmetallic materials.	Boring, turning, and facing. Light cuts under good average conditions. Also precision operations.	Light finishing *only* on metals. Also roughing on nonmetallic materials.	300–450	Essentially a high-speed finishing grade. When 883 *wears* at cutting edge use 905 for greater tool life. Usually produces better finish than 883. Grade 905 is particularly suited for high-speed, light-feed finishing to close limits. Requires care in brazing and grinding. Finish grind on fine-grained diamond wheel or lap.
	Operating conditions should be better than average. Not as tough as 883. Resists abrasion better than 883.						
999	92 5	140,000	All irons, nonferrous metals and nonmetallic materials.	Precision boring, turning, and facing. General operations on nonmetallic materials.	Continuous light finishing cuts *only*.	300 and up.	Use with considerable discretion as it will chip easily under adverse conditions. This grade is intended for special cases where conditions are ideal and high speed is available. Use when tool life or finish obtained with 905 is not satisfactory. Use tips of simple shape. Use extreme care in brazing and grinding. Sharpen with fine-grain diamond wheel or lap.
	Use where operating conditions are as much *above average* as possible. Hardest but least tough of tungsten carbide group.						

[a] Surface feet per minute.

Table continued

TABLE 125 (*concluded*)

Grade	Hardness Rockwell "A"	Trans. rupt. strength, psi	Materials machined	Suggested operations	Types of cuts	Suggested speed range[a]	General observations
TUNGSTEN CARBIDE AND TANTALUM CARBIDE GROUP (Commonly Called "Tantalum" Carbide)							
77B	86.8 The toughest grade of "tantalum" carbide. "Average conditions" desirable but not always necessary.	250,000	Steel in any form, up to 0.45–0.5 C and hardness up to 200 Brinell.	General turning, facing and boring.	Heavy continuous cutting with 0.030 to 0.050 feed.	200–300	Tough enough to stand up on heavy cutting. Good grade to use for steel when exact operating conditions not known. Used for cutting hot flash after welding. Not hard to braze Easily ground. Cutting edge should be honed smooth.
77A	88.8 Average conditions desirable. Stronger but not as hard as grade 907.	200,000	Steel bars, forgings, plates, stampings up to 0.65–0.75 C and most alloy steels up to 300 Brinell. Alloy irons with high steel content.	General turning, boring, and facing. Wear block in place of roller on back rest.	Continuous roughing and finishing.	250–400	Use when grade 77B wears dull but does not chip. Can be used for wear blocks in place of steel rollers on screw machine back rests. Not hard to braze. Easily ground. Hone cutting edge very slightly to a smooth land not wider than 0.003 after sharpening.
907	91.5 Average conditions should be met.	180,000	Steel bars, forgings, and stampings. Brake drums of a material that causes 883 and 905 to crater. Hard steel in the 300–350 Brinell range.	Turning, boring, and facing.	Light, high-speed, continuous cuts on precision work.	300 and up.	Principally for light, high-speed precision work in straight carbon steel range to 0.75 C. Tips should be simple shapes. Excellent for finishing steel brake drums; light cuts on steel tubing. Good on some grades of malleable iron. Not hard to braze. Grinds easily on diamond wheels just break cutting edge with hone.

TUNGSTEN CARBIDE AND TITANIUM CARBIDE GROUP (Commonly Called "Titanium" Carbide)							
1078A	90 5	225,000	Steel bars, castings, forgings, plates, and stampings up to 0.45 C and 250 Brinell.	General turning, boring, facing, etc.	Roughing continuous and interrupted.	200–400. Most economical speed is usually about 250.	A newer grade which has replaced 77A many times when 77A has proved to be a trifle hard. Will stand more speed than "tantalum" group, which usually aids cutting. Easily brazed and ground. Hone cutting edge.
	Use under average conditions. Is tougher than 77A. Resists abrasion better than 77B.						
831A	92 5	130,000	Hard and soft alloy steels. Bar stock, forgings, and stampings.	Precision turning, boring, and facing.	Continuous light cuts.	200–600	Excellent for close limit work where high speeds and fine feeds are used. Use tips of simple shapes. Brazing requires extreme care. Hold tips mechanically if possible. Not hard to grind. Finish on fine-grain diamond wheel or lap. Hone cutting edge very lightly.
	Conditions should be at least average.						
TUNGSTEN CARBIDE, TANTALUM CARBIDE, AND TITANIUM CARBIDE GROUP							
78A	89.9	190,000	Steel bars and castings.	General turning, boring, and facing.	Roughing for cuts as heavy as $^3/_8$ in. deep.	200 and up.	Essentially a strong grade for heavy cuts, permitting feeds up to $^3/_{64}$ in. per revolution.
	Average conditions desirable.						
78B	91.0	175,000	Steel bars, castings, etc.	General turning, boring, and facing.	For cuts as heavy as $^1/_4$ in. deep.	250 and up.	Tough and wear-resistant grade for general purpose machining; feeds up to 0.030 in./rev.
	Average conditions desirable.						
78	91.7	165,000	Any kind of S.A.E. steels.	General turning, boring, and facing.	Finishing light, high-speed continuous and interrupted cuts.	300 and up.	A grade of higher wear resistance and hardness than grade 78B, but less shock resistant. This grade is particularly adaptable to finishing and light roughing of all types of steel; feeds up to 0.030 in./rev.
	Average conditions desirable.						

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[a] Surface feet per minute

TABLE 126

Grade Analysis of Some Firthite Hard Metals[a]

Grade	Average hardness, Rockwell "A"	Nature and properties	Recommended field of use
GRADES FOR CUTTING CAST IRON, NONFERROUS, AND NONMETALLIC MATERIALS			
HC......	88	Strongest tungsten carbide; high binder content; withstands impact, vibration, and abuse; cannot be easily broken or chipped; will take an unusually keen edge even with steep rake and acute cutting angles and relief.	Heavy duty; severe interrupted cuts, coarse feeds on soft materials in old machines at relatively slow speeds; excellent for skiving brass; highly recommended for grooving aluminum alloy pistons.
HB......	89	Stronger than H; harder than HC; exceptionally tough and moderately wear resistant; wide latitude in manufacturing; freedom from cracking from brazing and grinding.	Rough and intermittent cuts on soft metals and irregular castings; large tools; light shaper and planer service; sharp edge and plunge cut form tools of intricate shape.
H.	89.5	Basic grade of tungsten carbide; best balance of strength and wear resistance; harder than HB; stronger than HA; oldest standard tungsten carbide and most dependable performance.	Best first choice for doubtful applications; general use in rough machining softer metals and less abrasive nonmetallic materials at moderate speeds; light interrupted cuts.
HD.... .	90	Harder and more wear resistant than H; stronger than HA; withstands light shock and vibration.	Light rapid intermittent cuts—particularly milling; preferable to HA for inside angle tools requiring more wear resistance than H.
HA.	90 5	Harder and more wear resistant than H and HD; stronger than HF; maintains size on long turning and boring jobs; most widely used tungsten carbide; highly versatile; inside angle form tool applications to be avoided (use HD or H).	Semifinishing hard and chilled irons; well adapted to turning, facing, sawing, boring, and reaming; extremely abrasive materials; uninterrupted cuts only on rigid machines with well-supported work and tools.
HF......	91	Hardest and most wear-resistant grade; limited strength; requires care in brazing, grinding and application; low binder content.	Lightest, highest speed service on most abrasive materials; precision boring, turning, and facing; solid cuts, rigid machines; must be well supported with minimum overhang; notches and sharp corners to be avoided.

[a] *Firthite User's Handbook*, Firth-Sterling Steel Co., McKeesport, Pa., 1941.

TABLE 126 (concluded)
Grade Analysis of Some Firthite Hard Metals[a]

Grade	Average hardness, Rockwell "A"	Nature and properties	Recommended field of use
		GRADES FOR CUTTING STEEL	
T-04	89	Strongest steel cutting grade; withstands impact and vibration as well as considerable abuse; tough and moderately wear resistant; remarkable uniformity and versatility of performance; will take a keen smooth edge and can be ground to steep rakes and clearances with deep chip curling grooves.	Heavy duty; severe interrupted cuts; coarse feeds and deep cuts in roughing softer steels at relatively low speeds in older machines; wears at speeds over 200 ft./min.; closest approach to a universal grade; machines both cast iron and chilled cast iron; use on large tools and in cases of limited tool support.
T-89	89 5	Triple carbide; high binder content confers considerable strength; alloys provide corrosion, erosion, heat, wear, and chip crater resistance; harder than T-04, stronger than TA.	Wide scope of application; first choice for doubtful cases; rough machining softer steels up to $^1/_2$-in. cuts, $^3/_{32}$-in. feeds up to 250 ft./min.; cuts both cast and chilled iron; stands shock and "jump" cuts.
TA	90 5	Wear and crater resistant; stronger and tougher than T-16; similar strength and hardness compared with T-90; harder and more resistant to wear and chip craters than T-89; balanced composition.	General purpose material for all types of steel—cast, rolled, and forged; limited to light, intermittent cuts; use for operations requiring higher speeds but lighter cuts and feeds than T-89.
T-90	90 5	Triple carbide; low coefficient of friction; tougher than T-16; harder than T-89; excellent heat, wear, and chip crater resistance; unique balance of hardness and strength.	High-speed finishing and light roughing medium and hard steels in rigid machines with steady cuts; ideal shell machining grade.
T-16	91	Very hard and wear resistant; limited strength; exceptional heat and chip crater resistance; harder than T-90 and TA.	Light, rapid finishing of harder steels in automatic machines up to $^3/_{16}$-in. cut 0.015-in. feed; rigid machines, well-supported work and tools; no intermittent cuts.
T-31	91.5	Hardest and most wear-resistant grade; premium material requiring extra charge based on calculated weight.	Lightest, highest speed, shallow cuts, fine feeds only—hard, alloy and treated steels; rigid machines; uninterrupted cuts only; precision boring at exceptionally high speed.

TABLE 127
Grade Analysis of Some Kennametal and Vascoloy-Ramet Hard Metals

Grade	Average hardness, Rockwell "A"	Transverse rupture strength, psi	Recommended field of use
KENNAMETAL GRADES[a]			
KH	91	224,000	For continuous cuts on all material except free-cutting steel and malleable iron.
K2H	—	—	For free-cutting steels and malleable iron.
K3H	—	—	For light fast finishing cuts on steel as in precision boring.
KM	90.3	305,000	For rough machining or discontinuous cuts.
KS	89.9	322,000	For intermittent cutting and rough machining; for "jump" cuts on intermittent cuts; for machining cast steel.
VASCOLOY-RAMET GRADES[b]			
EE	90.5	275,000	Heavy roughing cuts under shock conditions.
EM	91.3	255,000	General-purpose grade for steel.
E	92.3	217,000	Medium and finishing cuts where extra long tool wear is desired.
XX	88.6	260,000	Roughing steel castings, roughing S.A.E. 1112, 1010 to 1030.
X	90.4	240,000	High carbon, high chromium, tool steels; finishing S.A.E. 1112, 1010 to 1030.
AT	92.0	220,000	Stainless steel, high carbon, high chromium, tool steels, etc.
B	90.0	210,000	Roughing semisteel, nickel-iron, alloy castings, etc.
A	91.3	210,000	Finishing semisteel, nickel-iron, alloy castings, etc.
2A68	91.3	250,000	General-purpose roughing grade for cast iron and abrasive materials.
2A5	92.0	235,000	General-purpose finishing grade for cast iron and abrasive materials.
2A3	89.4	310,000	Heavy roughing cuts under shock conditions (cast iron).
2A7	92.5	215,000	Finishing cuts where extra long tool wear is desired (cast iron).
2A9	92.9	190,000	Light finishing cuts where extra long tool wear is desired (cast iron).

[a] Bulletin No. 740, Kennametal, Inc. (Successor to McKenna Metals Co.), Latrobe, Pa.

[b] Catalog, Vascoloy-Ramet Corp., North Chicago, Ill., Jan. 1942.

all cemented carbides produced being used for cutting tools, and the balance being equally divided between the other two types of applications. Of the last, a special field of application, namely, components for use at elevated temperatures, has branched off most recently.

COMMERCIAL CARBIDE GRADES

The number of commercial carbide grades available on the American market is considerable. The best known trademarks include Carboloy,[102] Firthite,[103] Kennametal,[104] and Vascoloy-Ramet.[105] A grade analysis for some Carboloy products[106] is reproduced in Table 125, and the fields of use of some Firthite materials[107] are indicated in Table 126. Some Kennametal[108] and Vascoloy-Ramet[109] grades are analyzed in Table 127.

The majority of commercial hard metal grades are of the multiple carbide type, for pure WC–Co hard metals can be used only for the machining of short-chipping materials. The multiple carbide materials based on solid solutions between tungsten carbide and titanium carbide and/or tantalum carbide are used exclusively for the machining of steel, but newest developments indicate that these hard metals may also become adapted to the machining of cast iron and other short-chipping materials.[110] It appears possible that the disadvantages due to poor thermal conductivity can be overcome and that straight WC–Co hard metals can be fully replaced by the more advantageous solid-solution type hard metals, so that eventually a universal hard metal alloy can be introduced in work shop practices.

CUTTING TOOL APPLICATIONS

Performance. A detailed survey of the cutting tool applications for cemented carbides has been given by MacKenzie,[111] and more recently by Hull and Schwartz.[111a] Cemented carbide tool materials are most valuable for their ability to perform many cutting operations more efficiently than is possible with other tool materials. Average production increases through the use of cemented carbides have been conservatively reported[112] as: cast iron: 10–200% (average about 60%); steel: 10–80% (average about 35%); and nonferrous materials (aluminum, brass,

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[102] Products of the Carboloy Company, Inc., Detroit, Mich.

[103] Products of Firth-Sterling Steel Co., McKeesport, Pa.

[104] Products of Kennametal Inc., Latrobe, Pa.

[105] Products of Vascoloy-Ramet Corp., North Chicago, Ill.

[106] Carboloy Catalog Nos. TA-371, GT-120, and GT-133.

[107] Firthite Catalogs 1938 and 1942; Users Handbook 1942.

[108] Kennametal, Bulletin No. 1740.

[109] Vascoloy-Ramet Catalog, Jan. 1942.

[110] P. Schwarzkopf, *Powder Metallurgy*. Macmillan, New York, 1947, p. 212.

[111] A. MacKenzie, *Metals Handbook*. Am. Soc. Metals, Cleveland, 1939, p. 909.

[111a] L. J. Hull and D. L. Schwartz, *Metals Handbook*. Am. Soc. Metals, Cleveland, 1948, p. 59.

[112] Progress Report No. 4, Sub-committee on Metal Cutting Materials, Am. Soc. Mech. Eng., Special Research Committee on the Cutting of Metals, 1935.

bronze, etc.): 15–500%. The savings in cost of production of the same materials were reported as: cast iron: 5–75% (average about 28%); steel: 5–50% (average about 22%); and other materials: 20–75% (average 20 to 40%). The same report gave the following data for cutting speeds, showing a tendency toward high speeds and light feeds: cast iron, roughing cuts: 55–500 ft./min. (average 175); cast iron, finishing cuts: 70–580 ft./min. (average 245); soft steel: 95–400 ft./min. (average 200); hard steel: 40–300 ft./min. (average 135); and brass and bronze: 150–2250 ft./min. (average 510).

The cemented carbide tool alloys are particularly advantageous in mass production applications because of their resistance to wear and shape changes—requiring considerably less frequent tool grinding and permitting faster removal of stock.

Materials Machinable. Among the materials that can be machined with cemented carbide tools are: (*1*) ferrous metals, including cast iron, malleable iron, cast steel, forged steel, rolled steel, and alloy steels; (*2*) nonferrous metals, including aluminum, copper, brass, bronzes, babbitt, zinc, and nonferrous alloys; and (*3*) nonmetallic materials, including carbon, wood, plastics, resins, rubber, casein, asbestos, transite, masonite, porcelain, and glass.

The entire range of steels up to a hardness of 500 to 550 Brinell in any classification is machinable by the multiple carbide tools which are able to retain a high degree of hardness at speeds 2 to 4 times greater than possible with high-speed steel tools.

Types of Tools Used. In most tool applications for turning, cutting, boring, planing, or milling, hard metals are used in the form of small tips that are brazed onto supporting shanks of steel. When used in this form, the hard metal is employed most economically. The tips should be anchored well in a strong supporting construction. Common copper-base or silver-base brazing alloys are suitable for the purpose. Direct welding is usually difficult because of the difference in the coefficients of thermal expansion of the carbides and steel (see also Volume I, page 724). A most recent development, however, is the mechanical insertion and fastening of carbide insert cutting bits to the supporting steel shanks. Apparently, this method of securing the carbide inserts by appropriate clamping and wedging locks in the tool holder under complete exclusion of any brazing or other joining operation requiring heating of the tool insert has been quite successful.[112a].

An assortment of what may be classified as "standard" tools is shown in Figure 352; some of the more specialized hard metal tools

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[112a] J. S. Gillespie, *Iron Age, 163,* No. 19, 84 (1949).

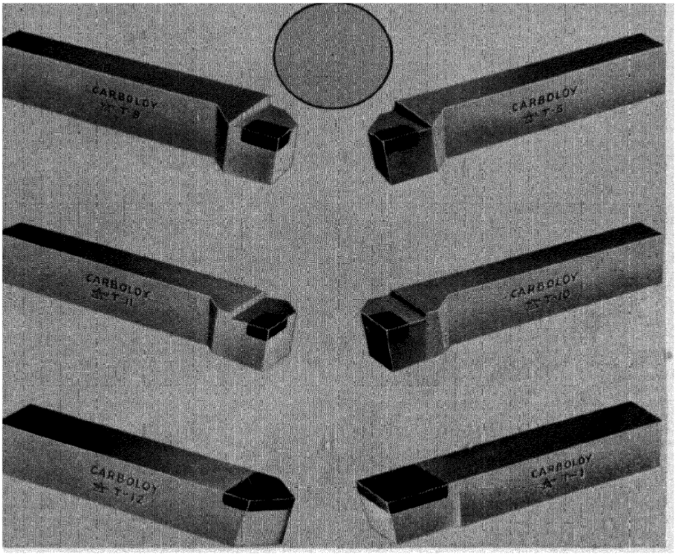

Fig. 352. Variety of standard hard metal tipped tools (courtesy of Carboloy Co., Inc.).

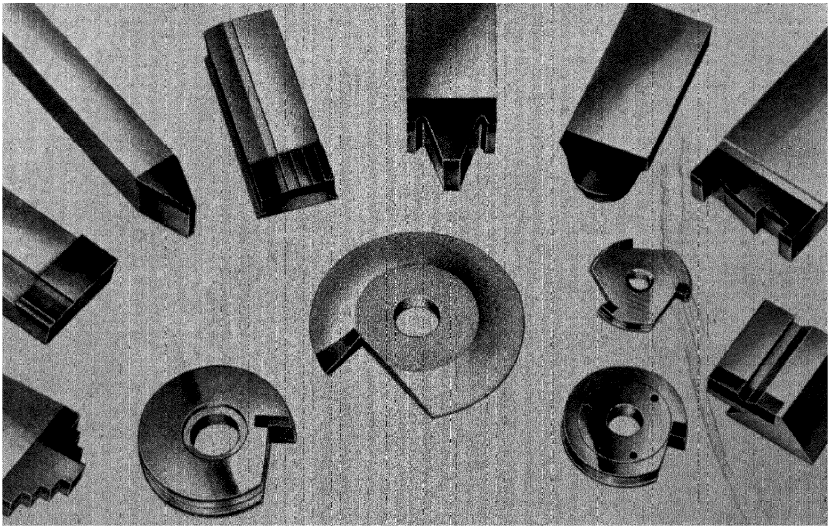

Fig. 353. Assortment of special-shaped hard metal form tools. They include flat, dovetail, and circular forms and tools for skiving, threading, radius forming, pulley grooving, and overshot and undershot cutters. (Courtesy of Carboloy Co., Inc.)

are shown in Figures 353 and 354. A partial list of the many types of tools that are being tipped with cemented carbides is given by MacKenzie,[111] as follows: (*1*) single point tools, for turning, boring, facing, chamfering, and planing; (*2*) grooving tools, for straight grooving and form grooving; (*3*) form tools, including flat tools and circular tools; (*4*) blades, for inserted type milling cutters, adjustable reamers, and saws; (*5*) drills, including flat drills and spiral drills; and (*6*) multiple tipped, solid shank tools, including end mills, side mills, hollow mills, profiling cutters, form tools, grooving tools, step drills, reamers, core drills, shot facers, counterbores, valve-seating tools, broaches, and saws.

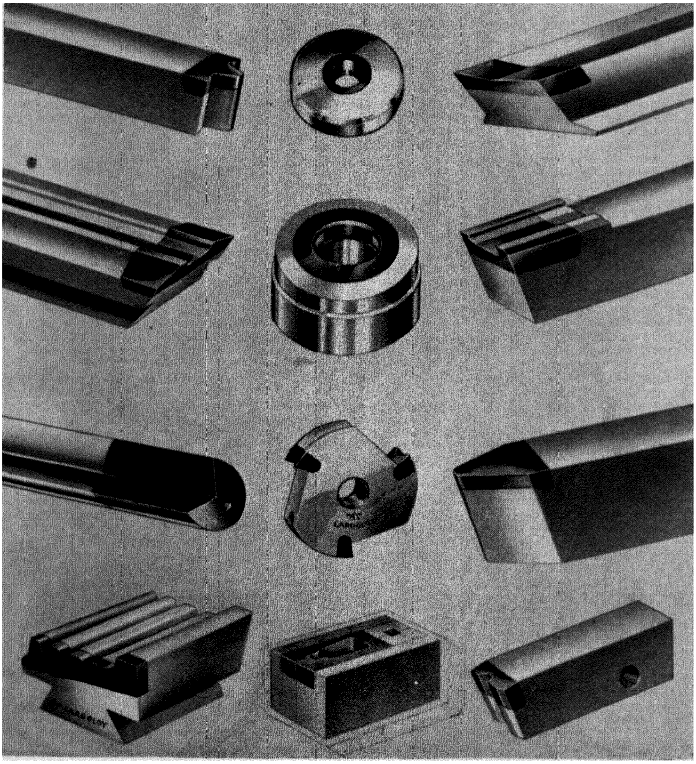

Fig. 354. Assortment of special-shaped hard metal form tools and dies. They include a gun drill (third row, left), a cartridge case die (first row, center), a sheet metal drawing die (second row, center), and a sheet metal stamping die (bottom row, center). (Courtesy of Carboloy Co., Inc.)

The attaching of carbide teeth to metal saws represents a typical example of the drastic increase in efficiency and cutting speed that is obtainable with hard metals. In one instance reported,[113] a difficult metal-sawing job was speeded up considerably by welding eight carbide teeth around the periphery of a circular saw. In addition to the gain in cutting efficiency, the saw did not require resharpening.

One of the most recent applications of cemented carbide alloys is for regular and rotating files. The smaller files—starting at $^1/_8$-in. diameter—are made entirely of hard metal, while the larger sizes consist of steel shafts tipped with cemented carbides. The life of these has been found to be 100 times more than usual[113a]

What may be considered one of the most promising fields for cemented carbides is rock drilling.[113b] Though cemented carbides have been used for many years for this purpose,[113c] it is only lately that their use as drill bits and tips has assumed major importance in the mining industry. The brittleness of tungsten carbide has in the past largely restricted the application to purely rotary drilling[113d] or to such cases where great shock resistance is not required, *e.g.*, the two-prong rotary drill bits for coal and soft rock, or boring crowns tipped with a brazed carbide insert or coated with a carbide weld deposit, which are used for deep hole drilling. Most recently, however, attempts with not altogether unfavorable results have been made to employ cemented carbides as tipped rotary percussive bits for shot hole drilling.[113e] A straight cobalt-cemented tungsten carbide composition with about 11% cobalt appears to be the most popular hard metal grade for this purpose; the tip is inserted in a slot in the alloy steel body, and copper-brazed, preferably using high frequency heating. In spite of the comparatively simple manufacture, uniform and reliable performance of the carbide-tipped percussion drill is still a problem; its final satisfactory solution may well depend upon a successful substitution of the presently employed slotting and brazing operations by a process that uses powdered metals for both the tip and the drill and permits sintering the steel-backed composite tool into a strong and shock resistant single unit.[113e] Results of percussion rock drilling tests made in Australia have recently been discussed by Wells.[113f]

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[113] Anonymous, *Am. Machinist, 90,* No. 10, 142 (1946).

[113a] P. Schwarzkopf, *Powder Metallurgy.* Macmillan, New York, 1947, p. 220.

[113b] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe.* Springer, Berlin, 1943, p. 308.

[113c] British Intelligence Objectives Sub-committee, Final Report No. 1727 (April 1948); see also *Met. Powd. Rept., 2,* No. 9, 135 (1948).

[113d] Anonymous, *Metal Ind., London, 73,* 174 (1948).

[113e] D. H. Shute, *Met. Powd. Rept., 3,* No. 2, 18 (1948).

[113f] E. J. Wells, *Chem. Eng. Min. Rev., 41,* 135 (1949).

DIE APPLICATIONS

Next in importance to the tool applications are the uses of hard metals for dies employed in metal-working processes. As in the case of tools, only a small proportion of hard metal is used in the dies (in the form of liners or nibs), the hard metal being solidly surrounded with a supporting material such as a forged steel ring. Figure 355 illustrates the hot-forging of a steel casing around the carbide die nib for a wire-drawing die. For this purpose tungsten carbide compositions have given entirely satisfactory performance. Cemented carbide dies enable the drawing of bars, rods, wires, and tubings in a wide variety of sizes and shapes. Hard

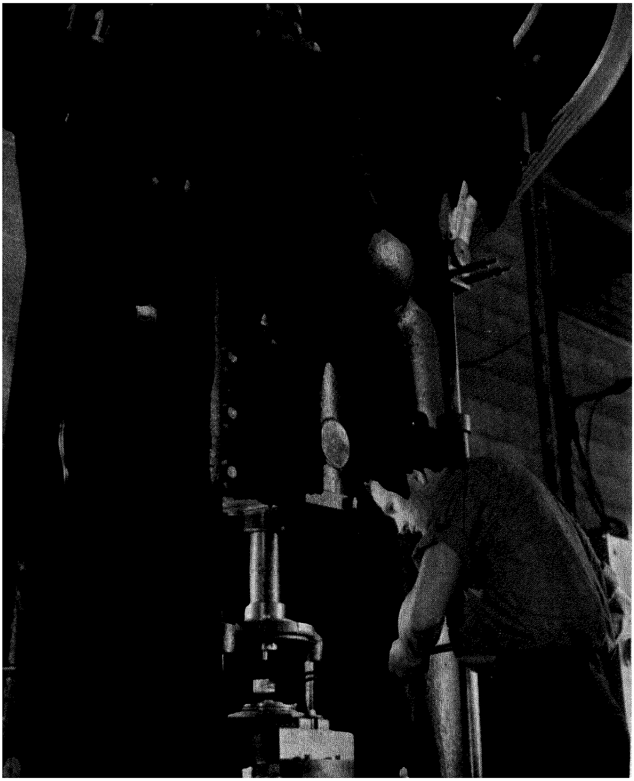

Fig. 355. Hot forging of steel casing around the cemented carbide die nib in a wire-drawing die (courtesy of Carboloy Co., Inc.).

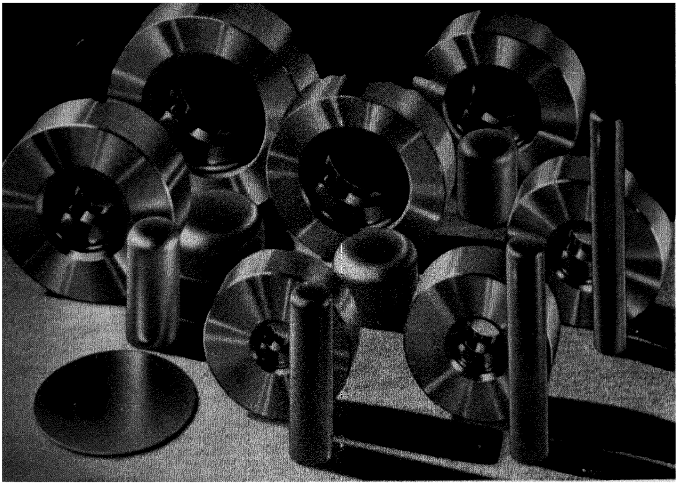

Fig. 356. Assortment of carbide-lined drawing dies and piercing mandrels (courtesy of A. C. Wickman Ltd.).

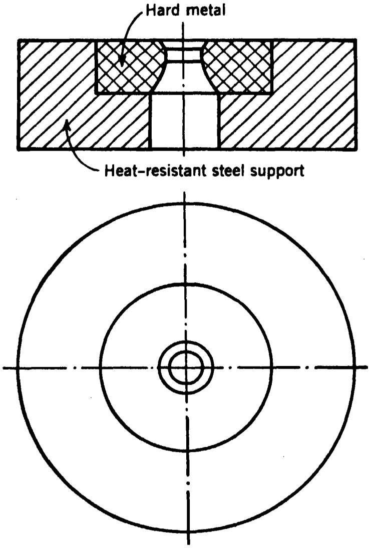

Fig. 357. Schematic drawing of an extrusion die with hard metal liner (according to Kieffer and Hotop[113g]).

[113g] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerstoffe*. Springer, Berlin, 1943, p. 311.

metal dies for extrusion, sizing, deep drawing, forming, or burnishing, as well as mandrels, are also in wide use. In Figure 356 a photograph is shown of an assortment of carbide-lined drawing dies, and in Figure 357 a sketch shows the cross section of an extrusion die. Figure 358 displays a number of forming, sizing, and calipering dies with hard metal liners.

According to MacKenzie,[111] the following materials can be reduced by hard metal drawing or extrusion dies: low carbon steels, high carbon steels, alloy steels, stainless steels, tungsten, molybdenum, precious metals, nickel, nickel alloys, aluminum alloys, copper, brass, and zinc. Of these, wires, bars, and tubing can be produced by hot drawing or extrusion, and bolt and screw stock by sizing and extrusion. Also, a great number of shapes can be produced by deep drawing and forming.

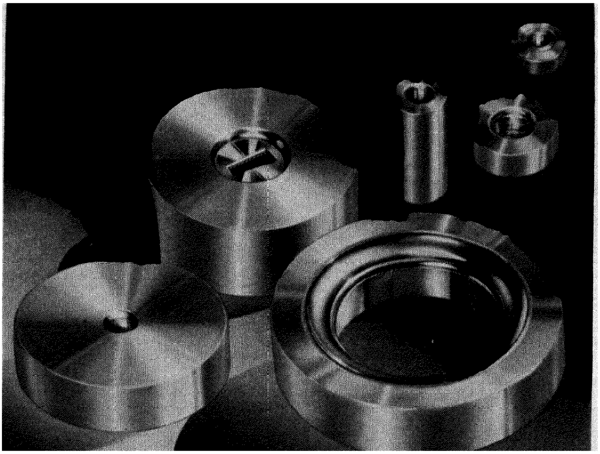

Fig. 358. Forming, sizing, and calipering dies with cemented carbide liners (courtesy of A. C. Wickman Ltd.).

As an example of improved performance and greatly increased tool life, the use of solid cemented carbides as punch and die material for the manufacture of stator laminations for electrical motors may be cited.[114] The dies, made in two pieces and clamped together, were produced from a highly shock-resistant carbide grade; the design permitted resharpening by grinding. A fiftyfold increase in punch and die life was obtained.

The application of carbide dies and punches for laminating and blanking is increasing steadily, and blanking of steel and other metals in thicknesses up to 0.025 in. has become possible.[115] In Figure 359 a

[114] Anonymous, *Mod. Ind. Press, 8,* No. 6, 8 (June 1946).
[115] E. Glen, *Iron Age, 157,* No. 17, 51 (1946).

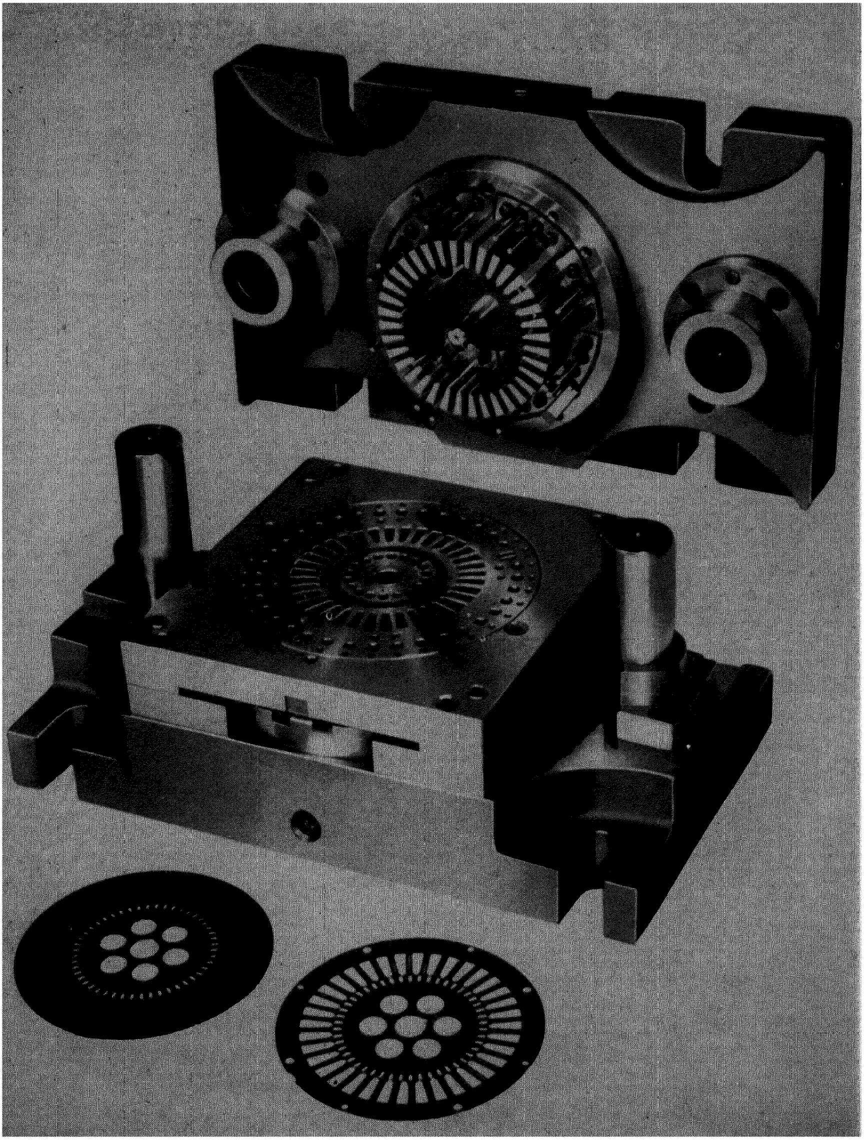

Fig. 359. Blanking die assembly for the production of stator laminations in electric motors. Built by Lincoln Park Industries for Westinghouse Electric Corp. The die is made to notch and pierce 36 notches and 12 rivet holes in approximately 6-in. diameter laminations. All of the functioning details in both the upper and lower halves of the die assembly are made of cemented tungsten carbide. (Courtesy of Lincoln Park Industries, Inc.)

very complicated blanking die is illustrated; this work may well be considered an outstanding example of the use of cemented carbide in the die field. The die assembly built for the production of stator laminations in electric motors about 6 in. in diameter consists of solid carbide sections and punches. During the war, the shell industry introduced carbide dies for the cold nosing of steel, and this procedure has been followed for projectile sizes up to 105 mm.[115]

The production of very large dies for the deep drawing of steel cylinders by a special hot-pressing process which combines molding, semisintering, and final sintering into a single operation, is another recent development in the carbide field. In one instance a nib has been produced with an internal diameter of 13.5 in., weighing more than 100 lb. Metals now being drawn economically in such dies include plain carbon steels, special alloy steels, brasses, bronzes, copper, aluminum alloys, zinc alloys, lead, and tin.[115]

Generally speaking, the size of cemented carbide components is now limited to about 100 square inches top surface, and the configurations required to fall within an 18-in. circle.[116] The maximum height of such large sections is approximately 8 in. and the weight does not exceed 120 lbs. These present size and weight limitations are determined chiefly by the equipment available; it is believed that, if necessary, the range can be greatly extended. As far as surface finish is concerned, it is claimed that cemented carbide products can be ground and lapped to a surface smoothness falling within a variation of $^{1}/_{80000}$ in.[116]

WEAR AND CORROSION RESISTANT APPLICATIONS

Cemented carbides are becoming increasingly important as materials displaying wear and corrosion resistance.[116a,b] The hard metal is used mainly in small tools, as well as in parts and accessories for production machines, where local wear or corrosion is a problem. This list of practical applications will give an idea of the extent to which carbides can be used as an engineering material[111,111a,117,118,118a]: centers for lathes and grinders; rests for lathe work; rests for centerless grinder work; grinder fingers, profiles, and cams; gages, micrometers, indicator points; coiling guides and arbors; guides of all kinds, including rayon thread and wire guides; valve stems and seats for hydraulic presses and refrigerators; ball valves and seats for pumps; meter fingers; valves in contact with

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[116] J. R. Longwell, *Steel, 119,* No. 23, 130 (1946).

[116a] R. Kieffer and F. Benesovsky, *Industrie u. Technik, 3,* No. 12, 251 (1948).

[116b] J. S. Gillespie, *Metal Progress, 56,* No. 4, 523 (1949).

[117] Progress Report No. 4, Sub-committee on Metal Cutting Materials, Am. Soc. Mech. Eng., Special Research Committee on the Cutting of Metals, 1935.

[118] Anonymous, *Machinery, New York, 53,* No. 2, 189 (1946).

[118a] P. M. McKenna, *Am. Machinist, 90,* No. 17, 117 (1946).

molten aluminum; sandblast nozzles, spray gun nozzles, and valve needles; burnishing tools and dies; chilling plates for hardening and tempering of thin stock; straightening dies; mold liners for pharmaceutical, ceramic, and powder metallurgy industries; grinder parts for grinding of pigments, pulverizing of coal and carbon products, and abrasives; balls for Brinell testing machines; precision balls for burnishing and polishing check valves; ball and sleeve bearings; small knives in sewing machines; swaging dies; ball mill slugs; liners for brick molds; milling collets; spindle bearings; vice components; knurl pins and wheel shafts; grooving tools; gripping devices; chuck jaws; and tongs for ingots or hot glass.

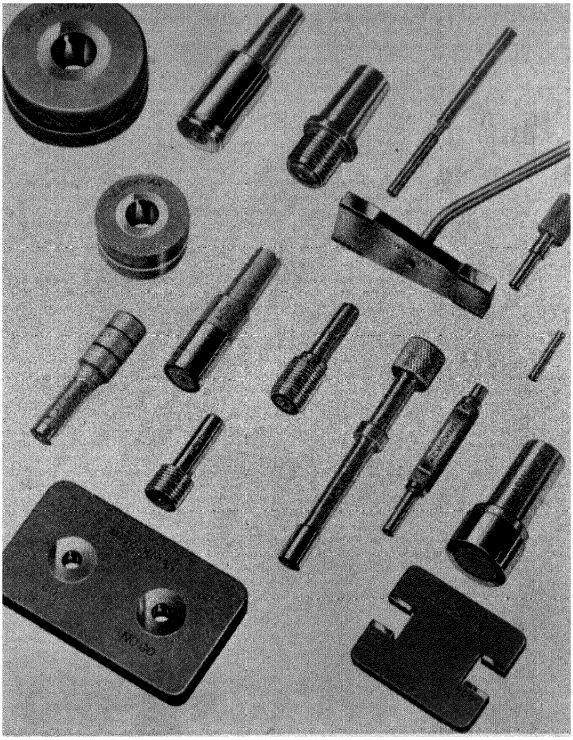

Fig. 360. Assortment of wear-resistant parts and dies with cemented carbide facings or liners (courtesy of Carboloy Co., Inc.).

Figures 360 and 361 show assortments of various carbide-lined parts requiring high wear resistance, and Figure 362 displays a large variety

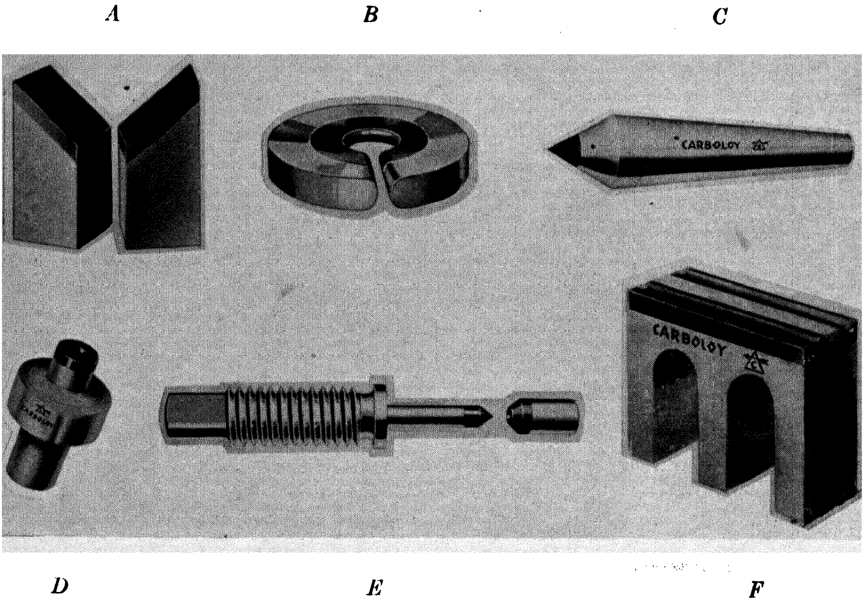

Fig. 361. Wear-resistant parts with hard metal facings: *A*, box tool blocks; *B*, textile guide; *C*, lathe and grinder center; *D*, coating die; *E*, hydraulic valve stem and seat; and *F*, wire-coiling guide (courtesy of Carboloy Co., Inc.).

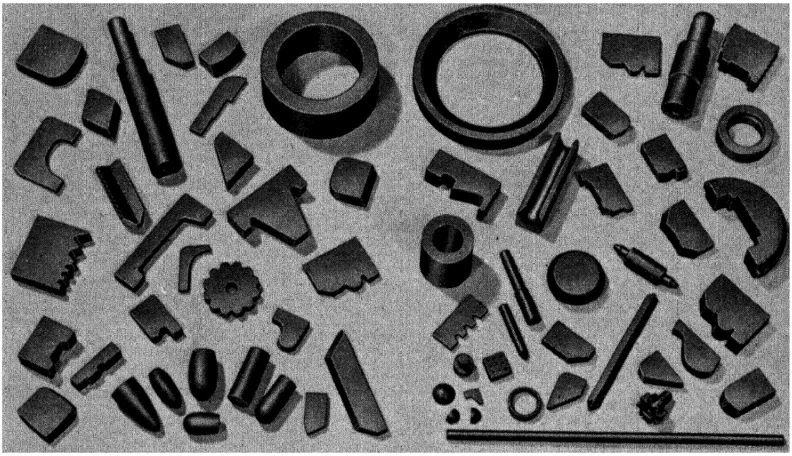

Fig. 362. Assortment of special-shaped hard metal blanks of accurate form for use in wear-resistance applications (courtesy of Carboloy Co., Inc.).

of hard metal blanks to be employed in wear resistance applications. In this connection, it is particularly interesting to note that carbide-lined dies have also been used successfully in powder metallurgy operations (see also Figure 358; and Figure 124 and Tables 36 and 38, Volume I, Chapter X). In molding operations requiring long production runs and close dimensional control, carbide dies have been used extensively during the past decade. More recently, carbide-lined molding, sizing, and coining dies have also been applied in the case of materials which cause abnormal wear of ordinary alloy steel dies. Sectional carbide nibs have found successful application for compacting brass, bronze, copper, iron–tungsten, silver–tungsten, and carbon powders.[119] (In this connection, reference is made to the recent development of *porous* cemented carbide die liners permitting saturation with a lubricant for the purpose of automatic lubrication during molding[119a,119b] (see also Chapter XXVII).)

One use of special interest, and already mentioned, has been as bullet cores in ammunition for antitank weapons as deployed by the Germans in the North Africa desert warfare[120] and later adopted on a large scale by the Allied armies. The material used was twice as dense and much harder than hardened alloy steel. In spite of the relatively low shock resistance of hard metals under normal conditions, Bridgman[121] has shown that bullet cores could be highly effective at the extremely high pressures and temperatures produced in penetrating armor plate.

Another interesting application is the use of cemented carbides for contact materials on relays and transmitters in telegraphic systems. With certain circuits, tungsten carbide with higher electrical resistance offers certain advantages over silver, gold, or platinum having a lower resistance.[122] Standard relay contacts for telegraphic transmission, consisting of tungsten carbide either cemented with cobalt ("Carboloy" type) or bonded with osmium ("Wilcoloy" type), have a life of over two years and meet the unusual requirements for polar relays in every respect (see also Chapter XXIII).

A comparatively recent development is high-speed bearings made from cemented carbides.[123] The installation of sleeve-type carbide-to-carbide bearings on a tool-post grinder used for grinding internal and

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[119] Anonymous, *Iron Age, 156,* No. 17, 50 (1945).

[119a] U. S. Pat. 2,444,282.

[119b] Brit. Pat. Application 6927/48 (March 5, 1947); see also *Met. Powd. Rept., 2,* No. 8, 117 (1948).

[120] F. H. Clark, *Mining and Met., 25,* 81 (1944).

[121] P. W. Bridgman, *J. Applied Phys., 12,* No. 6, 461 (1941).

[122] F. H. Clark, in J. Wulff, *Powder Metallurgy.* Am. Soc. Metals, Cleveland, 1942, p. 493.

[123] Anonymous, *Machinery, New York, 52,* No. 3, 148 (1945).

external surfaces or carbide die nibs has spearheaded this development. With the bearing surfaces properly lubricated with a mixture of kerosene and colloidal graphite, the life of the bearing was found to be about 50 times longer than that of the previously employed standard ball bearings. The wear after operation for more than two years was found to be only 4×10^{-6} in.

One of the most fascinating applications found lately for cemented carbides is for power mills, which have been produced for various applications and in widely differing sizes.[124] Standard rolls for cold strip mills are produced in two diameters, 0.470 and 0.810 in., and to lengths ranging from 10 to 20 in. Solid carbide rolls for rolling aluminum foil have been produced to a size 2-in. diameter and 40-in. long face; for cold rolling of steel, 3-in. diameter and 8.5-in. face. Hard metal rolls of the mounted type, 4-in. diameter and 2.25-in. face, have also been produced for the flattening of wire.

HIGH TEMPERATURE APPLICATIONS

The development of a special cemented carbide grade, known to the trade as K 138,[125] that endures temperatures at which conventional carbide compositions are rapidly destroyed has recently been publicized.[126] Containing the apparently highly oxidation-proof and heat-resistant titanium carbide as the chief component, and cobalt as major binder ingredient, the material is characterized by its light weight, high thermal conductivity, high thermal shock resistance, and high strength and corrosion resistance at elevated temperatures. Some of the reported properties most interesting from the point of view of high temperature resistance are:

Specific gravity	5.5
Transverse rupture strength at room temperature	175,000 to 210,000 psi
Transverse rupture strength at 985°C. (1800°F.)	100,000 psi
Tensile strength at 985°C. (1800°F.)	21,000 psi
Tensile strength at 1095°C. (2000°F.)	15,000 psi
Modulus of elasticity	55,000,000 psi
Hardness, Rockwell "A" scale	91.0 to 92.0
Thermal expansion	9.0×10^{-6} per °C. over range from 150 to 650°C. (5.0×10^{-6} per °F. over range from 300 to 1200°F.)
Thermal conductivity	0.085 cal./sec./°C./cm.
Electrical conductivity	5% of I.A.C.S.
Resistance to combustion gases up to 1150°C. (2100°F.)	No apparent attack in 48 hr.

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[124] Products of Kennametal, Inc., Latrobe, Pa.; catalog No. 47 (1947).

[125] Product of Kennametal, Inc., Latrobe, Pa.

[126] Anonymous, *Materials & Methods, 26,* No. 6, 85 (1947).

It is claimed that the strength at room temperature of this material is unaffected after heating at 1150°C. (2100°F.) for 48 hours. An indication for the good heat shock resistance of the material may be seen in the lack of change in pieces heated repeatedly to 985°C. (1800°F.) in a muffle furnace and quenched in water. Heating to the same temperature and cooling in air had no effect other than the initial discoloration of the exposed surface.

An impressive variety of shapes have been reported in which K 138 material can be produced, including rounds, flats, bars, plates, disks, and balls. Methods for making these shapes are apparently similar to those used in the manufacture of cemented carbide tool tips and shapes, and possibly center around the cold-press and vacuum-sintering or the hot-press techniques. Among the specific applications for the material, pins for supporting work going through porcelain enamel firing furnaces, and exhaust valve seats for Diesel engines have been emphasized. In the first instance, actual service has shown a useful life of at least six weeks as compared to 10 hours for cast nickel-chromimum alloy pins. Other suggested applications for the material are for furnace parts subjected to high temperatures and oxidizing or corrosive conditions, roll guides for hot-rolling mills, and other high temperature structures.

The use of this type of material for gas turbine buckets appears to be its greatest potential application (see also Chapter XXXII). First tests conducted in a quasiservice gas turbine unit by the National Advisory Committee for Aeronautics have given indications of a superior performance of the carbide blades over those made from conventional alloys (Vitallium).[126a,126b] Hoffman, Ault, and Gangler[126a] investigated the scale formed during service on the blade surfaces by x-ray methods and established an outer layer of TiO_2 and an inner layer of $CoTiO_3$. Short-time tensile tests of the 80–20 TiC–Co material gave peak values of 33,200 psi at 985°C. (1800°F.) and 13,200 psi at 1205°C. (2200°F.), which must be considered as exceptionally good figures.

Bobrowsky[126b] reported on tests with other TiC-base compositions, and also on experiments with ZrC as main constituent. Up to 20% Co, the short-time tensile strength of the TiC alloys increased rapidly at 870–1095°C. (1600–2000°F.), but further increases in binder proportion caused a drop in strength. Up to 1095°C. (2000°F.), cobalt-cemented TiC was found stronger than TiC cemented with W or Mo, and at 1320°C. (2400°F.) for the same binder content the short-time tensile strength increases in the order of Mo, W, and Co. Binder-free, hot-pressed TiC

[126a] C. A. Hoffman, G. M. Ault and J. J. Gangler, National Advisory Committee for Aeronautics, *Tech. Note* No. 1836 (1949).

[126b] A. R. Bobrowsky, *Trans. Am. Soc. Mech. Engrs., 71,* No. 6, 621 (1949).

was found stronger than ZrC at 1320°C. (2400°F.), but the reverse was found for 1205°C. (2200°F.).

TiC-base alloys have also been reported on by Redmond and Smith.[126c]

DIAMOND COMPOSITIONS

Historical Development

The basic principle of embedding hard particles into a comparatively soft matrix for producing materials suitable for cutting or abrasive purposes dates back more than three decades, and, as early as 1910, it was suggested[127] to incorporate silicon carbide, quartz, or glass particles into low-melting alloys by stirring in the hard particles while the alloys were in a mushy state. The fact that diamond is the hardest known matter, made it highly recommendable to use fine diamond splinters and dust particles as abrasive inclusions, and future developments were in this direction. Diamonds varying in size from $^1/_4$ to 3 carats (1 carat = 200 mg.) were, for example, anchored onto steel supports with the aid of easy flowing brazes; the diamonds were also pressed, forged, or rolled into the steel supports or into intermediate layers of a softer metal such as copper. These methods, however, found but limited applications in tools used for rock drilling and sawing on account of the large diamond sizes involved. The demand for less expensive products led to the use of finer diamond splinters and eventually to extremely fine dust particles. Various methods of bonding the diamonds were tried. One process involved the application of a paste from diamond splinters and oils onto a porous cast iron disk. Another process provided bonding of the splinters with resins and plastics during their molding. However, the comparatively low wear resistance and poor heat conductivity of these organically bonded diamond compositions have prevented their application as general-purpose cutting, polishing, or lapping tools, and have restricted their applications to lapping and polishing disks for hard metal tools.[128,129] A greatly improved method used in the manufacture of dental tools and cutting wheels for ceramics involves the electrolytic deposition of a nickel binder between the diamond splinters and the steel support. Before submersion into the nickel plating bath, the diamonds are rendered conductive by treatment with metal salts or graphite.[129a]

The bonding of diamond splinters with a matrix derived from metal powders such as electrolytic iron and steel was first suggested in

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[126c] J. C. Redmond and E. N. Smith, *J. Metals, 1,* 987 (1949).

[127] K. Friederich, *Metallurgie, 7,* 97 (1910).

[128] G. F. Taylor, *Gen. Elec. Rev., 37,* 97 (1934).

[129] French Pats. 803,212; 803,213.

[129a] German Pats. 4,042; 626,512; 659,019.

1922.[130,131] This method has been expanded during the last decade to include as matrix material various other metals, particularly copper and nickel-base alloys. Aside from impregnating these metals with diamond splinters alone, combinations with cemented carbides have also been successfully developed,[132] and products now made by metal powder bonding compete in importance with those made by plastic or electrolytic bonding.

Manufacture of Diamond-Impregnated Compositions

RAW MATERIALS

Diamonds. The size of the industrial diamond stones is important for the efficiency of the tool. The finer the grain (grit) size of the diamond, the slower is the cutting action, but the better the finish. In the manufacture of metal-bonded diamond dressing (truing) tools, somewhere between 5 and 35 diamond splinters are embedded per carat, their grain size ranging from 1.0–2.5 mm. (0.04–0.1 in.). For rough grinding and efficient removal of larger quantities of material, grain sizes of about 0.15–0.5 mm. (0.006–0.02 in.) are employed advantageously while for fine polishing the grain sizes fall within the range of 0.05–0.15 mm. (0.002–0.006 in.). Still finer grain sizes, particularly in combination with sintered tungsten carbides, are suitable for the grinding of cutting edges and high polishing of plane surfaces on hard metal tools, rolls, and other form pieces.[133] A typical procedure uses approximately 12 to 16% by weight of diamond dust in the tungsten carbide matrix.[134]

Metal Bonds. Of the many possible matrix materials based on sintered metals, alloys, and hard metal compositions, four principal groups have gained significance:

(*1*) Copper-base alloys, especially bronzes of the phosphor–bronze or beryllium–bronze types, or an alloy containing 47% Cu, 47% Ag, and 6% Co,[135] which permit a sufficiently low sintering temperature to protect the diamond from graphitization.

(*2*) Iron-base or nickel-base alloys, especially iron–nickel–chromium,[136,137] iron–nickel[138] of the Permalloy composition (80–20 Ni–Fe),

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[130] U. S. Pat. 1,625,463.

[131] German Pat. 386,776.

[132] German Pats., 590,707; 604,853; 611,860; 622,823; 627,862.

[133] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe*. Springer, Berlin, 1943, p. 367.

[134] Brit. Pats., 352,124; 419,126.

[135] W. D. Jones, *Principles of Powder Metallurgy*. Arnold, London, 1937, p. 170.

[136] U. S. Pat. 1,625,463.

[137] German Pat. 386,776.

[138] U. S. Pat. 1,959,422.

iron–tin–lead–antimony (70–15–7.5–7.5 Fe–Sn–Pb–Sb)[139] or nickel–beryllium containing 2–8% Be,[140] which must be sintered at higher temperatures, *e.g.*, 1100°C. (2000°F.) for 2 hours.

(*3*) Molybdenum and tungsten alloys such as molybdenum–copper–cobalt,[141] and tungsten–nickel–copper of the "heavy" alloy type[142,142a,142b] (see Chapter XXI), which must be sintered at still higher temperatures, *e.g.*, 1300°C. (2370°F.).

(*4*) Hard metal alloys, especially tungsten carbide–cobalt with 13% Co,[143] or tungsten carbide–titanium carbide–cobalt[144] and tungsten carbide–nickel alloys, with 25% Ni,[144a] which must be sintered between 1300 and 1400°C. (2340 and 2550°F.).

The last group, although requiring special manufacturing techniques to prevent graphitization of the diamond, has the particular advantages of having a firm hold on the diamonds in the matrix, a high hardness and wear resistance of the bonding metal that provides rigid anchorage for the diamonds, and a nearly equal expansion of the carbides and diamond retains a good thermal contact at elevated temperatures.

MANUFACTURING METHODS

The incorporation of diamond dust into the metal matrix can be accomplished by several methods. The diamond particles can be mixed with the metal powders and the mixture compacted at fairly high pressures. In the preparation of a Permalloy matrix, for example, pressures of about 80 tsi have been reported.[145] Sintering of the matrix must be conducted at temperatures sufficiently high to yield a strong and tough matrix. However, a temperature limit of about 1300°C. (2370°F.) is set by the tendency of the diamond to graphitize. Alloys consisting only of high-melting constituents, such as iron–nickel or iron–nickel–chromium, are generally not sintered above 1200°C. (2200°F.). If the matrix contains a low melting constituent, the compact is sintered above the melting

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[139] German Pat. 720,005.

[140] German Pat. 745,685.

[141] German Pat. 583,630.

[142] R. Kieffer and W. Hotop, *Stahl u. Eisen, 60,* 349 (1939).

[142a] F. Rollfinke, *Maschinenbau Betrieb, 19,* 109 (1940).

[142b] C. J. Leadbeater, *Symposium on Powder Metallurgy,* The Iron and Steel Institute, Special Report No. 38, London, 1947, p. 191.

[143] Brit. Pat. 359,637.

[144] W. Dawihl and A. Fehse, *Maschinenbau Betrieb, 18,* 526 (1940).

[144a] G. J. Trapp, B. E. Berry, H. Burden, A. E. Oliver, and T. Raine, *Symposium on Powder Metallurgy,* The Iron and Steel Institute, Special Report No. 38, London. 1947, p. 92.

[145] U. S. Pat 1,959,422.

point of this component, as, for example, in the case of copper–tin or tungsten–nickel–copper. Sintering in the presence of a liquid phase yields a denser and often stronger and tougher matrix.

Another method[146] of bonding the diamonds consists of first preparing a mixture of the diamond dust with powders of high-melting metals, such as tungsten, iron, or iron–nickel. The mixture is then pressed into a fairly dense skeleton body and sintered at a temperature below the melting point of the bonding metal. A subsequent infiltration of comparatively low-melting metals or alloys, such as lead, copper, bronze, or silver, yields a very dense body in which the diamonds are anchored solidly.

The hot-press method also provides a useful means of incorporating diamond dust in a metal matrix.[144a,147,148] Its chief advantage lies in very short sintering (hot-pressing) times, which even at comparatively high temperatures tend to protect the diamond from disintegration, and in the elimination of stresses which are normally caused by shrinkage of the matrix material. Mixtures of diamonds and metal powders such as tungsten–nickel–copper or tungsten carbide–cobalt can either be prepressed cold to facilitate their introduction into the hot press, or they can be subjected directly to the simultaneous action of heat and pressure. The method has made possible the production of very dense bodies in which the diamonds are anchored strongly in the matrix, even if no liquid phase exists during sintering.

Compositions in which diamonds are bonded by bronzes are usually prepared from mixtures that contain 10 to 20% by weight of diamonds added to a 90–10 copper–tin mixture. These mixtures are compacted at pressures ranging from 5 to 25 tsi and afterward sintered in a reducing atmosphere for a short time at 800–900°C. (1475–1650°F.). The density of the material can be improved by repressing and resintering at 600–800°C. (1100–1475°F.).[149]

Iron-base diamond impregnated tools were hot-pressed in Germany during the war by employing a temperature of 1000°C. (1830°F.) and a pressure of 43 tsi.[149a] Another procedure involved sintering diamond-impregnated iron powder directly onto steel backings or cylinders. After a presintering treatment at 1000°C. (1830°F.) the composite pieces were

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[146] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe.* Springer, Berlin, 1943, p. 365.

[147] Brit. Pat. 349,732.

[148] German Pats. 590,707; 604,853; 611,860; 622,823; 627,862.

[149] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe.* Springer, Berlin, 1943, pp. 366, 369.

[149a] British Intelligence Objectives Sub-committee, Final Report No. 860, Item No. 21 (January 1947); see also *Met. Powd. Rept., 1,* No. 7, 103 (1947).

immediately compressed while still hot. Infiltration of the sintered iron–diamond mixture with molten brass or bronze was also used in German diamond tool production work.[142b]

In hard cutting materials in which diamonds are embedded in cemented carbides, 5 to 20% by weight are added to a mixture of 80 to 90% WC and 10 to 20% Co, or to a mixture of 60 to 70% WC and 30 to 40% Ni. Sintering is carried out for a short time at temperatures of about 1400°C. (2550°F.); prolonged heating at this temperature leads to deterioration of the diamonds. During hot pressing, the liquid cobalt–tungsten–carbon eutectic is squeezed out, with the diamonds being brazed solidly into position.[149] One hot-press procedure found especially suitable for nickel-cemented carbide bonded compositions involved a temperature of 1150°C. (2100°F.) and a pressure of about 1400 psi.[144a]

The production of diamond tools bonded by tungsten–nickel–copper alloys is similar to that of the hard metal–diamond compositions. Again, 10 to 20% by weight of diamonds are added to a mixture of approximately 90% W, 6% Ni, and 4% Cu. The most favorable sintering temperature lies in the neighborhood of 1300–1350°C. (2370–2460°F.); the sintering time must be kept very short to prevent the possible breakdown of the diamonds accompanied by the formation of tungsten carbides through a reaction of the free graphite with tungsten.[149]

For equal volumetric proportions of diamonds, the compositions based on copper and iron alloys display less wear resistance than those based on the tungsten alloys, which, in turn, are far surpassed by the hard metal–bonded diamond tools. The grinding efficiency per unit time, however, is claimed to be inversely proportional to the hardness of the bonding metal.[150]

Industrial Applications

The industrial applications of metal-bonded diamond tools fall into five categories: cutting tools, grinding tools, dressing and truing tools, drills, and dental tools.

CUTTING TOOLS

Tools with single diamond points and solid or adjustable shanks have in the past been used to a considerable extent for certain metal-cutting operations on precision work—such as required in fine instrument work—but have lately been replaced to an increasing measure by the cemented

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[150] Brit. Pat. 359,637.

[151] W. D. Jones, *Principles of Powder Metallurgy.* Arnold, London, 1937, p. 170.

[152] R. Kieffer and W. Hotop, *Sintereisen und Sinterstahl.* Springer, Vienna, 1948, p. 511.

carbide cutting tools. Diamond tools, however, are especially suitable for applications demanding extreme durability of the tool to obtain the necessary accuracy of the cut. The metals cut advantageously by the diamond tools are generally of the nonferrous type, *e.g.*, brass, bronze, aluminum, nickel–silver; nonmetal substances include a host of materials ranging from fiber, plastics, and hard rubber to stones and masonware. The chief present-day use of the diamond cutting tool, however, is for the well-known cutting of glass and ceramics.

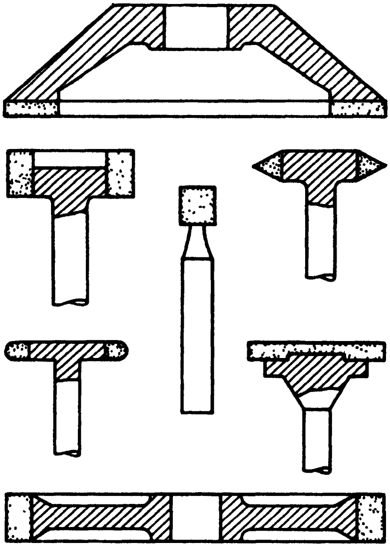

Fig. 363. Diagrammatic sections of grinding tools with diamond-impregnated hard facings (according to Kieffer and Hotop[149]).

GRINDING TOOLS

Carbide tools impregnated with diamond dust contain the diamond in various grit sizes. Their main application is to shape cemented carbide and other hard materials. Specific tools developed include internal and external grinding wheels, lapping wheels for grinding and polishing tools, and honing tools of different sizes and profiles. A number of diamond-impregnated grinding tools are schematically shown in Figure 363, and Figure 364 shows the photograph of a diamond-impregnated wheel for polishing carbide tools.

The diamond-impregnated hard metal tools are also used extensively for the shaping of ceramic materials, such as porcelain, silicon carbide, alumina, etc., and of glass, in particular for the optical industry. For the purpose of cutting sintered carbides and other hard materials, diamond-impregnated cut-off and slitting wheels are used exclusively. Grinding and slitting wheels in which the diamonds are set in softer bonding metals are used primarily for the rough cutting of hardened steels and other materials that are not quite so hard as carbides or so abrasive as most ceramics.

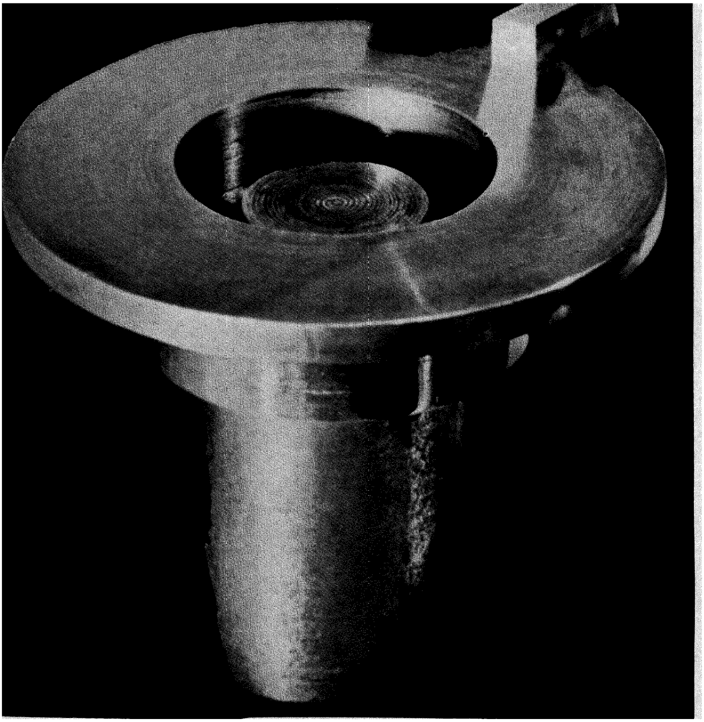

Fig. 364. Grinding of cemented carbide tool tip with a diamond-impregnated wheel (according to Jones[151]).

DRESSING AND TRUING TOOLS

Single diamonds in sizes varying from 1 to 3 carats have been used for dressing and truing grinding wheels as illustrated in Figure 365 (left bottom photographs and right). These comparatively expensive tools have more recently been replaced to a large extent by arrangements of a number of smaller diamonds which are available in greater quantities and at lower costs(Fig. 365 left top and Fig. 366). The small diamonds are embedded either in a sintered tungsten alloy of the "heavy metal" type or in a cemented carbide matrix. Typical wheel-dressing tools with diamond-impregnated hard alloy heads are also shown in Figure 367. This cluster type of tool has important advantages over the single-diamond type wheel dresser. Neither a complicated setting of the diamond nor its replacement after prolonged use is necessary. As the wheel dresser wears down, new diamond splinters are exposed continually, and the cutting faces remain sharp at all times. Thus, the total volume of diamond can be utilized, and the efficiency of the tool is greatly enhanced. Moreover, the multiple-set diamond arrangement is considerably more resistant to rough handling and shock than the single-diamond tool.

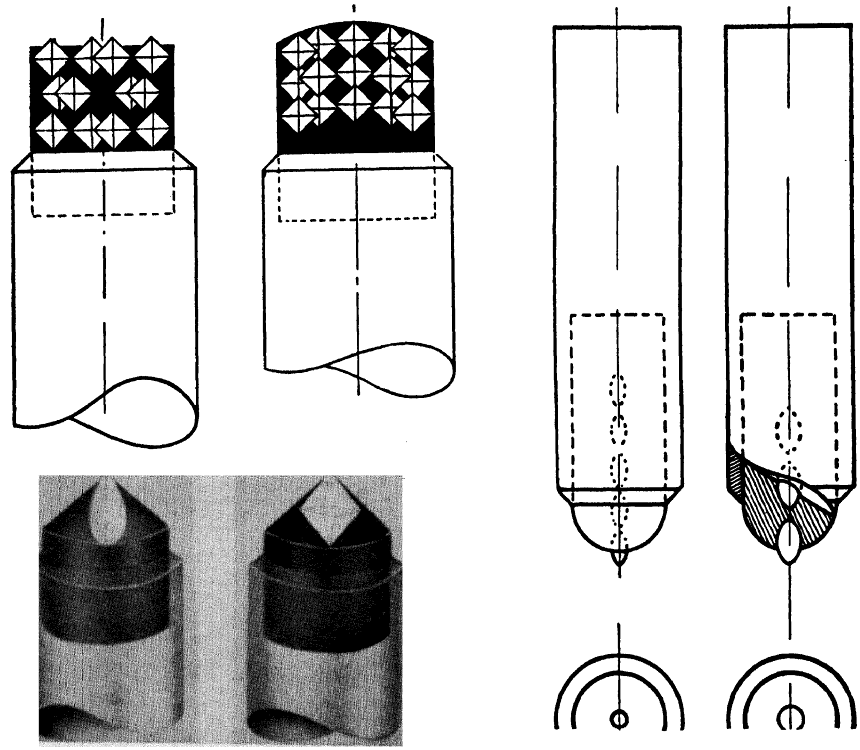

Fig. 365. Variety of single and multiple diamond wheel dressing tools (courtesy of P. Schwarzkopf and Consolidated Diamond Tool Corp.).

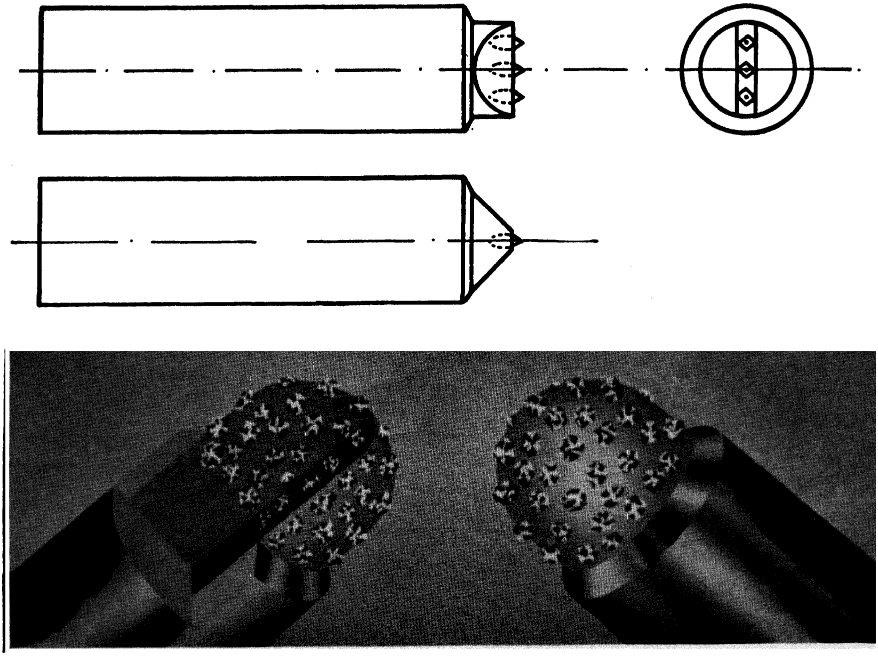

Fig. 366. Single, triple, and multiple diamond wheel dressing tools (courtesy of P. Schwarzkopf and Consolidated Diamond Tool Corp.).

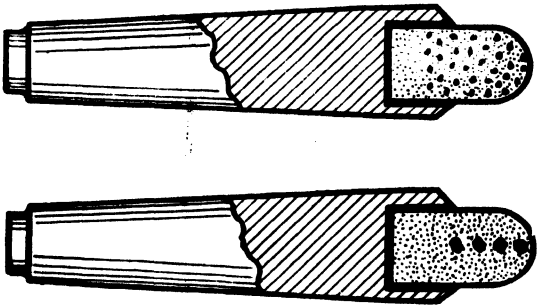

Fig. 367. Truing tools with differently constructed diamond-impregnated heads (according to Kieffer and Hotop[152]).

DRILLING TOOLS

Diamond-embedded hard metal tools have also gained increasing importance as core drill bits (jack bits) in rock boring, especially in mining work that involves piercing very hard rock. Depending on the type of rock to be drilled, new layers of diamonds must frequently be exposed by sand blasting the hard metal matrix. A typical core drill bit used in the mining field is shown in Figure 368. In comparison with individual diamond tools, the cluster-type arrangement has the advantage of a more efficient utilization of the total diamond volume, a better drill efficiency per unit time at higher speeds, and the elimination of replacements or resettings of the diamond.

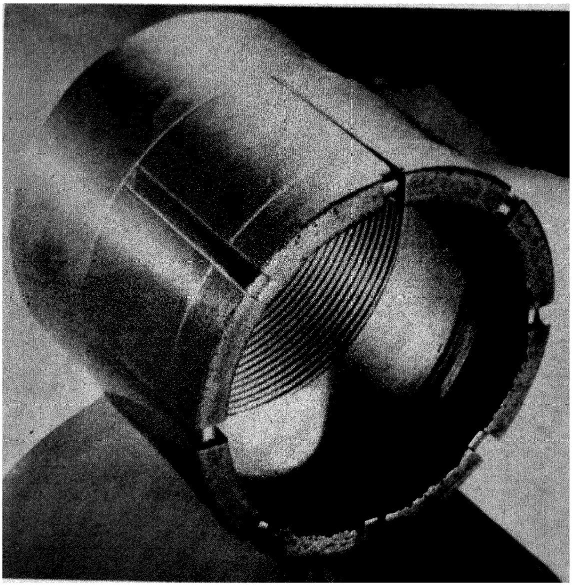

Fig. 368. Diamond-impregnated core drill bit (courtesy of R. Kieffer).

In addition to mining applications, diamond-impregnated drilling tools are also used in the ceramics and glass industries. In all these cases, cemented carbides are used exclusively as metal matrix.

DENTAL TOOLS

Small diamond-impregnated drills and grinding wheels have lately become important as dental tools. Whereas the bulk of these tools contain the diamond fragments embedded in a comparatively soft binder, *e.g.*, nickel, which is best applied electrolytically, special types are hard metal bonded in a sintering or hot-press operation.

Summary

Sintered hard metals and compositions constitute one of the most important branches of powder metallurgy, and, due to a remarkable increase in production achieved and, due to a consequent decrease in cost of the various carbide grades during recent years, they have gained tremendously in scope during the last decade. The advent of the industry producing these materials stems from the recognition of the fact that the addition of small amounts (from 3 to 20% by weight) of metallic constituents, such as cobalt, causes during sintering a cementing of the extremely hard carbides of tungsten and other refractory metals into hard and strong metal-like bodies. During this sintering operation, the metallic binder fuses and dissolves part of the carbide. Upon cooling, the carbide is reprecipitated at critical contact points between the carbide particles—transforming them into essentially rhombic or tetrahedral grains which form a network having great cohesive strength; at the same time the binder metal becomes almost entirely depleted of carbide and resumes its natural ductility.

The method of producing cemented carbide products is first to prepare the tungsten or multiple carbide powder, mix it with cobalt, and mechanically coat the hard particles with the soft binder metal through prolonged ball milling. In this treatment, a desired fine grain size is obtained, and, if required, other metal carbides can be added, as well as organic substances that facilitate compaction. The mixed powders are briquetted and presintered below the melting point of the binder metal to give the compact enough strength for shaping operations. Sintering is carried out at about 1400–1500°C. (2550–2730°F.) with the compacts placed on carbon supports and heated in a protective atmosphere. The treatment causes considerable shrinkage of the compact and results in a dense and hard product that can be shaped to final dimensions only by grinding and lapping operations. When a product of greatest density and hardness is desired, hot pressing is to be preferred as the production method.

The cemented carbides are used primarily as cutting tips in a variety of tools, and for a number of different materials. Plain tungsten carbides cemented with cobalt are suitable only for the high-speed cutting of short-chipping materials, such as cast iron, nonferrous metals, or nonmetallic materials. For the machining of the long-chipping steels, cobalt-cemented multiple-carbide compositions, particularly of the tungsten carbide–titanium carbide solid solution type, are required, and indications point toward a gradual substitution of the single-carbide compositions by the cemented multiple carbides for all tool applications.

Other fields of application for the sintered hard metals include die materials for drawing, sizing, extruding, or other operations, where only the shape of the article is deformed, but where no metal is removed. For nibs used in these dies the simpler tungsten carbide compositions are wholly satisfactory and many metals and alloys can be shaped in this way. A great variety of parts requiring wear and corrosion resistance can also be produced by using cemented carbide facings or tips. Included are such parts as burnishing tools and dies, pump valves, sand blast nozzles; gages, guides of many types, and, in particular, rock drills. Lately, titanium carbide-base compositions have found increasing interest for structural and engine components to operate at high temperatures.

A somewhat different hard cutting tool can be produced by incorporating industrial diamond fragments into a sintered metal matrix. Depending on the wear requirements, this matrix may consist of a soft sintered bronze; an iron–nickel alloy of the Permalloy type; a tungsten-base alloy of the "heavy metal" type; or a hard cemented tungsten carbide. In addition to a superb wear resistance, the latter combination has the added advantage of excellent heat transfer from the diamond to the hard metal, aided by a rigid bonding, which is retained at elevated temperatures, since both diamond and cemented carbides have approximately equal thermal expansion coefficients. For this reason the hard metal diamond tools have found their main applications in the mining field for core drill bits, and in the tool industry for wheel dressers and differently shaped tools for the lapping and polishing of carbides. The softer bonding metals are employed principally for rougher grinding or cutting of less hard materials, since the grinding efficiency increases with the softness and ductility of the matrix.

CHAPTER XXIII

Electrical Materials and Products

During the last two decades powder metallurgy has made a great inroad in the electrical field. Today, a large part of heavy duty electrical contact materials for switches, switch gear, and circuit breakers is produced exclusively by powder metallurgy techniques. Copper powders have been employed successfully for such diverse applications as current collectors, brushes, commutator segments, and rotors for squirrel cage motors. A somewhat specialized application developed in Germany is porous electrodes of aluminum, iron, or nickel for use in condensers and batteries. The manifold applications of tungsten, tantalum, and molybdenum, in incandescent lamps, x-ray tubes, and in the electronics field in general, have already been discussed in Chapter XXI.

The two chief reasons for applying the powder metallurgy approach are: (*1*) the inability to produce by fusion methods the hard, wear-resistant, and refractory metals such as tungsten in the ductile form; and (*2*) the desire to combine nonalloyable metals and metalloids such as copper and graphite or silver and tungsten in "pseudo-alloys" or "metal composites" which retain in proportion the specific electrical and mechanical properties of the components. Thus, for example, the low contact resistance, high current conveyance, and high thermal conductivity of a conducting metal (such as copper or silver) can be combined with the wear or arcing resistance of a refractory metal (such as molybdenum or tungsten), of a moderately high melting metal (such as nickel or cobalt), or of a nonmetallic material (such as graphite or certain metal oxides). Larsen[1] and Shobert[2] have lately surveyed the more general problems connected with these contact materials. Also, an excellent collection of data concerning electrical contacts has been published by the P. R. Mallory Co.[3] The reader interested in particular in the theoretical aspects connected with electrical contacts is referred to the

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[1] E. I. Larsen, *Trans. Am. Inst. Mining Met. Engrs.*, *161*, 554 (1945).

[2] E. I. Shobert, II, *Proceedings Third Annual Spring Meeting, Metal Powder Association*, New York, May 27, 1947, p. 57.

[3] *Electrical Contacts Data Book*. P. R. Mallory Co., Indianapolis, Ind., 1945.

book by Holm,[3a] whereas the books by Hunt[3b] and Windred[3c] are recommended for the student interested in the more practical problems.

HEAVY DUTY CONTACT METALS

Fundamentals

The theory underlying the functional mechanism and lifetime of heavy duty contacts has been outlined by Hausner,[4] Hausner and Blackburn,[5] and has also been described in detail in the Mallory data book.[3]

The lifetime of contact materials is limited by three deteriorating factors[4,5]: (*a*) heat developed due to their electrical resistance; (*b*) arcing caused by the switching operation; and (*c*) abrasion from mechanical motion. Direct current contacts which have been in operation for some time display material transfer from one contact face to the opposite one. This phenomenon, generally referred to as "pitting," is caused by electric sparking, which is in turn caused by arcing processes.

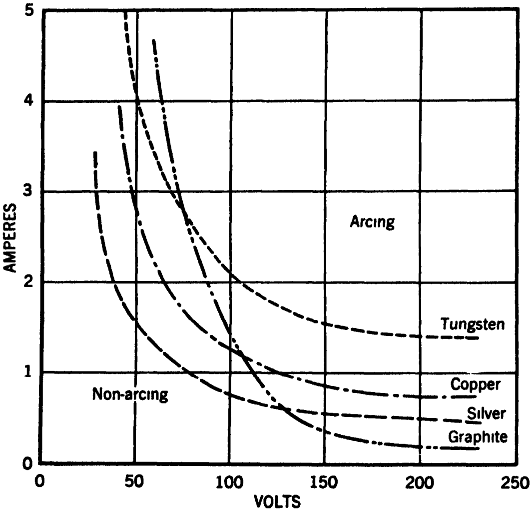

Fig. 369. Relation between arcing current and voltage for different materials (according to Hausner[6a]).

[3a] R. Holm, *Electric Contacts*. Almqvist and Wiksells, Uppsala, 1946 (in English).

[3b] L. B. Hunt, *Electrical Contacts*, Johnson, Matthey & Co., London, 1946.

[3c] G. Windred, *Electrical Contacts*. Macmillan, London, 1940.

[4] H. H. Hausner, *Schweiz. elektrotech. Ver. Bull.*, *33*, 29 (1942).

[5] H. H. Hausner and P. W. Blackburn, in J. Wulff, *Powder Metallurgy*. Am. Soc. Metals, Cleveland, 1942, p. 470.

Limiting and Critical Currents. In direct current resistance circuits a maximum current exists at various voltages that may be interrupted without the formation of an arc. This current is generally referred to as "limiting" current, whereas the current at which the contact shows a marked tendency to stick or weld is called the "critical" current.[6]

The formation of an arc is influenced by the dielectric medium between the contacts. For air, the arc may be formed when a direct current of at least 10 to 20 volts and 0.2 to 2.0 amperes is being closed or broken. If the temperature and humidity conditions of the air are kept stable, the commencement of arcing is dependent on the current. Each voltage has a definite current which just permits interruption of the circuit without producing an electric arc. This limiting current, in turn, is a characteristic material property, but depends also on the temperature and contact surface conditions. For most materials the limiting and critical currents are reduced by an increase in temperature because the electronic emission of a metal is also increased thereby. In Figure 369 and Table 128 the

TABLE 128

Average Characteristic Arc Voltages and Weight Losses of Contacts during Arcing and Critical Arcing Currents[3,5]

Material	Average characteristic arc voltage, volts	Specific weight loss, mg./coulomb	Critical arcing current for			
			25 volts, amperes	50 volts, amperes	110 volts, amperes	220 volts, amperes
Silver	11.8	0.17	1.7	1	0.6	0.25
Gold	15.0	—	—	—	—	—
Platinum	16.0	0.13	—	—	—	—
Tungsten	16.5	0.07	12.5	4	1.8	1.4
Molybdenum	16.5	0.01	18	3	2	1
Carbon (graphite)	18.0	0.0013	—	5	0.7	0.1
Nickel	14.0	0.02	—	1.2	1	0.7
Copper	12.4	0.045	—	1.3	0.9	0.5
Cadmium	10.0	—	—	—	—	—
Zinc	11.2	—	—	—	—	—
Chromium	16.0	—	—	—	—	—
Iron	13.5	—	—	—	—	—
Aluminum	14.0	0.014	—	—	—	—
Tin	13.5	—	—	—	—	—
Antimony	10.5	—	—	—	—	—
Lead	10.5	—	7.5	3	0.85	0.7
Bismuth	10.0	—	—	—	—	—
Silver-30% palladium	13.0	—	—	—	—	—
Silver-30% cadmium	10.0	—	—	—	—	—
Silver-4% magnesium	9.0	—	—	—	—	—
Brass	—	—	—	0.7	0.4	0.3

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[6] *Electrical Contacts Data Book*. P. R. Mallory Co., Indianapolis, Ind., 1945, p. 7 ff.

relation between critical arcing currents and voltage is given for different materials, and the superiority of the refractory metals tungsten and molybdenum in resistance to arc formation is apparent.

Conductivity. The adverse effects of rising temperature on the production of an arc can be controlled to a certain extent by selecting a properly designed contact and materials of high thermal conductivity.[5] It is known that a close relation exists between electrical conductivity and heat conductivity, since both depend upon the same electronic characteristics—including the effective number of free electrons in the atoms, charge, mass, average velocities, and average mean free path. This relationship is expressed by the Wiedemann-Franz law:

$$L = \lambda/xT$$

where L is a constant, λ is the thermal conductivity, x the electrical conductivity, and T the absolute temperature. This equation holds only for pure metals and not for alloys; it holds fairly well, however, for metal composites in which the mutual solubility between the components is insignificantly small.

Material Transfer. The transfer of material from one contact face to another through arcing depends on the physical characteristics of the contact material, as well as on the electrical characteristics of the arc as controlled by the operating conditions.[5] The quantity of material transferred is proportional to the current of the arc. A short arc is responsible for the evaporation of the anode material penetrated by the fast primary electrons. In a long arc, excessive ionization of the dielectric medium is responsible for the evaporation of the cathode material. The actual amount of metal evaporated depends on the time the arc is permitted to exist, *i.e.*, the faster the operating speed of the contacts, the smaller is the evaporation effect.

The quantity of metal transported can be expressed by the simple relationship: $G = g\gamma$ where g is the quantity of electricity in the arc and γ is the weight loss per unit electricity. The quantity of electricity passing during the life of the arc is determined by the arc's current and the time the arc operates. The specific weight loss per coulomb depends upon the characteristic arc voltage, the atomic volume of the metal, and the hardness.[7] Therefore a very hard contact metal is advantageous not only from the viewpoint of a greater resistance to mechanical wear but also with regard to a reduction of material losses. The characteristic arc voltage and specific weight losses are given for a variety of materials in Table 128. The material transfer is minimized by lowering the arc cur-

[6a] H. H. Hausner, *Product. Eng.*, *14*, No. 9, 618 (1945).

[7] R. Holm, F. Güldenpfennig, and R. Störmer, *Wiss. Veröffentl. Siemens-Konzern*, *14*, 30 (1935).

rent, by shortening the time of arcing, or by influencing the dielectric medium. For example, condensers placed between the contacts diminish arc voltage and current, and such expedients as a magnetic field, compressed air, or oil are employed for extinguishing the arc.

Welding. Coupled with a high hardness and resistance to mechanical abrasion is the requirement for a complete absence of welding of the contact faces at the operating pressure. This welding, often referred to as "sticking," is eliminated most efficiently if metals are selected that form slight oxide surface films or have a low atomic mobility at the operating temperature (due to their refractory characteristics).

Contact Resistance and Tarnishing. The surface resistance of contacts in actual operation will vary widely with the materials because of the difference in their ability to resist surface contamination. This contamination may originate from a number of sources, such as gas adsorption, formation of compounds at the surfaces, or formation of films of dust or grease. The factors which may affect contact resistance can be classified as follows[6]: (*1*) formation of films on contact materials as a result of corrosion and heat; (*2*) formation of high-resistance films by dust, grease, adsorbed gases, and other impurities; (*3*) formation of high-resistance films or roughened surfaces because of the operation of the contacts in electrical circuits; and (*4*) design of contacts.

Tarnish films which form on base metal contact surfaces as a result of atmospheric corrosion are among the most important of these factors. Such films are usually complex oxides often combined with sulfides, sulfates, or carbonates, and may cause a manifold increase in contact resistance. Among the base metals particularly susceptible to tarnishing is copper. In Table 129, a group of common contact materials are classified according to their resistance to tarnishing, showing that complete resistance to tarnishing and oxidation is obtained only in contacts from platinum, palladium, and gold, or certain of their alloys. Silver, though resistant to oxidation, is quite susceptible to sulfide tarnishing at room temperature, a characteristic which is not changed appreciably by alloying small amounts of noble metals with it. Only when as much as 30% Pd or 52% Au is alloyed with silver is there a marked increase in tarnish resistance.[6]

Refractory Metal Contacts

TUNGSTEN CONTACTS

Pure tungsten has proved to be very suitable as a contact metal for certain high voltage circuit breakers or similar applications, and particularly for points in automotive distributors and in spark plug electrodes for combustion engines. Tungsten is also used extensively for atomic hydrogen-welding electrodes. Its nonwelding characteristics produce metal–to–metal contacts that permit utilization of the good contact qualities and the high temperature resistance of the metal. If oxide films are formed at the contact faces and kept sufficiently thin, they may be beneficial in preventing sticking of the contact. If, however, these oxide films are allowed to become fairly heavy, which is possible at temperatures slightly below that of marked evaporation, or not enough time is allowed for their complete evaporation at higher temperatures, the resistance is

TABLE 129
Common Contact Materials Classified According to Their Resistance to Tarnishing[a]

Group	Material	Remarks
A: Completely resistant to tarnishing	Pure platinum	Tarnish above approximately 900 °C. (1650 °F.).
	Rhodium (electroplated)	
	Platinum-iridium 90–10	
	80–20	
	75–25	
	70–30	
	Platinum–ruthenium 95–5	
	Platinum–gold–silver 7–67–26	
	Gold–silver 70–30	
	Pure gold	
B: Resistant to sulfide tarnishing; subject to oxidation at temperatures above 350 °C. (660 °F.)	Palladium	
	Copper–palladium 40–60	
	Silver–palladium 50–50	
	Platinum–ruthenium 90–10	
	86–14	
C: Resistant to oxidation; subject to sulfide tarnishing	Fine silver	Silver alloys: tarnish little, if at all; more resistant to tarnishing than fine silver.
	Gold–silver 5–95	
	10–90	
	30–70	
	Palladium–silver 5–95	
	10–90	
	20–80	
	Silver–copper 92½–7½[b]	
	90–10[c]	
	80–20	
D: Subject to oxidation, sulfide tarnishing, or both	Tungsten	Used for heavy duty applications where higher forces are available; other factors, such as resistance to arcing, are more important.
	Silver–tungsten	
	Silver–tungsten carbide	
	Silver–molybdenum	
	Copper–tungsten	
	Silver–nickel	
	Silver–graphite	
	Silver–cadmium oxide	

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[a] *Electrical Contacts Data Book.* P. R. Mallory Co., Indianapolis, Ind., 1945, p. 11.
[b] Composition of sterling silver.
[c] Composition of coin silver.

increased to such an extent that the current flow becomes unsatisfactory. Only if high voltages (110 volts and higher) are applied can the oxide films evaporate or congeal sufficiently to permit the formation of metallic bridges, which in turn reduce the contact resistance.[8]

The contact metal is usually obtained by cutting thin disks, tips, or other suitable shapes from swaged tungsten rods (2.4–6-mm. diameter). Contacts produced in this manner have a fine-crystalline structure, since the contact face is cut perpendicular to the elongated fibers. This structure has been found to be more advantageous than that of disks stamped out of sheet, whose fibers lie parallel to the contact face.

The tungsten disks or tips are brazed with copper or silver solders to steel screws or other suitable backings. In the production of spark plug electrodes, the tungsten tips are either welded to nickel steels or are combined with copper shafts by first casting molten copper over the tip in graphite molds and then swaging the shaft to obtain accurate dimensions and greater rigidity.

During the war, a special tungsten powder of closely controlled particle size range (0.5–1 μ) was developed in Germany[8a] for contact purposes, the powder being produced from very light and fine tungstic oxide made by reacting sodium tungstate and HCl in a constant ratio.

OTHER REFRACTORY METAL CONTACTS

Pure molybdenum is used successfully as a contact material in high tension switch gear construction.[9] Tungsten alloys containing about 0.5% molybdenum have been reported to give better contact performance than pure tungsten because of their finer grain structure, while alloys with higher molybdenum content (up to 20%) appear to be less satisfactory. The lower conductivity and resistance to oxidation of the tungsten–molybdenum solid solution are considered to be chiefly responsible for the inferior contact qualities as compared with pure tungsten.[9]

Composite Refractory Metal Base Contacts

No pure metal exists that can furnish all the properties that are desirable in an ideal contact material. Table 130 shows the physical properties of a number of metals that can be used for contact purposes. The refractory metals, tungsten and molybdenum, are suitable where their hardness, density, and resistance to wear and material transfer are necessary properties. However, these metals are not satisfactory where

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[8] R. Holm, *Kolloid-Z.*, *104*, 231 (1943).

[8a] F.I.A.T., Final Report No. 785 (1947); see also *Met. Powd. Rept.*, *1*, No. 7, 105 (1947).

[9] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe*. 2nd ed.. Springer, Berlin, 1948, p. 332.

electrical conductivity requirements are high; moreover, the simultaneous lack of sufficient heat conductivity results in relatively high service temperatures for low voltage application, which in turn cause strong oxidation of the contact faces and an additional reduction in conductivity.

TABLE 130
Physical Properties of Some Pure Metals Used for Electrical Contacts
(Hausner[4,6a])

Properties	Tungsten	Molybdenum	Copper	Silver
Density, g./cc.....	19.1	10.2	8.9	10.3
Electrical conductivity, megmho-cm.	0.18	0.175	0.58	0.615
Electrical resistivity, microhm-cm.	5.51	5.70	1.724	1.62
Heat conductivity, cal./°C./cm./sec.	0.38	0.35	0.92	0.97
Brinell hardness.....	290	147	32	30
Melting point, °C.	3380	2620	1083	961
°F. . . .	6120	4750	1983	1761

Silver and copper, on the other hand, meet the conductivity requirements, but can only be used where their shortcomings of wear, pitting, or material transfer are not serious. The ideal material for most contact purposes would be one that has the hardness, density, and low material transfer of tungsten, in addition to the high electrical and thermal conductivity of silver. The nearest approach to such a material is a composite duplex structure in which the refractory metal particles are embedded in a continuous network of the conducting metal. Since, for all practical purposes, tungsten and molybdenum do not alloy with silver or copper, the individual properties of each metal can be retained in such a structure. The refractory metal component of most commercial grades of composite contact materials ranges between 40 and 85% by weight. Depending on the exact proportion of the refractory and conducting element as well as the degree and uniformity of dispersion of the different phases, a combined effect of the desired qualities of each component can be obtained over a large range of physical properties.

An important discussion of the general characteristics, composition, and history of the composite contact metals can be found in a paper by Kieffer.[9a]

MANUFACTURING METHODS

Two essentially different methods have been developed for the production of composite contact metals: the regular sequence of pressing, sintering, and subsequent working; and the infiltration process, wherein

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[9a] R. Kieffer, *Z. tech. Physik, 21*, 35 (1940).

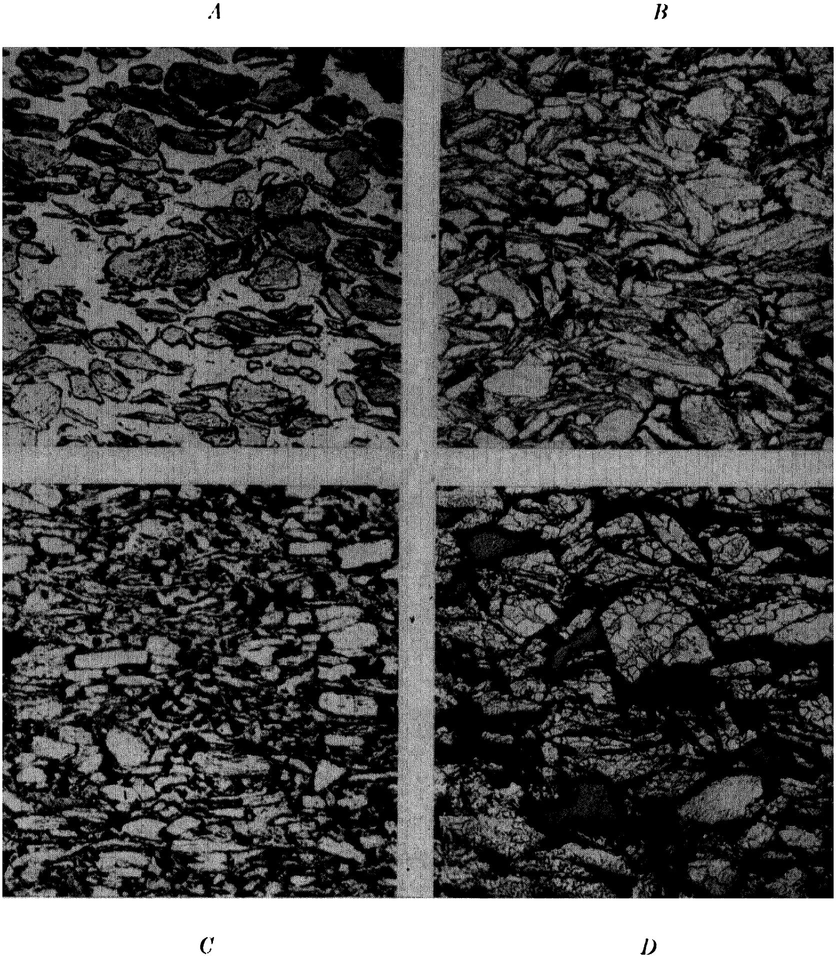

Fig. 370. Microstructures of representative composite contact materials made by the sintering technique (×150) (according to Hausner and Blackburn[5]): *A*, 60–40 Mo–Ag composition; *B*, 80–20 W–Ag composition; *C*, 82–18 W–Cu composition from fine electrolytic copper powder; and *D*, 82–18 W–Cu composition from coarse reduced copper powder.

either a preformed refractory metal skeleton compact is dipped into the liquid lower melting metal bath, or the liquid metal is allowed in other suitable manner to make contact and permeate the skeleton.

Sintering Method. The tungsten or molybdenum powder is mixed with copper or silver powder in the desired proportion and compacts are pressed from the mixtures, usually at pressures between 40 and 80 tsi. They may then be sintered at a temperature immediately below the melting point of the lower melting metal. The particle size and characteristics of the powdered ingredients have a very important bearing on the final properties. The finer the particle size the better is the dispersion throughout the structure and the better is the cohesion of the network formed by the lower melting metal phase, which in turn results in better conductivity. If, on the other hand, the freshly reduced fine tungsten or molybdenum powder is replaced by a coarser refractory metal powder obtained by crushing and milling high-sintered or swaged scrap,[10,10a] the wear resistance of the sintered product is improved at the expense of the conductivity.

In connection with the question of the most advantageous raw material for composite contact metals, it has been suggested to produce composite powders of suitable analysis by reduction of silver and copper molybdates and tungstates.[10b] The production of similar metallic agglomerates by chemical coprecipitation of the ingredients[10c] has already been described in Chapter VI, Volume I.

The structures of several typical compositions of low-sintered composite contact metals are illustrated in Figure 370, *A–D*. Sintering below the melting point of the copper or silver will cause little deformation, and many products can be pressed directly into final shape. If this is not practical, blanks can be pressed, and these must be machined to final dimensions after sintering.

The physical properties and especially the conductivity may be considerably improved if sintering is conducted at a temperature *above* the melting point of the high-conductivity metal. Analogous to the sintering of hard metal, the liquid phase acts as a cement, and, provided the temperatures reach 1400–1500°C. (2550–2750°F.), appreciable consolidation results. This has been found particularly true for composite materials containing silver, in which the solubility conditions are more favorable for the process than when combinations with copper are involved. There is no noticeable intersolubility between copper and tungsten or molybdenum; but silver dissolves several tenths of one per cent of tungsten, and more than a full per cent of molybdenum at 1400°C. (2550°F.).[10a] The dissolution of the very fine molybdenum or tungsten particles in the silver is accompanied by an appreciable shrinkage. Upon cooling, all molybdenum (or tungsten) is again precipitated on the larger

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[10] German Pats. 612,880; 643,567; U. S. Pats. 2,030,229; 2,096,924; 2,179,960.

[10a] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe*. 2nd ed., Springer, Berlin, 1948, pp. 321, 322.

[10b] U. S. Pat. 2,410,717.

[10c] Brit. Pat. Appl. 32,900/46 (Nov. 29, 1945); see also *Met. Powd. Rept.*, *2*, No. 5, 74 (1948).

refractory metal particles, which take on the uniform and spherical particle shape so typical for this kind of sintered product. Since the solubility of molybdenum or tungsten in silver is zero at room temperature, the high conductivity of the latter is restored. The pronounced shrinkage in these materials makes a direct molding or a forming (by machining) operation prior to the high-sintering operation impractical, and requires a final shaping operation after high-sintering. For compositions of comparatively low refractory metal contents, simple cold coining, sizing, or machining operations are possible. Hot forging or extrusion,[10d,e] however, is preferred for all those products that require maximum density and an optimum combination of hardness and conductivity. If the composite materials contain refractory metals in excess of about 80% by

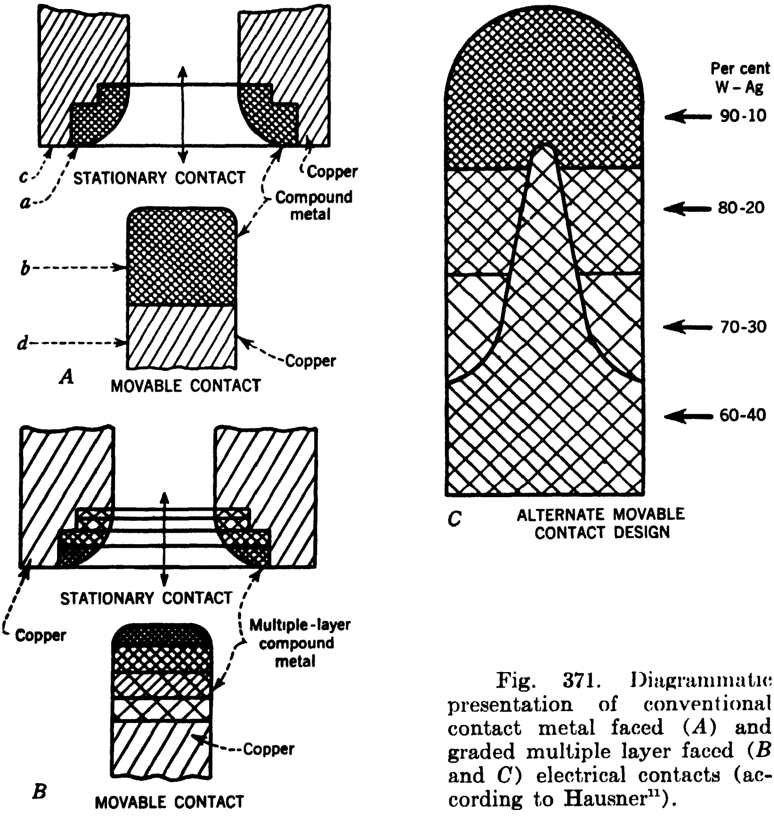

Fig. 371. Diagrammatic presentation of conventional contact metal faced (*A*) and graded multiple layer faced (*B* and *C*) electrical contacts (according to Hausner[11]).

[10d] R. Kieffer and W. Hotop, *Metallwirtschaft*, *23*, 379 (1944).

[10e] German Pat. 738,536.

weight, subsequent working and machining become extremely difficult, and hot pressing, possibly in several repeat operations, becomes the only effective way to achieve consolidation. Accurate dimensions may then be obtained by roughening with carbide tools, followed by finish grinding.

An interesting variation of the sintering method[11] has been described by Hausner for the production of multiple-layer contacts for certain switches, and is illustrated by the diagrammatic sketches of Figure 371, *A–C*. Very fine tungsten and crystalline silver powders are pressed into four layers of different composition. The bottom layer is pressed at 10 tsi from a 60–40 W–Ag mixture. A 70–30 W–Ag layer is pressed on top at 15 tsi. The third layer of 80–20 W–Ag is pressed again on top at 20 tsi, and the final layer of a 90–10 W–Ag composition is pressed on top of the three others at 75 tsi. After sintering at 905°C. (1660°F.) for two and one-half hours the sandwich is repressed cold at 90 tsi.

Infiltration Method. This method, known for the last three decades, is basically different from the one previously described. The closely graded refractory metal powder is lightly pressed into the desired shape (either the final form or a blank). The compact is then sintered at about 1000°C. (1830°F.) to give it a sufficient amount of strength to withstand further handling or machining to a more accurate shape. The resulting porous tungsten or molybdenum skeleton body is then heated in hydrogen to a temperature of at least 1100°C. (2000°F.), whereupon it is brought into contact with liquid copper or silver. The pores of the skeleton become impregnated with the molten copper or silver by means of capillary action, while little deformation of the outside contours will be encountered. Thus, direct molding or machining after sintering of the skeleton is quite feasible. Subsequent working, such as forging or extrusion, becomes necessary only when extremely good physical properties are required and final machining can be confined to those products that demand very exacting dimensional control.

Infiltration of the refractory metal skeleton bodies with copper or silver is conventionally performed by contacting the solid shapes with the infiltrant inside of suitable graphite or refractory oxide molds, so that the capillary forces of the skeleton can effect penetration of the liquid metal immediately upon liquefaction. Simple brazing or molybdenum resistor furnaces operating with hydrogen or dissociated ammonia are suitable; the latter has the advantage of a low dew point (see Chapter XVII, Volume I). However, a special tiltable furnace arrangement (see Fig. 254, Volume I) can provide for the low-melting metal to liquefy apart from the skeleton bodies before contact is made by

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[11] H. H. Hausner, *Product Eng.*, *14*, No. 9, 618 (1945).

reversing the slant of the furnace hearth (this procedure may have advantages for certain metal combinations that require spontaneous infiltration). The use of a vertical furnace allows the liquid metal to enter the skeleton and freeze from the bottom upward, driving the trapped gases ahead.[11a] Pouring the liquid over the skeleton bodies contained in graphite or refractory oxide molds, or submerging the skeletons in the liquid metal—possibly while simultaneously removing occluded gases by applying a vacuum to the system—are alternate procedures less generally employed.

Several variations of the basic method are of practical use. In the production of hard and wear-resistant materials possessing a predominant refractory metal phase, the skeleton body is heated in hydrogen to a temperature considerably above that necessary for the infiltration of the liquid high-conductivity metal phase. In fact, this treatment may resemble the regular sintering procedure employed in the manufacture of the pure refractory metals, *i.e.*, the tungsten or molybdenum may be heated to a temperature close to the melting point of the metal. According to the shape requirements, square or rectangular ingots would be treated in a bell jar type of furnace, while annular shapes would be sintered in a high-frequency furnace. After cooling to room temperature the ingots or blanks are machined to accurate shapes, whereupon the products are reheated in hydrogen to a temperature that permits the infiltration of the low-melting metal phase. The selection of the sintering temperature for the skeleton material is governed chiefly by the desired ultimate composition and the grade of refractory metal powder employed. With decreasing particle size and increasing temperature and time of sintering, grain growth and shrinkage progress with a tendency to alter the character and to diminish the volume of the intercommunicating pore system, thereby penalizing the subsequent infiltration process. This change in grain structure with rising sintering temperature is illustrated diagrammatically in Figure 372, according to Schröter.[12]

In the production of high-conductivity compositions containing 35–60% of the low-melting component, the refractory metal particles occupy a comparatively small volume of the structure. Therefore, the contact areas and cohesion between the tungsten or molybdenum particles are very limited, and the application of pressure would be of no avail. Instead, the powder is filled directly into graphite or ceramic molds and, after heating to the necessary temperature, the liquid copper or silver is permitted to penetrate the powder mass. The composite forms obtained are generally very uniform in composition, the concentration of the low-

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[11a] U. S. Pat. 2,422,439.

[12] K. Schröter, *Z. Metallkunde, 23,* 197 (1931).

melting metal not varying more than 4% throughout the entire body.[13] They are easily worked by forging, rolling, and, especially, extrusion, in order to increase hardness and toughness. When necessary, accurate dimensions are obtained by ordinary machining operations.

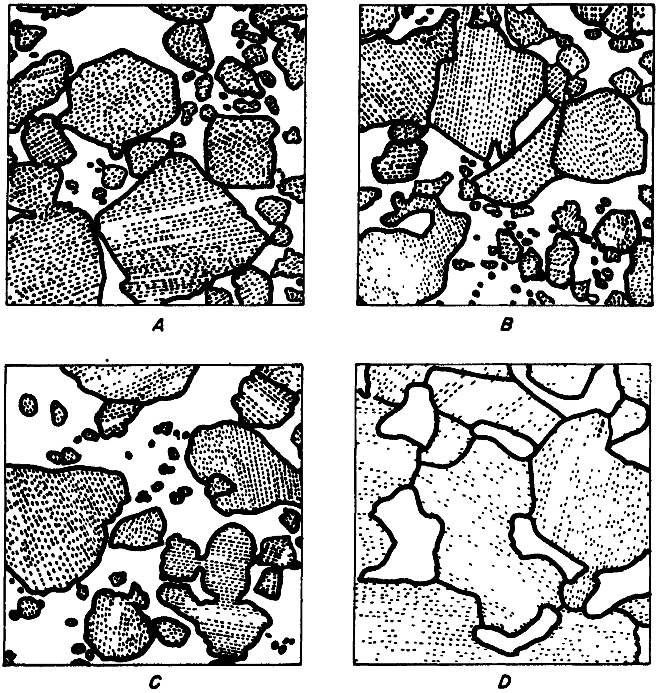

Fig. 372. Schematic presentation of the microstructure of pressed and sintered tungsten bars subsequently immersed in molten copper at 1100°C. (2010°F.), showing the effect of the sintering treatment on the grain size of the tungsten and the pattern of the copper phase at a magnification of 500 diameters (according to Schröter[12]): *A*, pressed tungsten bar heated to 1100°C. (2010°F.); *B*, bar sintered at 1350°C. (2460°F.); *C*, bar sintered at 1600°C. (2910°F.); and *D*, bar sintered at 2800°C. (5070°F.).

The refractory metal powder may vary considerably in nature and size. Originally, the freshly reduced tungsten powder of a particle size ranging from 1 to 50 μ was preferred,[14] but later on some European producers found it more advantageous to use a coarser powder with a particle size ranging from 50 to about 400 μ. This latter size is obtained by mechanical comminution of sintered or swaged tungsten scrap.[15]

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[13] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe*. Springer, Berlin, 1943, p. 321.

[14] German Pat. 436,678; U. S. Pat. 1,223,322.

[15] German Pats. 612,880; 643,567.

PROPERTIES

Tungsten–Copper. The mechanical and electrical properties of tungsten–copper have been thoroughly studied and discussed by Hausner and Blackburn,[16] Hensel, Larsen, and Swazy,[17] Kieffer and Hotop,[18] and others. The effect of an increasing percentage of tungsten on density hardness and electrical conductivity is shown diagrammatically in Fig-

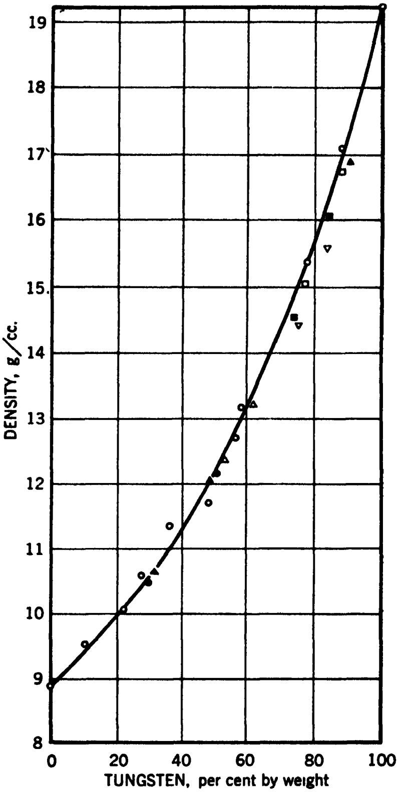

Fig. 373. Effect of composition on density of tungsten–copper alloys (according to Kieffer and Hotop[18]).

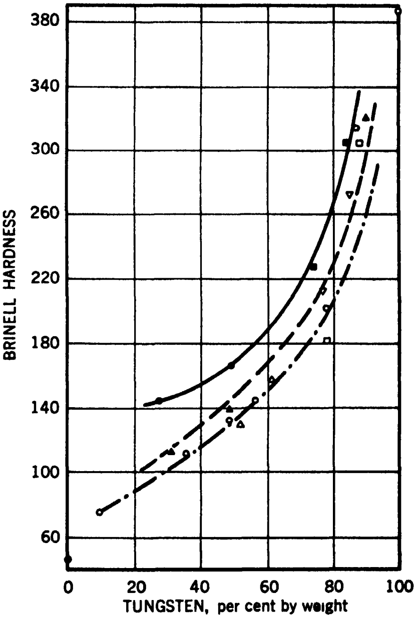

Fig. 374. Effect of composition on hardness of tungsten–copper alloys (according to Kieffer and Hotop[18]).

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[16] H. H. Hausner and P. W. Blackburn, in J. Wulff, *Powder Metallurgy*. Am. Soc. Metals, Cleveland, 1942, p. 470.

[17] F. R. Hensel, E. I. Larsen, and E. F. Swazy, *loc. cit.*, p. 483.

[18] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe*. Springer, Berlin, 1943, pp. 324 ff.

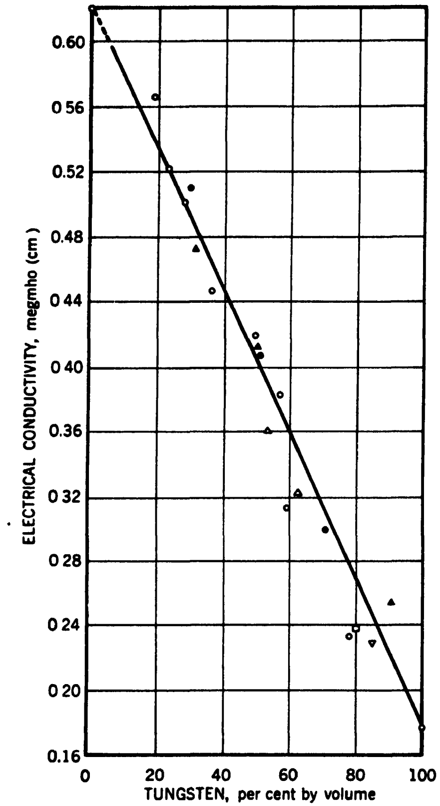

Fig. 375. Effect of composition on electrical conductivity of tungsten–copper alloys (according to Kieffer and Hotop[18]).

TABLE 131
Production Method and Designation of W–Cu Compositions Given in Figures 373–375 (Kieffer and Hotop[18])

Production method	Particle size of tungsten powder	Point designation
A: Mixing of the component elemental powders; briquetting; sintering; subsequent working	Coarse, 100–400 μ	○
	Medium, 50–100 μ	▲
	Very fine, 1–50 μ	●
B: Impregnation of the loosely filled tungsten powder in a mold; extrusion into shape	Coarse, 100–400 μ	△
C: Dip-impregnation of a pressed (and presintered) tungsten compact; machining to size	Coarse, 100–400 μ	□
	Medium, 50–100 μ	▽
	Very fine, 1–50 μ	■

ures 373 to 375, according to measurements made by Kieffer and Hotop.[18] Table 131 indicates the different procedures and raw materials used in this investigation. The materials obtained by sintering tungsten–copper powder mixtures containing up to 60% W (by weight) were extruded; compacts containing more tungsten were consolidated by hot-pressing. All compositions produced by impregnating a loose tungsten powder heap with liquid copper were extruded afterward, while the materials obtained by infiltrating precompacted and sintered tungsten skeleton bodies were simply machined to test bar shapes. As Figure 373 indicates, the experimental density values correspond closely to the theoretical curve despite differences in raw material and processing. The theoretical density of composites whose components are not soluble in each other is easily calculated according to the formula:

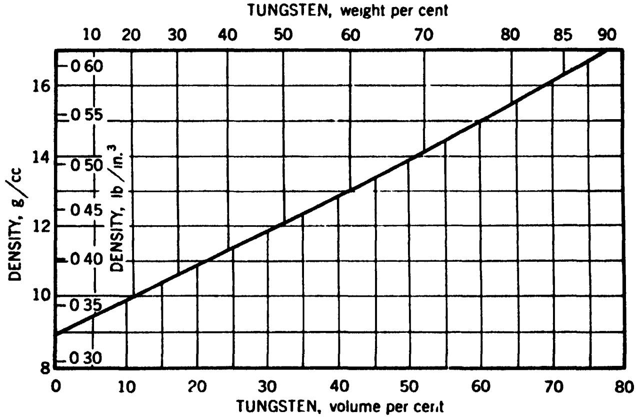

Fig. 376. Change in density with composition of tungsten–copper alloys as expressed by weight and volume per cent of tungsten (according to Hensel, Larsen, and Swazy[17]).

$$\rho_C = \frac{100}{(a/\rho_A) + (b/\rho_B)}$$

where ρ_C is the density of the composite, ρ_A the density of the component *A*, ρ_B the density of the component *B*, *a* the weight percentage of the component *A*, and *b* the weight percentage of the component *B*. If the density is plotted as a function of tungsten in volume per cent, a straight-line relationship is obtained, as can be seen from Figure 376.[17] The range of densities mostly used varies from about 12 to 16 g./cc.

The effect of particle size on hardness is pronounced, with finest powders yielding highest values (Fig. 374). According to Kieffer and

Hotop,[18] the reason for this effect should be sought in the method of Brinell hardness testing, which is not conclusive for such nonhomogeneous structures (see also Chapter XXXIV, p. 772). If very small tungsten particles are distributed uniformly, they tend to reinforce each other and to resist the impression of the Brinell ball. If only large tungsten particles are embedded in the copper, and if their weight proportion is not extremely high, fewer contacts are made between these particles, and upon impression of the ball, the hard particles will sink into the soft copper mass and indicate lower hardness values.

The curve for the electrical conductivity (Fig. 375) resembles in character that for the density (Fig. 376). The conductivity is theoretically (according to the rule of mixed proportions) a linear function of the composition (given in volume per cent) in any system that contains nonalloyable components. In other words, it can be calculated by the rule of mixed proportions, provided no impurities are present. Kieffer and Hotop's results (Fig. 375) approach reasonably closely the theoretical straight line between the conductivity values of pure tungsten and copper.

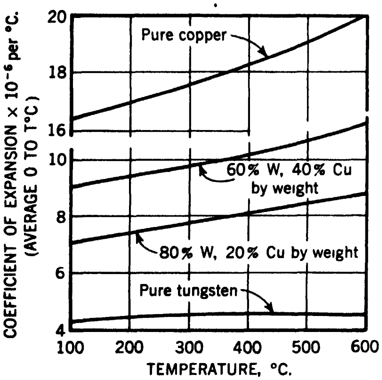

Fig. 377. Thermal expansion properties of composite tungsten–copper alloys. Average coefficient of expansion from 0 to T°C. of tungsten, copper, and two mixed proportions. (According to Hensel, Larsen, and Swazy[17]).

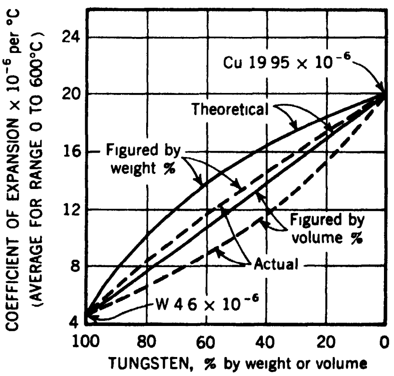

Fig. 378. Thermal expansion properties of composite tungsten–copper alloys as affected by the composition expressed in weight and volume per cent (according to Hensel, Larsen, and Swazy[17]).

Also of particular interest are the thermal expansion characteristics. The coefficient of expansion of pure tungsten does not change materially over a temperature range from 0 to 600°C. (30 to 1110°F.), the value being about 4.6 × 10^{-6} per degree centigrade. For pure copper, on the other hand, the value increases from 16.4 × 10^{-6} at room temperature to about 20 × 10^{-6} at 600°C. (1110°F.). Since the two metals are nonalloyable, it must be expected that the coefficient of expansion of their composite structure lies proportionally between the values established for the pure metals. This has been proved by Hensel, Larsen, and

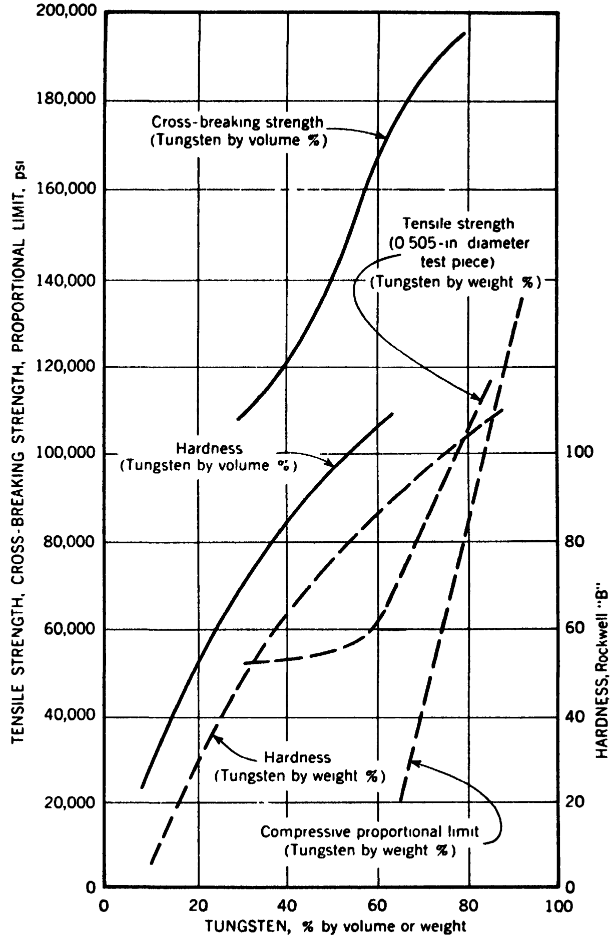

Fig. 379. Physical properties of composite tungsten–copper alloys as affected by composition (according to Hensel, Larsen, and Swazy[17]).

Swazy,[17] and their results for composites with 20 and 40% Cu are compared with the data for the pure metals in Figure 377. The values given on the curve indicate the average coefficient of expansion between 0°C. and the plotted temperature. The change in thermal expansion coefficient with composition is a linear function of the volume concentration in all

TABLE 132
Physical Properties of W-Cu Alloys Containing 0.5% Nickel (Hausner[20])

Specimen No.	Composition, % W	Composition, % Cu	Composition, % Ni	Compacting pressure, tsi	Density, g./cc.	Volume change after sintering, %	Electrical conductivity, % I.A.C.S.	Sample thickness mm. Before hot hammering	Sample thickness mm. After hot hammering	Reduction in thickness after hammering, %	Density after hammering, g./cc.	Increase in density after hammering, %	Electrical conductivity after hammering, % I.A.C.S.	Increase in electrical conductivity after hammering, %	Brinell hardness after hammering
171	20	79.5	.5	10	7.55	−22	24.4	5.18	1.52	71	9.1	20	31.5	29	78
172	30	69.5	.5	10	7.60	−15	17.3	5.70	1.70	70	9.9	30	30.5	76	92
173	40	59.5	.5	10	7.35	−8	15.7	6.04	1.73	71.3	10.4	41	29	86	96
174	50	49.5	.5	10	7.75	−6	13.9	6.08	1.78	70.3	11.4	47	28.8	108	114
175	60	39.5	.5	10	8.20	−3	10.6	5.83	1.78	65	11.9	45	26.7	150	133
176	70	29.5	.5	12	9.40	—	8.2	5.53	2.05	61	13.1	39	23.8	190	172
177	80	19.5	.5	17	9.65	+3	5.8	5.38	3.32	56.6	14.3	48	23.2	300	222
178	20	79.5	.5	50	8.65	−3	27.6	3.95	1.35	65.8	9	4	32.4	17	77
179	30	69.5	.5	50	9.05	−1	25.8	4.20	1.35	67.8	10	10	28.2	10	84
180	40	59.5	.5	50	9.55	−2	23.2	4.32	1.40	67.4	10.3	8	28.9	24	98
181	50	49.5	.5	50	10.15	−2	23.8	4.26	1.54	64	11.2	11	26.4	11	120
182	60	39.5	.5	50	10.4	+2	18.9	4.40	1.75	60.2	11.9	14	24.4	29	136
183	70	29.5	.5	50	11.2	+2	15.4	4.40	2.05	53.5	12.7	13	23	49	176
184	80	19.5	.5	50	12	None	12.5	4.34	2.00	54	14.2	18	22.8	85	208

TABLE 133

Physical Properties of W–Cu Alloys Containing 1% Nickel (Hausner[20])

Specimen No.	Composition, % W	Composition, % Cu	Composition, % Ni	Compacting pressure, tsi	Density, g./cc.	Volume change after sintering, %	Electrical conductivity, % I.A.C.S.	Sample thickness, mm. Before hot hammering	Sample thickness, mm. After hot hammering	Reduction in thickness after hammering, %	Density after hammering, g./cc.	Increase in density after hammering, %	Electrical conductivity after hammering, % I.A.C.S.	Increase in electrical conductivity after hammering, %	Brinell hardness after hammering
185	20	79	1	10	7.56	−21	21.5	5.25	1.58	70	9.2	20	25.9	20	80
186	30	69	1	10	7.58	−15	14	5.56	1.62	71.3	10.0	32	24.3	73	84
187	40	59	1	10	7.60	−8	12.6	5.88	1.72	70.8	10.3	36	23.1	83	90
188	50	49	1	10	7.75	−4	10.1	6.02	1.90	68.5	11.4	47	23.1	129	102
189	60	39	1	10	8.15	−2	9.3	5.85	2.08	64.5	12.1	49	22	136	123
190	70	29	1	12	9.60	+1.5	9.1	5.20	2.25	56.7	13.5	41	21.4	135	162
191	80	19	1	17	9.80	+3	5.3	5.38	2.38	55.6	14.5	48	20.5	286	206
192	20	79	1	50	8.65	−2.5	23.1	4.00	1.25	69	8.9	3	26.4	14	76
193	30	69	1	50	8.69	−2	17.9	4.28	1.45	65	10.1	16	24	34	82
194	40	59	1	50	9.55	None	18.0	4.28	1.55	63.8	10.4	9	22.9	27	94
195	50	49	1	50	10.2	−1	17.0	4.30	1.65	61.7	11.0	8	22.9	35	114
196	60	39	1	50	10.65	+2	16.5	4.40	1.78	59.5	12.1	14	22.5	36	144
197	70	29	1	50	11.4	+2	13.9	4.35	2.00	54.0	12.9	13	20.5	47	172
198	80	19	1	50	11.8	+3	11	4.33	2.20	49.2	14.3	21	18.1	56	218

compositions that contain only nonalloyable components. Therefore, the theoretical curve for tungsten–copper mixtures based on volume per cent is a straight line, while the one based on weight per cent is a slightly concave-upward curve. In Figure 378 the actual values of the coefficient of expansion of tungsten–copper alloys are shown together with the theoretical curves for the entire range of 0 to 100% W, both expressed in weight per cent and in volume per cent, according to Hensel, Larsen, and Swazy.[17] It can readily be seen that the actual values fall consistently *below* the theoretical; this comparatively low thermal expansion of copper–tungsten composites is usually beneficial, since it assures a minimum of stresses in brazed joints of contact metal facings and supporting members made of other materials that have a lower coefficient of expansion than copper (*e.g.*, steel).

The mechanical properties of tungsten–copper composites have also been studied by Hensel, Larsen, and Swazy.[17] In Figure 379 the Rockwell "B" hardness, tensile strength, transverse rupture strength, and proportional limit in compression are shown as a function of the tungsten content. The hardness increases consistently with tungsten content. The tensile strength rises slowly in the copper-rich compositions, but, above 50 to 60% W, it increases rapidly at the expense of ductility. Only compositions up to about 60% W are sufficiently ductile to permit cold working without failure. Very interesting is the fact that the tensile strength of annealed tungsten–copper compositions is considerably greater than that of pure tungsten rod of equal cross section. Apparently, strong bonding is produced between the copper and tungsten even though no alloying occurs. Equally impressive are the increments in cross breaking strength and in compressive proportional limit. By improving their technique, Hensel and coworkers were even able to increase hardness and tensile strength without changing the copper content, thus retaining a high electrical conductivity and some ductility. The improved material displayed a Rockwell hardness of B 102–108 against B 85–90 for the standard material, a tensile strength of 125,000 psi against 80,000 psi, and a cross breaking strength of 210,000 psi against 130,000 psi. The same investigators reported copper–tungsten materials having such rare combinations of physical properties as a tensile strength of 175,000 psi, a Rockwell hardness of B 110, an electrical conductivity of 30% I.A.C.S. (International Annealed Copper Standard), and a density of 14.5 g./cc.[17]

Tungsten–Copper–Nickel. The addition of nickel to the tungsten–copper system has a marked effect on electrical conductivity and hardness. Due to the fact that nickel effects a partial solubility between copper and tungsten,[19] even minute additions (*i.e.*, a fraction of one per

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[19] G. H. Price, C. J. Smithells, and S. V. Williams, *J. Inst. Metals, 62,* 239 (1938).

cent) raise the hardness of the material and decrease the electrical conductivity[20,21] as shown in Tables 132 and 133.

Products with higher nickel content in which the alloying effects are still more pronounced have been discussed in Chapter XXI in connection with high-density tungsten alloys ("heavy metal"). The original claim,[21a,21b] that these alloys have also proved their value as contact materials for high current applications (in the order of 100,000 amperes) when great wear resistance is essential, could not be entirely confirmed by subsequent long-time performance records.[21c]

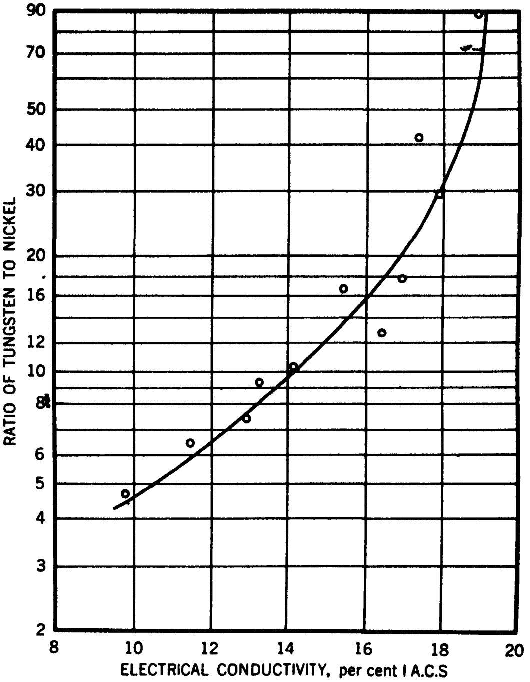

Fig. 380 Effect of nickel as expressed by the ratio W–Ni on the electrical conductivity of tungsten–copper–nickel compositions (according to Hausner[21]).

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[20] H. H. Hausner, *Powder Met. Bull.*, *2*, No. 1, 6 (1947).

[21] H. H. Hausner, *Metals & Alloys, 18*, No. 6, 1335 (1943).

[21a] G. H. S. Price, S. V. Williams, and C. J. O. Garrard, *Gen. Elec. Co.* (*London*), *11*, No. 4, 223 (1941).

[21b] P. Schwarzkopf, *Powder Metallurgy*. Macmillan, New York, 1947, p. 233.

[21c] R. Kieffer, *private communication.*

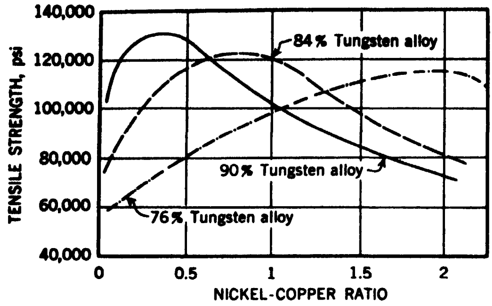

Fig. 381. Variation of tensile strength of tungsten–copper–nickel alloys with increasing nickel–copper ratio (according to Hausner and Blackburn[22]).

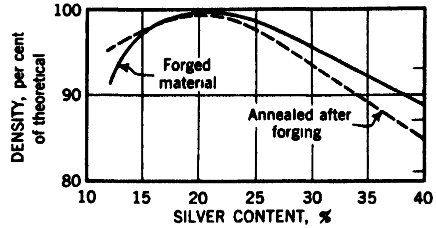

Fig. 382. Effect of composition on the density of tungsten–silver compacts, as forged, and annealed after forging (according to Hausner and Blackburn[23]).

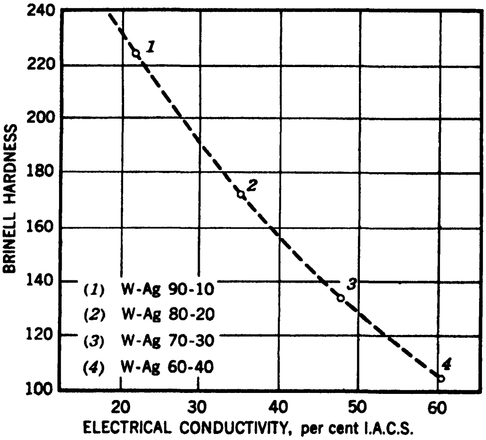

Fig. 383. Relation between hardness and electrical conductivity for tungsten–silver contact alloys of different composition (according to Hausner[23]).

Some of the more important physical properties have been given previously in Table 104, Chapter XXI. The effect of the tungsten-nickel ratio on conductivity is shown in Fig. 380,[21] and that of the nickel–copper ratio on tensile strength in Fig. 381.[22] Several different compositions can give nearly the same tensile values between 115,000 and 130,000 psi, but the nickel–copper ratio for a constant tungsten content affects the tensile strength greatly. It is also interesting that the maximum is shifted toward an increased copper content in the nickel–copper

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[23] H. H. Hausner and P. W. Blackburn, in J. Wulff, *Powder Metallurgy*. Am. Soc. Metals, Cleveland, 1942, p. 470.

ratio for compositions high in tungsten. This observation indicates that in these materials the cementing action is not so much an alloying phenomenon but rather more of a surface bonding effect, with greatly increased surface adhesion forces similar to the case of plain tungsten–copper structures.

Tungsten–Silver. The physical properties of tungsten–silver contact materials compare favorably with those of the tungsten–copper compositions of corresponding tungsten concentration. Table 134 gives some data for a number of technically important compositions. The effect of tungsten concentration on the density of forged and annealed material is shown in Figure 382, according to Hausner and Blackburn.[22] The theoretical density is obtained with both the forged and the subsequently annealed materials for a tungsten content of about 80%. Figure 383 shows the relationship between hardness and electrical conductivity for such forged materials, and indicates the position of four different tungsten–silver proportions. In properly prepared materials, optimum hardness and conductivity can be obtained simultaneously, the actual values depending on the composition.

TABLE 134
Physical Properties of W–Ag Contact Materials[a]

Composition, %[b]		Density, g./cc.	Brinell hardness	Cross breaking strength, psi	Electrical conductivity		Estimated contact resistance[c]
W	Ag				megmho-cm.	Per cent I.A.C.S.	
90	10	17.5	230–250	180–200,000	0.20–0.23	35–40	1000
85	15	17.0	210–230	160–180,000	0.24–0.25	42–44	700
80	20	16.3	200–220	140–160,000	0.26–0.28	45–49	500
75	25	15.8	160–180	125–140,000	0.28–0.30	49–53	350
70	30	15.2	140–160	115–120,000	0.30–0.33	53–57	250
65	35	14.7	120–140	105–110,000	0.33–0.35	57–61	200
60	40	14.4	110–120	95–105,000	0.35–0.37	61–65	180
50	50	13.5	90–100	80– 85,000	0.39–0.41	68–72	150
30	70	12.0	50– 60	55– 60,000	0.47–0.51	82–89	120

[a] Data constitute the composite findings of Europeans (Kieffer and Hotop[18]) and Americans (Mallory, *Electrical Contacts Data Book*; Stackpole Carbon Co., St. Mary's, Pa., Catalog No. 12, 1945; H. H. Hausner, *private communication*).

[b] Composition in weight per cent.

[c] As compared to bulk Ag = 100.

By varying selectively the tungsten concentration over the depth of the contact metal, as, for example, by Hausner's[23] method of pressing multiple layers of different tungsten–silver proportions (for manufacture, see page 194 and Figs. 371, *B* and *C*), the contact metal can be equipped

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[23] H. H. Hausner, *Product Eng.*, *14*, No. 9, 618 (1945).

with the most desirable properties for each section. Such multiple-layer contact materials can combine high spark resistance at the contact surface with a considerably improved over-all conductivity. The bottom layer containing 60% W, balance Ag, has a very good conductivity, while its coefficient of thermal expansion matches more closely that of the brazed-on copper support than would a composition richer in tungsten. At the same time, the larger low-melting metal phase facilitates brazing to copper or other backing materials, and less field distortions caused by abrupt changes in conductivity will be encountered. The comparatively low hardness of this layer has no significance because of its distance from the contact face. In the superimposed layers the tungsten content increases in 10% steps, and with it, density and hardness, while conductivity changes inversely. The top layer constituting the contact face contains the heaviest tungsten concentration (tungsten–silver ratio: 90–10) and is therefore the densest, hardest, and most resistant to sparking. Figure 384 shows how its critical current is increased over that of the better conducting compositions, especially for lower voltages.

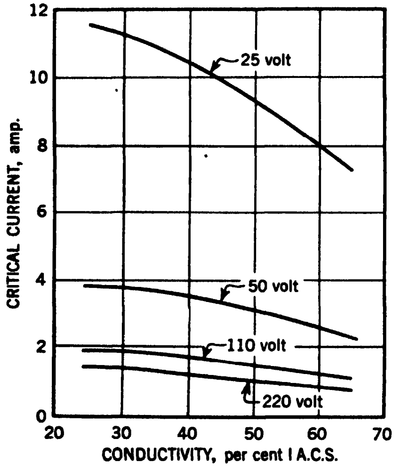

Fig. 384. Critical currents of silver–tungsten contact material as a function of the conductivity of the compact and the voltage imposed (according to Hausner and Blackburn[22]). Conductivity is expressed as per cent of the International Annealed Copper Standard (I.A.C.S.).

Molybdenum–Silver. The physical properties of some industrially important molybdenum–silver contact materials are given in Table 135. They correspond closely to the tungsten–silver group, except for the density—which is practically constant for all ratios (about 10.3 g./cc.). Although in many cases molybdenum–silver can be used interchangeably with tungsten–silver, its easier machinability and slightly lower raw material cost make it often more desirable. However, the molybdenum-base compositions have proved to be somewhat less arc resistant and

TABLE 135

Physical Properties of Mo–Ag Contact Materials[a]

Composition, %[b]		Density, g./cc.	Brinell hardness	Cross breaking strength, psi	Electrical conductivity		Estimated contact resistance[c]
Mo	Ag				megmho-cm.	per cent I.A.C.S.	
80	20	10.25	190–210	160–180,000	0.28–0.30	49–53	500
75	25	10.27	180–190	140–160,000	0.30–0.32	53–56	400
70	30	10.28	160–170	125–140,000	0.32–0.34	56–60	325
65	35	10.29	140–150	110–125,000	0.34–0.36	60–63	275
60	40	10.30	120–130	100–110,000	0.36–0.38	63–67	250
50	50	10.32	90–100	90– 95,000	0.40–0.42	70–74	225
30	70	10.33	50– 60	60– 65,000	0.48–0.50	84–88	175

[a] Data constitute the composite findings of Europeans (Kieffer and Hotop[18]) and Americans (Mallory, *Electrical Contacts Data Book*; Stackpole Carbon Co., St. Mary's, Pa., Catalog No. 12, 1945; H. H. Hausner, *private communication*).

[b] Composition in weight per cent.

[c] As compared to bulk Ag = 100.

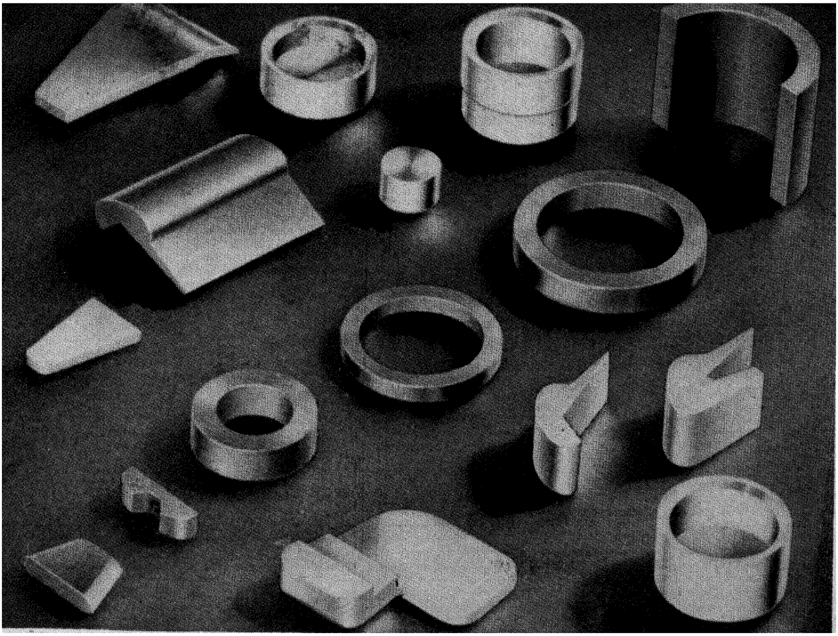

Fig. 385. Variety of shapes of tungsten–copper contact metals (according to Hensel, Larsen, and Swazy[27]).

more easily attacked by atmospheric corrosion. At certain conditions, molybdenum–silver compositions will form a surface film that increases the contact resistance. On material which is not constantly in service, the film may have detrimental effects.

APPLICATIONS

The refractory metal base composite materials have found a wide field of applications where heavy duty contact metals are required, and a variety of shapes made from tungsten–copper contact metals is shown in Figure 385. The composite materials are fastened to their supporting members (usually made from copper, brass, or bronzes) by means of copper or silver brazing in a protective hydrogen atmosphere. In some cases, a thin coating of tin facilitates the brazing operation. A particularly solid joint is obtained if the supporting material is cast directly onto the composite facing. When tungsten–copper facings are to be joined with copper supports, the copper-impregnation method can readily be combined with such a step.

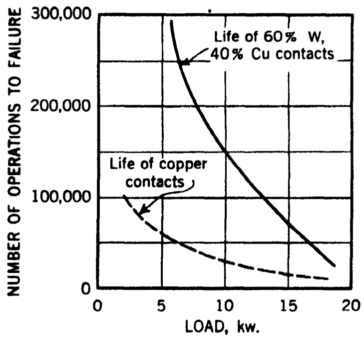

Fig. 386. Comparison of the life of tungsten–copper and plain copper contacts for oil circuit breakers (according to Hausner and Blackburn[29]).

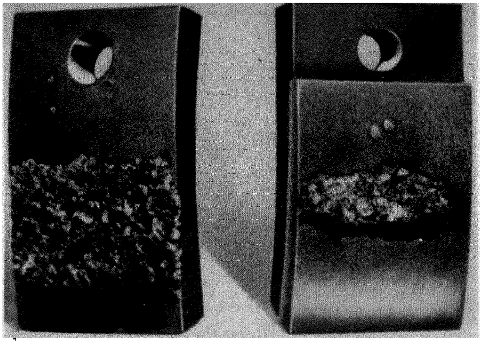

Fig. 387. Comparative performance of transformer tap-changer contacts of plain copper (left) and copper with copper–tungsten contact metal facing (right) according to Parsonage[26]).

The selection of the contact material depends primarily upon the particular application. Tungsten–copper materials are favored for high voltage applications where pitting and burning must be overcome and long life is essential. Figure 386 compares diagrammatically the life of two 60–40 W–Cu contacts with plain copper contacts in an oil circuit

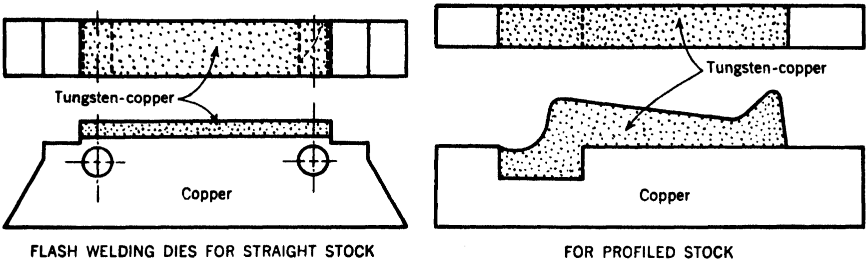

Fig. 388. Schematic drawing of tungsten–copper facings of two typical flash welding dies designed to withstand heavy pressure (according to Hensel, Larsen, and Swazy[27]).

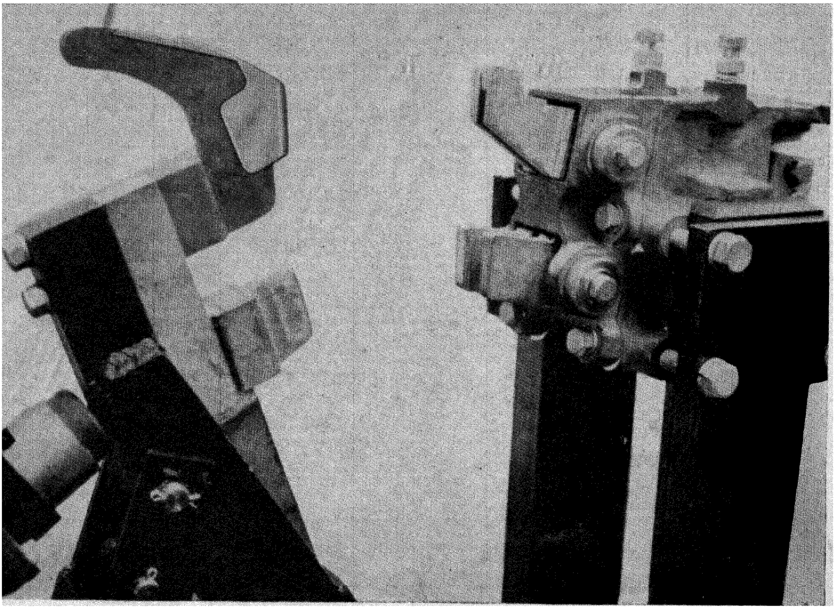

Fig. 389. Circuit breaker where lower connection of considerable mass of copper carries the current, and the upper contact, faced with tungsten–copper alloy, withstands the arc when the switch is opened (according to Hensel, Larsen, and Swazy[27]).

breaker, according to experiments by Windred[24] and Meier.[25] The life of the composite material is more than six times as long as for ordinary copper contacts, the latter lasting only 25,000 operations at 10-kw. load as compared with more than 150,000 operations for the 60–40 W–Cu

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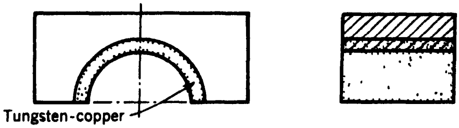
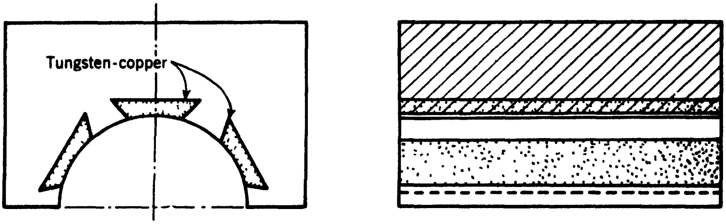
[24] G. Windred, *Elec. Eng.* (*London*), *4*, 1045 (1937); *Engineer* (*London*), *169*, No. 4406, 558; No. 4407, 567 (1940).

[25] K. Meier, *Elektrotech. Z.*, *57*, 493 (1936).

contacts. Similar results have been obtained with tap-changer contacts for transformers[26] (Fig. 387). According to Hensel, Larsen, and Swazy,[27] tungsten–copper contact facings in flash welding dies (Fig. 388) will increase the life of the contact from 10 to 80 times as compared with plain copper-faced dies. Furthermore, the uniformity and quality of the welds produced with the composite material are greatly improved. The most typical field of application for tungsten–copper contacts is for oil circuit breakers and for air circuit breakers having two- or three-stage contacts. The individual stages serve to carry the load and to provide auxiliary and final arcing contacts. A typical circuit breaker with contact fingers is shown in Figure 389. Other applications of tungsten–copper contact metals include current-carrying bearing inserts (Fig. 390); contact facings for various butt, flash, and projection welding dies or disks; combination contact metals and arcing tips for high voltage, high amperage (up to 10,000 amperes) applications; and arcing tips for handling peak currents (up to 40,000 amperes).



SHORT BEARINGS WITH SMALL DIAMETERS



LONG BEARINGS WITH LARGE DIAMETERS

Fig. 390. Schematic drawing of tungsten–copper bushing and bearing inserts for current-carrying shafts (according to Hensel, Larsen, and Swazy[27]).

Tungsten–copper–nickel contacts, containing 90% W, 7.5% Ni, and 2.5% Cu, have proved to be useful for high-current applications, since they exhibit very high resistance against material transfer and high hardness, while their electrical conductivity, although less than in binary

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[26] S. H. Parsonage, *Elec. Eng. (London)*, *10*, 828 (1940).

[27] F. R. Hensel, E. I. Larsen, and E. F. Swazy, in J. Wulff, *Powder Metallurgy*. Am. Soc. Metals, Cleveland, 1942, p. 492.

tungsten–copper contacts, is still fairly good. Typical applications include arcing contacts, especially in alternating current oil circuit breakers[28] (see Fig. 330, Chapter XXI).

Tungsten–silver contact metals have been very useful in voltage regulators for low voltages, but can also be used for medium and high voltage applications. They are particularly suitable for medium currents, when wear resistance is important. They are also being widely employed in circuit breakers, contactors, motor starters, and aviation relays, and, generally, for arcing tips that operate under oil.

Molybdenum–silver contact metals are most suitable for low and medium voltages and high currents, especially for high conductivity requirements. In addition to application in switch gear, these materials are also used in circuit breakers, contactors, transformer-protecting equipment, motor controls, aviation relays, and aviation engine starting relays, and, generally, for arcing tips that operate in air.

Compositions containing a low percentage of tungsten or molybdenum are, generally speaking, most suitable for contacts requiring comparatively high conductivity coupled with good arc-resisting characteristics. Materials that include a higher percentage of tungsten and molybdenum are most advantageously employed in the important field of arcing tips.

Composite Hard Metal Base Contacts

Sintered tungsten carbide hard metals are successfully used for contact materials in the telegraph service (see also Chap. XXII, p. 167). Tungsten carbide cemented with 6% cobalt, for example, has been found by Clark[29] to perform very satisfactorily for compacts in standard polar relays. Other cementing metals that may be used are osmium, platinum, iridium, and rhodium. Tungsten borides cemented with osmium or other noble metals performed equally well, but had the disadvantage of distorting during sintering. In the German patent literature a number of hard metal compositions suitable for contact purposes are mentioned which contain tantalum carbide and columbium carbide[30] and titanium carbide.[31] Cobalt-cemented tungsten carbide contacts have been suggested for vacuum contacts,[32] and hard metals containing a large proportion of titanium carbide for electrode facings in welding machine dies operating on stainless steels and aluminum.[33]

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[28] G. H. S. Price, S. V. Williams, and C. J. O. Garrard, *J. Gen. Elec. Co. (London), 11,* No. 4, 223 (1941).

[29] F. H. Clark, in J. Wulff, *Powder Metallurgy.* Am. Soc. Metals, Cleveland, 1942, p. 493.

[30] German Pat. 554,931.

[31] German Pat. 622,522.

[32] German Pat. 497,472.

[33] I. Gabler, *Z. Ver. deut. Ing., 82,* 1399 (1938).

Contact materials containing tungsten carbide and silver, with the content of the former varying from 20 to 80%, have been developed for air circuit breakers.[34] Their Rockwell "B" hardness ranges from 80 to 100; these contact materials have a very high current capacity, coupled with excellent nonwelding characteristics, resulting in long contact life and increased efficiency of the switch. Compositions containing tungsten carbide, cobalt, and silver (*e.g.*, 90–8–2 WC–Co–Ag) have been suggested for airplane engine applications.[35] In Table 136, the physical properties of tungsten carbide base composite materials are compared with those of the plain refractory metal base compositions.[36]

TABLE 136

Properties of WC-, W-, and Mo-Base Contact Metals[36]

Principal composition	Electrical conductivity, per cent I.A.C.S.	Hardness, Rockwell "B"	Ultimate tensile strength, psi	Cross breaking strength, psi
Cu-WC	47	90–98	70,000	140,000
Cu-W	38	72–82	63,000	110,000
Cu-W	34	85–92	75,000	130,000
Ag-WC	55	50–65	35,000	65,000
Ag-WC	50	70–85	40,000	90,000
Ag-WC	35	95–105	55,000	120,000
Ag-W	62	60–65	35,000	80,000
Ag-W	52	82–90	50,000	120,000
Ag-W	45	92–99	70,000	130,000
Ag-Mo	52	70–80	45,000	110,000
Ag-Mo	47	80–90	60,000	135,000

Other Composite Contact Materials

SILVER-GRAPHITE

Silver–graphite composites have been used in those applications in which the nonwelding properties are of paramount importance, and when high conductivity is also desirable.[37] The commercial grades of silver-graphite vary in graphite content from 1 to 15% by weight, the balance being pure silver; for special applications, combinations containing up to 50% graphite have been developed. The contact resistance of a 95–5 Ag–C material is shown as a function of contact pressure in Figure 391,

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[34] Anonymous, *Materials and Methods, 23,* No. 2, 570 (1946).

[35] Brit. Pat. 583,067.

[36] *Electrical Contacts Data Book.* P. R. Mallory Co., Indianapolis, Ind., 1945, p. 55.

[37] U. S. Pat. 1,802,718.

and of the number of operations in Figure 392. It compares favorably with silver–nickel in the former case, and equals pure silver in the latter case. The physical properties of silver–graphite composites are given in Table 137. In these compositions, high conductivity is combined with satisfactory lifetime and desirable nonsticking characteristics. The chief applications are for ordinary and aviation circuit breakers, relays, switches, contactors, sliding contacts on instruments, motor control equipment, and low voltage motors and generators.

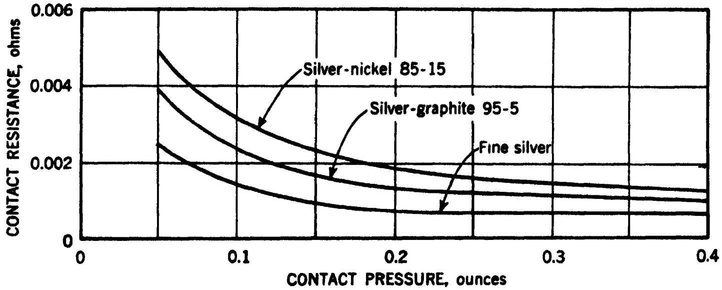

Fig. 391. Contact resistance of fine silver, silver–graphite, and silver–nickel contact metals as a function of contact pressure. Contacts carrying current only, without interruptions (circuit "makes" and "breaks"); contacts $^3/_8$ in. diameter, one flat, one domed with $^3/_4$ in spherical radius. (Courtesy of Gibson Electric Co.)

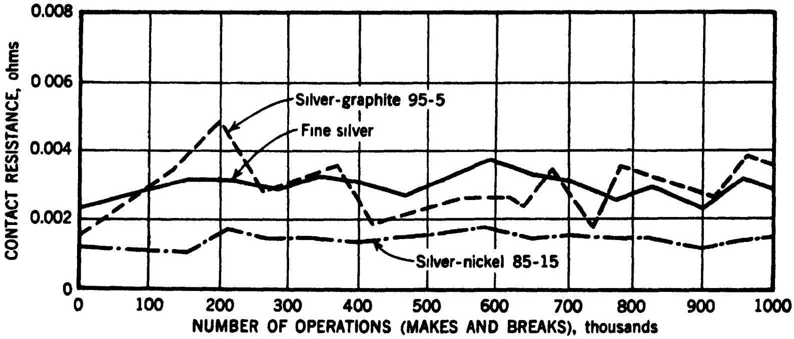

Fig. 392 Endurance characteristics of fine silver, silver–graphite, and silver–nickel contact materials as illustrated by change in contact resistance with the number of operations (circuit "makes" and "breaks") for alternating current. *Test conditions*: contact pressure, 1 ounce; resistive load, 9.0 amp., 115 volts, a.-c.; operated at 44 makes and breaks per minute; contacts $^3/_8$ in. in diameter, one flat, one domed with $^3/_4$ in. spherical radius. Weight loss in 1,000,000 operations: fine silver, 0.005 g.; silver–graphite, 0.130 g.; silver–nickel, 0.004 g. (courtesy of Gibson Electric Co.).

SILVER-NICKEL

The properties of sintered silver–nickel contact materials have been investigated by Comstock.[38] The materials are usually produced by compressing the correctly proportioned powder mixture and sintering below the melting point of silver. Subsequent cold or hot coining results in completely solid structures. The nickel content usually varies from 5 to 50% by weight; the composite structures have a very high conductivity which approaches that of pure silver in the case of silver-rich

TABLE 137

Physical Properties of Silver–Graphite Contact Materials[a]

Composition, %		Cross breaking strength, psi	Hardness, Rockwell superficial	Density, g./cc.	Electrical conductivity (Ag = 100)	Contact resistance[b]
Ag	Graphite					
99	1	50,000	15T68	10.0	92	—
98	2	45,000	15T65	9.6	85	115
98	2	37,500	15T67	9.1	—	120
97	3	37,000	15T64	9.3	78	—
96	4	32,000	15T66	9.1	70	130
96	4	31,000	15T64	8.9	—	—
95	5	23,000	15T50	8.6	60	200
93	7	20,000	15T45	8.0	50	225
90	10	15,000	15T40	7.0	54	—
80	20	5,000	15T50	5.7	—	—
75	25	6,000	15T10	3.8	—	—
50	50	5,000	15T30	3.0	—	—

[a] Stackpole Carbon Company, St. Mary's, Pa., Catalog No. 12, 1945, p. 21.
[b] On 30-ampere, 110-volt a.-c. gravity-type relay (Ag = 100).

TABLE 138

Physical Properties of Ag–Ni Contact Materials[a]

Composition, %		Cross breaking strength, psi	Hardness, Rockwell superficial	Density, g./cc.	Electrical conductivity (Ag = 100)	Contact resistance[b]
Ag	Ni					
85	15	46,000	30T38	9.4	78	130
80	20	58,000	30T40	9.2	70	140
70	30	60,000	30T42	8.8	65	165
60	40	64,000	30T40	8.2	50	—
60	40	50,000	30T46	9.6	60	—
40	60	65,000	30T68	9.3	45	—
40	60	40,000	30T15	8.0	40	—

[a] Stackpole Carbon Company, St. Mary's ,Pa., Catalog No. 12, 1945, p. 23.
[b] On 30-ampere, 110-volt a.-c. gravity-type relay (Ag = 100).

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[38] G. J. Comstock, *Metal Progress, 35,* 576 (1939).

materials. The contact resistance, on the other hand, is improving over that of fine silver if the nickel content is not above 15%. At the same time, the composites are harder and show less tendency to "stick" than pure silver. The physical properties of some silver–nickel contact materials are given in Table 138 (the materials containing 60 and 40% Ag having been manufactured in two different ways). In Figure 391 the contact resistance of an 85–15 Ag–Ni composite contact metal is plotted as a function of contact pressure, and compared with that of pure silver and with a silver–graphite material. Although the contact resistance is somewhat higher than for pure silver, it is still low. As Figure 392 shows, however, the contact resistance remains lower than that of fine silver even when the contacts make and break a circuit up to 1,000,000 times.

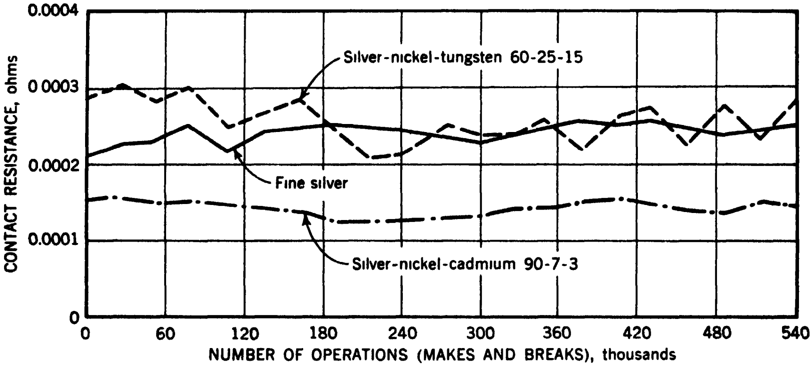

Fig. 393. Endurance characteristics of fine silver, silver–nickel–tungsten and silver–nickel–cadmium contact materials as illustrated by the change in contact resistance with the number of operations (circuit "makes" and "breaks") for direct current. *Test Conditions*: contact pressure. 4 ounces; resistive load, 15.5 amp., 6 volts, d.-c.; operated at 1800 makes and breaks per minute; contacts $^3/_{16}$ in. in diameter (courtesy of Gibson Electric Co.).

This low and constant contact resistance combined with the non-sticking properties at heavy pressures make nickel–silver contacts very suitable for high voltage disconnect switches involving applications up to 200,000 volts. The materials are also useful for main current carrying contacts on circuit breakers rated up to 10,000 amperes. Other applications include relays, motor starters, safety switches, selector switches, heavy duty contactors, and transformer protectors operating in oil.

SILVER-NICKEL-TUNGSTEN

Compositions containing from 1 to 30% W, 1 to 35% Ni, balance Ag are also useful as contact metals. They may be used primarily for equipment that must operate under relatively high current density conditions, where the material must have a satisfactory conductivity, as well as good resistance to arcing caused by the opening and closing of the circuit. In Figure 393 the contact resistance of a 60–25–15 Ag–Ni–W material is plotted against the number of operations and compared with pure silver and with a composition containing cadmium instead of the refractory metal (see p. 219). The contact resistance of the material containing refractory metal is as low as that of fine silver when operated under direct current load at high frequency. Figure 394 shows the temperature rise of a pair of 55–25–20 Ag–Ni–W contacts when operating under severe test conditions on a circuit breaker. A low contact resistance is indicated by the low temperature rise at the heavy load imposed by the high current density for relatively long periods.

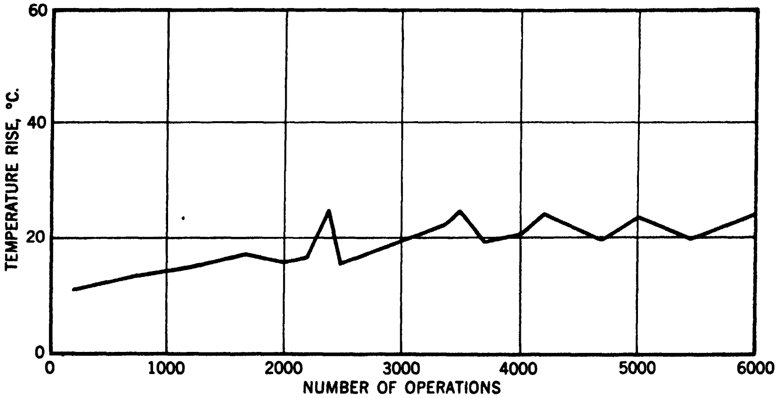

Fig. 394. Increase in temperature of a 55–25–20 silver–nickel–tungsten contact with the number of operations for alternating current. *Test Conditions*: contact pressure, 16 ounces; resistive load, 50 amp., 220 volts, a.-c.; operated 3 seconds on, 4 seconds off on a single-pole circuit breaker; contacts $^3/_{16}$ in. in diameter, one flat, one domed (courtesy of Gibson Electric Co.).

Applications for which such complex contact metals have proved satisfactory include small circuit breakers, motor starter switches, line starters, and relays.

SILVER-NICKEL-MOLYBDENUM

Compositions containing 1 to 35% Mo, 1 to 35% Ni, and balance Ag have also been developed, and are employed in essentially the same applications as their tungsten-containing counterparts. Their principal advantage stems from their somewhat lower raw material costs.

SILVER-NICKEL-CADMIUM

Materials containing cadmium in addition to silver and nickel have also been developed for special contact purposes. Compositions of such materials contain from 5 to 25% Ni and from 1 to 10% Cd, the balance being fine Ag. Their exceptionally low contact resistance can be seen from Figure 393, in which a material containing 7% Ni and 3% Cd is compared with pure silver and with a tungsten-containing nickel–silver composition. The addition of cadmium to the silver–nickel composite structure results in a comparatively hard and tough material which possesses good wearing qualities and very low contact resistance. The ternary composition is more resistant to wear than either pure silver or binary silver–cadmium combinations. This complex material is used principally in small circuit breakers and relays.

SILVER-CADMIUM

Binary silver–cadmium alloys with up to approximately 10% Cd have also been mentioned in the literature as contact material. Due to the solid solubility of these alloys, however, their conductivities are below those obtainable with silver–cadmium oxide materials (p. 220). A series of alloys containing from about 3 to 11% Cd has been studied by Hensel and Larsen,[39] and the electrical conductivity of these alloys is reproduced in Table 139 for cold-worked and annealed specimens.

TABLE 139

Electrical Conductivity of Ag–Cd Solid Solution Alloys (Hensel and Larsen[39])

Composition, %			Electrical conductivity, per cent I.A.C.S.
Ag	Cd	Condition	
96.98	3.02	Cold worked,	67.0
		Annealed ½ hr. at 650 °C. (1200 °F.)	72.5
94.32	5.68	Cold worked,	52.6
		Annealed ½ hr. at 650 °C. (1200 °F.)	59.2
89.16	10.84	Cold worked,	39.25
		Annealed ½ hr. at 650 °C. (1200 °F.)	44.2

SILVER-IRON

Compositions containing from 10 to 40% Fe, balance Ag have also been suggested as contact material.[40] The iron is added in the form of carbonyl iron powder, and the mixture is compacted at 12 tsi, sintered at 900°C. (1650°F.) for half an hour in a hydrogen atmosphere; a reduc-

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[39] F. R. Hensel and E. I. Larsen, *Trans. Am. Inst. Mining Met. Engrs.*, *161*, 569 (1945).

[40] Brit. Pat. 578,936.

tion of 20% by cold rolling is followed by annealing under the same conditions as used for sintering, and stamping of the contacts out of the resulting sheet. Incorporation of carbonyl iron reduces sticking and pitting and increases the mechanical strength of the material. The silver–iron composition may be used for facings with a pure silver backing or in conjunction with another silver-base contact.

MISCELLANEOUS COMPOSITIONS

Among other sintered metal compositions that are suitable for contact materials, silver combinations with lead oxide, cadmium oxide, and iron oxide appear most interesting. The silver–cadmium oxide materials can be used in heavy duty relays, since they withstand heavy overloads without sticking or welding. They also maintain low contact resistance over extended periods of operation.[41] Table 140 shows the physical properties of three typical compositions. The silver–iron oxide contacts

TABLE 140
Physical Properties of Ag–CdO Compositions after Various Treatments (Hensel and Larsen[41])

Composition, %		Treatment	Density, g./cc.	Electrical conductivity, per cent I.A.C.S.	Hardness, Rockwell "F"	Ultimate tensile strength, psi	Elongation in 1 in., %
Ag	CdO						
97.5	2.5	Pressed at 10–15 tsi	7.85	—	—	—	—
		Sintered in air 1 hr. at 800°C. (1470°F.)	8.43	—	—	—	—
		Re-pressed at 50 tsi (full hard)	10.1	88.7	74	25,200	1.6
		Annealed ½ hr. at 600°C. (1110°F.)	—	94.9	18	18,000	16.8
95	5	Pressed at 10–15 tsi	7.72	—	—	—	—
		Sintered in air 1 hr. at 800°C. (1470°F.)	8.19	—	—	—	—
		Re-pressed at 50 tsi (full hard)	9.99	83.6	76	25,000	1.6
		Annealed ½ hr. at 600°C. (1110°F.)	—	93.5	30	17,000	8.6
90	10	Pressed at 10–15 tsi	7.50	—	—	—	—
		Sintered in air 1 hr. at 800°C. (1470°F.)	7.8	—	—	—	—
		Re-pressed at 50 tsi (full hard)	9.8	69	81	26,000	0
		Annealed ½ hr. at 600°C. (1110°F.)	—	80	40	17,000	4

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[41] F. R. Hensel and E. I. Larsen, *Trans. Am. Inst. Mining Met. Engrs., 161,* 569 (1945).

are being used successfully on aviation-type circuit breakers up to 125 amperes direct current at 30 volts. These contacts combine the low contact characteristics of the silver with the arc resistance characteristics of the iron oxide in such a manner that the material resists the action of altitudes. A composition of 90% silver and 10% iron oxides is claimed to excel by its resistance to wear and welding, and its chemical stability.[41a] Contact materials containing lead oxide have acquired uses on account of their nonwelding characteristics and resistance to arcing on direct current circuits. The physical properties of two typical compositions, each manufactured in two ways, are given in Table 141. The range of silver–lead oxide compositions is narrower than that of other silver composites, the lead oxide generally not exceeding 5% by weight. Typical applications of this material include low-voltage apparatus for fairly heavy currents, especially where vibrating contacts are involved.

TABLE 141

Physical Properties of Ag–PbO Contact Materials[a]

Composition		Cross breaking strength, psi	Rockwell hardness, superficial	Density, g./cc.	Electrical conductivity (Ag = 100)	Contact resistance[b]
Ag, %	PbO, %					
97.5	2.5	37,000	30T39	9.8	70	—
97.5	2.5	45,000	15T67	9.0	65	—
95	5	42,000	15T67	9.7	50	115
95	5	27,000	30T25	9.4	45	—

[a] Stackpole Carbon Company, St. Mary's, Pa., Catalog No. 12, 1945, p. 22.

[b] On 50-ampere, 110-volt a.-c. gravity-type relay (Ag = 100).

During the war, an intensive study in Germany of the systems tungsten, oxygen and nickel or silver, respectively, has disclosed a surprisingly high electrical conductivity of the lower tungsten oxides and of some ternary phases containing oxygen, indicating that tungsten–nickel–oxygen alloys with up to 10% Ni content can give excellent performance for certain contact applications.[42]

Other sintered alloys suggested for special contact purposes are chiefly copper-base. They include compositions containing copper and silver, and copper, silver, and graphite. The latter have been developed especially for heavy duty sliding contacts on rheostats.[42a] Other compositions in use contain copper and cadmium (nonequilibrium structures

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[41a] U. S. Pat. 2,394,501.

[42] Staatl. Forschungsinst. f. Metallchem., Marburg, British Intelligence Objectives Sub-committee Doc. F.D. 1594/46; see also *Met. Powd. Rept.*, *1*, 76 (Jan. 1947).

[42a] Stackpole Carbon Company, St. Marys, Pa., Catalog No. 12, pp. 26, 27.

lacking alloy formation)[42b]; copper, silver, and cadmium[43]; copper, cadmium, and boron, with or without silver[44]; and copper alloys with cadmium, chromium, and iron.[45] Binary compositions of copper and chromium can also be used as welding electrode material, and copper–graphite compositions with 80 to 95% Cu qualify for heavy duty contactors, rheostat sliding contacts, arcing tips, as well as for brushes (see below).[42a] One type of material of unusual corrosion resistance plus good conductivity has been produced from stainless steel and silver powder mixtures,[46] the former having been obtained by intercrystalline corrosion of scrap metal. Another material of exceptional chemical stability, especially suitable for contacts on control equipment operating in certain types of industrial atmospheres where silver–graphite compositions undergo early failure, is gold–graphite, which, in spite of its obviously higher cost, is claimed to result, in certain instances, in considerable savings in time and production.[42a]

Special contact metal developments in Germany during the war included a corrosion resistant titanium contact metal (produced from the hydride), an abrasion resistant tungsten boride material, and a 95–5 silver–graphite composition for sliding contacts for which special grades of silver powder were developed.[46a]

CURRENT COLLECTOR BRUSHES

Development of Composite Structures

ALL-CARBON BRUSHES

The development of electrical machinery promoted the use of sliding contacts to enable the transfer of electrical current between the moving and stationary elements of the equipment. Current collector brushes were first produced from carbon alone, whereby carbon (*e.g.*, lampblack, coke, graphite) powders were pressed with a pitch binder into bars that were sintered into bulk graphite. The required brush shapes were formed by simple machining. These carbon brushes, however, did not entirely fill the needs of modern electrical engineering—except in high-voltage, low-current applications where all-carbon brushes usually perform satisfactorily.

[42b] U. S. Pat. 2,370,400.

[43] U. S. Pat. 2,119,965.

[44] U. S. Pats. 2,116,252; 2,170,431.

[45] U. S. Pat. 2,218,073.

[46] U. S. Pat. 2,426,659.

[46a] F.I.A.T. Final Report No. 785 (1947); see also *Met. Powd. Rept., 1,* No. 7, 105 (1947).

METAL-GRAPHITE MATERIALS

In high-current, low-voltage applications a higher current-carrying capacity is required than can be obtained by ordinary carbon materials. Furthermore, for a brush to be deemed satisfactory there must be a minimum of sparking, a minimum of electrical and mechanical losses, a minimum of wear of the commutator or slip ring, uniform contact with a lubricating film over the commutator or slip ring, as well as quiet operation and good brush life. While the electrical and thermal conductivities of copper and some of its alloys are satisfactory from the standpoint of current transfer in high-current applications, the comparatively high frictional characteristics lead to nonuniform contact and incomplete surface lubrication. External lubricants such as greases or oils would help to overcome the wear problem, but would tend to impair the electrical properties on account of their insulating properties. The solution of the problem was found in combining in a composite structure the lubricating properties of solid graphite with the current-carrying characteristics of metallic conductors such as silver, copper, or certain bronzes. The development of these nonabrading, highly conducting, metal–graphite composites represents one of the oldest phases of powder metallurgy and has resulted in the modern method of manufacturing uniform fine-grained products which combine to a high degree of perfection the principal requirements of low friction, high wear resistance, low electrical resistance and high heat conductivity. In a uniform structure of the composite material, the graphite phase tends to form a continuous film between the moving parts, reducing friction and wear. The lubrication value of the graphite is not sacrificed by the addition of the metal powders if their particles are dispersed uniformly. On the other hand, the electrical resistance is lowered and the heat conductivity improved proportionally with the metal powder addition. Thus, for increasingly high-current applications, an increasingly large metallic phase is required in the brush.

LAMINATED STRUCTURES

An improvement in the current-carrying properties of the composite material is achieved by imparting to the brush a laminated structure that results in a lower electrical resistance in the direction of current flow than in the direction perpendicular to it. Such structure is accomplished by using flake copper powders, and applying the pressure at right angles to the direction in which the current is to flow in the finished brush.

Laminated brushes of this type have given valuable performance in commutator-type machines.[46b]

BRUSHES FOR AVIATION EQUIPMENT

Standard types of metal–graphite brushes were found unsatisfactory for equipment in planes flying above 20,000 feet.[47] At these altitudes the rise in current density and lower temperature have but little effect on the wear of the brushes, but the low pressure and moisture content of the atmosphere tend to pulverize the structure. Thus, the development of an improved material became necessary. The recently perfected high-altitude copper–graphite type of brush contains a complex organic lubricant that resists oxidation and provides a stable film which gives satisfactory brush life, contact drop, and low coefficient of friction even under extremely adverse service conditions.

Manufacture

The metal–graphite brush materials are produced by conventional powder metallurgy techniques. In the case of simple copper–carbon combination, the copper powder is generally of fine grade. Either electrolytic or reduced powder is closely sized: in one specific grade, all particles must pass through a 230-mesh sieve, but not more than 15% can pass through a 325-mesh sieve. Another powder favored by some manufacturers is extremely fine and has a very low apparent density (all —325 mesh, apparent density 0.7–1.0 g./cc.) and is produced electrolytically. This powder resembles graphite powder with respect to particle size, structure, and unit weight, and facilitates uniform distribution of both phases during mixing which, in turn, inhibits classification or segregation during molding. In the case of bronze–graphite compositions, up to 10% Sn is

TABLE 142

Chemical Composition of Typical Copper–Graphite and Bronze–Graphite Brush Materials (Kieffer and Hotop[49])

Type No.	Composition, %				
	Copper	Graphite	Tin	Lead	Zinc
1	85	5	—	10	—
2	80	10	—	10	—
3	80	10	10	—	—
4	70	20	—	10	—
5	70	30	—	—	—
6	68	12	8	—	12
7	30	70	—	—	—

[46b] R. R. Hoffman, *Trans. Am. Inst. Mining Met. Engrs.*, *161*, 550 (1945).

[47] D. Ramadaroff and S. W. Glass, *J. Am. Inst. Elec. Eng.*, *63*, 825 (1944).

added to the copper; more complex materials contain up to 10% each of zinc, nickel, and lead, in addition to the copper and tin. The purpose of these additions is to increase the bonding or wear resistance, or, in the case of lead, to improve the smoothness of operation. Small amounts of silver and cadmium have also been suggested for this purpose.[48] The composition of a number of typical copper-base brush materials is given in Table 142.

The powder mixtures are molded into desired shapes at moderate pressures (up to 40 tsi), usually in automatic mechanical presses. The resulting compacts are sintered at temperatures between 750 and 900°C. (1400 and 1650°F.) in a neutral or reducing atmosphere. In the case of bronze structures, a liquid phase is formed during the initial stages of the treatment. To maintain close size control, the sintered brushes are repressed at pressures similar to those first used. If the percentage of metal is comparatively large, a sufficiently strong bond is obtained between the metal particles during sintering to provide good mechanical strength for the brush. For material high in graphite, a tar or pitch binder is required.

According to Kieffer and Hotop,[49] porous bronze–graphite brushes, containing 1.5–2% C, 5–20% Sn, balance Cu, can be impregnated with insulating oils or fluids that promote better contact. The production of these porous materials varies from the standard procedure only in certain details, such as the use of coarser and more uniformly sized powders, a lower molding pressure, and the application of organic substances that volatilize during sintering.

The physical design of brushes varies widely, and includes blocks and complicated shapes having bevels, slots, recesses, or grooves, often being further complicated by attachments, such as, flexible shunts, pigtails and clips. Consequently, only simple-shaped high production items such as brushes for small motors or automotive starters and generators are molded to the exact size and shape required, the tolerances in this case generally falling between 0.004 and 0.020 in.—depending on the over-all size.[46b] For some purposes, brushes are molded to approximate shape and size, and require only minor finishing operations. Frequently, however, the material is molded into the shape of large blocks from which a number of parts may be cut. Conventional machining and grinding operations give the finished size. The tolerances obtained in machined parts are approximately of the same order as those held by the directly molded simple shapes.

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[48] U. S. Pat. 2,053,662.

[49] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe*. Springer, Berlin, 1943, pp. 319, 320.

Properties

The current-carrying capacity of the metal–graphite products depends upon the proportion of the metallic phase in the material. Roughly, the following relation exists:[49a,50]

Material	Current density, amp./in.²	
	Minimum	Maximum
All-carbon	35	50
High-graphite metal composites (containing about 70% C)	70	100
Low-graphite metal composites (containing about 5% C)	125	250

According to Hoffman,[50] composite materials high in metal content withstand momentary loads up to 500 amp./in.². The specific resistance of metal–graphite materials suitable for brushes varies between 50 and 0.4×10^{-5} ohm/in.³. The scleroscope hardness ranges from approximately 5 to 35, and the transverse rupture strength from 2500 to 25,000 psi. At conventional operating conditions, the coefficient of friction ranges from 0.04 to 0.13 and the total positive and negative contact drop ranges from about 0.25 to 1.50 volts.

In Table 143, a comparison is made between the physical properties of copper–carbon brushes and typical graphite bronze composites that were produced in Germany during the war.[51] The electrical resistivity of various compositions of copper–graphite brushes that are suitable for high-altitude service in aviation equipment is given in Table 144.[52] Table 145 shows the influence of atmospheric conditions on the coefficient of friction and brush life for a high-altitude brush material containing 45% copper.[52]

Applications

The metal–graphite composite materials are used principally in brushes. These brushes are used extensively in motors and generators of both the commutator and slip-ring types, *e.g.*, in rotary converters, low-voltage generators for electrolytic installations, starters and generators in automobiles, battery chargers, and similar machines. Other, though more specialized, uses for the material include current-carrying washers, bushings, and rollers. Parts that serve to transfer current in relatively

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[49a] P. Schwarzkopf, *Product Eng.*, *17*, No. 4, 268 (1946).

[50] R. R. Hoffman, *Trans. Am. Inst. Mining Met. Engrs.*, *161*, 550 (1945).

[51] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe*. Springer, Berlin, 1943, p. 318.

[52] D. Ramadaroff and S. W. Glass, *J. Am. Inst. Elec. Eng.*, *63*, 825 (1944).

slow or intermittently moving equipment, such as rheostat controllers or switches, are considered to be outside the family of brushes, being referred to generally as contacts; they are discussed as such in the previous section of this chapter. Figure 395 shows an assemblage of metal–graphite brushes with pigtail shunts attached, as used in aircraft and automotive applications. Although copper is the chief constituent in most metal–graphite brush materials, silver–graphite composite structures have been used increasingly during recent years. In spite of their higher cost, they are now used in many applications where their slightly higher conductivity and their better lubricating properties yield a superior performance.

TABLE 143

Physical Properties of German Metal–Graphite Brush Materials (Kieffer and Hotop[51])

Properties	Low graphitic bronze	High graphitic bronze	Copper-graphite
Specific gravity	5.0	3.5	2.5
Brinell hardness	38	32	15
Scleroscope hardness	10	20	15
Thermal coefficient of expansion, per °C., $\times 10^{-6}$			
Longitudinal	12.0	4.0	2.9
Transverse	13.0	5.0	5.9
Specific electrical resistance, microhm-cm.	10	50	800
Breaking strength, psi	4250	5000	1420
Appearance (color)	Coppery	Chocolate	Graphitic with copper strata

TABLE 144

Electrical Resistivity of High-Altitude Copper–Graphite Brushes (Ramadaroff and Glass[52])

Grade type No.	Per cent copper	Resisitivity in ohm-in.
1	75	0.0000091
2	65	0.000019
3	45	0.00035
4	25	0.00055

TABLE 145

Effect of Atmospheric Conditions on Coefficient of Friction and Life of Copper-Graphite Brushes, Containing 45% Copper (Ramadaroff and Glass[52])

Atmospheric conditions	Coefficient of friction	Life, hr./in.
Room air, 50% humidity	0.21	6.000
Room air, 100% humidity	0.25	38,000
Dry air, sea level	0.18	1,200
Dry air, 18.2 cm. Hg	0.19	1,500
Vacuum, 0.1 cm. Hg	0.12	25,000

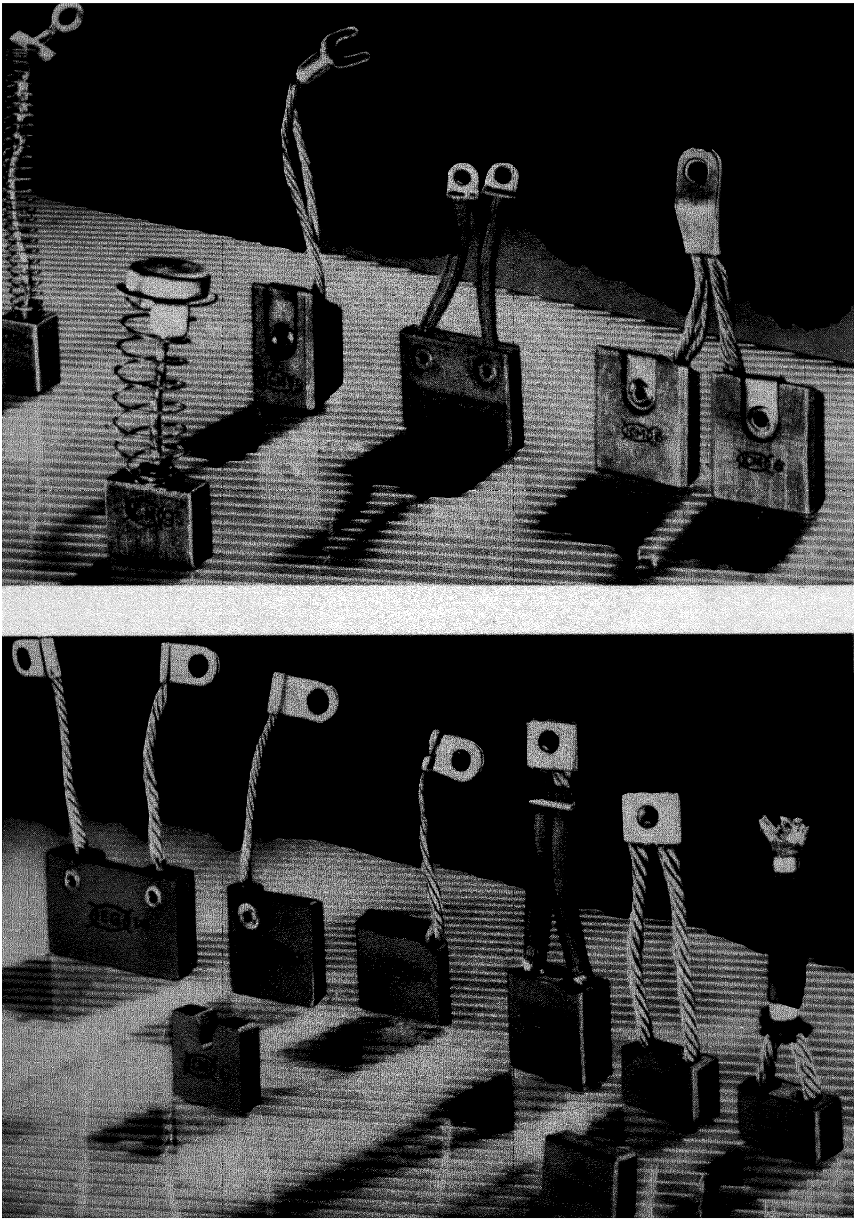

Fig. 395. Assortments of copper–graphite and plain graphite current collector brushes consisting of types used in aircraft (top) and automotive (bottom) applications (courtesy of Morganite, Inc.).

MISCELLANEOUS ELECTRICAL PRODUCTS

Sintered Copper Components

Among other products developed by powder metallurgy methods for the electrical field, pure copper parts for commutators and rotors are of some interest. Hardy[53] has reported on the development work for both of these applications. Requirements for commutator segments, implying a minimum copper content of 99.5%, a Brinell hardness of 100, and close dimensional tolerances, could apparently be met with electrolytic copper powder. The conductivity specifications, originally set at 96% I.A.C.S., however, could not be reached simply with pressed, sintered, and repressed powders, and were accordingly reduced to 65% I.A.C.S. (a value still satisfactory in view of the larger cross section of the commutator segment in comparison with the lead-in wire). Segments of very high density, produced by pressing at 50 tsi, sintering at 800°C. (1470°F.) for one hour, and repressing at 65 tsi, reached conductivity values of 90% I.A.C.S., and slightly higher values were obtained with copper segments having an integral silver facing. The conductivity originally required could be reached only with drop-forged or hot-pressed copper.

Apparently, several factors have so far been in the way of large-scale production of commutator segments from copper powders. Aside from the economic aspect (which would become favorable with increasing production), size control has been a major obstacle. While the rounding of corners during stamping of the segments from hard-rolled sheet is the principal disadvantage of the conventional manufacturing method, the powder molding process must work to fractions of one-thousandth of an inch in every direction. Whereas it is not particularly difficult to achieve this for the length and width dimensions, it is very difficult to control the thickness to that accuracy. Moreover, a serious tool problem results from the fact that the segments are strongly tapered and the powder has a tendency of shifting toward the thinner end upon compression into the wedge shape; shear stresses are thus exerted on the ear-shaped protrusion of the die. However, the use of carbide dies is believed to give a satisfactory solution to this problem.

The production of squirrel-cage rotors involves the pressing of resistance rings from pure copper powder. These rings are pressed onto both ends of a rotor assembly consisting of a stack of core iron lamellae that are held together by means of copper pins. According to Hardy,[53] compression of accurately weighed powder allotments in a hydraulic press and a suitable mold permitted a limitation of compression stroke to $^1/_8$ in., while at the same time an even weight distribution and proper balance

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[53] C. Hardy, *Metal Progress, 36,* 57 (1939).

could be maintained. Rotors produced in this manner performed as well as their cast and fabricated counterparts.

The use of sintered copper products of intricate design in the electronics field has been reported recently by Chase.[54] Some of these products are in electron tubes in which gas-free components of very high purity are a prerequisite. Furthermore, exceedingly close tolerances are required on certain critical dimensions, which cannot be produced readily by machining. One specific application for pure, sintered copper mentioned by Chase is an oblong shading coil with a wall thickness of only $^1/_{32}$ in. (see also Chapter XXVI.)

Resistor Materials

The use of the pure refractory metals, molybdenum and tungsten, as electrical resistor elements has already been discussed in Chapter XXI; the applicability of sintered iron–chromium–aluminum type alloys for heating elements is discussed elsewhere (Chapter XXXII). Of particular significance, however, seems to be the recent developments of combinations of metals and ceramics into composite structures of controlled or predetermined resistivity. Distinct from the simpler approach of encasing a refractory metal (molybdenum) rod or wire[54a,55] by a refractory oxide (Sillimanite) tubing and sealing the assembly gas-tight, the new developments are in the direction of mixing the metallic and nonmetallic constituents and producing a duplex structure embodying the electrical characteristics of each material (see also Chapter XXX). Thus it has been found possible for certain systems (*e.g.*, TiO_2–Ni, ZrO_2–Cu or ZrO_2–Fe_2O_3–Cu) by careful control of mixing and particle size distribution to produce resistor materials of predetermined (positive or negative) temperature coefficient of resistivity, and to assess the electrical behavior on the basis of a simple circuit diagram which relates the total resistivity to the inherent resistivity of the materials and the ensuing contact resistivities.[56-59] An 80–20 Al_2O_3–Fe material was found suitable as resistance material only up to 200°C. (390°F.) because the temperature coefficient of resistivity became negative at higher temperatures.[60]

The theoretical background of such metal–metal oxide semiconduc-

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[54] H. Chase, *Materials and Methods*, *24*, No. 6, 1439 (1946).

[54a] P. Schwarzkopf, *Metals and Alloys*, *13*, No. 1, 45 (1941).

[55] G. S. Lewin, *Proc. Inst. Radio Engrs.*, *35*, 494 (1947).

[56] H. H. Hausner, *J. Am. Ceramic Soc.*, *30*, 290 (1947).

[57] H. H. Hausner, *Powder Met. Bull.*, *3*, No. 1, 4 (1948).

[58] H. H. Hausner, *Proc. International Powder Metallurgy Conference*, Graz, July 12–17, 1948, Referate No. 51.

[59] H. H. Hausner, *Bull. Am. Phys. Soc.*, *24*, No. 1, 40 (1949).

[60] British Intelligence Objectives Sub-Committee, Document F. D. 1179/46; see also *Met. Powd. Rept.*, *1*, No. 5 (1947).

tors has recently been investigated by Meyer-Hartwig,[61] who found that with increasing temperature an equilibrium resistance is reached according to the characteristics of the finely dispersed metal and ceramic components. A controlled electrical behavior of the semiconductors depends on the possibility of arraying the metallic particles before sintering in the form of capillaries.

Porous Electrodes

The development of sintered porous metallic elements for electrodes in condensers, plates in batteries, and the like, was originated in Germany some twenty years ago, and introduced in the United States sevtral years later. An extensive patent literature covers a host of metals and alloys for this purpose, including silver,[62] tantalum,[63] molybdenum and tungsten,[64] aluminum,[65] and especially nickel,[66] iron,[67] and numerous iron alloys.[68,69] The suggested applications for porous iron alloys include electrodes for alkaline electrolytes[68] and for secondary elements[69]; those for nickel, tantalum, or silver include contacts and collectors operating in water, anodes for electrolytic cells and condensers, and plates (nickel) for alkaline nickel–cadmium batteries.

Only the last mentioned application has been described recently in the literature, so that production details and results of laboratory and performance tests are available. Fleischer[70] assembled sintered porous plates (plaques) into experimental cells and established discharge curves for different rates for a five-plate unit. The preparation of the porous plates was based on reports by American and British investigators[71-76]

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[61] E. Meyer-Hartwig, *Proc. International Powder Metallurgy Conference*, Graz, July 12–17, 1948, Referate No. 21.

[62] German Pat. 747,370.

[63] U. S. Pat. 2,359,970.

[64] German Pat. 732,433.

[65] German Pat. 708,895.

[66] German Pat. 721,887.

[67] U. S. Pat. 2,366,402.

[68] German Pats. 491,498; 493,593; 519,456.

[69] German Pats. 469,917; 523,029; 583,869; 608,122; 666,010.

[70] A. Fleischer, *J. Electrochem. Soc.*, *94*, No. 6, 289 (1948).

[71] G. B. Ellis, U. S. Dept. of Commerce, Office of Publication Board, PB 13806 (1946).

[72] L. E. Lighton, U. S. Dept. of Commerce, Office of Publication Board, PB 22928 (1946).

[73] P. E. Plehn, U. S. Dept. of Commerce, Office of Publication Board, PB 42771 (1946).

[74] H. B. Lunn, British Intelligence Objectives Sub-committee, Final Report No. 708 (1946).

[75] M. Barak and B. L. Davies, British Intelligence Objectives Sub-committee, Final Report No. 1129 (19) (1947).

[76] F. X. Brennan, "Investigation of Foreign Electrical Batteries," Summary Report No. F-SU-1155-ND (Project No. DQ126), Headquarters Air Materiel Command, Patterson-Wright Air Base, Dayton, Ohio (not published).

covering the development and production of 10 and 20 ampere-hour batteries for aircraft and special types of military equipment in Germany during the war. The porous plaques, designed as support for the active masses of the positive and negative plates, were prepared by sintering carbonyl nickel powder of low apparent density. They were then impregnated with nickel or cadmium salt solutions, preferably the nitrates, followed by precipitation of the heavy metal ions in the pores of the plaque by cathodic polarization in alkali hydroxide solution.

Summary

Two distinct lines of sintered electrical products have been established: heavy duty contact materials and compositions suitable for current-collector parts. In both instances, composite structures containing two fundamentally different elements have performed better than products made from only one element.

Electrical contacts fabricated from metal powders fall in two classes. One is comprised of a highly conductive metal and a refractory metal (or compound). Contact materials of this class have been developed primarily for use as facings for heavy duty circuit breakers and similar devices. The composite structures combine the refractory properties and great resistance to wear, material transfer, and similar electrical erosion phenomena of molybdenum, tungsten, or tungsten carbide with the low contact resistance and high thermal and electrical conductivities of silver or copper. The second class of material contains a predominant amount of silver, and a refractory material, such as graphite, nickel, or certain metal oxides. Composite structures of this nature are generally used for lighter duty or specialized applications.

The principal prerequisites of contact materials are: (*1*) high density, approaching theoretical; (*2*) good physical properties; (*3*) high thermal and electrical conductivity; (*4*) low contact resistance; (*5*) resistance to welding, shock, wear, material transfer, electric erosion, and atmospheric corrosion; and (*6*) ability to be brazed or soldered to other materials. The demand for combining all of these properties in the electrical contact material requires a rigid control of raw materials and fabricating processes. Two fundamentally different methods of manufacture are in general use: the pressing of powder mixtures into desired shapes followed by sintering, forging, or hot pressing; and the infiltration of loosely heaped or compacted refractory metal powders with the low-melting liquid conducting metal. Accurate shapes are generally produced by machining, but may also, under certain favorable circumstances, be molded directly.

The contact material used to facilitate the transfer of electrical current from fast moving elements to stationary parts of electrical machinery is a composite of graphite and copper or bronzes. Current-collecting brushes and current-carrying bushings or rollers containing the metal component are more wear resistant and have a greater current-carrying capacity than all-carbon materials. Graphite combinations with silver have found specialized applications.

Sintered commutator segments, squirrel-cage rotors, rings, and elements in electronic apparatus, all from pure copper, mark attempts to widen the field of application of powder metallurgy products to other branches of electrical engineering.

Besides the refractory metal heating elements, combinations of metals and nonmetals in form of sintered composite bodies have recently been developed and studied for the purpose of electrical resistors; certain oxide–metal combinations were found to possess unique electrical properties that could be influenced by selection of composition and particle size distribution.

Sintered porous electrodes of iron, nickel, aluminum, silver, tantalum, or of certain ferrous alloys have been suggested for use in condensers, batteries, secondary elements, or special contacts, but, with the exception of porous nickel plates in nickel–cadmium batteries, little is known so far about the extent of their actual use or performance.

CHAPTER XXIV

Magnetic Materials and Products

PHYSICAL CHARACTERISTICS OF MAGNETIC MATERIALS

Although the bulk of magnetic materials is produced by conventional fusion methods and is used either in the cast state or as forged or rolled products, in certain, quite important, cases the powder metallurgy technique yields highly desirable products. During the last two decades, working procedures have been perfected to such a degree that in spite of the need for delicate controls of raw materials and treatments, the powder metal approach has now become a highly competitive production method for a variety of products falling in the groups of both magnetically soft and permanent magnet materials.

As an introduction, it appears advisable to discuss briefly the fundamental physical characteristics of magnetic materials; but the reader is urged to consult the pertinent literature for a more detailed study.[1–10]

Fundamentals

MAGNETIC MATERIALS

According to their behavior in the presence of a magnetic field, magnetic materials may be classified into permanent magnetic and soft magnetic materials.

Permanently Magnetic Materials. Into this class belong those materials that require a strong field for complete magnetization, but retain their magnetization to a large extent afterward. These materials are generally termed "permanent" magnets. Included in this group are high carbon steels, chromium steels, tungsten–cobalt steels, aluminum–

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[1] R. M. Bozorth, *Elec. Eng.*, *54*, 1251 (1935).

[2] W. C. Ellis and E. E. Schumacher, *Metals & Alloys*, *5*, 269 (1934); *6*, 26 (1935).

[3] A. Kussmann, *Z. Ver. deut. Ing.*, *83*, No. 16, 445 (1939).

[4] R. L. Sanford, U. S. Dept. Commerce, Circ. Bur. Standards, No. C448, Aug. 10, 1944.

[5] A.S.T.M. Committee A-6, Report on Magnetic Properties, 1944.

[6] C. E. Webb, *J. Inst. Elec. Engrs. London*, *82*, 303 (1938).

[7] J. H. Goss, *Product Eng.*, *17*, No. 1, 47 (1946).

[8] K. Hoselitz, *J. Sci. Instruments*, *23*, 65 (1946).

[9] H. E. Fiske, *Materials and Methods*, *25*, No. 6, 72 (1947).

[10] E. I. Shobert, II, *Proceedings Third Annual Spring Meeting of Metal Powder Association*, New York, May 27, 1947, p. 57.

nickel–cobalt–iron alloys, vanadium–cobalt–iron alloys, and nickel–copper alloys containing cobalt and/or iron, all in a hardened state.

Soft Magnetic Materials. Into this class belong those materials that are more easily magnetized and demagnetized. They are usually termed "soft" magnetic and include pure ingot and sheet iron, nickel, cobalt, nickel–iron alloys, and silicon–steel sheet, all in a soft-annealed condition.

MAGNETIC PROPERTIES

Hysteresis Loop. A magnetic field is produced in a coil when an electric current is passed through it. This field can be represented by a certain number of lines of force. If a ferromagnetic material (*e.g.*, iron) is then placed inside the coil, the number of lines of force is materially increased. An increase in electric current or an increase in the number of turns of the coil causes the number of lines of force (also called magnetic flux) to increase further until a saturation is reached. The number of lines per square centimeter (or square inch) is called magnetic induction B. The magnetic field causing the induction B is measured by the number of ampere turns per unit length, and is designated by the symbol H. As mentioned before, an increase in H increases B up to a certain saturation value, but if H is then decreased, B falls off at a *slower* rate than at which it was built up. Thus, it follows a somewhat different curve, so that a certain residual induction B_r exists, even when the magnetizing force has gone back to zero. A reverse magnetizing, called coercive force or coercivity, H_c, must be applied to demagnetize the material completely, *i.e.*, to bring B back to zero. As the negative magnetizing force increases, a negative induction is caused, which increases until a saturation value is again reached that is identical with the positive maximum induction value B_m. From this point, the

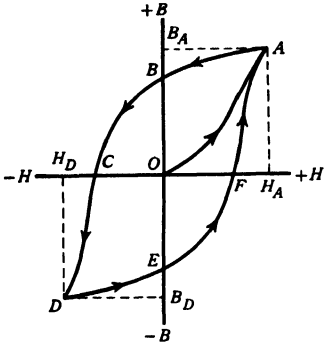

Fig. 396. Hysteresis loop.

H	Magnetizing force (oersteds)
B	Induction (gauss)
$\mu=B/H$	Magnetic permeability
$O-C=O-F=H_c$	Coercive force
$O-B=O-E=B_r$	Residual induction
$O-H_A=O-H_D$	Magnetizing force for saturation
$O-B_A=O-B_D$	Induction at saturation

cycle proceeds toward completion of a closed curve, which is called "hysteresis loop," and is shown in Figure 396. However, the initial magnetization curve is not retracted. The ratio B/H at any stage represents the magnetic permeability of the substance, designated by the symbol μ.

The saturation B_m, residual induction B_r, coercive force H_c, and permeability μ constitute the characteristic properties of ferromagnetic materials and impose typical complexions on the hysteresis loop. By alloying and heat treatment a variety of combinations of these properties can be achieved, and specific materials have been developed that boost one property to suit a special purpose, often at the expense of the others.

Soft magnetic materials are, in general, characterized by a steeply ascending magnetization curve. Large values of flux density are produced by small magnetizing forces. The slope of the magnetization curve, *i.e.*, the permeability, is therefore rather great in the case of soft magnetic materials. Since the coercive force is very low, the area within the hysteresis loop is small (Fig. 397*A*)—which is an important factor for alternating current applications, since it represents energy losses in the form of heat.

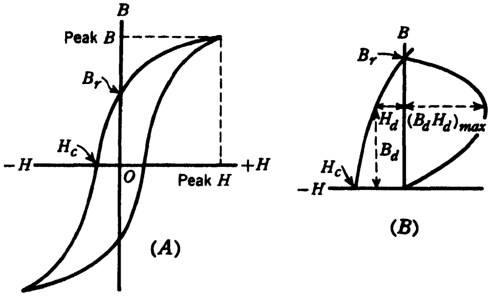

Fig. 397. Fundamental characterization of magnetic materials (permanent magnets): *A*, symmetrical hysteresis loop (B_r = residual induction; H_c = coercive force); *B*, demagnetization and external energy diagram [B_r–H_c = demagnetization curve; $(B_dH_d)_{max.}$ = external energy curve].

Hard or permanent magnetic materials are characterized by a gradually ascending magnetization curve. The permeability is low at all magnetizing forces, and to attain practical saturation requires magnetizing forces of considerable proportion. The hysteresis loop comprises a comparatively large area (Fig. 396). The important properties of permanent magnet materials are associated with the demagnetization curve (second quadrant) of the hysteresis loop. Both a large coercive force and residual induction are desirable. The maximum value of their product

TABLE 146

Composition and Magnetic Properties of Permanent Magnet Materials

Material	Composition, %	Coercive force, H_c, oersteds	Residual induction, B_r, gauss	External energy, $(BH)_{max}$ × 10^{-6}
Carbon–manganese steel	0.60 C 0.80 Mn 0.20 Si	40	9,000	—
Low-chrome steel	0.90 Cr 0.60 C	50	9,500	—
Carbon steel	1.20 C	60	8,000	0.18
Chrome steel	2.00 Cr 1.00 C	60	9,500	0.24
	6.00 Cr 1.00 C	70	9,500	0.28
Tungsten steel	6.00 W 0.60 C	60	11,000	0.28
	6.00 W 0.9 C	80	10,000	0.34
High-chrome steel	3.50 Cr 0.90 C	68	9,500	0.29
Cobalt–chrome steel	9.00 Co 9.00 Cr	150	8,500	0.55
	15.0 Co 10.0 Cr	200	9,000	0.7
Cobalt steel	35.0 Co 7.0 W 4.0 Cr 0.75 C	260	9,500	1.05
Iron–cobalt–tungsten alloys	—	150	11,500	0.8
Iron–cobalt–molybdenum alloys	—	300	10,000	1.25
Iron–nickel–aluminum alloy, cast	—	550	6,000	1.3
Sintered	—	550	3,500	0.6
Alnico V, cast	—	550	12,500	4.5
Sintered	—	575	10,000	3.5
Iron–nickel–aluminum–cobalt alloy cast	—	600	7,300	1.6
Copper–nickel–iron alloy, cast	60.0 Cu 20.0 Fe 20.0 Ni	550	5,400	1.5
Sintered	—	525	7,000	1.45
Copper–nickel–cobalt alloy, cast	50.0 Cu 29.0 Co 21.0 Ni	710	3,400	0.8
Sintered	—	810	2,500	0.7
Oxide magnets	—	600	4,000	1.3
Iron–nickel–cobalt–titanium alloys	—	900	6,000	2.1
Iron–platinum alloy	78.0 Pt	1800	4,000	2.0
Cobalt–platinum alloy	77.0 Pt	4000	3,000	2.5
Iron–neodymium alloy	—	4300	800	0.15
Silver–manganese–aluminum alloy	87.0 Ag 9.0 Mn 4.0 Al	5500	500	0.06

may be considered to be an index of the quality of the permanent magnet. This property is usually expressed in a combined diagram (A) hysteresis loop and (B) demagnetization and external energy curves as indicated in Figure 397. Tables 146 and 147 give coercive force and residual induction for a number of typical permanent magnet materials.

Effect of Air Gap. The hysteresis loop can only be measured in a closed magnetic circuit. Therefore, it can alone serve as a pure material property index in a ring sample. If an air gap is introduced, as is predominantly required for industrial designs of electrical appliances, the magnetic performance is no longer determined solely by the magnetic characteristics associated with the hysteresis loop, but also to a considerable extent by design factors, and in particular by the relation between the size of the air gap and the length of the magnetic material involved. The introduction of this air gap has a flattening (shearing) effect on the hysteresis curves, as shown in Figure 398. As a result, the permeability is reduced, but is also stabilized over a wider range of flux densities.

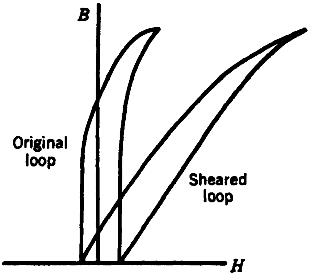

Fig. 398. Flattening ("shearing") effect of an air gap on the hysteresis loop of a soft magnetic material.

APPLICATIONS

The typical magnetic characteristics of each class of magnetic material suggest very definite fields of application. High coercive forces are required to obtain sufficiently large residual flux densities in permanent magnet materials having comparatively large air gaps. Since the hard permanent magnet materials are difficult to machine, accurate dimensions of the gap are only possible by grinding, unless combinations with soft iron are used, as, for example, in pole piece assemblies for direct current applications (see page 242).

Soft magnetic materials in alternating current applications are particularly concerned with the magnetic characteristics associated with the hysteresis curves: a small area of the loop is desirable for the sake of low hysteresis losses. The hysteresis loss, which for one cycle is represented by the area of the loop, is proportional to the frequency according to the formula:

$$L_H = a\, fB_m{}^{1.6}$$

where L_H represents the hysteresis loss, f the frequency, B_m the maximum value for flux density, and a a proportionality factor. However, losses caused by eddy current must be reduced; these losses, caused in a magnetic core or a magnetic part by the flow of induced currents, are proportional to the square of the frequency and the maximum flux density, and are therefore more potent in high frequency applications than are the hysteresis losses. Eddy current losses in sheet materials can be expressed according to the formula:

$$L_{EC} = a\ (b/\rho)\ f^2B^2{}_m$$

where L_{EC} represents the eddy-current losses, b the thickness of the sheet, ρ the resistivity of the metal, f the frequency, B_m the maximum induction, and a a proportionality factor. Accordingly, the eddy-current losses are reduced by a high resistivity of the material. They are diminished appreciably if the magnetic substances are used in subdivided form: for low frequency applications, alloy steels in the form of stacked sheets insulated from each other are generally employed, while for higher frequencies iron or iron–nickel alloys in the form of finely divided and possibly insulated powder particles are used.

Properties of Metal Powder Magnets

SINTERED PRODUCTS

Sintered products distinguish themselves from their fused counterparts in two respects: the structure is obscured by the presence of porosity and the grain size is of considerably smaller order. Both characteristics have a profound influence on the physical behavior of the sintered alloys and are especially significant for magnetic materials. The finer grain size of the sintered metal is important in the case of permanent magnets of the "Alnico" type, where great difficulties are encountered in the machining of cast, coarse-grained products.

Inherent Porosity. As previously shown (see Volume I, Chapters XIV and XVIII), the porosity in sintered metals varies in character with a number of factors that are inherent in the raw materials, with the molding conditions, and with the conditions during sintering. Therefore, the effects of porosity on the various powder metallurgy products must always be considered in conjunction with the size, shape, and distribution of the pores. In magnetic materials, the internal pores not only reduce the effective cross section of the metal, thereby increasing the tendency of the material to become saturated, but they also are connected with an internal demagnetization, which is the reason that the hysteresis loops observed on porous ferromagnetic materials generally appear as sheared curves (see also Fig. 398); thus the internal pores have a similar effect as an air gap by forcing the magnetic flux to travel through them. Hence, the pore effects must be added to those of the structural air gap.

In this connection reference is made to the recent theoretical work by Néel[10a] in France, who investigated the influence of porosity in ferromagnetic substances upon the coercive force and the approach to saturation. Tests were conducted on sintered iron with porosities of 0.05 to 0.4%, *i.e.*, of a much smaller order than encountered in commercial sintered iron products, and the effect of ultrafine pore sizes (in the region of 0.05 μ), as well as that of an anisotropic distribution of the pores, was studied and compared with the effect of pores and inclusions in cast metal.

Effect of Porosity on Permanent Magnets. In the case of permanent magnets the porosity effects are not very serious, since the air gaps incorporated in the design are relatively large, and the added pore effects are comparatively insignificant. The magnetic properties of sintered permanent magnets compare well with those of fused magnets even if the structure is not completely dense.

Effect of Porosity on Soft Magnets. The effect of internal porosity is most significant, however, where soft magnetic products are involved. For direct current applications the magnetic performance becomes markedly dependent on the density, and sintered pole pieces generally require a density of at least 85–90% of theoretical. When the soft magnetic parts are combined with permanent magnets in designs having comparatively large air gaps the effects of the internal pore volume are overcome sufficiently to permit the use of slightly more porous materials in electric motors and generators.

The problem relating to alternating current applications is infinitely more difficult. The magnetic circuits are often entirely closed, and internal porosity has the effect of cumulative air gaps decidedly affecting the magnetic characteristics of the material. Further complications result from the fact that the continuous metal structure promotes eddy-current losses. Thus, a reduction in pore volume would be helpful in overcoming the gap effects, but would simultaneously be harmful from the standpoint of eddy-current losses. In view of the contrary nature of these complications, and particularly in view of the great difficulties encountered in producing a truly dense sinter product, it is not surprising that no sintered magnetic material has yet been developed that is universally acceptable

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[10a] L. Néel, *Proc. International Powder Metallurgy Conference,* Graz, July 12–17, 1948, Referate No. 16.

for low frequency alternating current applications. In fact, in most cases, powder metallurgy products are completely unacceptable from this point of view.

Combined Magnet Systems. New possibilities in designing magnetic systems for very small meters and motors stem from the successful production of combined permanent magnet and soft magnetic pole pieces in one pressing operation. In spite of certain difficulties in applying a sintering and heat-treating cycle that satisfies both materials, Howe[11] was able to produce a strong and shock-resistant composite assembly during sintering whose joints were not disrupted by the subsequent heat treatment needed to attain optimum magnetic properties.

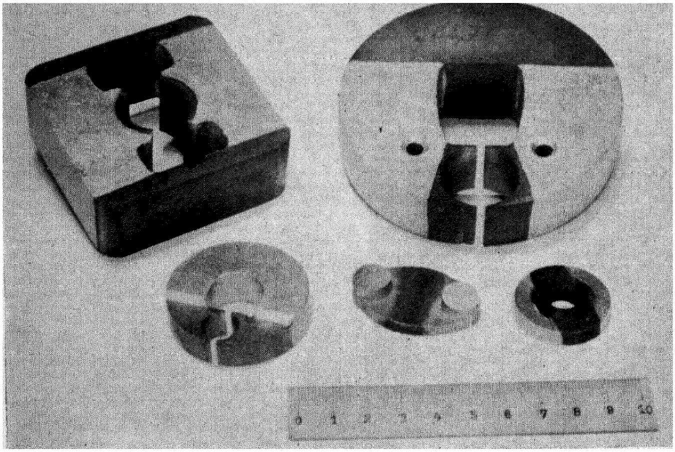

Fig. 399. Sintered permanent magnets and composite magnet systems (according to Kieffer, Benesovsky, and Bartels[13]). (Scale in centimeters.)

During the war, composite soft and permanent magnetic elements were developed in Austria, where they are now produced in quantity.[12,13] The magnets are generally of circular shape (Fig. 399) with one portion of the circle consisting of Alnico and the other of soft iron (with 3% aluminum added to prevent scaling during heat treatment). The soft

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[11] G. H. Howe, *Iron Age, 145,* No. 1, 27 (1940).

[12] G. M. Butler, U. S. Dept. Commerce, Office Publ. Board, P.B. 1834; Combined Intelligence Objectives Sub-committee (*C.I.O.S.*) (London) 21 XXX-8, 1946, p. 14; see also *Powder Met. Bull., 1,* No. 3, 51 (1946).

[13] R. Kieffer, F. Benesovsky, and H. J. Bartels, *Powder Met. Bull., 2,* 54 (May 1947).

portion may be machined (*e.g.*, accurately slotted and drilled) to pole piece shape after sintering. According to Leadbeater,[13a] the composite magnets can be made by placing the different powders in paper compartments inside carbide-lined dies.

MOLDED PRODUCTS

For alternating current applications involving high frequencies (*e.g.*, cores for communication systems), solid ferromagnetic metals are entirely unsuitable. Not only are the eddy-current losses prohibitively high, but permeability varies beyond an acceptable range. Thus, the requirements are of such a nature that only a very finely divided structure may be used; the individually separated particles suppress the eddy current, while the interstices function as air gaps and result in a low and stabilized permeability. This type of magnetic material provides a natural application for metal powders. Extremely fine powders of ferromagnetic metals or alloys (*e.g.*, carbonyl iron and Permalloy) can be used as compacted cores without any need for sintering. Nonmagnetic substances (*e.g.*, plastics) may be used advantageously as insulating envelopes around the particles and may serve as binders at the same time. The air gaps in loosely compacted cores cause a pronounced flattening of the hysteresis loop, resulting in permeability values as low as a fraction of one per cent of those for solid metal cores.

Another interesting application for metal powders in the magnetic field involves permanent magnet powders molded with plastic materials as binders; resins and other plastics are mixed with the powdered permanent magnet alloy in suitable proportion, and are warm-pressed at low temperatures and pressures. The high hardness and brittleness of permanent magnet materials of the Alnico type impose great difficulties in machining the parts to close tolerances. Although the insulating materials reduce the effective flux density, they have the great advantage of facilitating direct molding into the desired shape, thus contributing to greater economy.

EFFECT OF POWDER METALLURGY VARIABLES

As opposed to the disadvantage of the inherent porosity in sintered metals, the powder metallurgy process offers a good many variables that are worth while considering when comparing its products with those obtained by fusion and machining. The nature of the porosity can be changed in a number of ways (see also Volume I, Chapter XIV). Both

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[13a] C. J. Leadbeater, *Symposium on Powder Metallurgy,* The Iron and Steel Institute, Special Report No. 38, London, 1947, p. 191.

particle shape and size distribution have their effects. The rate of heating, the evolution of gases or vapors from possible addition agents, the sintering atmosphere, and the time allowed for diffusion at the maximum sintering temperature all influence the shape, size, and distribution of the pores. For example, fine powders with equiaxed particles tend to give mostly equiaxed small interstices that are uniformly distributed throughout the cross section. Coarse powders, particularly if containing a majority of irregularly shaped particles, tend to produce nonuniform pores. High pressures tend to depress the porosity, but gas evolution during sintering tends to counteract this effect. High sintering temperatures applied for prolonged periods enable plasticity and surface tension forces to round off angular cavities and deep crevices, thus producing spherelike pores. Sintering in vacuum tends to produce sausagelike or near-spherical cavities. Finally, condensation after sintering by coining also has a reducing effect on pore size and quantity.

One of the most recent and significant developments in the permanent magnetic field stems from the fact that pressing[14] (*i.e.*, of magnet–resin compositions), as well as heat treating and cooling in a magnetic field,[15,16] produces a magnetically oriented structure, and has a considerable influence on the magnetic properties. Sintered material produced by employing the latter procedure has passed the stage of mere academic interest, and is now produced commercially in the form of intricate shapes having higher external energy than is possible with other sintered materials.[16a]

Another interesting development that had its origin shortly before the war in Germany is the application of powder mixing procedures for the purpose of obtaining materials displaying specific relations between the magnetization and temperature.[16b] By mixing magnetic alloy powders having Curie points covering the desired range of temperature, it is claimed that practically any temperature–magnetization relationship can be obtained reproducibly. Thus, an approximately rectilinear curve of the magnetization as a function of temperature between 100 and −20°C. (212 and −4°F.) was established with a material compacted from a 6:4:3 mixture of three iron–nickel alloys, and then sintered at 900–1200°C. (1650–2190°F.) for 30–60 minutes (the alloys contained 29.5, 28.5, and 27.5% Ni, respectively, and 0.2% C, 0.2% Si, and 0.5% Mn, in each case). No change of these magnetic characteristics was found when the alloy powders were bonded with 5–10% by weight of synthetic resins.

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[14] U. S. Pat. 2,188,091.

[15] W. Jellinghaus, *Tech. Mitt. Krupp—Forschungsber.*, *A10*, No. 2, 143 (1940).

[16] G. B. Jonas and H. J. Meerkamp van Embden, *Philips Tech. Rev.*, *6*, 8 (1941).

[16a] "Sintered Alnico V," product of General Electric Co., Catalog CDM-15A.

[16b] German Pats. 743,249 and 748,069; see also *Met. Powd. Rept.*, *2*, No. 6, 90 (1948).

In the present efforts to develop a sintered magnetic material suitable for low frequency alternating current applications, the approach of powder metallurgy offers various interesting possibilities. They include the fine subdivision of the structure by means of foreign inclusions or films around the particles; preferred orientation of the grain structure by employing special flake powders (*e.g.*, obtained by hot working) with nonmetallic separators (*e.g.*, mica, graphite); production of a special alloy structure by partial or complete diffusion of the ferromagnetic base metal with other elements (*e.g.*, Fe with Ni, Cr, Si, C).

It is also of some interest to consider the close alliance of the ferromagnetic properties with alloying. For example, the highly sensitive methods for measuring magnetic properties such as permeability or Curie-point[16c] can be used to advantage in studying the progress of diffusion in powder metallurgy alloys. In this connection the recent work by Rostoker[16d] deserves special mention (see also page 284); this investigator could show that the development of time–temperature–property (magnetic) relationships give an accurate picture of the degree of diffusion-alloying in iron–silicon, iron–nickel, and iron–cobalt compositions. When following the homogenization process by this approach, and also by x-ray studies, it was found that the x-ray technique is not too sensitive to small degrees of inhomogeneity, as compared with permeability and coercive forces—which, on the contrary, are very sensitive.

SPECIAL PROPERTIES OF ULTRAFINE FERROMAGNETIC POWDERS

It was discovered that quite unique permanent magnetic properties can be obtained from pure iron powders if the particles are of colloidal size, (*i.e.*, between about $^1/_{10}$ and $^1/_5$ μ, or even smaller) and if, during the process of manufacture, temperatures and pressures are selected so that agglomeration of the particles and grain growth are avoided. Thus, the surprising fact was established that permanent magnetic material—with properties comparable with the best permanent magnets obtainable by standard alloying practices—could be produced from pure iron, which in the cast and rolled state is generally the ideal material for the *opposite* purpose, namely, for soft magnetic applications.

Theories connected with this extraordinary phenomenon have been advanced by Weil,[17,17a] and Néel[10a,17b] in France, by Kittel[17c] in the United

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[16c] P. W. Selwood and J. Nash, *Trans. Am. Soc. Metals, 35,* 609 (1945).

[16d] W. Rostoker, *Trans. Am. Inst. Mining Met. Engrs., 180,* 672 (1949).

[17] L. Weil, *Proc. International Powder Metallurgy Conference,* Graz, July 12–17, 1948, Referate No. 17.

[17a] L. Weil, *Compt. rend., 225,* 229 (1947).

[17b] L. Néel, *Compt. rend., 224,* 1488, 1550 (1947).

[17c] C. Kittel, *Phys. Rev., 73,* 810 (1948).

States, and by Koenigsberger[17d] and by Stoner and Wohlfarth[17e] in Great Britain, who followed to some extent the fundamental thoughts of Kersten.[17f] Consequently, the effect has been fairly well explained, and it has been shown that below a critical particle size the shape becomes of equal importance for the stabilization of the permanent magnetic properties.

According to the theoretical concepts by Néel,[10a,17b] magnetization in a particle that represents a complete domain is directed parallel to the longest axis of the particle, and also along the path of easiest magnetization, such as along the edge of the particle in the case of iron. The coercive force is dependent on the crystal energy in the case of strictly spherical particles, but in nongeometrical particles (*e.g.*, Permalloy), where the crystal energy is dependent on direction, the coercive force is caused only by the average geometrical anisotropy. In practice, there is an overlapping of the two effects. Theoretical values for iron were found to be 600 oersteds for the spherical powders and 1400 for the others, but they are, of course, not additive; experimental values were 1000 oersteds for iron, 1200 for a 73–27 iron–cobalt alloy, 500 for cobalt, and 200 for nickel. The experimental values for loose powders are always lower than the theoretical ones due to agglomeration of the particles; if, however, the powders are pressed into compacts of *isotropic* porosity, the coercive force rises proportionally with the density in the case of iron and nickel. The effect of anisotropic porosity appears to be particularly significant with nickel, while with cobalt the coercive force appears independent of compacting pressure due to interfering conglomeration. Weil and collaborators[17g,17h] used these theoretical concepts for calculating the coercive forces and the effects of temperature on this property.

Information on details of producing permanent magnets from these ultrafine ferromagnetic powders, and on the range of magnetic properties obtainable, is given in a number of British patents.[17i] Ultrafine powders can be produced by low-temperature reduction or decomposition, respectively, of oxides, oxalates, formates, carbonates, etc., or by thermal decomposition of dilute carbonyls. In this way, aggregates of 1–10 μ are produced, which can be further comminuted to particles of 100–300 Å. (as shown by line broadening during x-ray examination). Powders of this kind yield compacts of remarkably high densities, with 95% of the

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[17d] J. G. Koenigsberger, *Phil. Mag.*, *38*, 640 (1947).

[17e] E. C. Stoner and E. P. Wohlfarth, *Trans. Roy. Soc. London*, *A240*, 599 (1948).

[17f] M. Kersten, *Grundlagen einer Theorie der Ferromagnetischen Hysterese und der Koerzitivkraft.* Hirzel, Leipzig, 1943.

[17g] L. Weil and S. Marfoure, *J. Phys. Radium*, *8*, No. 8, 358 (1947).

[17h] L. Weil, S. Marfoure, and P. Bertaut, *J. Phys. Radium*, *9*, No. 8, 203 (1948).

[17i] Brit. Pats. 590,392; 594,681; 596,875.

theoretical value attained by iron compacted at 12 tsi and sintered for one hour at 1000°C. (1830°F.), and values even closer to the theoretical mark being obtained with cobalt and nickel processed in the same manner. Furthermore, these ultrafine powders can be alloyed readily.

A short review of the underlying principles and production methods connected with these pure iron powder magnets has recently been given by Steinitz[17j]; additional production details are also described later on in this Chapter (page 267).

PERMANENT MAGNETS

Aluminum–Nickel–Iron Alloys

With powder metallurgy methods, the production of permanent magnets has been broadened considerably to include small size applications as well as designs requiring close dimensions. Many types of permanent magnet materials were developed during the last three decades. To these belong the chromium and tungsten steels, the Honda-type cobalt steels first produced in 1916, and the alloys containing aluminum, nickel, cobalt, iron, titanium, and copper of the Mishima type[18] produced from 1930 on. Alloys containing 5–14% Al, 12–33% Ni, 0–30% Co, balance iron, are generally referred to as "Alnico" magnets. During the last five years the magnetic properties of the Alnico-type material have been still further improved by producing a magnetically oriented structure through heat treatment in the magnetic field; the material type Alnico V reaches a residual induction of 12,500 gausses and a coercive force of 550 oersteds The application of the magnetic field during cooling is performed at temperatures between 750°C. (1380°F.) and the Curie point, and the effect is further increased by raising the Curie point through the addition of cobalt to the Al–Ni–Fe alloys. In Figure 400 a graphic comparison is given of the magnetic properties of five grades of Alnico, according to Smith[19] (see also Table 147); in Figure 401 the magnetic properties of several Alnico and Honda-type permanent magnet materials are shown through demagnetization and energy-product curves.[20] In general, it may be stated that the advantages of Alnico over other less powerful permanent magnet materials lie mainly in a shorter and more compact magnet, because the higher coercive force permits a reduced length, the lower residual induction permits a greater cross-sectional area, and the high external energy product permits a smaller volume. Figure 402 gives a schematic dimensional comparison of equivalent permanent magnets, all

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[17j] R. Steinitz, *Powder Met. Bull.*, *3*, No. 6, 124 (1948).

[18] Anonymous, *Iron Age*, *130*, No. 9, 346 (1932).

[19] B. M. Smith, *Gen. Elec. Rev.*, *45*, 210 (1942).

[20] R. L. Sanford, U. S. Dept. Commerce, Circ. Bur. Standards No. C448, Aug. 10, 1944.

TABLE 147. Permanent Magnet Characteristics of Alnico Alloys

Material	Chemical composition, nominal, %					H_m, oersteds	B_m, gauss	Residual induction, B_r, gauss	Coercive force, H_c, oersteds	External energy, $(B_dH_d)_{max}$	Approx. relative cost per lb.
	Al	Ni	Co	Cu	Fe						
Cast Alnico I	12	20	5	—	Bal.	2000	12,350	7,300	440	1,400,000	1.00
Cast Alnico II	10	17	12.5	6	Bal.	2000	12,600	7,350	560	1,600,000	1.20
Sintered Alnico II	10	17	12.5	6	Bal.	2000	12,300	6,900	520	1,430,000	3.50
Cast Alnico III[a]	12	25	—	—	Bal.	2000	12,000	6,900	475	1,380,000	0.80
Cast Alnico IV	12	28	5	—	Bal.	3000	11,850	5,300	730	1,300,000	1.10
Cast Alnico V	8	14	24	3	Bal.	3000	17,200	12,500	550	4,500,000	4.00
Sintered Alinco V	8	14	25	3	Bal.[b]	—	—	10,000[c]	575	3,500,000[c]	—

[a] For sections up to ⅝ in. by ⅝ in. For larger sections the magnetic characteristics are the same as for Alnico I.
[b] Except for 1% Ti. [c] Minimum values.

TABLE 148

Magnetic Properties of Sintered Magnets in Comparison to Cast Magnets of Same Composition (Kieffer and Hotop[22])

Alloy	Method of production		Residual induction, B_r, gauss	Coercive force, H_c, oersteds	External energy value, $(BH)_{max} \times 10^{-6}$, gauss × oersteds	$(BH)_{max}$ / $(B_r \times H_c)$	Density, g./cc.
28% Ni 14% Al	Sintered	Maximum values[a]	6500	560	1.3	0.39	6.8
		Average values	6000–5500	480–530	1.1–0.95	0.36–0.33	6.6
	Cast	Maximum values[a]	7000	560	1.35	0.40	7.0
		Average values	6300–5800	480–530	1.20–1.05	0.37–0.34	6.9
22% Ni 12% Al	Sintered	Maximum values[a]	7800	360	1.25	0.48	6.8
		Average values	7700–7300	280–330	1.1–0.85	0.44–0.42	6.7
	Cast	Maximum values[a]	7900	350	1.25	0.46	7.05
		Average values	7800–7400	180–250	1.0–0.75	0.44–0.42	6.95

[a] The individual values indicated do not necessarily occur simultaneously.

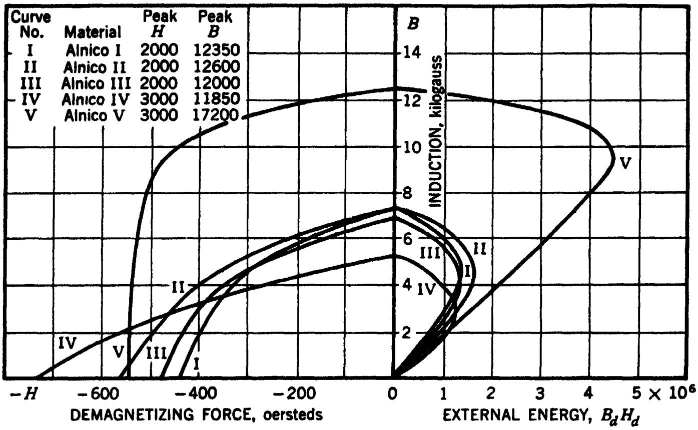

Fig. 400. Comparison of the magnetic properties of the five grades of Alnico permanent magnets (according to Smith[19]).

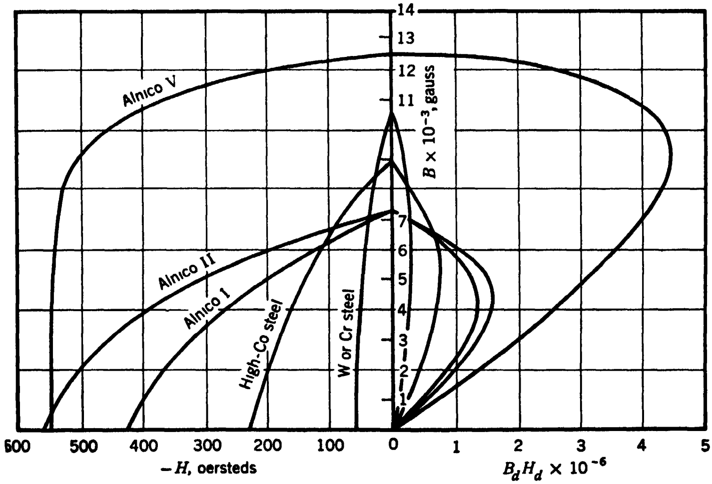

Fig. 401. Demagnetization and energy-product curves for typical permanent magnet materials (according to Sanford[20]).

having the same magnetic strength.[21] Besides offering the advantage of the design of smaller precision apparatus, Alnico magnets also excel in their greater stability, in their greater resistance to vibrations, elevated temperatures, and stray magnetic fields, and in their higher stored energy for a given volume.

[21] General Electric Co., Catalogs GEA 3682B, CDM-1, and CDM-2.

The production of the Al–Ni–Fe and, particularly, Al–Ni–Co–Fe alloys by conventional fusion methods results in certain distinct disadvantages. These include oxidation of the melt, reaction of the fused metal with the crucible material, introduction of casting defects, boundary segregation, and, particularly, a coarse grain structure. The resulting metal often has a nonuniform flux density and is always mechanically weak and brittle. It cannot be machined, except by grinding, and the part must by necessity have a comparatively simple shape; this in turn requires the use of pole pieces in the assembly. Thus, part of the power of the Alnico magnet is frequently lost because of its particular design requirements.

The powder products have none of these disadvantages, while their magnetic properties closely approach those of their fused counterparts. Comparative data on the properties of sintered and cast permanent magnets of two typical compositions are given in Table 148; further data can be found in Chapter XXXI. From an economic point of view, the sintering method compares favorably with the fusion method for magnets weighing up to about 1.5 ounces; this is why the method is widely employed for the manufacture of small, permanent magnets of intricate design in a large variety of shapes.

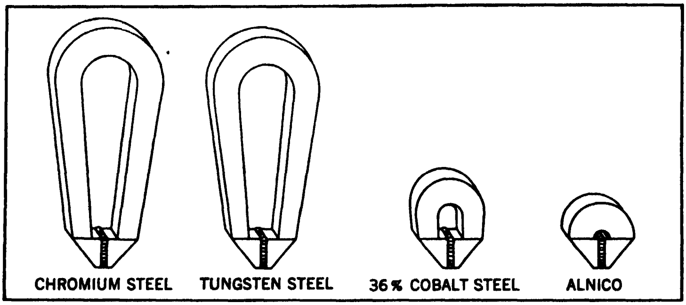

Fig. 402. Comparison of equivalent permanent magnets of different composition and of the same magnetic strength (courtesy of General Electric Co.).

The principal advantages of sintered materials falling in this weight group are as follows.

(*1*) Direct molding makes possible more intricate shapes and greater design efficiency and flexibility; many parts can thus be produced directly to close tolerances without grinding.

(*2*) Better technological properties are possible, especially cohesive strength, shock resistance, and machinability, on account of a fine-grain structure without cracks or blow holes; the tensile and transverse rupture strengths may be three to ten times as high as those of the cast material of the same composition.

(*3*) More uniform magnetic flux distribution is obtained because of the fine-grained, more homogeneous structure.

(*4*) Less raw material is used per part on account of savings in scrap, grinding, etc.

PRODUCTION METHODS

Permanent magnets of the Alnico type can be produced from metal powders by several methods: (*a*) Pulverization of the fused, brittle alloy or its shot; forming by pressing with a binder and sintering, or hot-pressing; or molding with plastics. (*b*) Mixing of the virgin metal powders; cold pressing followed by sintering. (*c*) Mixing of metal powders with prealloyed components obtained by pulverization of fused master alloys; cold pressing and sintering. However, only the last-mentioned method has been developed to an industrial level.

Magnets from Pulverized or Shotted Fused Alloy. The extreme brittleness of cast Alnico facilitates mechanical comminution to a fine-grained product. Small castings, as well as shot available as a by-product of the casting process, can be crushed in hammer mills or between rolls; ball milling or pulverizing in jaw crushers produces fairly fine grades. Such powder, however, is very hard and brittle and can only be briquetted with the aid of binders (such as used with refractory metals or carbides) and at very high molding pressures. The possibility of obtaining molded permanent magnets containing a major proportion of a plastic binder has already been mentioned. These molded products can be produced to accurate shapes, but distinguish themselves from the sintered magnets by the fact that the individual particles are only bonded together by the plastic, and that sintering of the Alnico phase into a coherent structure is not possible. Of course, the magnetic properties of these products are very much inferior to the cast material.

The plasticity of the Alnico particles is considerably improved at elevated temperatures, suggesting the hot-press approach. If the alloy powder is heated to about 1100–1200°C. (2000–2200°F.) and then pressed at 60 to 90 tsi, a good structure and magnetic properties of about 70–80% of energy values of the original cast alloy are obtainable,[22] but the severe service conditions caused by the high temperature and pressure require special precautions against oxidation and die wear, and render the method impractical.

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[22] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe.* Springer, Berlin, 1943, p. 354.

Magnets from Virgin Powder Mixtures. In applying to permanent magnets the conventional method of producing sintered alloys—by compacting *mixtures* of the constituents in their elemental form—the compacting difficulties encountered in the brittle alloy powders are overcome, since all four individual metal powders (iron, nickel, cobalt, and aluminum) are relatively soft and susceptible to plastic deformation. As is often the case, however, when comparing (as raw material) alloy powders with mixtures of the elemental powders, increased compactibility goes hand in hand with impaired diffusion; conversely, improved homogeneity of the alloy, particularly for short sintering cycles, can only be obtained by prealloying the particles and rendering them less susceptible to compaction. The main obstacle to an adequate alloying during sintering of Al–Ni–Fe and Al–Ni–Co–Fe alloys can be found in the strong oxidizing tendencies of the aluminum. During the production of the aluminum powder, tenacious oxide films are formed which are not reducible during sintering in hydrogen atmosphere. As a matter of fact, the oxide films are bound to increase in thickness with rising temperatures during sintering unless the hydrogen is extremely well desiccated. Apparently, the situation is not improved when the sintering temperature rises above the melting point of the aluminum: the liquid phase tends to promote segregation and distortion, and diffusion is hampered due to an isolating effect of the oxide films surrounding the aluminum droplets.

The technique of prealloying by diffusion sintering of the mixture of loose powders in pure hydrogen at moderate temperatures, so successfully employed in the manufacture of cemented carbides and certain copper alloys, does not give the same satisfactory results in the case of the aluminum-bearing permanent magnet alloys. The initial oxidation of the aluminum powder particles is sufficient to inhibit complete diffusion during prealloying in the solid state. Even if the presintering temperature is raised above the melting temperature of the aluminum, *e.g.*, to 700–900°C. (1300–1650°F.), the liquid aluminum shows only a limited tendency to diffuse into the other constituents due to the formation of the solid oxide films; where exposed, the liquid aluminum tends to cement the solid particles of the other metals into a coherent porous mass that requires mechanical pulverization before compaction into the desired magnet shape. The sintered products fall short in magnetic properties when compared with the cast alloys, especially if the aluminum powder used initially is of fine grade. This fact indicates that oxide films surrounding the particles are directly responsible for the unsatisfactory alloying conditions, since the oxide formation is, of course, more pronounced for the fine aluminum powder having a considerably larger effective surface area. In Table 149 the properties of 60–27–13 Fe–Ni–Al magnets prepared by prealloying coarse as well as fine aluminum powder at 700–900°C. (1300–1650°F.) and sintering at 1300°C. (2370°F.) are compared with those of cast material of the same composition, according to Hotop.[23]

Magnets from Partly Fusion-Alloyed Powder Mixtures. The production method that was finally developed on an industrial scale constitutes a compromise of the two previously described procedures. The adverse effect of the aluminum oxide barriers is greatly reduced by prealloying the aluminum by fusion with nickel,[24] cobalt,[25,25a] or, especially, iron.[26,27] Brittle master alloys containing approximately 50% Al form only a minor constituent in the mix, the bulk of the ingredients consisting of the plastic iron, nickel, and cobalt particles. Thus, the advantages of the prealloying effects are combined with those of the satisfactory compactibility of elemental powder mixtures. In fact, the latter are sufficiently plastic to permit, in certain cases, the inclusion of a minor proportion (up to 40%) of the pulverized cast alloy or shot of final composition; this, in turn, advances homogenization and improves the magnetic properties of the final product. The master alloy (about 50–50 Al–Fe) is sufficiently brittle to be easily disintegrated by milling, and the

TABLE 149

Magnetic Properties of a 60% Fe, 27% Ni, and 13% Al Alloy Produced by Different Methods (Kieffer and Hotop[22])

Method of production	Residual magnetism, B_r, gauss	Coercive force, H_c, oersteds	Energy value, $(BH)_{max} \times 10^{-6}$, gauss × oersteds	$(BH)_{max}/(B_rH_c) \times 100$, %
Sintered alloy, made from coarse aluminum powder; mixture of elemental powders prealloyed at 700–900°C. (1300–1650°F.)	4600	440	0.575	28
Sintered alloy, made from very fine aluminum powder; mixture of elemental powders prealloyed at 700–900°C. (1300–1650°F.)	2550	230	0.17	28
Cast alloy of the same composition	6500	510	1.26	38

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[23] W. Hotop, *Stahl u. Eisen, 61,* 1105 (1941).

[24] G. Ritzau, *Wiss. Veröffentl. Siemens-Werke (Werkstoff Sonderheft),* 1940, p. 37.

[25] S. J. Garvin, *Symposium on Powder Metallurgy.* The Iron and Steel Institute, Special Report No. 38, London, 1947, p. 67.

[25a] Brit. Pat. 592,506; see also *Met. Powd. Rept., 2,* No. 6, 89 (1948).

[26] G. H. Howe, in J. Wulff, *Powder Metallurgy.* Am. Soc. Metals, Cleveland, 1942, p. 530.

[27] U. S. Pat. 2,192,741. French Pat. 799,798.

oxidation of the aluminum is substantially minimized. The alloy has a melting point of about 1175°C. (2150°F.) and is liquid in the initial stage of the high temperature sintering, thereby facilitating diffusion. The liquid phase is absorbed gradually by the solid phase as the alloy approaches a homogeneous solid state of equilibrium. It is generally agreed that this transitory type of liquid phase is most helpful in securing proper sintering conditions without undue segregation or loss of shape. The claim that the prealloyed phase should melt at a temperature close to that of the final alloy, as advanced by Ritzau,[24] has not been substantiated by other investigators[23,26]; neither has Ritzau's suggestion to substitute Al–Ni alloys with nickel contents up to 70% for the conventional Al–Fe master alloys. The Al–Fe prealloy has a definite affinity to oxygen, although not quite as marked as in the case of pure aluminum. While molecular hydrogen does not reduce the Al_2O_3 films, atomic hydrogen derived from the decomposition of titanium hydride or zirconium hydride at about 450°C. (840°F.) apparently is capable of reducing these films during sintering.[28,29]

COMMERCIAL MANUFACTURE

Detailed accounts of the commercial manufacture of sintered Alnico magnets have been given by Howe,[26] Fulton,[30] Kieffer and Hotop,[31,31a] Garvin,[25] Franks,[31b] and others. The sintering techniques have been discussed by Kalischer,[28] Hotop,[23] and Ritzau.[24]

Pressing. Because of the fact that the majority of sintered permanent magnets are small, they may be pressed in automatic mechanical presses. The friction between the powder and the die wall causes loss in pressure in the center region of the compact, resulting in increased porosity; during sintering this produces more shrinkage in the center than at the ends of the compacts facing the plungers. The "hour glass" shape of the sintered product can often be corrected by a grinding operation, but it is preferable to produce magnets of greater height by stacking thinner sections after grinding the flat faces. The compacting pressures employed for Alnico magnets vary over a wide range. According to Howe, the pressure may be as low as 10 tsi. Hotop indicates pressures varying

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[28] P. R. Kalischer, *Trans. Am. Inst. Mining Met. Engrs.*, *145*, 369 (1941).

[29] P. R. Kalischer, in J. Wulff, *Powder Metallurgy*. Am. Soc. Metals, Cleveland, 1942, p. 537.

[30] C. R. Fulton, *Trans. Am. Inst. Mining Met. Engrs.*, *161*, 557 (1945).

[31] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe*. 2nd ed., Springer, Berlin, 1948, pp. 352 ff.

[31a] R. Kieffer and W. Hotop, *Sintereisen und Sinterstahl*. Springer, Vienna, 1948, pp. 479 ff.

[31b] A. E. Franks, *Iron Age*, *161*, No. 15, 82 (1948).

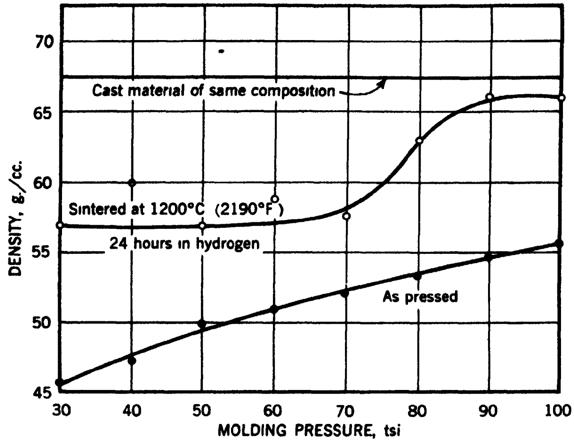

Fig. 403. Effect of the molding pressure on the density of a pressed and a sintered 65–25–10 iron–nickel–aluminum bar (according to Kalischer[28]).

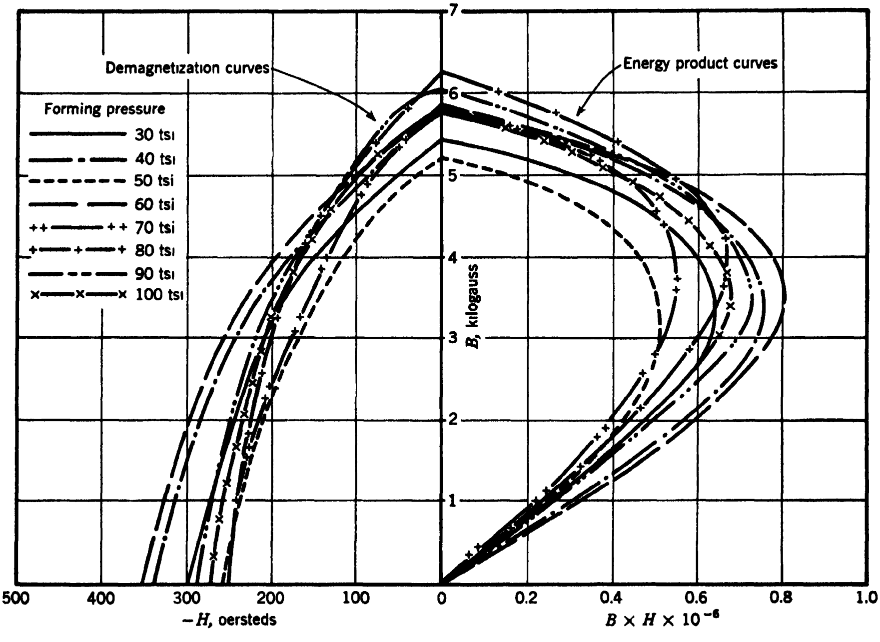

Fig. 404. Relationship between forming pressure and magnetic properties of sintered 65–25–10 iron–nickel–aluminum magnets (according to Kalischer[28]). The apparent loss in magnetic properties at pressures above 60 tsi is attributed to minute internal pressing cracks, which could be eliminated in later tests by lubrication of the molding die with "Aquadag."

between 20 and 60 tsi. Kalischer mentions pressures ranging from 30 to 100 tsi. Maximum magnetic properties were obtained by the last investigator when using 60 tsi, while at least 90 tsi were found necessary for the attainment of complete density. (Incidentally, the same high pressure of 90 tsi was also employed in German prewar work on 63–23–14 Fe–Ni–Al cylindrical magnet bodies.[31c]) The effect of molding pressure on the density of a 65–25–10 Fe–Ni–Al alloy used by Kalischer is shown in Figure 403, and the effect on the magnetic properties in Figure 404.

Sintering. The sintering temperatures used in the production of Alnico range between 1200 and 1330°C. (2200 and 2400°F.). In order to obtain complete consolidation and alloying by diffusion, sintering must take place in the presence of the liquid phase formed by the fusion of the 50–50 Fe–Al prealloy (about 1175°C.; 2150°F.). Depending on temperature, the time during which the material is kept at sintering temperature may vary over a considerable range. According to Hotop, a period of one to six hours is satisfactory for 1300°C. (2370°F.); Kalischer investigated periods from five to forty hours at 1200°C. (2200°F.). The effect of sintering time upon the magnetic properties of 65–25–10 Fe–Ni–Al compacts molded at 100 tsi is shown in Figure 405. According to

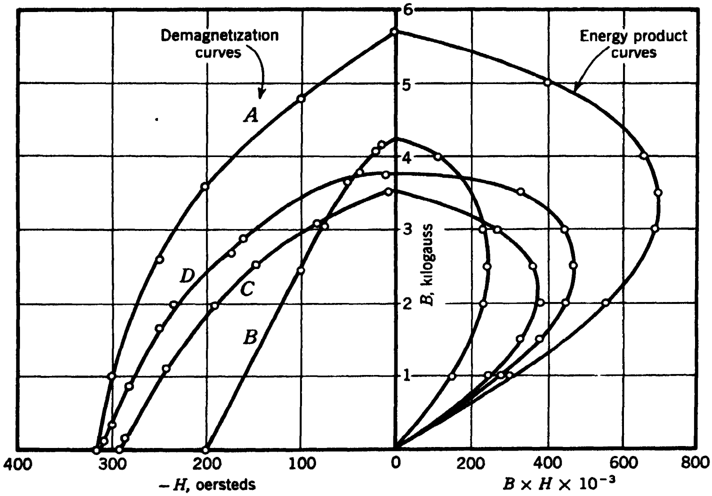

Fig. 405. Effect of sintering time at 1200°C. (2190°F.) on the magnetic properties of 65–25–10 iron-nickel-aluminum alloy (according to Kalischer[28]): sample *A*, sintered 20 hr., density 6.85 g./cc.; sample *B*, sintered 5 hr., density 5.73 g./cc.; sample *C*, sintered 10 hr., density 5.77 g./cc.; sample *D*, sintered 15 hr., density 6.62 g./cc.

[31c] British Intelligence Objectives Sub-committee, Document F. D. 1230/46; see also *Met. Powd. Rept.*, *1*, No. 5, 77 (1947).

Kalischer, the compact sintered at twenty hours results in better performance than the ones sintered for shorter periods, while an extension beyond the twenty-hour limit results in no further improvement.

Sintering operations must be conducted in purified hydrogen whose dew point should be *ca.* —60°C. (—76°F.). Passage over hot copper to catalyze the reaction of free oxygen with hydrogen must be followed by careful drying of the gas by means of condensers, activated alumina and chemical drying agents. The passage over powdered silicon, ferrosilicon,[32] or calcium[28] has also been found adequate. The most effective way to eliminate the detrimental effects of oxygen on the aluminum involves the use of a commercially available metal hydride powder. For example, titanium hydride added to the powder mixture evolves the hydrogen at 450°C. (840°F.); at the instant of evolution the hydrogen is nascent (in the atomic state). 2% titanium hydride is, according to Kalischer, sufficient to reduce all Al_2O_3 in the compact.

In commercial practice, the magnets are placed either into sealed iron boxes containing hydrogen under slightly above atmospheric pressure, or they are placed on open trays. The charge is transported through molybdenum-wound Alundum muffle furnaces (see Fig. 255, Volume I). The trays are constructed so that they slide easily along the bottom of the furnace retort. Composite trays consisting of slabs from iron powder or mixtures of iron and Alundum powder, respectively, prevent welding of the magnets to the surface of the tray. Certain German practices involved burying the magnets in an iron—aluminum powder pack inside sealed iron boxes contained in graphite boats (see also Volume I, Chapter XV).

Since the material is of the precipitation hardening type, solution treatment by rapid cooling in hydrogen atmosphere is essential for satisfactory magnetic performance. The continuous furnace operation permits combination of the sintering treatment with the controlled cooling rate; sintering of Alnico magnets in batch-type furnaces usually results in slower cooling, making reheating and controlled, rapid cooling mandatory. The heat treatment of the special grade Alnico V[32a] differs from the foregoing to the extent that a magnetic field is applied to the charge during the latter stage of the sintering cycle and during cooling in the continuous furnace, resulting in a material with anisotropic magnetic properties.

European sintering practice, as developed in Reutte, Austria, during the war, distinguishes itself from the above by introducing an atmosphere gettering process.[33] The unsintered magnet components are stacked in

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[32] G. H. Howe, *Iron Age, 145,* No. 1, 27 (1940).

[32a] Product of General Electric Co.

[33] *Met. Powd. Rept. 2,* 36 (Nov. 1947); British Intelligence Objectives Subcommittee, F.I.A.T., Final Rept. No. 1130 (Sept. 1947).

iron boats, which in turn are placed on top of a layer of powdered alumina inside the furnace trays. In order to prevent the sintering together of the magnets, they are separated by a thin layer of fine, powdered spinel ($MgO.Al_2O_3$). A protecting cover of sheet iron is placed inside each iron boat; the space between the cover and boat is filled with a powdered getter material consisting of 20–50% aluminum powder, 5–10% powdered alumina or spinel, and the remainder iron powder. As an alternate getter material, powdered silicon has also proved effective. Oxidation of the compacts is completely avoided by this procedure, and the resulting magnetic properties are practically identical with those of cast magnets.

Machining. In order to shorten the sintering period and to obtain the highest possible density, sintering is generally conducted near the upper limit of the previously mentioned temperature range (1300°C.; 2370°F.) just below the temperature of formation of blisters and segregation. As a consequence of the partial fusion of the alloy at this high temperature, considerable distortion and shrinkage will take place. In Table 150, the linear shrinkage is shown together with the density and the magnetic properties for various forming pressures.[34] Linear shrinkage figures ranging from 3 to 7% are generally encountered and frequently require a presintering and machining operation. Howe[26] recommends a presintering treatment in hydrogen at 600°C. (1100°F.) followed by rapid cooling, *i.e.*, a treatment analogous to that employed in hard metal manufacture. Machining of unsintered compacts is also possible, accord-

TABLE 150

Linear Shrinkage, Specific Gravity, and Magnetic Properties of Iron–Nickel–Aluminum Sintered Magnets, as a Function of Different Pressures in Production (Kieffer and Hotop[34])

Pressure, tsi	Linear shrinkage, %	Specific gravity, g./cc.	Residual magnetism, B_r, gauss	Coercive force, H_c, oersteds	Energy value, $(BH)_{max} \times 10^{-6}$, gauss × oersteds
21.3	11.2	6.75	6700–6600	570–480	1.10–1.25
34.8	8.9	6.77			
42.6	8.1	6.78			
49.8	7.2	6.79			
57.6	6.3	6.78			
65.9	5.4	6.76			
71.8	4.9	6.77			
Cast alloy of the same composition........		6.9	6500	510	1.25

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[34] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe.* Springer, Berlin, pp. 356 ff.

ing to Kieffer and Hotop,[34] who claim that even threads can be machined into the compressed powder compacts. The machining of compacted or presintered forms is advantageous where special shapes or short production runs make it impossible to use molding dies containing the actual contours. Machining of fully sintered magnets is difficult but not impossible. Grinding operations produce most accurately dimensioned products. Cutting operations such as drilling, milling, turning, or shaping require hard metal tools, but produce clean surfaces and no broken edges.

PROPERTIES AND APPLICATIONS

The difference in structure of sintered and cast Alnico-type permanent magnets becomes apparent from Figures 406 to 408, in which the respective fractures and microstructures are compared. The sintered structure distinguishes itself by its fine grain size; the comparatively low porosity and insignificant amount of impurities in the grain boundary areas are rather impressive. The clean and fine-grain appearance of the fracture is responsible for the high transverse rupture strength, which is in the order of 140,000 to 200,000 psi as compared with 40,000 to 70,000 psi for the cast magnets.

A comparison between the magnetic properties of sintered and cast Alnico-type permanent magnets has already been given in Table 148. The sintered materials are but slightly inferior to the cast alloys in accordance with the difference in the respective densities (see also Chapter XXXI). In Figures 409 to 410,[35] the properties of a sintered Alnico material containing 10% Al, 17% Ni, 12.5% Co, 6% Cu, balance Fe, are compared with those of various other permanent magnets made by conventional fusion methods. Figure 409 gives demagnetization and energy product curves, while in Figures 410*A* and *B*, sintered Alnico and 2 other permanent magnet materials are compared with regard to resistance to vibration and resistance to stray magnetic fields. These properties were tested on $^1/_4$ sq. in. bars, $1^{13}/_{32}$ in. long, one impact being equivalent to a 1-meter drop of the test bar on a steel plate. The superiority of the sintered Alnico is apparent in all cases.

Sintered Alnico V, containing 8% Al, 14% Ni, 25% Co, 3% Cu, 1% Ti, balance Fe, has remarkable magnetic and physical properties. The diagram of Figure 411 shows typical minimum demagnetization and external energy curves as obtained in the direction of heat treatment. A minimum residual induction B_r of 10,000 gausses, a minimum coercive force H_c of 575 oersteds, and a minimum external energy $(B_d H_d)_{max}$ of

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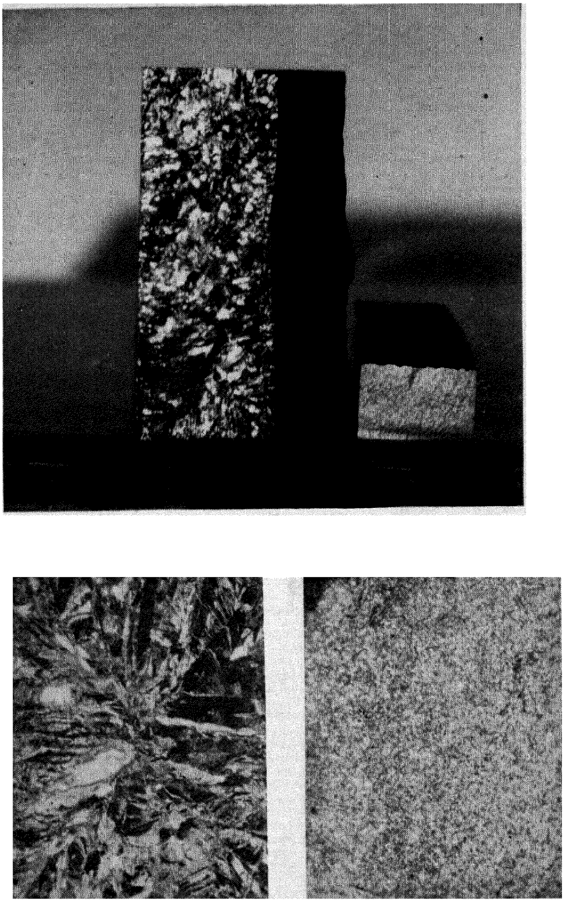
[35] General Electric Co., Catalogs GEA 3682B, CDM-1, and CDM-2.

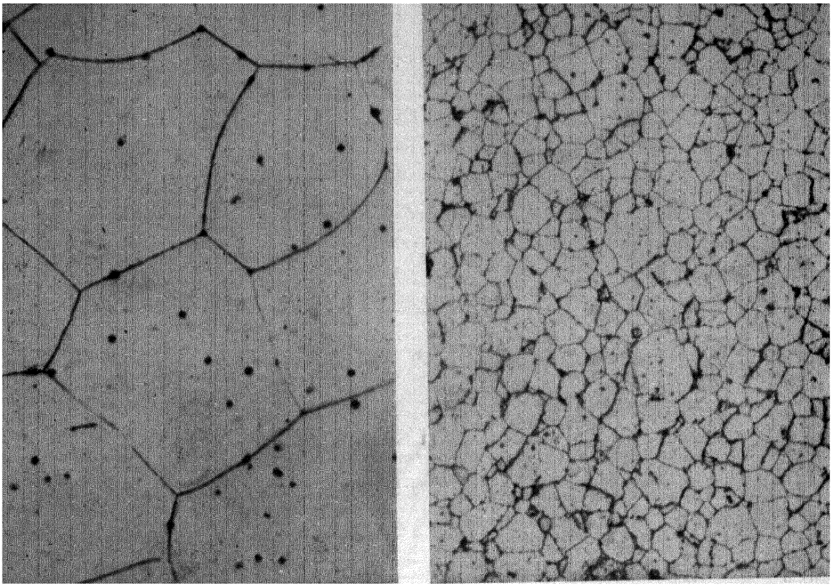


B C

Fig. 406. Comparison of fracture of cast (*A*, left; and *B*) and sintered (*A*, right; and *C*) iron–nickel–aluminum permanent magnets (courtesy of R. Kieffer).

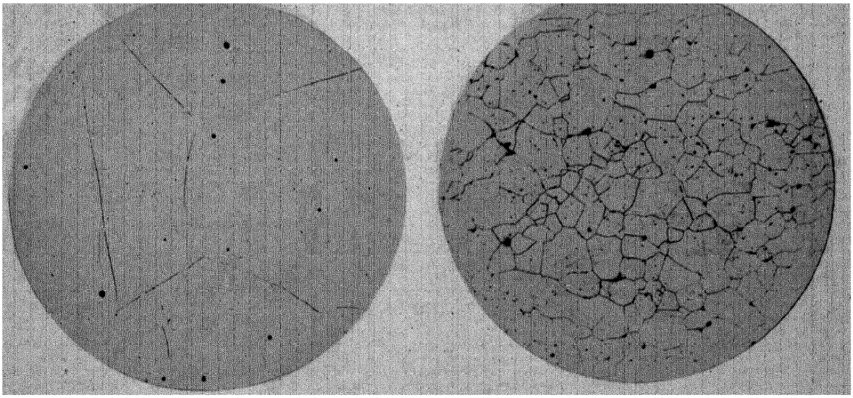
3,500,000 gauss-oersteds are guaranteed by the manufacturer.[35a] The physical properties are essentially the same as those common to all sintered Alnico-type magnets. The material is hard, though less brittle than cast Alnico V; fine-grained, but not forgeable; and possesses tensile properties about ten times better than those of cast Alnico V.

[35a] General Electric Co., Tech. Rept. on Sintered Alnico V, Catalog CDM-15A.



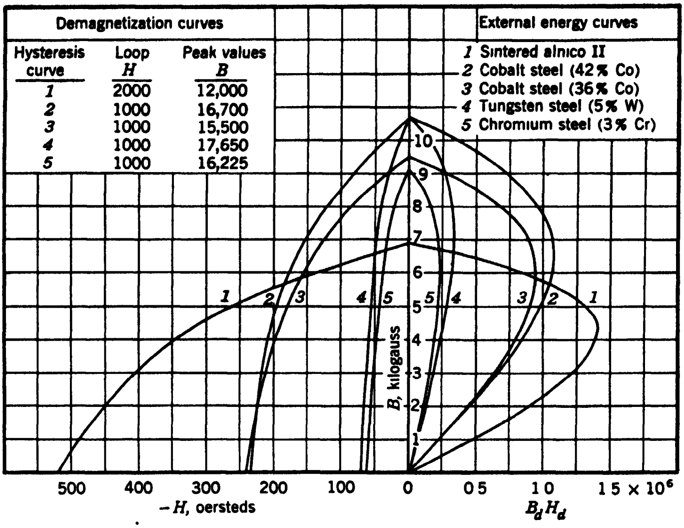
A *B*

Fig. 407. Microstructure (×150) of 60–27–13 iron–nickel–aluminum permanent magnets (according to Kieffer and Hotop[34]): *A*, cast alloy; *B*, sintered alloy.



A *B*

Fig. 408. Microstructure (×250) of 54–17–13–10–6 iron–nickel–cobalt–aluminum–copper permanent magnets ("Alnico II"), showing similar grain-size contrast as in Figure 407: *A*, cast alloy; *B*, sintered alloy (courtesy of General Electric Co.).



Demagnetization curves

Hysteresis curve	Loop H	Peak values B
1	2000	12,000
2	1000	16,700
3	1000	15,500
4	1000	17,650
5	1000	16,225

External energy curves
1 Sintered alnico II
2 Cobalt steel (42% Co)
3 Cobalt steel (36% Co)
4 Tungsten steel (5% W)
5 Chromium steel (3% Cr)

Fig. 409. Comparison of demagnetization and external energy curves of sintered Alnico and various other permanent magnets (courtesy of General Electric Co.).

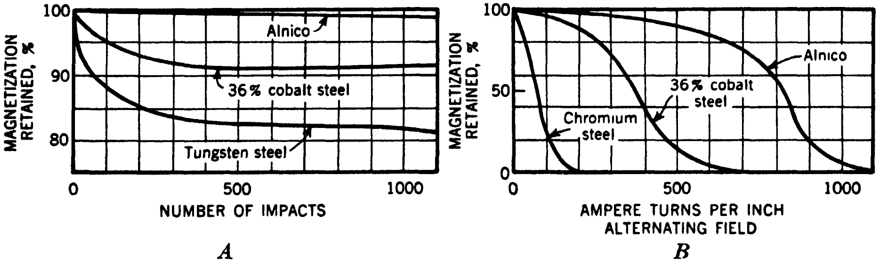


Fig. 410. Resistance of sintered Alnico to vibrations (A) and to stray magnetic fields (B) as compared with that of other permanent magnet materials. Tests were made on bars $^1/_4 \times {}^1/_4 \times 1^{13}/_{32}$ in. One impact is equivalent to a one-meter drop of the Alnico bar on its end on a steel plate. (Courtesy of General Electric Co.)

Sintered permanent magnets of the Alnico type are used in a large variety of electrical appliances, including magnetos, galvanometers, oscillographs, speedometers, tachometers, regulators, circuit breakers, switches, contactors, relays, transmitters, telephone receivers, hearing aids, and compasses. Also mentioned in the literature is their use in motors, generators, loudspeakers, small lifting magnets, and amplifiers. Figure 412 shows an assortment of typical, commercial sintered small Alnico magnets.

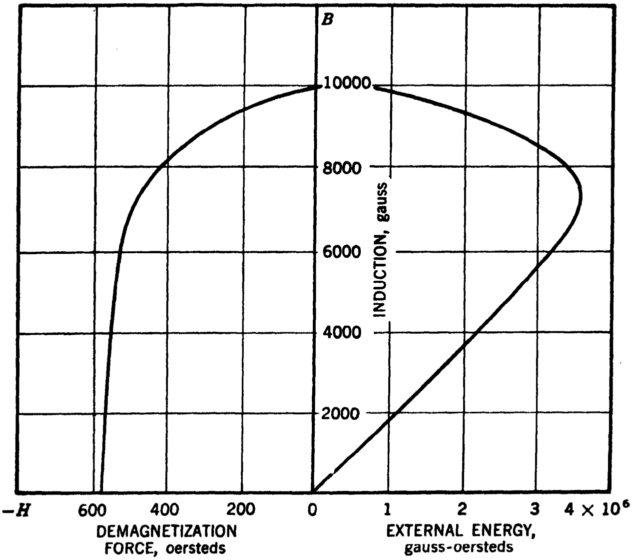


Fig. 411. Demagnetization and external curves of sintered Alnico V.

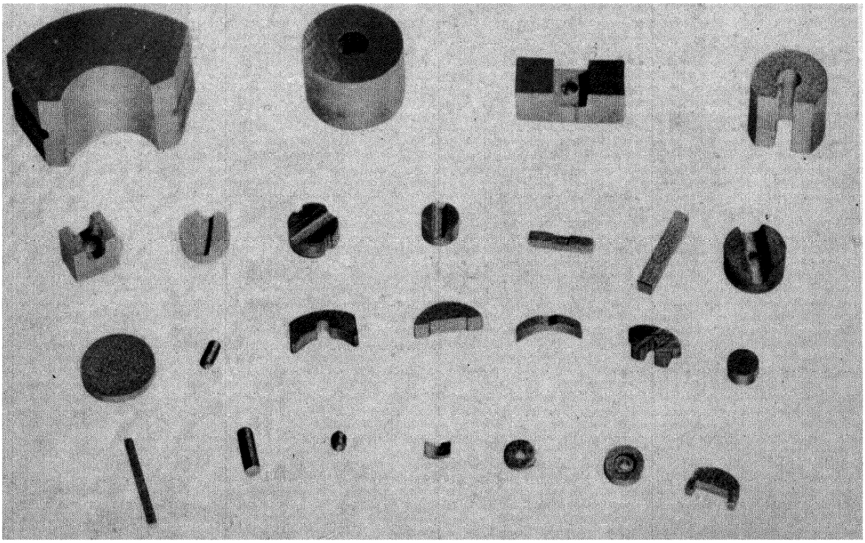


Fig. 412. Assortment of sintered Alnico permanent magnets of various sizes and shapes (courtesy of General Electric Co.).

Sintered Alnico V finds increasingly wide applications in several different fields. The high magnetic properties invite its use for all those cases that require small powerful magnets. In particular, the material is now being used in the fields of electronics, instruments, relays, novelties, and mechanics. Especially noteworthy applications are a rotor for a sensitive magnetic relay, and the G. E. Electronic Reproducer[35a] which derives its magnetic field from a small sintered Alnico V permanent magnet.

Other Permanent Magnet Alloys

Other permanent magnet materials that have been developed from metal powders include copper–nickel alloys with cobalt and iron, and steels containing cobalt and tungsten or molybdenum. None of these alloys however offers the same magnetic properties as sintered Alnico, and their commercial importance is of second order. Compacted iron-base materials produced from ultrafine powders, which apparently possess very high coercivities, may become a possible exception.

COPPER–NICKEL–COBALT

Alloys containing about 45% Cu, 25% Ni, and 30% Co possess important magnetic properties [$B_r = 2500$ gausses, $H_c = 810$ oersteds, $(B \times H)_{max} = 800{,}000$] which are comparable to a medium-strong Alnico magnet material. The alloy known as "Cunico,"[32a] can be readily produced by casting, but also by powder metallurgy methods ("Permet").[36] In the latter instance, fine powders are mixed in the proper proportions, pressed to size at comparatively low pressures (10–20 tsi), and sintered at 1050–1150°C. (1920–2100°F.) in hydrogen atmosphere. Rapid cooling after a prolonged period of sintering (up to ten hours) results in a maximum solution. Densification is obtained by coining at high pressures (50–75 tsi), either before or after precipitation treatment at 600°C. (1100°F.). The magnetic properties of both types[36,37] are compared with several Alnico compositions[38] in Table 151; in Figure 413 a hysteresis loop is shown for the sintered alloy.[36] Alloys of the Cunico composition have a lower energy value and, accordingly, require a larger magnet size than the customary Alnico grades. The high coercive force, however, permits relatively short magnets and makes the material suitable for bridging comparatively large air gaps. Also, the alloys are easily machinable and can be used in designs having narrow air gaps. Thus, the inferiority in magnetic properties is compen-

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[36] R. Steinitz, *Powder Met. Bull., 1,* No. 3, 45 (1946).

[37] J. H. Goss, *Product Eng., 17,* No. 1, 44 (1946).

[38] General Electric Co., Catalog CDM-1.

TABLE 151
Magnetic Properties of Copper–Nickel–Cobalt and Iron–Nickel–Aluminum Alloys[a]

Type	Composition, %	Residual induction, B_r, gauss	Coercive force, H_c oersteds	Energy product $(B_d \times H_d)_{max} \times 10^{-6}$	Process and heat treatment
Alnico I........	12 Al, 20 Ni, 5 Co	7,300	440	1.40	Cast; oil-quenched from 1200°C. (2190°F.), reheated at 600°C. (1100°F.) for long time
Alnico II.......	10 Al, 17 Ni, 12.5 Co, 6 Cu	7,350	560	1.60	Cast; oil-quenched from 1200°C. (2190°F.), reheated at 600°C. (1100°F.) for long time
Alnico V.......	8 Al, 14 Ni, 24 Co, 3 Cu	12,500	525	4.50	Cast; oil-quenched from 1200°C. (2190°F.), reheated at 600°C. (1100°F.), cooled in magnetic field
Alnico II.......	10 Al, 17 Ni, 12.5 Co, 6 Cu	7,000	560	1.50	Sintered; quick-cooled, reheated at 600°C. (1100°F.) for long time
Cunico.........	50 Cu, 21 Ni, 29 Co	3,400	710	—	Cast; cold-rolled, machined, oil-quenched, reheated at 600°C. (1109°F.) for long time
Permet.........	45 Cu, 25 Ni, 30 Co	2,500	810	—	Sintered; quick-cooled, reheated at 600°C (1100°F.) for long time

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[a] Data for Permet from R. Steinitz, *Powder Met. Bull.*, *1*, No. 3, 45 (1946), for Cunico from J. H. Goss, *Product Eng.*, *17*, No. 1, 44 (1946).

sated, but the high price of cobalt, as well as the long periods necessary for satisfactory diffusion during sintering, permit use of the alloy only for special applications. Attempts to substitute in the sintered alloy part or all of the cobalt by iron have not been particularly successful to date.

IRON-COBALT STEELS WITH TUNGSTEN OR MOLYBDENUM

Magnetic alloys, containing about 17% Co, 9% W or Mo, 3% Cr, balance Fe or Fe plus 1% C, can be produced readily by sintering.[39] The mixed powders are pressed at 15–30 tsi, and sintered in hydrogen or vacuum at 1150–1300°C. (2100–2370°F.). Since cast alloys of the same composition can easily be rolled or machined, there is little advantage in using the powder alloys, especially in view of the fact that magnetic properties of the sintered metal are not superior to those of the cast materials, and the Alnico materials are more economical on account of their greater efficiency.

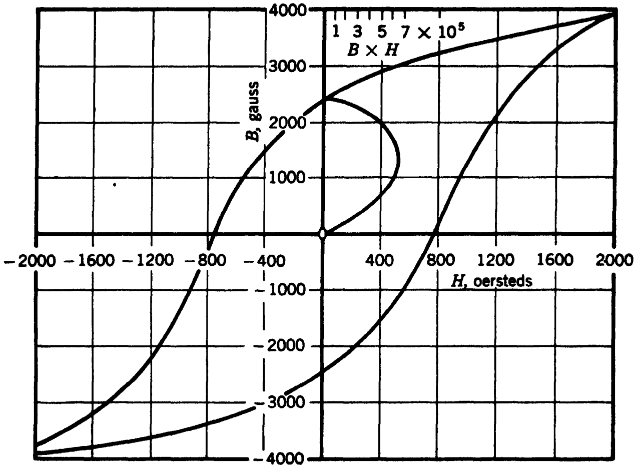

Fig. 413. Hysteresis loop and external energy diagram for sintered copper–nickel–cobalt permanent magnet material (according to Steinitz[38]). Composition of the alloy is 45% Fe, 30% Co, and 25% Ni.

ZIRCONIUM–NICKEL ALLOYS WITH IRON OR COBALT

Zirconium-bearing sintered permanent magnets have been suggested by Alexander.[40] The alloys are produced by reduction of the powdered

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[39] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe*. Springer, Berlin, 1943, p. 362.

[40] U. S. Pat. 2,184,769.

oxides of the alloy components with calcium hydride. No particular applications are known for this material.

IRON-BASE MAGNETS FROM ULTRAFINE (COLLOIDAL) POWDERS

During the war a number of iron-base permanent magnet alloys were developed in France which were based on extremely fine powders as starting material, and which possessed properties comparable to sintered Alnico magnet material.[41,42] Thus, it was found that permanent magnets made from magnetic powders of colloidal size (average particle size 0.1 μ, smallest size 0.01 μ) would possess amazingly high coercivities, with values recorded up to 2000 oersteds. Even straight colloidal iron powder gave magnets with a coercivity of up to 430 oersteds. Moreover, these magnetic properties could be obtained without the need for heat treatment.

In a subsequent patent[43] it is claimed that magnets made from colloidal iron powder can be further improved in both coercive force and residual magnetism by incorporating into the powder a small amount of calcium oxide, aluminum oxide, or magnesium oxide. This can be accomplished by adding lime or one of the other oxides to an iron formate solution at 100°C. (212°F.) to give a solution of 10% each of iron formate and calcium formate, which upon cooling precipitates iron formate crystals containing 1% CaO; these are subsequently reduced in hydrogen at 320°C. (610°F.). The loose powder and compacts pressed from it at 30 tsi, and then magnetized, have the following magnetic properties:

Material	Coercive force, H_c, oersteds	Residual magnetism, B_r, gausses
Loose iron powder containing 1% CaO from iron and calcium formate solution, reduced at 320°C. (610°F.)	400–430	5500
Same powder after compaction at 30 tsi	550	5800
Same powder, but reduced at 350°C. (660°F.), after compaction at 30 tsi	425	6500
Iron powder containing 1.5% MgO from iron and magnesium formate solution, reduced at 320°C. (610°F.)	520	5400
Iron powder containing 3.2% MgO from iron and magnesium formate solution, reduced at 320°C. (610°F.)	550	4900

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[41] Brit. Pat. 590,392; see also *Met. Powd. Rept.*, *2*, No. 2, 24 (1947).

[42] L. Weil, *Proc. International Powder Metallurgy Conference*, Graz, July 12–17, 1948, Referate No. 17.

[43] Brit. Pat. 594,681; see also *Met. Powd. Rept.*, *2*, No. 6, 89 (1948).

The original patent referring to these products enumerates several different methods of producing the ultrafine powders.[41]

(*1*) Iron and nickel powders as a reaction product of iron–aluminum and nickel–aluminum alloys, respectively, with sodium hydroxide (Raney method).

(*2*) Iron, nickel, and cobalt powders as a decomposition product of the respective formates, oxalates, hydroxides, or carbonates, the decomposition being accompanied by a reduction process at stated conditions.

(*3*) Alloy powders by the same process, with suitable mixtures of the compounds as starting material.

(*4*) Colloidal carbonyl powders by emanating a mixture of hydrogen and the respective carbonyl vapor or a mixture of vapors of different carbonyls at 300°C. (570°F.) through oil containing ether to promote precipitation.

(*5*) Colloidal carbonyl iron powder by emanating hydrogen through iron carbonyl at 50°C. (122°F.).

The powders produced under (*2*) and (*3*) are generally pyrophoric and require coverage in benzene, acetone, or ether immediately upon entering the cooling chamber of the furnace. The wet powders are pressed either cold or at temperatures below 250°C. (480°F.). Compacting pressures ranging from 6 to 60 tsi are sufficient to give compacts with a density of 5 to 6 g./cc.

The pressed magnets are protected from oxidation by immediate coverage with oil or by immersion in some organic or inorganic binding substance which solidifies thereafter and increases the coherence of the product.

Some of the extraordinary magnetic properties obtained with these ultrafine powder products are as follows:

Material	Coercive force, H_c, oersteds	Residual magnetism, B_r, gausses
Iron powder by reduction for 1 hour at 320°C. (610°F.) of iron formate, pressed slightly to a density of 3.0 g./cc.	530	3000
Same, but pressed to a density of 6.0 g./cc.	410	5700
Iron powder by reduction for 1 hour at 320°C. (610°F.) of ferric hydroxide, pressed to a density of 5.0 g./cc.	430	4100
Raney iron, pressed to a density of 5.5 g./cc.	380	4300
Carbonyl iron by emanating iron carbonyl vapor and hydrogen through oil at 300°C. (570°F.), pressed to a density of 5.0 g./cc.	450	4200
Cobalt powder by reduction for 1 hour at 320°C. (610°F.) of cobalt formate, pressed to a density of 6.0 g./cc.	350	5700
73–27 iron–cobalt alloy powders by reduction of the mixed formates under various conditions, pressed to various densities	560–1400	9400–1225

The surprisingly high coercivities quoted—which become truly remarkable when compared with the corresponding properties of sintered Alnico II magnets (average values for coercivity 520 oersteds and for residual magnetism 6900 gausses)—may be explained by a number of reasons. The most important one is the geometrical anisotropy of the ultrafine particles (see page 246). Also to be considered (though probably of minor consequence) are gaseous or solid inclusions. The Raney-type powders contain considerable percentages of hydrogen and aluminum, while the powders produced from the formates, oxalates, and other compounds contain unknown amounts of oxide, and the carbonyl powders contain a certain quantity of dissolved or occluded hydrogen. Another reason may be that strains are not so much caused by inclusions as by the high surface energy in the colloidal particles themselves, which may cause the grain boundaries to affect the coercivity in a manner similar to the distorting effect of precipitated aluminum in the Alnico-type magnet.

While it is known that these new methods of producing magnetic materials have taken roots in France, their broader development, especially in the U. S., must await the answer to such questions as powder production difficulties, powder costs, and performance of actual products in extended service—with particular attention to adequate mechanical strength of the unsintered structures. (Apparently, it is possible to increase the mechanical strength at least four to five times by a heat treatment between 300 and 450°C. (570 and 840°F.), which, however, slightly decreases the coercive force and increases the residual magnetism without changing the energy value[43a].) Indications are that the method should be of particular interest in connection with very small magnets of the kind weighing less than one gram.

OXIDE MAGNETS

Permanent magnets based on magnetic oxides of iron deserve brief mention. According to a process developed by Kato and Tokai,[44] mixtures of powdered Fe_2O_3 and Fe_3O_4 are sintered at 1000°C. (1830°F.), and the sintered products are magnetized at slightly elevated temperature, *e.g.*, 300°C. (575°F.). The magnets have a very low density (4 g./cc.) and good temperature and shock resistance, but the residual induction is too low to be useful for most purposes. An additional disadvantage of the material lies in its extreme brittleness, making handling difficult and tending to cause early service failures.

[43a] Brit. Pat. 612,879; see also *Met. Powd. Rept.*, *2*, No. 6, 89 (1948).

[44] Y. Kato and I. Tokai, *J. Inst. Elec. Engrs. Japan*, *53*, 408 (1933).

MOLDED PERMANENT MAGNETS

The possibility of bonding permanent magnet alloy powders with plastics into accurately shaped products has already been mentioned. The most frequently used plastics are polyvinyl chloride and phenol-formaldehyde resins.[44a] Crushed and pulverized Alnico castings, scrap, or shot is mixed with the resin powders and pressed at low pressure (about 1–4 tsi) at the temperature required for the polymerization or consolidation of the particular plastic (100–150°C.; 200–300°F.). This procedure makes it possible to attain very close tolerances, and permits accurate holes to be pressed directly. The possibility of inserting metal or plastic sections which can be utilized for mounting the magnet is an additional advantage of the method. The incorporation of the plastic causes a moderate decrease in the magnetic properties. A typical commercial molded magnet product has the following properties:[45]

Bending strength, psi	1,700	Residual induction, gausses	3,500–4,800
Tensile strength, psi	17,000	Coercive force, oersteds	500–800
Density, g./cc.	5.5–6	Energy product	$0.6\text{–}1.2 \times 10^6$

It is claimed that the magnetic properties of such molded magnets can be further improved if the material is subjected to a magnetic field during the process of molding.[46]

Leadbeater[46a] reports a war-time German development of pressed, unsintered, resin-bonded magnets based on powder mixtures instead of pulverized fully alloyed materials; the mixtures contained 9–13.5% Al, 18–28% Ni, 0–19% Co, 0–4% Cu, 0–4% Ti, balance Fe powder.

SOFT MAGNETIC PRODUCTS

Direct Current Applications

The most important soft magnetic materials consist of iron of very high purity, or of alloys of iron and silicon, nickel, cobalt, or molybdenum, respectively. The powder metallurgy approach has made an important inroad during the last decade in producing these materials, thereby competing with vacuum fusion of electrolytic iron, or hydrogen-annealing of Armco-iron sheets. Pole pieces and armatures made from electrolytic or hydrogen-reduced iron powders have found their principal field of usefulness in small electric motors and generators for direct current applica-

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[44a] P. Schwarzkopf, *Powder Metallurgy*. Macmillan, New York, 1947, p. 246.

[45] H. Dehler, *Stahl u. Eisen, 62,* 985 (1942).

[46] U. S. Pat. 2,188,091.

[46a] C. J. Leadbeater, *Symposium on Powder Metallurgy,* The Iron and Steel Institute, Special Report No. 38, London 1947, p. 191.

tions, and, more generally, for instruments where the electrical and magnetic requirements are not too severe.

The chief advantages in making pole pieces and armatures by powder metallurgy methods lie in the direction of easier manufacture. If the parts are to be produced by conventional fusion and machining methods, it is necessary to purify the metal, and particularly to remove such elements as carbon, phosphorus, or sulfur, since these impurities affect the magnetic characteristics adversely. No special purification is necessary, however, if in the powder metallurgy process commercially pure iron powders (98.0% Fe, minimum), and dissociated ammonia or pure hydrogen as sintering atmosphere, are used. (Purity of the powder or minor alloying additions remain almost ineffective, as long as the density of the part remains below approximately 90% of the true theoretical value, and sintering is performed at a temperature below that necessary for a pronounced spheroidizing of the pores.) The rapid method of manufacturing parts renders the process quite economical, especially where standard designs permit large production runs. On the other hand, the powder method offers greater design flexibility, which is often more advantageous than the superior electrical behavior of laminated structures. The elimination of waste material in machining and of special tool machinery, as well as the substantial saving of labor in manufacture, are additional advantages inherent in the powder method.

In the beginning of this chapter it has been explained that for soft magnetic parts to be used in direct current motors and generators, the magnetic permeability, *i.e.*, the ratio of the flux density to the magnetizing force, is the principal magnetic property. The entire design of the motor, its speed, and its torque are based on the magnetic flux, a property dependent on the induction (flux density) in the different sections of the magnetic circuit. Permeability should be as high as possible, *i.e.*, a good flux should be obtained with the least number of ampere turns, since this would require a minimum of space and result in a maximum efficiency (minimum power loss through resistance in the winding). High permeability of the pole piece material is also important in view of the low permeability of the air gap. Still more significant from a practical standpoint is the fact that the permeability must be uniform from piece to piece; otherwise it would be necessary to have a different number of windings for each pole piece.

Hysteresis and eddy-current losses are only of minor importance for small direct current electric motors because the current passing through the field coils is constant and, therefore, the magnetic field is also constant except for small fluctuations caused by the slots or teeth of the armature. Only in large motors and generators or in armatures of rotating direct current machines do the hysteresis and eddy-current losses become sufficiently strong to be taken into account when selecting material and design. An addition of 2–6% Si to the iron, suitably in form of ferrosilicon powder, has been found to increase the resistivity and to reduce the eddy-current losses appreciably without very serious effects on the compactibility of the powder or on the densification during coining.[47]

MANUFACTURE

The manufacture of soft magnetic parts from iron powders has been described in detail by Lenel[48] and some of the inherent press problems have been emphasized by the author.[49] The process consists essentially of molding the required shape in a briquetting press, sintering in hydrogen atmosphere, and coining to the required final dimensions. To facilitate molding, especially in the case of more complicated designs, powdered nonmetallic lubricants are mixed with the iron powder. The magnetic performance, as well as the toughness and shock resistance, of the product is improved if the coined parts are subjected to a final hydrogen annealing. For strongly curved sections, molding and sintering may be carried out in several steps, as outlined in detail in Volume I, Chapter IX.

Raw Material. The raw material for making soft magnetic parts is usually straight iron powder without alloying ingredients. The type and grade of iron powder used are of importance in so far as final density is concerned, since this has a distinct bearing on the magnetic properties of the part. Although the purest powders such as electrolytic or carbonyl iron generally give the best ultimate density and, therefore, magnetic performance, molding problems as well as economic considerations may often indicate the use of a lower cost powder of less purity, but better compactibility. Even within a particular type of powder, different grades as distinguished from each other by their particle size distribution or apparent density, may have to be considered for different designs, although the magnetic requirements may be in the same order. Depending on the complications of the design and the machinery available for molding, from 0.5 to 2% by weight of internal lubricant (stearic acid, metal stearates) is generally added to the iron powder.

Molding. The pressing of soft magnetic parts, such as pole pieces and armatures, follow the same procedure as in the molding of other iron parts. Pressures are applied from two opposite ends, either through action of a double-action press or through the operation of a spring-loaded

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[47] R. Steinitz, *Powder Met. Bull., 2,* No. 6, 135 (1947).
[48] F. V. Lenel, *Trans. Am. Inst. Mining Met. Engrs., 161,* 535 (1945).
[49] C. G. Goetzel, *Trans. Am. Inst. Mining Met. Engrs., 166,* 506 (1946).

floating die, since most parts have several cross sections (*e.g.*, most pole pieces have heavy round hubs and strongly curved thin wing sections). An even density throughout the piece, and uniformity from piece to piece, are essential for optimum mechanical and magnetic properties. The molding pressures range from 10 to 50 tsi, the simpler flat shapes permitting high densification during molding at pressures near the upper limit. Lower pressures (up to 30 tsi) are used for curved parts to avoid undue straining of the press tools. A satisfactory densification is obtained either by coining after sintering or by high-temperature sintering. The application of a porous preform may be indicated by certain designs, the powder being pressed into a shape differing from that of the finished part and the final form and density being produced by the coining operation. (For further details see Volume I, Chapter IX.)

Sintering. The sintering temperature is determined not only by the need for adequate consolidation of the compact but also by the magnetic requirements of the end product. High densities are required for optimum magnetic performance, necessitating sintering temperatures well within the austenitic range. Where densification is achieved primarily by the subsequent coining operation, a sintering temperature of about 1100°C. (2000°F.) has proved satisfactory for reasonably short sintering times of one-half to one hour at temperature. This cycle permits the use of standard continuous-transport furnace equipment, thus being particularly advantageous for large production runs.

Without subsequent densification in coining, higher temperatures must be used. According to Lenel[48] the most favorable magnetic properties are obtained by sintering at 1315°C. (2400°F.). A continuous sintering furnace is impractical for this high temperature. Instead, a box-type furnace heated with Globar heating elements and an attached cooling zone is employed. Depending on the size of the parts and the magnetic properties required, sintering is carried out in hydrogen for 90 minutes to 3 hours.

Coining. The subsequent coining operation may serve solely as a sizing operation, or may also densify the part further when high densities are not achieved during sintering. Sizing consists of a one-step coining operation in punch presses, using moderate pressures. Coining for the purpose of densification or reshaping the form requires considerable pressures, usually in the range of 40 to 80 tsi. Hydraulic presses and spring-loaded dies may be used for this operation.

Annealing. Coining of the parts into high-density products, which is usually connected with a marked change in contours, implies severe strain hardening of the structure. A subsequent annealing treatment in hydrogen is necessary to make the part sufficiently ductile and shock resistant for further handling in finishing operations and for assembly and service. It is also desirable for optimum magnetic properties. The choice of the proper annealing or resintering cycle depends on the shrinkage characteristics of the material and on the stress concentrations caused by the individual design. In order to retain the advantage of an accurate size after coining, no noticeable shrinkage or expansion is permissible during the annealing treatment. This requirement limits the annealing temperature range to about 700–850°C. (1300–1550°F.), *i.e.*, above the recovery temperature but below the transformation temperature of pure iron. If annealing is carried out above this range, marked shrinkage and possible distortion result.

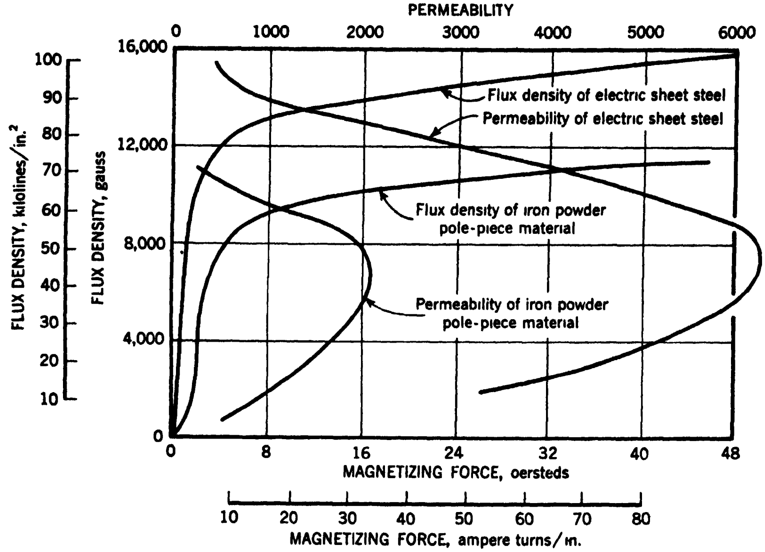

Fig. 414. Magnetization and permeability of magnetic material made from iron powder and of electrical sheet steel (according to Lenel[48]).

PROPERTIES

Lenel[48] has investigated the magnetic properties of pole pieces produced from iron powders under different conditions. In Figure 414 the induction and permeability of sintered pole pieces are compared with the corresponding values for the electric sheet steel material formerly used. It may be seen that the sintered material is inferior, and at the operating flux density of about 60,000 lines per square inch more ampere turns per inch are required in the field coil. However, the difference is small in comparison to the number of turns necessary to bridge the air

TABLE 152

Magnetic Properties of Ring Samples from Sintered Iron (Lenel[48])
Briquetted at 30 tsi, Sintered 3 Hours at 1315°C. (2400°F.) in Hydrogen

Source of iron powder	Radial shrinkage of samples in sintering, in./in.	Density of sintered sample, g./cc.	Maximum permeability	Magnetizing force, oersted, for flux density of 10,000 gauss	Flux density, gauss, for magnetizing force of 40 oersteds	Residual induction, gauss, from 10,000 gauss	Coercive force, oersted from 10,000 gauss
Electrolytic.	0.008	6.82	3100	3.9	12,700	9300	1.6
Decarburized comminuted steel shot.	0.012	6.69	2150	14	11,000	9000	2.0
Hydrogen-reduced mill scale.	0.018	6.20	1340	30	10,300	8500	3.1
Hydrogen-reduced oxide from steel scrap . .	0.023	6.01	1380	40	10,000	8300	2.9

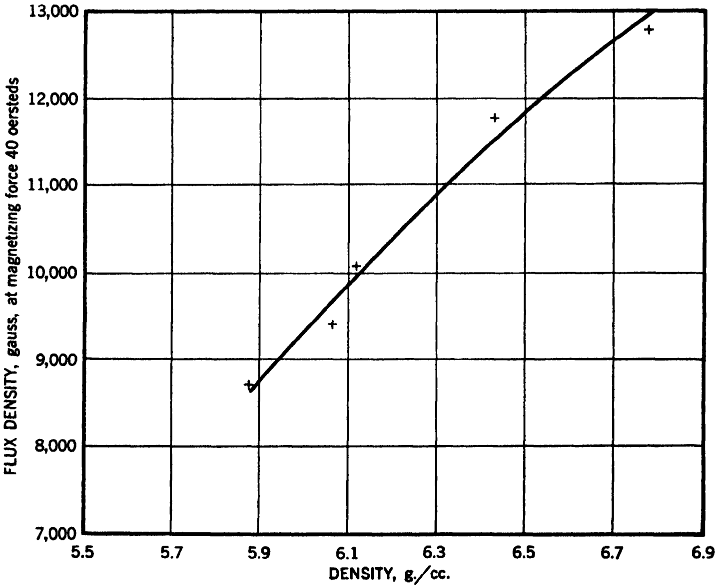

Fig. 415. Relation between sintered density and flux density of sintered iron magnets at a magnetizing force of 40 oersteds (according to Lenel[48]).

gap, and the design modifications possible with the powder part compensate to a large extent for the extra turns necessary in the coil.

The effect of type (source) of iron powder used is shown in the data of Table 152. The best induction and permeability properties are obtained for electrolytic iron. Next in line is iron powder, obtained by decarburization of mechanically comminuted steel shot. Reduced from powders give the least satisfactory performance. The relationship between sintered density and flux density is shown in Figure 415; the flux density increases with increasing density of the sintered part. The effect of sintering temperature upon the magnetization curve and hysteresis loop is shown in Figure 416. The curves demonstrate that the permeability values rise

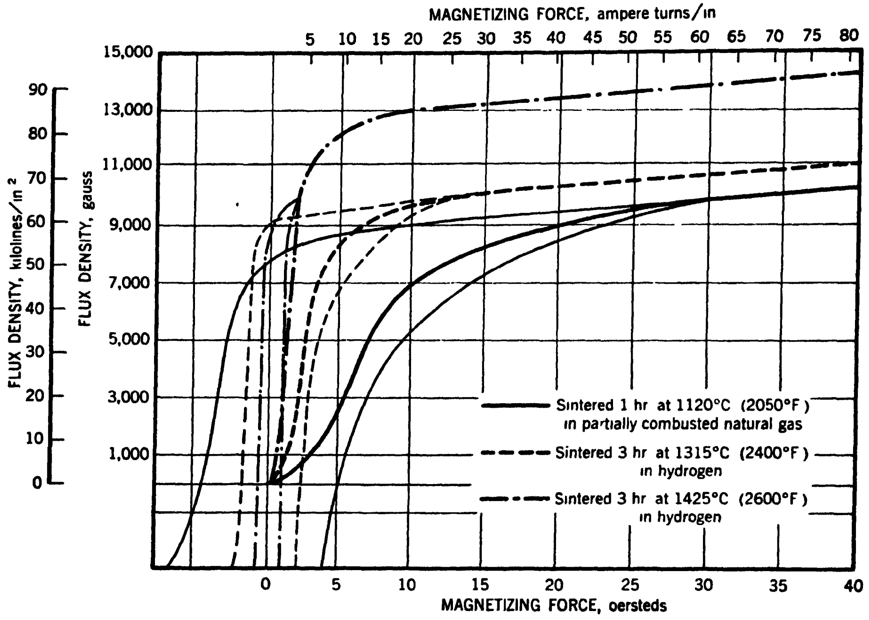

Fig. 416. Effect of heat treatment on magnetization curve and hysteresis loop of magnetic material made from iron powder (according to Lenel[48]).

and the hysteresis loop becomes very narrow with increasing sintering temperatures and times. The density of sintered pole pieces must be carefully controlled since the characteristics vary widely with variations in density. This is shown in Figures 417*A* and *B* and 418, where the characteristics of pole pieces of 96% density produced from electrolytic iron powder are compared with those of similar pole pieces of 90% density produced from reduced iron powder.[50,51] A comparison of the

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[50] P. Schwarzkopf, *Powder Metallurgy*. Macmillan, New York, 1947, pp. 251–252.
[51] R. Hradecky and R. P. Seelig, *Iron Age*, *156*, No. 13, 50 (1945).

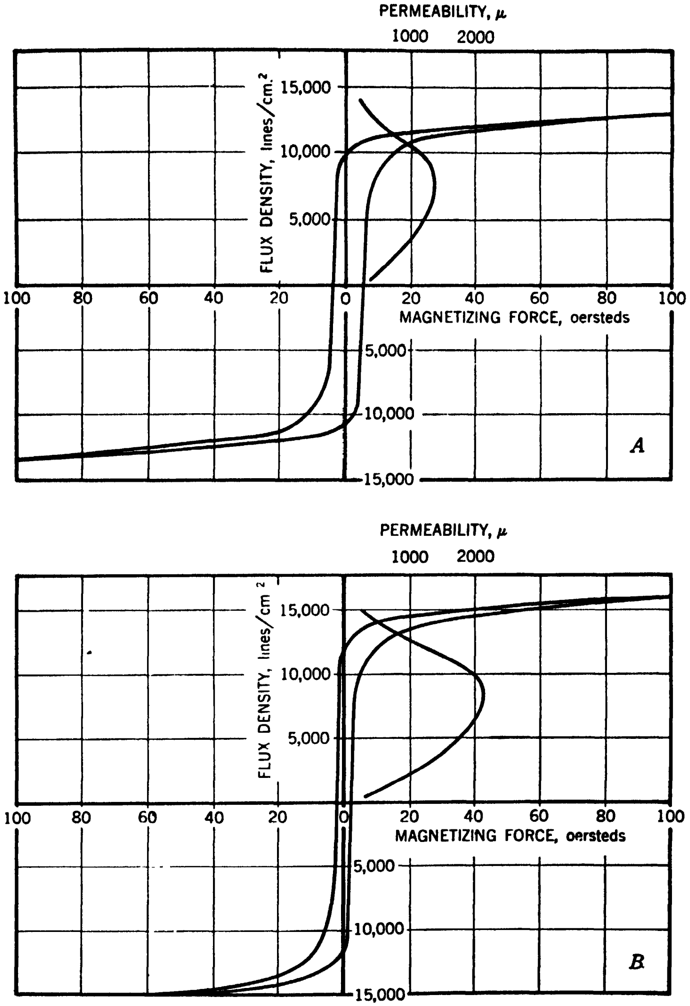

Fig. 417. Hysteresis loop and permeability curves of sintered soft iron magnets (according to Schwarzkopf[50]): *A*, material of 84–88% density; *B*, material of 94–96% density.

hysteresis curves of the sintered material with pure iron and cast iron is shown in Figure 419.

Oliver,[52] in a discourse presented at a symposium in England,

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[52] D. A. Oliver, *Symposium on Powder Metallurgy*, The Iron and Steel Institute, Special Report No. 38, London, 1947, p. 63.

surveyed the field of sintered magnetic iron components, *e.g.*, pole pieces for small electric motors, generators, instrument relays, etc., and analyzed their magnetic characteristics and methods of manufacture. The presentation was broadened by the addition of some experimental data, and Table 153 gives the processing particulars and magnetic properties of the test specimens used; both American and British raw materials were employed. The relation between permeability and magnetic induction for the different materials is shown graphically in Figure 420, and the same diagram also shows curves for an American sintered product ("Pomet 300") and for solid Armco iron for the sake of comparison.

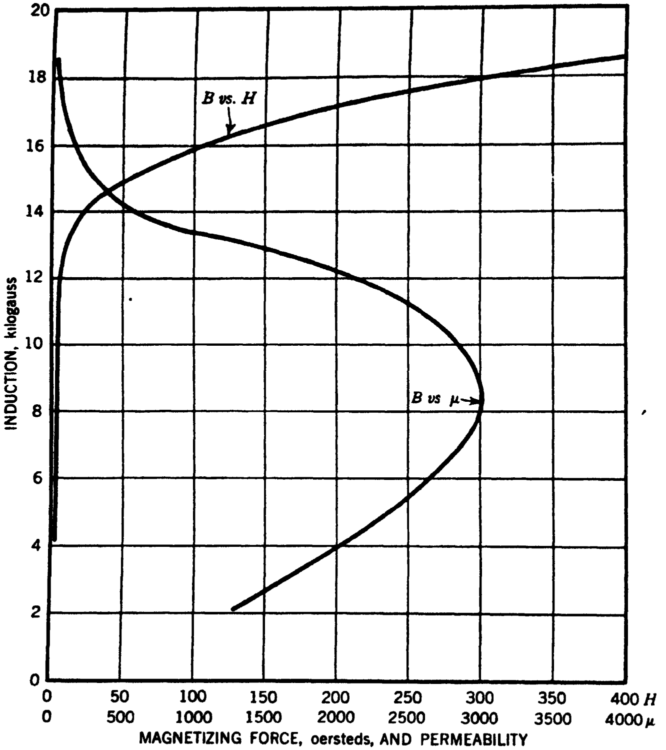

Fig. 418. Magnetization and permeability of high-density sintered iron (according to Hradecky and Seelig[51]). Maximum permeability is reached for an induction of approximately 8300 gauss.

One of the latest studies of the properties of sintered soft iron magnet parts has been reported by Steinitz,[53,53a] who investigated the relationship

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[53] R. Steinitz, *Trans. Am. Inst. Mining Met. Engrs.*, *175*, 834 (1948).

[53a] R. Steinitz, *Proc. International Powder Metallurgy Conference*, Graz, July 12–17, 1948, Referate No. 58.

between magnetic properties and densities or sintering temperature of differently prepared iron compacts. Steinitz essentially reaffirmed previous findings, and arrived at the conclusion that, in general, the coercive force of porous iron is higher, while the residual magnetism and permeability are lower, than for Armco iron. The results further seem to indicate that the raw material has a negligible influence on the magnetic properties (two electrolytic and three-reduced powders with variations in carbon from 0.01 to 0.25% and in oxygen from about 0.3 to above 1% were used), if these are compared for identical densities and not for identical processing cycles. A beneficial effect of high sintering temperatures (1315–1370°C.; 2400–2500°F.) on the magnetic properties may be attributed to the spheroidizing of the residual pores. Steinitz also shows

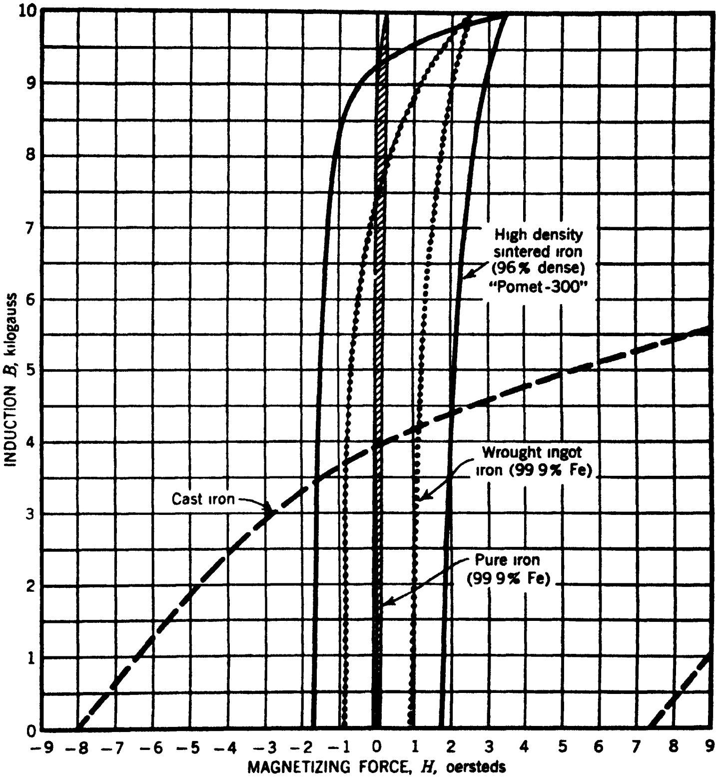

Fig. 419. Comparison of hysteresis curves for high-density sintered iron with chemically pure iron, wrought ingot iron, and cast iron (according to Hradecky and Seelig[51]).

TABLE 153

Properties of Soft Magnet Test Pieces[a] (Oliver[52])

Designation	Iron powder	Compacting pressure, tsi	Sintering temperature °C.	Sintering temperature °F.	Sintering time, hr.	Atmosphere	Sintered density,[b] g./cc.	Maximum permeability μ_{max}	H for μ_{max}	B for μ_{max}	Specific resistivity, ohm-cm. × 10^6 at 20°C.
A[c]	American origin: Hydrogen-annealed .	35	1300	2370	1	Dissociated ammonia	6.40	650	8.9	5750	20
B	M.P.C. electrolytic iron (standard grading)...	35	1400	2550	1	"	7.00	900	6.4	5800	—
C	M.P.C. electrolytic iron (standard grading).........	35	1150	2100	3	"	6.80	1630	4.2	6750	16
D[d]	M.P.C. electrolytic iron (standard grading).......	35	1150	2100	3	"	7.46	2510	3.6	9000	13

[a] Supplied by Metal and Plastic Compacts Ltd., Birmingham.

[b] Density of pure iron = 7.88 g./cc.

[c] Sintered hardness approximately 55 (diamond pyramid hardness, 30-kg. load).

[d] Specimen D had an intermediate coining operation followed by final annealing at 950°C. (1920°F.).

the feasibility of following cold working by coining and stress relief by subsequent annealing with the aid of magnetic measurements.

APPLICATIONS

The principal applications for sintered field poles and armatures can be found in small electric motors and generators as used for controls, instruments, and similar appliances, for which a very high flux density in a given design is not as important as the advantages inherent in the powder metallurgy approach, *i.e.*, the more rapid and inexpensive method of manufacture, and a greater flexibility of design than is possible with parts made from laminated sheet metal. Figure 421 shows a number of different designs for pole pieces, and Figure 422 an assortment of poles, shunts, bridges, and armatures made by the sintering process.

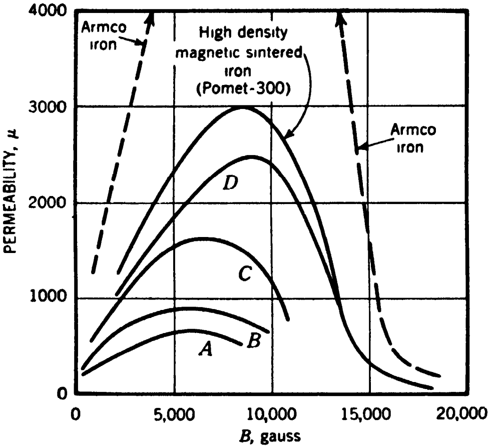

Fig. 420. Permeability curves of soft magnetic specimens *A* to *D*, investigated by Oliver[52] as compared with American data for high-density sintered iron and solid Armco iron (μ_{max} about 7000).

Alternating Current Applications

LOW FREQUENCY PRODUCTS

Directly Molded Parts. Soft magnetic parts from sintered iron are suitable only where a constant magnetic field is applied. In alternating current equipment where the magnetic field alternates between positive and negative values, hysteresis and eddy-current losses predominate. The hysteresis losses are a function of the purity of the iron, and may therefore be influenced to a certain extent by careful selection of the iron powder. The eddy-current losses are largely controlled by the electrical resistivity of the material. They may be reduced by increasing the elec-

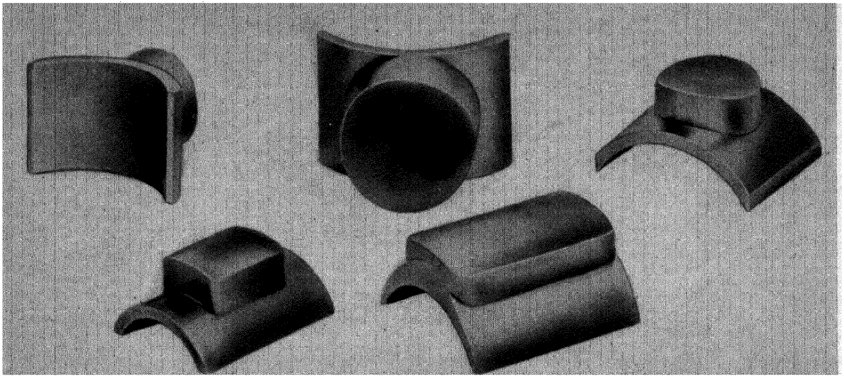

Fig. 421. Pole pieces **made** from iron powder (according to Lenel[48]).

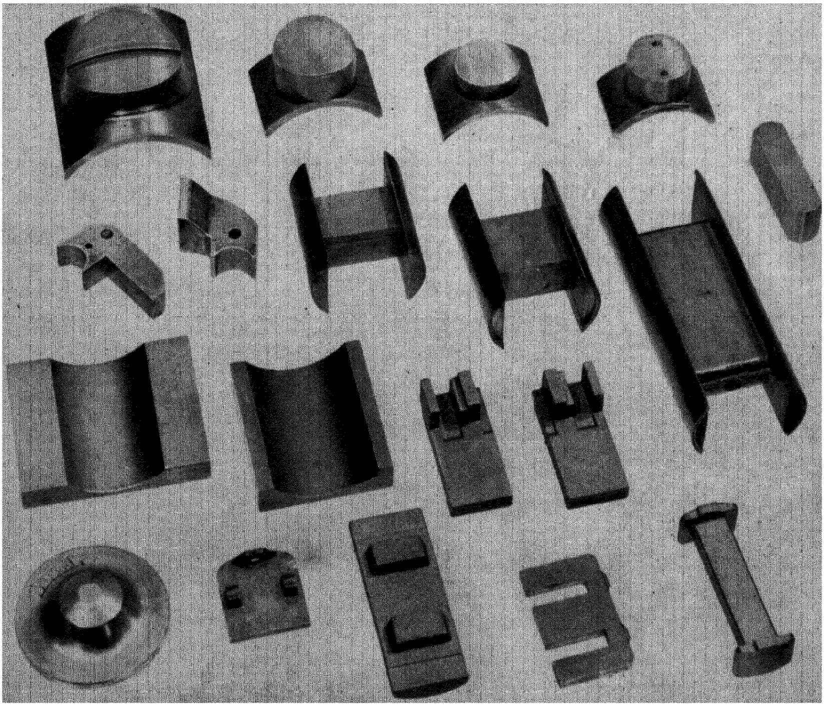

Fig. 422. Assortment of soft magnetic sintered iron components, including pole pieces, **shunts, bridges, and armatures** (**courtesy** of American Electro Metal Corp.).

trical resistance along the path of the eddy current. This is generally accomplished by employing parts composed of punched sheet steel laminations which are insulated from each other and riveted together.

Although the porosity in sintered iron increases the resistivity to about 150 to 200% that of pure iron, this increase is not sufficient and compares quite unfavorably with the resistivity of silicon steel. Hence, it has not been possible to use plain sintered iron for alternating current applications.

Alloying of the iron with silicon, nickel, cobalt, chromium, aluminum, and other elements tends to increase the resistivity, thereby reducing the eddy-current losses. Unfortunately, however, the permeability is reduced and the hysteresis losses are increased at the same time, and there appears to be no alloy that will perform entirely satisfactorily. The addition of silicon, which is standard in the manufacture of electrical sheet steel, has proved quite satisfactory in the powder metallurgy production of armatures for small electric generators or motors. Steinitz[53b] investigated four different alloys containing 1.5, 3, 4, and 6% silicon. The silicon was added to reduced iron powder in the form of 15% ferrosilicon powder which, in spite of its abrasive qualities, could be molded satisfactorily into the complicated armature shapes if mixed with the iron powder up to a ratio of 40% ferrosilicon to 60% iron. The alloying effect of the silicon on the resistivity could be controlled by arresting the sintering process before complete equilibrium through diffusion was attained. The effect of two sintering cycles, 1100°C. (2000°F.) for 90 minutes and 1400°C. (2550°F.) for 45 minutes was studied on $3 \times {}^1/_2 \times {}^1/_2$ in. bar samples (for resistivity measurements) and 2 in. diameter ring samples (for magnetic measurements) which had been molded at 35 tsi. After coining at 42 tsi and annealing at 760°C. (1400°F.) the resistivity of the low-temperature sintered material was found to increase with increasing silicon content from 20 microhm-cm. for the 1.5% silicon alloy to 100 microhm-cm. for the 6% alloy; at the same time, the maximum permeability decreased from 700 to below 400. The higher sintering temperature was found to improve considerably the permeability for the 4% silicon alloy (giving values in the order of 1500), while at the same time the density was also somewhat increased by shrinkage (from 5.9 g./cc. for the low-temperature sintered alloy to 6.6 g./cc. for the high-temperature sintered alloy).

With the aid of resistivity measurements, Glaser[53c] was able to follow the progress of sintering and diffusion in compacts containing 6 and 10% Si.

[53b] R. Steinitz, *Powder Met. Bull.*, *2*, 135 (Nov. 1947).

[53c] F. W. Glaser, *Powder Met. Bull.*, *4*, No. 1, 19 (1949).

An iron–silicon alloy with 3% Si, obtained by molding a mixture of reduced iron with ferrosilicon powder at 25 tsi, sintering at 1175°C. (2150°F.) in dry hydrogen, coining at 50 tsi, and annealing at about 800°C. (1500°F.), was found to have a resistivity of about five times that of Armco sheet iron, and a permeability of about 1000. The hysteresis loop of this material is shown in Figure 423.[50]

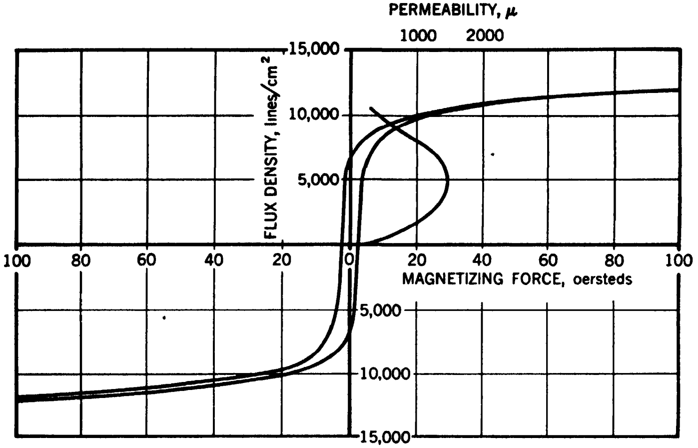

Fig. 423. Hysteresis loop and permeability curve of sintered 97–3 iron–silicon magnets (according to Schwarzkopf[50]).

Rostoker[53d] recently gave further information on iron–silicon alloys. In addition to alloys containing 4% silicon for which he established time–temperature–property relationships, compositions with 6, 7, 8, and 9% silicon were studied. In the first instance, the sintering temperature for high-density ring-shaped compacts, pressed at 30 tsi, was varied from 1400°C. (2550°F.) to 1000°C. (1830°F.), and the sintering time from 2 to 24 hours. The electrical resistivity for the 4% alloy after sintering at 1300°C. (2370°F.) was 51.3 microhm-cm., the density 98.1% of the solid alloy. After repressing at 75 tsi and annealing, the magnetic properties were as follows.

Temperature of 24-hr. sintering treatment	μ_m	B for μ_m, gauss	B_r, gauss	H_c, oersteds
			(for B = 10,000 gauss)	
1400°C. (2550°F.)	9750	5650	7910	0.355 (μ_0 = 1100)
1350°C. (2460°F.)	9000	6700	7680	0.38
1250°C. (2280°F.)	8200	8200	8250	0 44
1150°C. (2100°F.)	5500	5500	7850	0.66
1000°C. (1830°F.)	1560	4680	6150	1.8

[53d] W. Rostoker, *Trans. Am. Inst. Mining Met. Engrs., 180,* 672 (1949).

In the study of alloys of higher silicon content, the ring samples were sintered at 1300°C. (2370°F.) for up to 24 hours, and then, as before, repressed at 75 tsi and annealed. Electrical resistivities ranged from 83.5 microhm-cm. for the 6% silicon alloy to 98.6 microhm-cm. for the 9% silicon alloy, while the density ranged from 94.2 to 96.0% for the group. In the case of samples sintered for 24 hours, the following magnetic properties were recorded.

Sample	μ_m	B for μ_m, gauss	B_r, gauss (for B = 10,000 gauss)	H_c, oersteds (for B = 10,000 gauss)
6% silicon alloy	9,900	5140	7760	0.295 ($\mu_0 = 1000$)
7% silicon alloy	17,500	7000	8410	0.19 ($\mu_0 = 1000$)
8% silicon alloy	14,500	4900	6700	0.20 ($\mu_0 = 1400$)
9% silicon alloy	10,800	4200	6000	0.215 ($\mu_0 = 1130$)

Thus, it was found that the alloys high in silicon (above 6%) have definite merits despite their comparatively low saturation values, since the maximum permeability (μ_m) and coercivity values are very good, and the electrical resistivities are very high.

Rostoker also investigated iron–nickel alloys with the high nickel contents of 50, 65, and 78.5%. High-density ring samples pressed from mixtures of electrolytic iron, −150 mesh, and carbonyl nickel, all finer than 4 microns, were sintered at 1400°C. (2550°F.) for up to 24 hours; they were tested thereafter, and also after a series of heat treatments in which they were cooled at different rates from above their Curie temperatures. The resistivities were, in the order of increasing nickel contents, 37.1, 20.2, and 16.1 microhm-cm.; the density ranged from 95.6 to 94.3%. For the alloys sintered for 24 hours, the magnetic properties were as follows.

Sample	μ_m	B for μ_m, gauss	B_r, gauss (for B = 10,000 gauss)	H_c, oersteds (for B = 10,000 gauss)
50% nickel alloy	6,760	2030	2050	0.19
65% nickel alloy	7,950	1590	1750	0.10
78.5% nickel alloy	12,000	2400	2500	0.10

Heat treatment of the sintered nickel–iron alloys, *i.e.*, cooling at different rates from above their Curie temperature, showed a definite effect of the cooling rate on the initial (μ_0) and maximum (μ_m) permeability values: air cooling or oil quenching approaches the critical cooling rates, whereas water quenching sets up injurious stresses.

Last, Rostoker also studied iron–cobalt alloys containing 30, 40, and 50% cobalt. These alloys are significant, since their saturation magnetizations are about 10% higher than those for pure iron. High-density ring samples produced from —150 mesh electrolytic iron and —200 mesh cobalt powders were sintered at 1400°C. (2550°F.) for up to 24 hours. Their resistivities were, in the order of increasing cobalt content, 13.0, 9.8, and 7.2 microhm-cm.; their densities ranged from 94.2 to 93.3%. For the alloys sintered for 24 hours, the magnetic properties were as follows.

Sample	μ_m	B at μ_m, gauss	μ_0	B_r, gauss (for B = 10,000 gauss)	H_c, oersteds (for B = 10,000 gauss)
30% cobalt alloy	1450	8,600	240	6050	2.4
40% cobalt alloy	1900	7,550	400	6410	2.0
50% cobalt alloy	3720	11,150	600	6950	1.3

Heat treatment involving quenching rates of increasing severity from above the Curie temperature had a similar effect as noted on the nickel–iron samples. Especially the 40% cobalt alloy responded to this treatment to a marked extent, with maximum permeability being doubled by an oil quench. An optimum quench rate was again apparent.

In view of the large field of potential uses of directly molded powder metallurgy products in alternating current machines the development of a soft magnetic material of low eddy-current losses that is more suitable than the iron–silicon alloys appears most desirable. The use of experiences gained in the production of laminated structures in current collector brushes with the aid of flake powders is indicated in developing a magnetic material of directional resistivity.

Parts from Wrought Material. Sintered and rolled iron–nickel alloys obtained by the decomposition of carbonyl mixtures are superior

TABLE 154

Permeabilities of Sintered Iron–Nickel Alloys (Duftschmid, Schlecht, and Schubardt[55])[a]

Magnetizing force, oersteds	Heated 4 hr. at 1100°C. (2010°F.) and slowly cooled: 42% Ni, 58% Fe	Heated 4 hr. at 1100°C. (2010°F.) and slowly cooled: 50% Ni, 50% Fe	Heated 4 hr. at 1100°C. (2010°F.), cooled to 650°C. (1200°F.) and quenched: 78% Ni, 22% Fe
0.005	9,500	8,200	14,700
0.010	13,600	13,250	27,300
0.025	24,200	33,000	80,100
0.050	31,000	55,500	—
0.100	32,000	—	—
Maximum permeability	33,200	56,200	85,900
for magnetizing force, oersteds	0.078	0.056	0.029
and coercive force, oersteds	0.038	0.037	0.021

[a] According to experiments by F. Duftschmid and A. Heinzel, and measurements by F. Bergmann.

to cast alloys of corresponding composition due to their greater purity. In Figure 424 permeability curves are shown for several sintered carbonyl iron–nickel alloys.[54] The magnetic characteristics of such alloys rolled to 0.35-mm. sheet are shown in Table 154. According to Duftschmid,

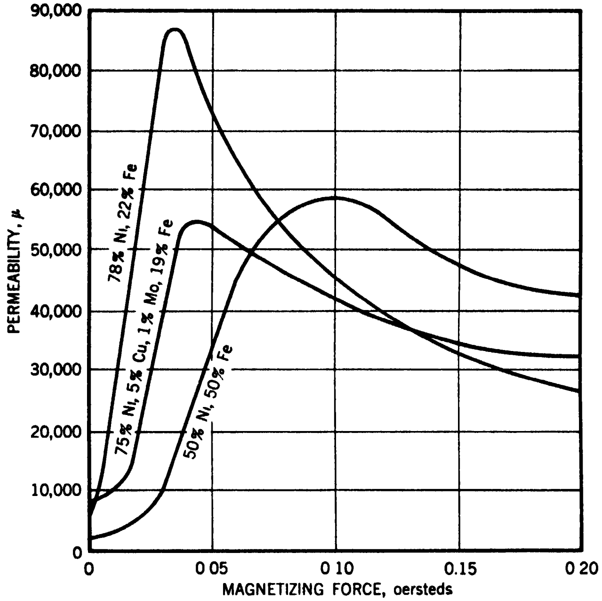

Fig. 424. Permeability curves of three sintered carbonyl nickel–iron alloys (according to Hamprecht and Schlecht[54]).

Schlecht, and Schubardt,[55] the high permeability and comparatively high saturation make these alloys well suited for use in loudspeakers and radio transformers.

HIGH—FREQUENCY CORES

One of the most important applications of metal powders for magnetic purposes is the production of cores for self-inductance coils (loading and filter coils) for alternating current, especially for high-frequency applications in telephone and radio systems. The position of these products in the frequency scale is indicated in Table 155.[56] Coils with cores devel-

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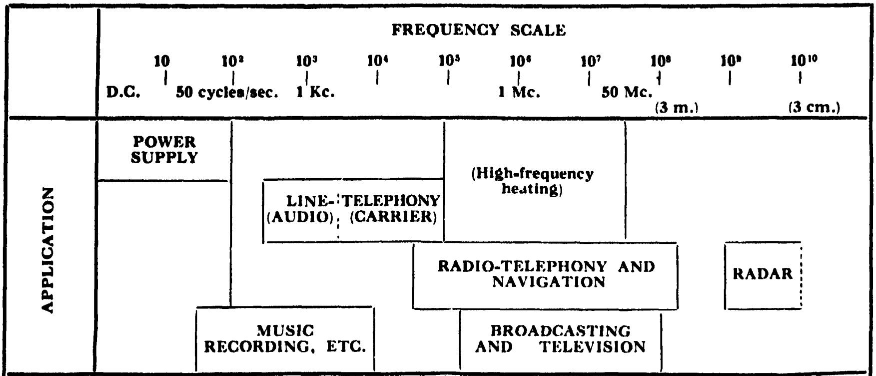
[54] G. Hamprecht and L. Schlecht, *Metallwirtschaft, 12,* 281 (1933).

[55] F. Duftschmid, L. Schlecht, and W. Schubardt, *Stahl u. Eisen, 52,* 845 (1932).

[56] G. R. Polgreen, *Symposium on Powder Metallurgy,* The Iron and Steel Institute, Special Report No. 38, London, 1947, p. 52.

TABLE 155

Magnetic Requirements and Electrical Applications for Frequency Ranges (Polgreen[56])



REQUIRED MAGNETIC PROPERTIES	High permeability 1000-10,000	Powder cores (toroids) of higher permeability up to 120μ	Cores of lower permeability (8 12μ) for fixed inductances	Low permeability
		Low hysteresis and viscosity for telephone applications	Low eddy-current losses	Very low eddy currents and low dielectric loss
		All closed magnetic circuits (toroids)	Open and closed magnetic circuits	Open-magnetic-circuit cores
REMARKS	Stampings most suitable for chief uses		High-permeability (50μ) cores with low eddy-current losses have been developed for variable-inductance units	Mostly in development stage

oped from powders were a considerable improvement over the earlier coils, which consisted chiefly of cores from fine iron wires surrounded by copper wire coils. The modern radio tuning cores are produced by simply compressing suitably insulated metal powder particles without subsequent sintering. Heat treatment below the sintering temperature of the metal powder for the purpose of thermal stabilization may cause a strong bonding between the insulating mass and the metal particles. Fine iron powders of the electrolytic or carbonyl type are used as core material (the latter gaining steadily in importance). Also, fine grades of reduced iron powders have been reported in use for certain special applications. To the latter belong high-voltage transformer cores used in television deflection circuits, which consume about 1.3 pounds per set of combined reduced and electrolytic powders.[56a] Iron powder obtained by a hydro-

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[56a] Anonymous, *Iron Age, 163,* No. 12, 74 (1949).

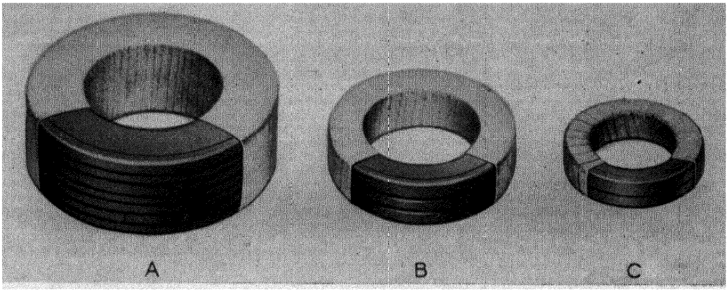

Fig. 425. Relative size of equivalent telephone cores made from electrolytic iron powder (A), Permalloy powder (B), and Molybdenum-Permalloy powder (C) (according to Legg[57]).

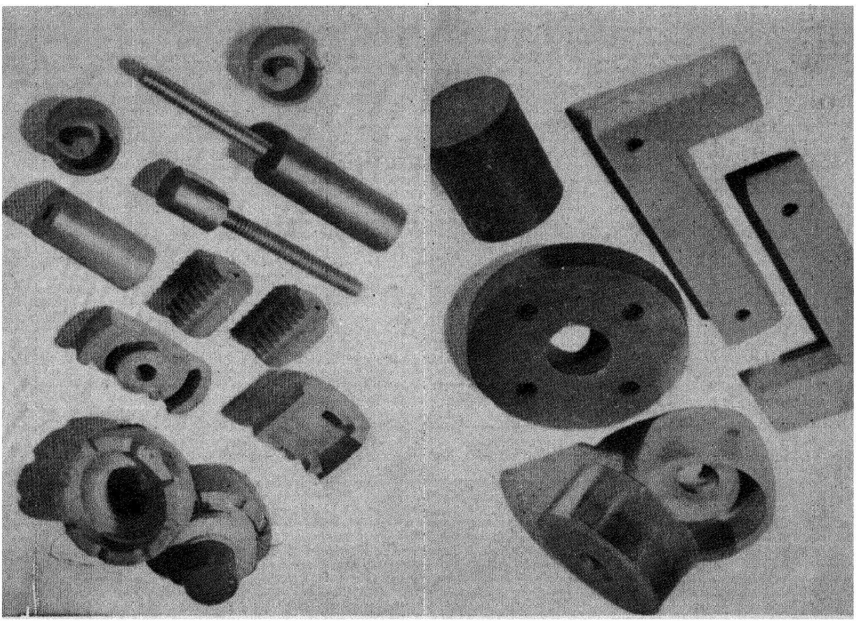

Fig. 426. Assortment of various types of radio cores made from magnetic iron powder (according to Shea[58]).

gen reduction of iron formate (*e.g.*, at 550°C.; 1020°F.) has also been claimed to be satisfactory for dust cores.[56b]

[56b] Brit. Pat. 610,514; see also *Met. Powd. Rept.*, *3*, No. 5, 67 (1949).

Recently, "Permalloy" alloy powders (70–90% Ni, balance Fe) and a variation thereof, "Molybdenum-Permalloy" powders (with 2–5% Mo, 78–81% Ni, and balance Fe), were used successfully along with the plain iron powders for core material. The reduction in size made possible by using the Permalloy powders is illustrated in Figure 425.[57] By using the finely divided magnetic powder whose particles are thoroughly insulated from each other, the eddy currents can be reduced sufficiently to permit operation of the cores in coils functioning over a wide range of frequencies in communication circuits (*i.e.*, from voice frequencies up to millions of cycles per second). Figure 426 illustrates a variety of different radio cores made from magnetic iron powders.[58]

Several recent field investigation reports[58a–d] give considerable details of the production of cores in Germany during the war, including descriptions of the different procedures used for insulating and bonding the individual powder particles.

Magnetic Characteristics. Cores for inductance coils must meet the following magnetic and electric requirements[58e]: (*1*) Eddy-current and hysteresis losses must be kept at a minimum; (*2*) frequency modulation effects produced by hysteresis must be kept to a minimum; (*3*) the permeability must remain constant over the range of inductance (corresponding to the normal range of telephone currents); and (*4*) the permeability must always return to approximately its original value after the application of large magnetizing forces.

Eddy currents are of great significance in practically all alternating current applications and are especially important when high frequencies are involved; their losses are reduced appreciably by insulating films. Insulated and compressed pure iron or Permalloy powders of very small particle size also have the tendency of reducing the modulation effects produced by the hysteresis. The permeability of the cores is a function of the compacting pressure and can be kept constant over a considerable range of magnetizing forces. Figure 427 shows the effect of compacting

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[57] V. E. Legg, *Bell System Tech. J.*, *18*, 438 (1939).

[58] G. Shea, *Electronics Inds.*, *4*, No. 8, 86 (1945).

[58a] F. R. Hensel, F.I.A.T., Final Rept. No. 792 (1947); see also *Met. Powd. Rept.*, *1*, No. 7, 106 (1947).

[58b] H. L. Krebs, F.I.A.T., Final Rept. No. 1101 (1947); see also *Powder Met. Bull.*, *3*, No. 1, 10 (1948).

[58c] British Intelligence Objectives Sub-committee, Final Rept. No. 1203 (1947); see also *Met. Powd. Rept.*, *1*, No. 9, 133 (1947).

[58d] British Intelligence Objectives Sub-committee, Misc. Rept. No. 10 (1917); see also *Met. Powd. Rept.*, *2*, No. 2, 26 (1947).

[58e] H. H. Hausner, *private communication.*

pressure on the permeability of cores from Permalloy powder.[59] The relationship between permeability and hysteresis, eddy-current, and residual (permeability shift) losses is shown for iron and permalloys in

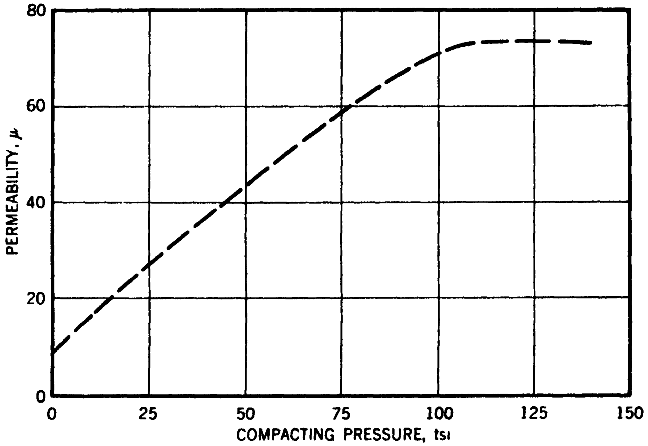

Fig. 427. Effect of forming pressure on permeability of compressed Permalloy (according to Shackelton and Barber[59]).

TABLE 156

Loss Coefficients of Powdered Core Materials (Legg and Given[60])

Material	Permeability	Hysteresis		Residual		Eddy current	
	μ	$\alpha \times 10^6$	$\mu\alpha \times 10^3$	$c \times 10^6$	$\mu c \times 10^3$	$e \times 10^9$	$\mu e \times 10^6$
Grade B iron	35	49	1.7	109	3.8	88	3.1
Grade C iron	26	81	2.1	139	3.6	31	0.8
Permalloy	75	5.5	0.41	37	2.8	51	3.8
	26	11.5	0.30	108	2.8	27	0.7
Molybdenum–Permalloy	125	1.6	0.20	30	3.8	19	2.4
	26	6.9	0.18	96	2.5	7.7	0.2
	14	11.4	0.16	143	2.0	7.1	0.1

Table 156[60]; the low loss coefficients of Molybdenum–Permalloy are significant.

The different core materials react differently at different frequencies. This is shown in Figure 428, where the so-called quality factor "Q" (also known as "energy factor" or "coil magnification factor") is shown as a function of the frequency. "Q" is the usual designation for the ratio of the reactance of a coil to its series resistance:

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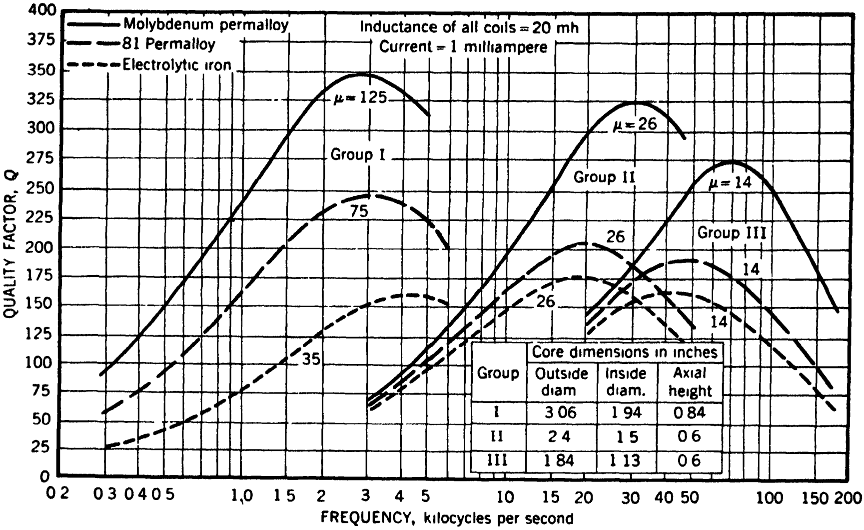
[59] W. J. Shackelton and J. G. Barber, *Am. Inst. Elec. Engrs. J.*, *47*, 429 (1928).

[60] V. E. Legg and F. J. Given, *Bell System Tech. J.*, *19*, 385 (1940).

$$Q = 2\pi f L/R$$

where L is the coil inductance (henries), R is the series coil resistance (ohms), and f is the frequency at which L and R are measured. The Q value will generally increase with increasing coil inductance or frequency and decrease with an increase in coil resistance. An iron core causes an increase in inductance but produces eddy-current and hysteresis losses at the same time, which in turn represent an increase in effective coil resistance. If carbonyl iron is used, and the cores are properly designed,



Group	Core dimensions in inches		
	Outside diam	Inside diam.	Axial height
I	3 06	1 94	0 84
II	2 4	1 5	0 6
III	1 84	1 13	0 6

Fig. 428. Comparative Q-frequency characteristics on typical filter coils made from electrolytic iron, Permalloy (81–19 Ni–Fe), and Molybdenum–Permalloy (according to Legg and Given[80]).

the Q value of the coil may be considerably increased within a specified frequency range. The permeable core material tends to keep the coil resistance low by permitting a high coil inductance with the same number of windings.

Iron Cores. The first compressed iron cores were produced from fine, pure electrolytic iron powders whose particles were insulated from each other by means of surface oxide films and shellac coatings. The powders were compacted at about 100 tsi, followed by drying at 125°C. (260°F.). Cores of this kind were successfully employed for loading coils in telephone circuits, for inductance elements in filters of carrier current systems, and for resistance coils in radio telephone circuits. More recently, carbonyl iron powders have taken the place of much of the electrolytic iron for cores, especially for radio cores. Oxidation of the surface has in most cases given way to coating with plastic insulators (*e.g.*, phenol derivatives).[60a] The type of powder shown in Fig. 429 exhibits a beneficial "shell" structure of each particle which is believed to be the cause for a low electric conductivity of each particle, resulting in very low eddy-current losses. The high purity helps keep the hysteresis losses at a minimum, while the extremely small particle size (more than 80% by weight, from 2 to 7 μ) tends to reduce the eddy-current losses. Because of the spherical particle shape, good insulating effects are obtained with a comparatively small amount of insulating material. The finest grades (80% by weight, from 1 to 5 μ) result in cores having the highest Q values (for high-frequency applications in the range above 3 megacycles) combined with good permeability, and at the same time exhibit extremely

Fig. 429. Sectioned carbonyl iron powder (type "E") showing specific "shell structure" of each individual particle (courtesy of General Aniline Works).

[60a] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe.* Springer, Berlin, 1943, p. 349.

low eddy-current losses due to the small particle size. It is claimed[61] that the hysteresis loss can be reduced by 50% without affecting the permeability when carbonyl iron powder is used that has been ball milled after it has been given several coatings of insulating material. A good summary of the development and present status of cores from carbonyl iron powder has been published by Pfeil,[61a] while Swazy, Busch, and Suggs[61b] described valuable details concerning insulation and binders for the different iron powders used in the cores.

Permalloy Cores. Compressed Permalloy cores surpass plain iron cores in constancy of permeability and low hysteresis and eddy-current losses.[62] The high permeability at low inductions indicates the use of Permalloy cores in small coils with low-resistance windings. An essential feature of the Permalloy cores is that each particle must consist of the Permalloy composition, which means that only *completely* alloyed powders are suitable. This requirement necessitated the development of a special procedure for preparing the powder.[63] Mechanical comminution was feasible only if the fused alloy was artificially embrittled by small sulfur additions, which formed films of complex sulfides in the grain boundaries. Hot-rolled sheets of the embrittled material are readily pulverized in attrition mills, and can, in fact, be reduced to extremely fine sizes which usually do not exceed 15 μ. A final anneal softens the powder sufficiently to permit molding into the cores later on. The application of insulating films (usually of ceramic nature) to the individual particles aids appreciably in suppressing the eddy-current losses. The cores are pressed at about 100 tsi and are generally annealed at low temperatures to remove pressing strains and to restore optimum magnetic properties. (For the effect of molding pressure upon the permeability of Permalloy cores, see Fig. 427.)

Molybdenum-Permalloy Cores. The favorable magnetic characteristics and, in particular, the high permeability and low loss properties are further improved by the use of Molybdenum-Permalloy cores. The production of these alloys[64,65] varies little from that of plain Permalloy. (An exception is a special atomizing process developed in England.[66])

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[61] German Pat. 700,751.

[61a] L. B. Pfeil, *Symposium on Powder Metallurgy,* The Iron and Steel Institute, Special Report No. 38, London, 1947, p. 47.

[61b] E. F. Swazy, L. S. Busch, and A. M. Suggs, *Proc. Fourth Annual Spring Meeting of Metal Powder Association,* Chicago, April 15–16, 1948, p. 51.

[62] S. E. Buckley, *Symposium on Powder Metallurgy,* The Iron and Steel Institute, Special Report No. 38, London, 1947, p. 59.

[63] W. C. Ellis and E. E. Schumacher, *Metals & Alloys, 5,* 269 (1934); *6,* 26 (1935).

[64] E. E. Schumacher, in J. Wulff, *Powder Metallurgy.* Am. Soc. Metals, Cleveland, 1942, p. 166.

[65] V. M. Legg and F. J. Given, *Bell Tel. System, Tech. Pub. Monographs,* 1940, B-123.

[66] Brit. Pat. 587,138; see also *Met. Powd. Rept., 1.* No. 12, 190 (1947).

The particles are usually somewhat coarser (mean diameter 42 μ); their ceramic coatings average 0.5 μ in thickness. The improvements in magnetic properties resulting from the replacement of pure iron by Permalloy or finally by Molybdenum-Permalloy become apparent from Figure 428. The use of Permalloy and, especially, Molybdenum-Permalloy (*e.g.*, "Supermalloy" containing 79% Ni, 5% Mo, 0.5% Mn[67,67a]) cores enables savings in magnetic material as well as in coil wire and space; it also makes possible intricate designs. Core material of a stabilized permeability over a given temperature range is claimed possible by the addition to the insulated Permalloy or Molybdenum-Permalloy particles of a special molybdenum-rich alloy powder (12–13% Mo, 80% Ni, balance Fe) in amounts of 0.2–1.0%.[68]

Miscellaneous Core Materials. Ternary alloys of iron with small amounts of silicon and aluminum (*e.g.* 84–9.5–6.5 Fe–Si–Al), developed in Japan and known under the name of "Sendust,"[69,70] are of interest because of their high magnetic quality and brittle nature which facilitates pulverization of the cast alloy.

Lately, certain nonmetallic ferromagnetic materials, based on solid solutions of cubic nonmagnetic ferrites of zinc and cadmium with cubic magnetic ferrites of iron, nickel, cobalt, manganese, magnesium, or copper have gained considerable interest because of the very high permeabilities coupled with high resistivities (which almost entirely eliminate eddy current losses in certain compositions) that are obtainable.[71-74] Some applications for these cubic ferrites (also known as "Ferrox-cube" materials) are high-frequency transformers, tuning devices, and filters.

Summary

The production of ferromagnetic materials represents a significant powder metallurgy application. Both from a technical and an economical viewpoint, certain types of sintered products have successfully replaced fusion products, and, with further advancement of the field, it may be

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[67] O. L. Boothby and R. M. Bozorth, *J. Appl. Phys., 18,* No. 2, 173 (1947); *Bell Telephone System, Tech. Pub. Monograph* B-1451.

[67a] Anonymous, *Bell Laboratory Records, 26,* No. 3, 111 (1948).

[68] U. S. Pat. 2,393,295.

[69] H. Masumoto, *Science Repts. Tôhoku Imp. Univ., Honda Anniversary Volume,* 388 (Oct. 1936).

[70] G. R. Polgreen, *Symposium on Powder Metallurgy,* The Iron and Steel Institute, Special Report No. 38, London, 1947, p. 52.

[71] J. L. Snoek, *New Developments in Ferromagnetic Materials*. Elsevier, New York-Amsterdam, 1947.

[72] J. L. Snoek, *Philips Tech. Rev., 8,* 353 (1946).

[73] Brit. Pat. 629,031; French Pat. 937,076; U. S. Pat. 2,452,529; 2,452,530; 2,452,531.

[74] Brit. Pat. 594,474; see also *Met. Powd. Rept., 2,* No. 6, 90 (1948).

expected that applications for magnetic purposes will be further broadened in scope. Three distinct types of magnetic products have gained practical importance during the last decade and a half: (*1*) small permanent magnets, particularly of the Alnico type; (*2*) soft magnetic parts from iron powders for direct current applications; and (*3*) compacted ferromagnetic powders for alternating current applications involving high frequencies.

Alnico magnets of small size are produced by sintering. Provided that suitable raw materials are used in the process, magnetic properties comparable with those obtained by the casting technique may be obtained in the sintered magnets. Complete alloying is possible during sintering if the readily oxidizing aluminum component is prealloyed with part of the iron phase by fusion, and if this material is pulverized and added to the other ingredients of the powder mixture. The sintered product can be molded directly to final size and shape, and the dimensions usually held within commercially acceptable tolerances during subsequent sintering; on the other hand, the production by casting of Alnico magnets to close dimensional tolerances is impractical and may be accomplished only by finish grinding. As a result of the finer grain size obtainable in the sintered magnets, the magnetic flux distribution is comparatively more uniform, and the mechanical strength is several times that of cast Alnico. As a rule, magnets weighing up to 1.5 ounces are produced economically from powders.

Soft magnetic products have become a major part of the iron powder parts production. Pole pieces, shunts and armatures for direct current electric motors and generators can be made satisfactorily from iron or iron-alloy powders. The main advantage in molding, sintering, and coining such parts from powders lies in the rapid and economical method of manufacturing and in a greater flexibility of design. The electrical and magnetic properties, though of major importance, do not necessarily have to be superior or even equal to parts made from laminated electrical sheet steel stock. The principal magnetic property that determines the quality of the soft magnetic part is the permeability; this must be high, and uniform from piece to piece, to permit a constant and minimum number of turns for the winding in order to reduce space requirements and resistance losses. Flexibility in design compensates appreciably for a certain loss in permeability caused by the inherent porosity in the sintered product. The soft magnetic materials based on pure iron powders are suitable only for applications in which a constant magnetic field is involved, since in these cases hysteresis and eddy-current losses are only of minor importance. But these losses become significant in larger direct current motors and generators, as well as in armatures of rotating direct current machines, and silicon or other elements may have to be added to the iron to increase the resistance and thereby reduce the eddy-current losses.

For low-frequency alternating current applications, the eddy-current and hysteresis losses become the predominant factors controlling the magnetic performance of the part. In this field, directly molded powder metallurgy products have proved unsuccessful so far, and the road is open for interesting development work.

One particular alternating current application where metal powders have resulted in very satisfactory performance is in the high-frequency range for induction coils in communication circuits. By the use of finely divided ferromagnetic powders, whose individual particles are thoroughly insulated from one another, the eddy-current losses in the magnetic cores are sufficiently reduced to permit operation over a wide range of frequencies. Iron powders of extreme purity and fineness, such as electrolytic or carbonyl powders, or powdered nickel–iron alloys of the Permalloy type, possibly with the addition of several per cent of molybdenum, are particularly suitable as raw materials. The individual particles are coated with a thin film of a plastic, ceramic, or oxide, and the powders are molded under high pressure to form substantially solid cores. Before use in telephone and radio applications, the products are baked to obtain stress relief and optimum magnetic performance.

CHAPTER XXV

Ferrous Materials for Structural Parts

For the fields of applications described earlier the powder metallurgy method produces structures and properties of a special nature that cannot be readily obtained by other manufacturing methods. In the production of machine elements and general structural parts from iron and steel powders, however, there is a great deal of competition with other and long-established methods of fabrication. Only on two counts can the sintered products hope to compete successfully with their machined counterparts. Either they must be *superior* in strength or other physical properties if marketed on the same price basis, or they can be equal or even inferior in physical characteristics, though still satisfactory for the particular purpose, but then must be brought on the market at a *lower* price. It is here that, in the author's opinion, the entire future of the powder metallurgy of iron and steel hinges. Today, the production of ferrous powder parts is at the cross roads. If it should prove possible to obtain comparatively good physical properties through inexpensive methods of manufacture, including tooling, supported by the use of low-priced iron powders, a reduction in engineering and overhead charges, fully mechanized production methods, and, perhaps, radically new processing steps, iron and steel powder metallurgy may rapidly grow into one of the biggest fabrication methods for engineering materials. In that event the consumption of raw material may be measured in terms not of tons, but of tens and possibly hundreds of tons per day, thus amounting to a really significant part of the thousands of tons of iron and steel that are consumed annually for the fabrication of machine parts by countless American manufacturers. On the other hand, it is quite obvious from the record of the powder parts production industry during the war and immediate postwar period that few new fields of application have been opened, and success has been mainly in the direction of expanding the use of sintered ferrous parts in established fields, and boosting their competitive qualities through improved production techniques. The relatively low mechanical quality has so far restricted the use of the sintered material to soft magnetic parts from pure iron powders (see Chapter XXIV), special steel-like porous parts such as certain types of gears requiring wear resistance coupled with antifriction properties (furnished by graphite or other lubricants incorporated in the structure), simple structural or machine parts which are normally produced from cast iron (*e.g.*, wheels and casters), and certain machine or tool parts which possess a desired combination of mechanical or technological advantages unobtainable from cast or wrought metals of similar composition. But the fact remains that the tremendous field of application involving closely dimensioned structural members of all types of engineering machinery remains barred to the powder metallurgist as long as he is unable to custom-mold *economically* on a mass production basis *precision* parts of *higher quality* (especially better strength, ductility, and impact resistance) than so far produced.

The inherent porosity has been generally recognized as the chief cause for the obvious limitations in mechanical quality of the ferrous powder metal parts (for further discussion of this subject see Chapter XXXIII). Thus the tendency prevails to produce parts of maximum density. In practice, however, the so-called "technically dense" parts, though produced without the intention of producing a porous part, may still exhibit a marked degree of porosity—with densities generally being between 80 and 90% of the theoretical value.

The limitations imposed on the molding process by adverse design features are of similar importance. This point has been extensively covered in Volume I, Chapter IX.

It is the purpose of this chapter to review the principal manufacturing methods and properties so far recorded in the powder metallury of iron and steel, to indicate potential applications, and, finally, to point the way for certain developments that should help in the drive to place custom-molded ferrous powder parts in the competitive class, both from the technical and economic point of view. While it is beyond the scope of this book to discuss the economic aspects of the problem to any appreciable extent, it is believed worth while to draw the reader's attention to a novel idea that has recently been presented and may possibly lead to a renaissance of the ferrous parts business. According to Patch,[1] the production of powder metallurgy parts should be considered a self-sustaining process which can readily be incorporated as an independent operational unit by the parts' *consumer*. In other words, the consumer assumes the role of producer in much the same manner as is the case with other processes, such as automatic screw machine, grinding, or heat-treating operations. By applying the "captive plant" principle to the powder metallurgy process, full advantage can be taken of the labor-saving and scrap reduction possibilities of the process, while a more favorable burden rate can be arrived at than if the parts production

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[1] E. S. Patch, *Iron Age, 159,* No. 21, 64 (1947).

remained in the hands of the independent manufacturer. Regardless of the pros and cons which such a new approach will undoubtedly invoke, Patch's idea of the "Parcel-Package Powder Metallurgy Plant" in every medium or large-size metal manufacturing concern is certainly worth serious thought—more so since the presently existing division of *producer* and *consumer* of custom-molded articles appears hardly capable of coping with the desired expansion of the metal powder industry to its potential capacity. An excellent example of a steady development in this direction was recently given by Bonanno,[1a] whose report on the economic and technical aspects of a captive powder metallurgy parts plant in the toy industry appears to be most encouraging.

For a more detailed survey of the economy of production of iron-base structural parts the reader is also referred to a recent publication by Fischer and Seelig.[2]

SINTERED IRON

Sintered pure iron parts are of considerable usefulness for certain applications in the electrical industry (see Chapter XXIV), but due to the inherent softness and weakness of the structure, they are not very applicable for machine parts, except if hardness and wear resistance in certain exposed surfaces are improved by localized alloying (carburizing, siliconizing, chromizing) and heat treatment (see Volume I, Chapters XIX and XX). Nevertheless, a thorough appraisal of the manufacturing methods and properties obtainable with pure sintered iron is most instructive, the more so since the major part of ferrous powder metallurgy is still based on pure iron powders.

Industrial Development

The preparation of compact objects by pressing and sintering iron powders constitutes one of the oldest procedures in powder metallurgy (see Volume I, Chapter II), and sintered iron produced by various methods has been the object of many an investigation since the turn of the century. But only during the middle of the 1930's had the development work in the iron powder field advanced to the extent that production of custom-molded parts from iron powder could be attempted on an industrial scale. In the beginning, a pure, cheap iron powder was made from Swedish sponge iron, but the supply of this material was cut off at the beginning of the war, and domestic brands had to be used instead. Scrap steel is today the principal raw material for iron powders. With the end

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[1a] J. L. Bonanno, *Proc. Fifth Annual Spring Meeting of Metal Powder Association,* Chicago, April 4–5, 1949, p. 74.

[2] H. W. Fischer and R. P. Seelig, *Powder Met. Bull., 2,* No. 6, 128 (1947).

of World War II, the Swedish powder has also reappeared on the American market. Until the entry of the United States into the war, iron powder was used mainly for bearings, gears, cams, and miscellaneous parts containing an appreciable degree of porosity (rendering the part resistant to wear or corrosion by filling the pores with oil). One application of particular interest was found in the textile machinery, where corrosive conditions precluded the use of copper-base alloys, and where internal lubrication was required to avoid contamination of the fabrics with lubricating oil.

The direct molding of iron powder parts was found advantageous in many ways. Important scarce stock materials, as well as machining time, were saved; the manufacturing methods could be simplified and readily geared to large-scale production; surface smoothness and comparatively close tolerances became fundamental properties of the products. Eventually, molding techniques could be perfected to such a degree that certain, comparatively complicated shapes, including irregular curves and holes, eccentrics, recesses, keyways, splices, or radial projections could be molded more readily than they could be machined. In general these sintered iron parts compared well in physical properties with low-grade cast iron, but a considerable range in properties could be obtained by proper selection of raw material and treatment. Grading of parts from iron powder into three classes, according to their specifications for chemical composition and density, has been suggested by Lenel[3,4] and Langhammer:[5]

Type A: Materials having mechanical properties similar to ordinary cast iron. Minimum total iron content 95%, containing up to 2.5% C. Minimum density 5.4 g./cc. (75% of cast iron). Only suitable for applications where stresses are very low.

Type B: Materials similar to Type A but having improved tensile strength, a definite yield point, and a noticeable elongation. Minimum total iron content 97.5%, maximum total carbon content 0.4%. Minimum density 5.8 g./cc. (75% of fused pure iron). Suitable for application where stresses are moderate, but impact stresses are low.

Type C: Materials having mechanical properties approaching ordinary malleable iron. Minimum total iron content 98.5%, maximum total carbon content 0.2%. Minimum density 6.5 g./cc. (82.5% of fused pure iron). Suitable for applications where stresses, including impact, are moderate.

In materials of Type A, carbon could be added to the powder mixture in the form of graphite and allowed to combine with the iron during sintering, or could be partly or fully contained in combined form in the original particles (steel or cast iron powders). Further reference to these

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[3] F. V. Lenel, *Metallurgia, 28,* No. 166, 189 (1943).

[4] F. V. Lenel, *Mech. Eng., 65,* 489 (1943).

[5] A. J. Langhammer, in *Symposium on Powder Metallurgy.* ASTM, Philadelphia, Pa., 1943, p. 23.

materials will be made when discussing sintered iron–carbon alloys (p. 344).

During the war, increased production requirements produced a certain effect on iron part production; rigid physical specifications suggested the addition of a fourth class of iron powder parts with mechanical properties equivalent or slightly superior to those of malleable iron. The stipulated chemical requirements of a minimum total iron content of 99% and a maximum total carbon content of 0.1%, coupled with a minimum density of 7.0 g./cc. (89% of fused pure iron), made the use of electrolytic iron powders mandatory. The specification failed to be generally endorsed by the parts-producing industry, since the approach appeared to be prohibitive for the mass production of machine parts from the viewpoints of powder cost and quantities available. Moreover, the comparatively high density requirements would have necessitated molding and coining at high pressures (leading to considerable die and tool wear) and sintering operations at high temperatures, which, in turn, would have constituted an additional technical and economic burden. For these reasons, materials falling in the last class have so far been used almost exclusively for certain soft magnetic parts requiring high permeability and low hysteresis losses (see Chapter XXIV).

The most spectacular development of iron powder metallurgy took place during World War II in Central Europe because of the manufacture on a huge scale of paraffin-impregnated rotating iron bands for various sized shells. The production of up to 3500 tons per month of these bands[5a] during the peak era was only possible by employing inexpensive types of powders that could be produced and handled on a scale never before encountered by the powder metallurgy industry. It became obvious that mechanically comminuted or fusion-disintegrated types of powder were resorted to for the most part in spite of their inferior forming characteristics as compared with the more plastic reduced sponge iron types. While repeated reference to the mechanically comminuted (Hametag) and liquid-disintegrated (DPG-rotating disk) or atomized (RZ) powders have been made in Volume I (pages 40 to 45), and some of the characteristics of the products made from these powders will be described later in this chapter, a full discussion of this particular phase of iron powder metallurgy is not possible in this book. In addition to the individual references, the reader interested in this development is referred to the comprehensive presentation of the subject in the recent book by Kieffer and Hotop.[5b]

[5a] G. J. Comstock, *Communication at Powder Metallurgy Colloquium,* New York University, April 26, 1946.

[5b] R. Kieffer and W. Hotop, *Sintereisen und Sinterstahl.* Springer, Vienna, 1948, pp. 21–35.

Manufacture of Iron Parts

Manufacturing methods for iron powder parts are by now well established.[6–8] It may therefore suffice to stress only the principal steps involved. For further details the reader is advised to consult those sections of Volume I dealing with iron powder metallurgy (especially Chapters III and VI on domestic powder production and specifications; Chapter IX on design of iron powder parts; and Chapters XIX and XX on heat treating and finishing).

RAW MATERIAL

In the main, four principally different types of iron powder have been found suitable for parts production in the United States: (*1*) reduced Swedish sponge iron; (*2*) reduced domestic iron powder; (*3*) decarburized steel and cast iron shot or scrap; and (*4*) electrolytic iron powder. In Germany, powders obtained by atomizing and liquid disintegration have been used widely during the war. Carbonyl iron powders—in this country as well as abroad[9]—have been employed only for the manufacture of magnetic cores.

The Swedish iron powder is obtained by direct reduction with charcoal of extremely pure magnetic ore concentrates. The type available on the United States market before the war combined the advantages of low price (about 8 cents per pound on a tonnage basis) with good molding characteristics. Low carbon content and almost complete lack of other alloying ingredients (Mn and Si) have been considered to be mainly responsible for the plasticity of the iron particles, in spite of the presence of noticeable oxide films surrounding them. The powder that is now imported from Sweden shows an improvement in purity (lower oxygen content) without a departure from the prewar cost level. This fact makes Swedish powder one of the most important raw materials in the iron powder parts industry in this country.

Domestic iron powders have been available in quantity since 1940; they are produced almost exclusively today by gaseous reduction (with carbonaceous atmospheres or hydrogen, sometimes preceded by prereduction with solid carbon or gases containing carbon monoxide or hydrocarbons) of pulverized rolling mill or hammer scales, or of pulverized, oxidized steel sheet scrap (*e.g.*, from tin cans). The inexpensive grades

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[6] Anonymous, *Machinery, (N. Y.), 48,* No. 12, 111 (1942).

[7] P. Schwarzkopf and C. G. Goetzel, *Metal Progress, 49,* 539 (1946).

[8] U. S. Pat. 2,411,073. (This specification can be considered an excellent summary of the manufacturing principles underlying the powder metallurgy of iron and steel.)

[9] H. L. Krebs, Field Information Agency, Technical (F.I.A.T.) Final Report No. 1101, Apr. 29, 1947); U. S. Dept. of Commerce, Office of Publ. Board, P.B. 78,996.

obtained by carbon reduction compare in price with the Swedish material, but are generally inferior in chemical analysis and physical performance. Grades equaling the Swedish powder in purity or plasticity, or both, exceed the price range of the latter by about 50% (10–12 cents per lb.), while the best domestic grades are superior to the imported material, but cost nearly twice as much (14–16 cents per lb.). The domestic powders are available, however, in a considerable variety of properties (*i.e.*, size range, purity, apparent density, and particle plasticity), so that a selection of a definite type for a specific purpose is possible. Thus, powders of high apparent density and moderate compactibility are generally used for the mass production of simple prismatic parts for which quick loading and large production rates are most essential. Powders of lower apparent density and very good compactibility are required for the molding of parts of complicated shapes (*e.g.*, having curved faces or axial projections).

Iron powders produced by decarburizing crushed steel, cast iron scrap, or cast iron shot are distinguished by their compact, rugged or near-spherical particles, and compare unfavorably with reduced sponge-like powders as far as ease of molding is concerned. They have found use for special structures as, for example, where controlled pore volume and pore distribution are needed for impregnation (*e.g.*, with oil or lead).

Powders produced by electrolysis resemble decarburized steel powders in many respects. Common grades have a comparatively high apparent density. The purity, however, is of the highest order. Depending on details of manufacture, the particles are either fernlike, flaky and nodular, or solid and globular. Accordingly, the compactibility varies; powders composed chiefly of particles of the first kind often resist compaction and tend to form laminar products, while powders containing primarily the second kind of particles usually display excellent compressibility and high green strength.[10] Large-scale production capable of yielding 10 to 12 tons of powder per day has recently been reported[11] to take place at the Pacific coast[12] (the process involves dissolving about 36,000 tons a year of machine shop steel scrap in an acidic ferric chloride solution from which the iron is electrolyzed and deposited on stainless steel cathodes).

Atomized iron powders were developed during World War II as a major source of material in Germany, and the best-known type, known as RZ-powder, was used in considerable quantities in the production of the porous iron driving bands. In contrast to other processes, a low-melting iron–carbon alloy was used as a starting material, and atomiza-

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[10] H. V. Trask, *Metal Progress, 50,* 279 (1946).

[11] Anonymous, *Internatl. Industry, 28,* 349 (July 1947).

[12] W. J. Granberg, *Iron Age, 160,* No. 26, 70 (1947).

tion was performed under controlled *oxidizing* conditions, so that in a subsequent heat treatment the powder could be freed from carbon and oxygen simultaneously.[12a] Centrifugally disintegrated iron powders produced by passing a molten stream of iron–carbon alloy over a rotating mechanical disk[12b,c] (see Volume I, Chapter III) were also used in large quantity by the Germans in the production of porous iron driving bands during the war.[13] The powder, generally known as "DPG" powder, was usually mixed with up to an equal portion of mechanically disintegrated, eddy-milled powder of the "Hametag" type[14] (see also Volume I, Chapter III) and with up to 20% sponge iron. The former addition was made to increase the production volume, the latter to improve the poor compactibility. Figure 430*A–D* shows the particle shape of the four different types of powders used in the process.[15] The solid structure of the atomized and liquid-disintegrated powder particles, and the disk-shaped contours of the eddy-milled particles make a thorough annealing and purifying treatment before use mandatory. This treatment, usually performed in wet hydrogen at 700–900°C. (1300–1650°F.), has the main purpose of reducing both the carbon and oxygen content of the powders from about 2–3% each to less than 0.5% total, and of transforming the particle surfaces into spongy, plastic, soft iron skins. According to recent reports,[15,16] the atomized and milled powders have been retained as major sources of supply for the postwar iron parts production in Central Europe.

A survey of the present-day methods of manufacturing iron powder, the raw material requirements, and the economic aspects (*i.e.*, power and coal consumption, labor, and installation costs), with special reference to wartime and post-war conditions prevailing in Germany, has recently been published by Buchholtz.[16a]

The commercially available iron powders are usually given a conditioning treatment before molding, as discussed in detail in Volume I, Chapter VII. Blending of parts of different shipments results in a homo-

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[12a] G. Naeser, *Proc. International Powder Metallurgy Conference,* Graz, July 12–17, 1948, Referate No. 5a.

[12b] F. Rapatz and F. Schmidt, *Proc. International Powder Metallurgy Conference,* Graz, July 12–17, 1948, Referate No. 37.

[12c] H. Timmerbeil, *Proc. International Powder Metallurgy Conference,* Graz, July 12–17, 1948, Referate No. 9.

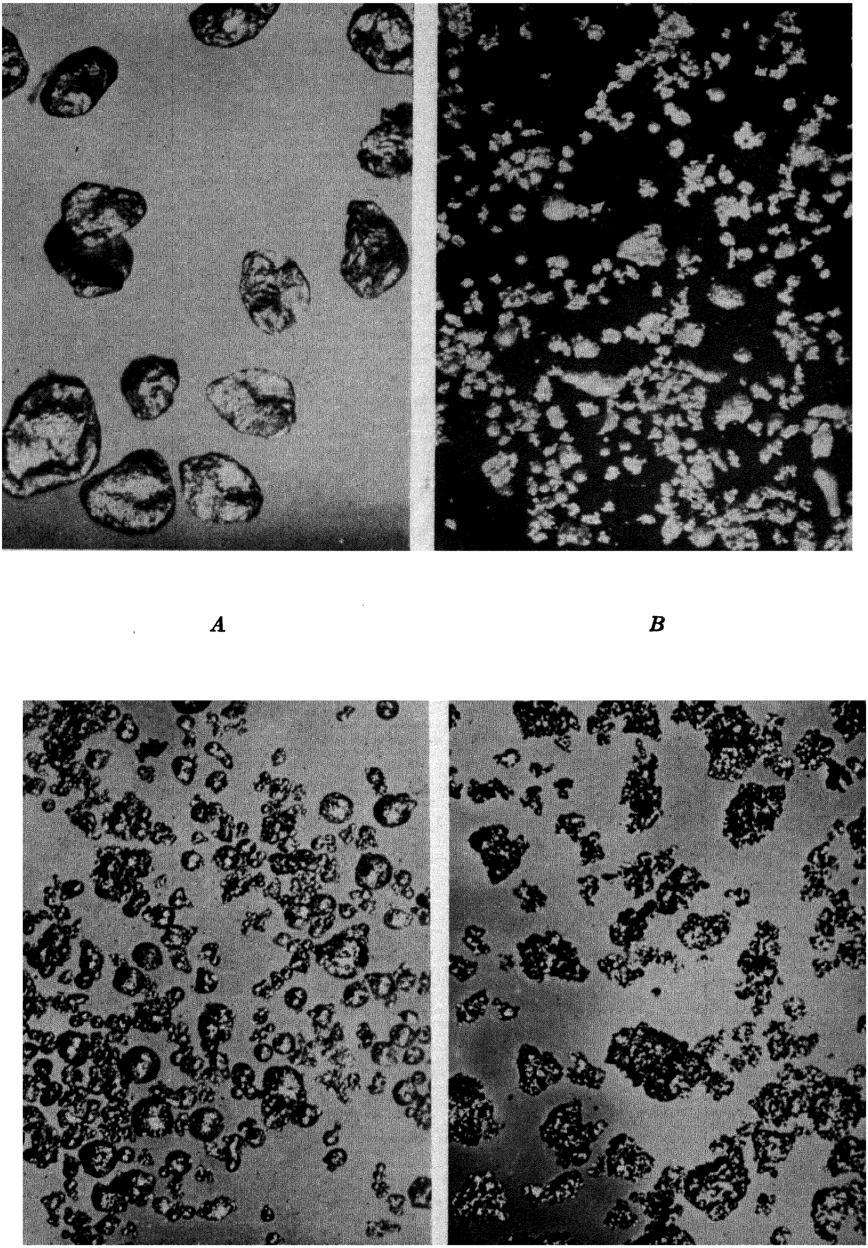
[13] G. M. Butler, U. S. Dept. of Commerce, Office of Publ. Board, P.B. 1834; Combined Intelligence Objectives Sub-committee (London), 21, XXX-8, 13 (1946).

[14] U. S. Dept. of Commerce, Office of Publ. Board, P.B. 63,061; British Intelligence Objectives Sub-committee, Final Report No. 908. See also *Powder Met. Bull.,* *2,* No. 4, 93 (1947).

[15] R. Kieffer, F. Benesovsky, and H. J. Bartels, *Powder Met. Bull., 2,* No. 3, 54 (1947).

[16] R. Kieffer and W. Hotop, *Sintereisen und Sinterstahl.* Springer, Vienna, 1948, pp. 380, 403.

[16a] H. Buchholtz, *Stahl u. Eisen, 69,* 247 (1949).



A *B*

C *D*

Fig. 430. Particle shape and appearance of German commercial iron powders (×22) (according to Kieffer, Benesovsky, and Bartels[15]): *A*, eddy-milled powder, screened—particle size 400–500 μ; *B*, liquid-disintegrated ("DPG") powder, screened—particle size 10–200 μ; *C*, atomized powder, screened—particle size 10–300 μ; *D*,

geneous, reproducible powder mix from which production allotments are drawn. It is common practice to add a small proportion of a nonmetallic lubricant to the powder to facilitate briquetting. In certain cases (*e.g.*, Swedish powder) a low-temperature hydrogen-annealing treatment may precede the mixing operation. The losses in carbon, sulfur, and oxygen during such a treatment have been investigated by Hüttig and Sedlatschek.[17]

Two interesting conditioning treatments have recently been reported. One affects the flow characteristics of the powder; by coating the particles with a water-repellent substance (*e.g.*, methyl chlorsilane vapors) the flow rate is markedly improved without impairing the final properties of the sintered metal.[18,19] The other treatment relates to shrinkage control during sintering, which is especially difficult with chemically produced powders, *e.g.*, reduced oxides or carbonyl iron. Whereas the common expedients of preheating in hydrogen and prepressing followed by pulverization proved inadequate, rolling of the powder into strips of a maximum thickness of 1 mm. and repeat-rolling of several superimposed strips followed by grinding was found successful.[20] Carbonyl powder compacts from materials treated in this manner showed a shrinkage of less than 1% after sintering at 1200°C. (2190°F.), as compared with a shrinkage of 23% for the untreated powder.

MOLDING

The molding of metal powder parts has been discussed in detail in Volume I, Chapter IX. Iron powder parts are molded conventionally in automatic machines at pressures ranging from 25 to 50 tsi with production rates varying from about 5 to 50 pieces per minute. Parts of more intricate shape are preferably pressed at pressures near the lower limit but must be molded into a shape sufficiently strong for subsequent handling. Pressures near the upper limit are necessary if strong and dense compacts are required, or if powders of poor compactibility must be used. Both mechanical and hydraulic presses are used for the molding of iron parts, the former generally preferred for low-pressure applications. The mechanical presses (and lately also some of the hydraulic machines) are equipped

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[17] G. F. Hüttig and K. Sedlatschek, *Powder Met. Bull.*, *2*, No. 4, 80 (1947).

[18] A. Squire, *Watertown Arsenal Lab. Rept. WAL 671/25* (June 1, 1945); U. S. Dept. of Commerce, Office of Publ. Board, P.B. 30277; see also *Met. Powder Rept.*, *2*, No. 3, 38 (1947).

[19] A. M. Burghardt and E. M. Rubino, *Watertown Arsenal Lab. Rept. WAL 671/34*; U. S. Dept. of Commerce, Office of Publ. Board, P.B. 39590; see also *Powder Met. Bull.*, *2*, No. 2, 38 (Mar. 1947); *Met. Powder Rept. 2*, No. 3, 41 (Nov. 1947).

[20] British Intelligence Objectives Sub-committee, Doc. F. D. 1765/46; *Met. Powd. Rept.*, *1*, No. 5, 69 (1947).

with automatic feeding devices for mass production operation. For precision work requiring very close weight tolerances, manual feeding of the powder into the die cavity may be preferred; the individual allotments must then be weighed rapidly and accurately (for details see Volume I, Chapter XI). Where parts with several axial projections or steps are involved, each section must be molded correctly and to a density equaling that of the entire part, since failures will otherwise occur. Each of these sections is molded individually by employing multiple, sometimes telescoping, punches that may be moved by individual drives of the press (for details see Volume I, Chapters IX and XI). Another method frequently employed involves the use of dies with spring-loaded members which permit the proper location of the powder during filling of the die cavity and the shift or transfer of the powder into the desired sections during molding. Double-action presses or spring-floated dies apply uniform compression from top and bottom. Uniform filling of the die cavity is essential in order to obtain reproducible size or density. Vibrating feed-shoes or pulsating press tools are frequently necessary to produce this result.

SINTERING

After being molded, the iron powder parts are usually sintered in continuous furnaces under controlled atmosphere. Gas-heated or electric furnaces of the type employed in brazing practices are used with a partially burned natural gas or hydrocarbon atmosphere, or with dissociated ammonia (see also Volume I, Chapters XVI and XVII). Both for the sake of economy and in order to control the amount of shrinkage in the parts, the time of heating is usually kept short, rarely exceeding one hour at maximum heat. In order to obtain sufficient consolidation, a high sintering temperature is essential; its maximum is given by the temperature limitations of the heating elements or the alloy material used for the furnace retort. European practice[21] involves sintering in molybdenum resistor furnaces, as shown in Figure 431, at 1000–1200°C. (1830–2190°F.). In the United States commercial sintering of iron parts is usually carried out at a temperature ranging between 1050 and 1150°C. (1920 and 2100°F.). The rate of heating the compacts to maximum temperature has a certain effect on the dimensional changes occurring during sintering. Rapid heating may result in distortion or growth caused by the spontaneous escape of trapped air or volatilizing lubricants. Therefore, slow heating and, possibly, drawing at moderate temperature (*e.g.*, red heat) prior to heating to maximum sintering temperature are often re-

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[21] R. Kieffer, F. Benesovsky, and H. J. Bartels, *Powder Met. Bull.*, *2*, No. 3, 54 (1947).

sorted to. In fact, it may even be advantageous to remove the harmful gases in an independent presintering operation. The rate of cooling is of no particular significance for very pure iron compacts, and cooling in water-jacketed chambers attached to the furnace muffle is sufficient, provided that the parts remain protected from contact with the oxygen of the air until they are quite cold. If carbon is a major impurity in the iron, slow cooling may become necessary to render the part sufficiently plastic to withstand subsequent sizing, coining, or finishing (machining) operations.

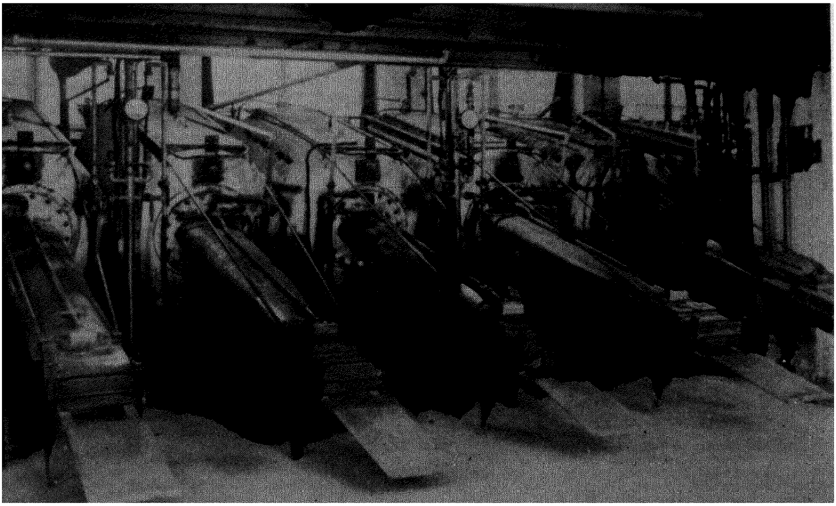

Fig. 431. Battery of pusher-type incline molybdenum resistor furnaces operated at 1000–1200°C. (1830–2190°F.) in the sintering of iron parts (according to Kieffer, Benesovsky, and Bartels[21]).

SUBSEQUENT OPERATIONS

Even though the shrinkage of sintered iron parts may be closely controlled and often kept to less than 0.5% of any linear dimension, precision parts require further sizing. This operation may simply deform the surface sufficiently to produce the required dimensional accuracy without affecting the internal structure. It is accomplished by forcing the part through sizing dies in mechanically operated presses.

For dense and strong iron parts, additional densification is achieved by cold coining. Dies are usually of simpler construction than used for molding, since no powder transfer problems have to be considered, and densification is obtained by simple axial compression. But because of the rigidity of the sintered iron structure, high specific pressures are usually necessary (*e.g.*, 40 to 80 tsi), which in turn require strong die and tool constructions. Hydraulic presses are used to good advantage for larger-size parts; small and medium-size parts (up to about two square inch cross-sectional area) are coined in heavy mechanical punch presses as shown in Figure 432 (see also Volume I, Chapter XI).

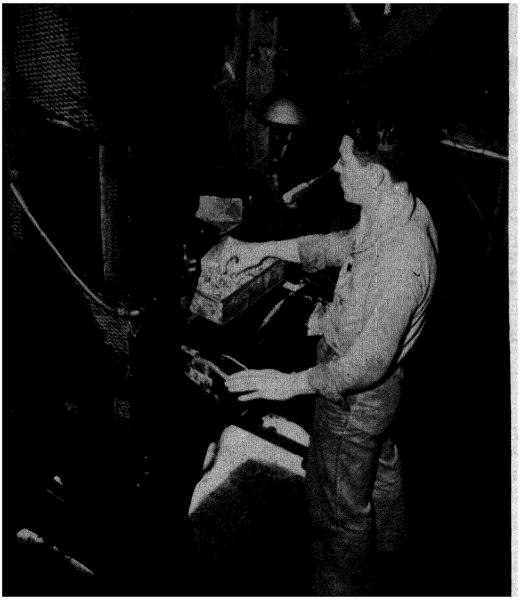

Fig. 432. Automatic coining of sintered iron centering buttons for universal joints in 75-ton mechanical punch press (courtesy of American Electro Metal Corp.).

Heat treatments for the purpose of stress release and annealing are usually necessary for parts severely work hardened during coining. If the treatment is conducted at temperatures above the alpha–gamma transformation, shrinkage will again be considerable and a subsequent second sizing may become a necessity.

Sintered iron parts are usually finished by simple cleaning or machining operations. Deburring (by tumbling or belt grinding of edges) and broaching or reaming of cored holes are most common operations; so are drilling of lateral bore holes or machining of lateral grooves or recesses. Machining of sintered pure iron is more difficult than that of bar stock, and special tools and procedures are often required. Due to the inherent porosity, sintered iron parts tend to rust strongly, and rust proofing of the exposed surfaces is indicated (for details concerning the finishing of parts see Volume I, Chapter XX).

Properties of Sintered Iron

The influence of the type of powder and the various processing conditions on the structure and properties of pure iron compacts has been extensively studied by a number of investigators, and much interest is still concentrated on this problem. In fact, a rather comprehensive investigation has been reported in England by Leadbeater, Northcott, and Hargreaves.[22] These investigators made an attempt to correlate iron powder characteristics with the ultimate properties of sintered compacts, and much attention was given to standardization and development of testing methods. The standardized powder testing methods were applied to 28 commercial iron powders, and correlation coefficients were established on the basis of statistical analyses according to the formula:

$$r = \frac{\Sigma\,(x - \bar{x})\,(y - \bar{y})}{\sqrt{\Sigma\,(x - \bar{x})^2\,(y - \bar{y})^2}}$$

where r is the correlation coefficient, x and y are single values of two variables, $\bar{x}$ and $\bar{y}$ are the average values of all the data for the two variables, and $\Sigma(x - \bar{x})$ and $\Sigma(y - \bar{y})$ are the sums of the individual deviations from the mean values. Coefficients derived by this formula can range between +1 and −1 with a positive value for r indicating that one factor increases simultaneously with the other, whereas a negative value for r generally indicates that one factor increases while the other decreases. It is important, however, to consider that Leadbeater, Northcott and Hargreaves found that no casual relationship exists for any one combination of properties, since many factors usually affect any one final property.

EFFECTS CAUSED BY POWDER VARIABLES

The sintering of loose carbonyl powders was studied by Schlecht, Schubardt, and Duftschmid[23] and by Delisle.[24] Microscopic examination indicated two types of effects: those limited to individual particles, such as rounding of particle shapes and intraparticle recrystallization at low

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[22] C. J. Leadbeater, L. Northcott, and F. Hargreaves, *Symposium on Powder Metallurgy*. The Iron and Steel Institute, Special Report No. 38, London, 1947, p.15.

[23] L. Schlecht, W. Schubardt, and F. Duftschmid, *Z. Elektrochem., 37,* 485 (1931).

[24] L. Delisle, *Steel, 115,* No. 12, 131 and 154 (1944); *Trans. Electrochem. Soc., 85,* 135 (1944).

temperatures; and effects concerning several adjacent particles, such as surface bonding and grain growth at higher temperatures. With rising temperatures the density of the powder increases over the range of 400 to 900°C. (760 to 1650°F.); a decrease in density for increasing temperatures up to about 1000°C. (1830°F.) must be attributed to the alpha–gamma transformation; a renewed increase in density takes place if the temperature is raised to 1300°C. (2370°F.), with grain growth becoming apparent. Complete consolidation, however, is only accomplished by a subsequent cold- or hot-working operation.

TABLE 157

Effect of Method of Powder Manufacture on Iron Powder Characteristics (Dawihl and Schmidt[25])

Powder	Powder characteristics	Particle diameters, microns	Particle shape	Apparent volume, cc./100 g.	Carbon, %	Oxygen, %	Insoluble in HCl, %
I	Fine eddy powder, prepared by eddy-milling sheet material	5–40	Irregular, dense	50	0.23	1.22	0 10
II	Coarse eddy powder, prepared by eddy-milling sheet material	100–500	Irregular, dense	48	0.11	0.38	0.21
III	Stamped powder, prepared by stamping wire	200–600	Flaky	282	0.81	1.84	0.47
IV	Reduced powder, prepared by reducing oxide in H_2 at 600°C. (1110°F.)	0.5–2	Acicular	123	0.10	3.95	0.33
V	Pressure-reduced powder, prepared by reducing Swedish ore in H_2 under pressure at 550°C. (1020°F.)	15–70	Angular, porous	47	0.08	3.87	0.92
VI	Sponge powder, prepared by reducing ore with carbon and subsequent mechanical comminution	100–500	Irregular, spongy	46	0.08	1.20	0.67
VII	Atomized powder, prepared by directing a stream of liquid metal against a rotating disk	10–30	Spherical	32	0.03	1.75	0.24

The extent to which the method of powder production affects certain properties of sintered iron compacts was investigated by Dawihl and Schmidt.[25] Seven different powders were studied; they included three milled or stamped powders, three reduced powders and one atomized powder. Table 157 gives the physical and chemical characteristics of each of the powders. The effect of sintering temperature on the porosity of the powders compacted at 37 tsi is indicated in Table 158, which also

TABLE 158

Effect of Powder History on Porosity, Microstructure, and Microhardness of Sintered Iron Compacts Compressed at 37 Tsi (Dawihl and Schmidt[25])

Powder	Volume of pores in per cent, unsintered	Volume of pores in per cent, sintered at:					Linear shrinkage, %, at
		600°C. (1100°F.)	800°C. (1470°F.)	1000°C. (1830°F.)	1200°C. (2190°F.)	1450°C. (2640°F.)	1450°C. (2640°F.)
I	50	48	44	32	21	4	17
II	25	25	25	25	21	11	3
III	37	37	37	37	30	12	9
IV	44	38	11	11	11	9	16
V	39	39	38	37	35	17	10
VI	32	32	32	32	30	13	5
VII	28	28	28	28	25	7	8

Microstructure after sintering at 1450°C. (2640°F.)

Powder	Pore distribution	Pore size	Grain shape	Grain size distribution
I and II	Uniform	Fine	Polygonal	Uniform
III	Laminar structure		Longitudinal	Uniform
IV	Uniform	Medium	Polygonal	Uniform
V	Uniform	Very coarse + fine	Angular with sharp corners	Very wide distribution
VI	Irregular	Coarse + fine	Irregular with smooth corners	Wide distribution
VII	Uniform	Medium	Polygonal	Uniform

Microhardness

Material	Hanemann microhardness				
	Powder		Compact sintered for 2 hr. at 1400°C. (2550°F.) after compacting at		Forged and annealed
	Original	Annealed at 700°C. (1290°F.)	7 tsi	43 tsi	
I and II	100	95	115	132	135
III	—	—	200	200	153
IV	—	—	153	185	—
V	—	—	129	170	123
VI	120	120	125	157	126
VII	98	98	112	129	134

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[25] W. Dawihl and U. Schmidt, *Stahl u. Eisen, 65,* 9 (1945).

lists the microscope findings on compacts sintered at 1450°C. (2640°F.), and the microhardness of the original powders and the sintered and subsequently worked compacts. The values have only relative importance, since the tester used did not record absolute values,[26,27] but they indicate that stresses are produced by grain growth taking place during sintering. This was confirmed by x-ray diffraction measurements which also indicated the presence of stresses—even after sintering the compacts for two hours at 1450°C. (2640°F.). The method of powder manufacture also influenced the ductility and susceptibility to plastic deformation in subsequent swaging or bending, the results being in good agreement with the microhardness tests. Thus, the differences in the original powder which were due to the different production methods were still reflected in the microstructure, microhardness, and ductility of the sintered compacts, even after sintering at 1450°C. (2640°F.).

The effect of particle size distribution on the final properties of iron powder compacts has been studied by Kuzmick and collaborators.[28] The tests were made on four domestic iron powders, two of the electrolytic and two of the oxide-reduced types. Each powder was separated into three different screen fractions (—100 +150, —150 +200, —200 +325 mesh), and into three different subsieve fractions, corresponding to an average particle size of 37, 25, and 15 microns. Each fraction, as well as the original powder, was tested for apparent density, flow, and oxygen content [hydrogen loss at 1100°C. (2010°F.), for 30 minutes] before being compacted at 25 and 50 tsi and sintered in purified hydrogen at 1100°C. (2010°F.) for 30 minutes. The test results indicate that, in general, shrinkage and tensile strength increases with decreasing particle size, while apparent density and compressibility compensate for each other to the extent that both green and sintered densities are little affected by the particle size of the powder. But the true effect of particle size is believed masked by the fact that such factors as cold working during the manufacture of the powder, as well as the individual density and shape of the particles, are not sufficiently considered. Also in agreement with common experience is the observation that the subsieve fractions have a very great effect on the properties of the original powder, which in turn points to the need for careful control of the size distribution of the —325 mesh powder fraction.

A study of the effect of particle size distribution on the physical properties of pressed and sintered iron powders has been reported by

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[26] H. Hanemann and E. O. Bernhardt, *Z. Metallkunde, 32,* 35 (1940).

[27] H. Hanemann, *Metallwirtschaft, 21,* 315 (1942).

[28] J. F. Kuzmick, J. D. Shaw, C. L. Clark, T. W. Frank, W. V. Knopp, and A. S. Margolis, *Iron Age, 158,* No. 23, 72; No. 24, 76 (1946).

Rostoker.[29] In this work a special technique of packing mixtures of selected sizes was used. A 25-cc. graduated glass cylinder mounted on a rubber-cushioned electromagnetic vibrator plate was filled with the test mixture and exposed to a vertical vibration until constant volume was reached (approximately 30 seconds). Compacting at 30 and 50 tsi was followed by sintering in purified hydrogen for 1 hour (plus the 10 minutes required for the charge to reach temperature) at different temperatures ranging from 850 to 1400°C. (1560 to 2550°F.). The results concerned with the relationship between packed densities and physical properties of the compacts are of special interest. Mixtures that *pack* to higher densities do not necessarily *press* to higher densities, and the effect of packing is apparently overshadowed by the effects of plastic flow. No correlation between packing ability of the powder, and any of the measured physical properties of the sintered compacts (density, tensile strength, etc.) could be established. It was concluded that the particle size distribution for any given sintering temperature must be a compromise between the desirable features of the coarse, medium, and fine size fractions. Work hardening during compaction, which is more pronounced in finer particles, reduces the pressed (green) density, but has a beneficial effect on diffusion during sintering. At low sintering temperatures, the effect on diffusion is predominant, and fine sizes sinter more rapidly. At higher temperatures the effect of work hardening during pressing becomes the determining factor, and sintering proceeds faster with coarser sizes. This conclusion, however, does not appear entirely justified, since it fails to take into consideration the more pronounced annealing and grain growth effects at the higher temperatures.

Measurements of the electrical resistivity of iron and iron-base powder compacts have also disclosed a relationship between the type of powder and the ultimate properties. Based on studies by Kantorowicz[30] and Skaupy and Kantorowicz[31] of the changes taking place in metal powders during compacting, Steinitz[32] applied the same method to an investigation of the reactions taking place during sintering, thereby following the development of metallic bonding. Experiments were confined to a reduced and an electrolytic iron powder, both commercial grade (—100 mesh), two mixtures of electrolytic iron and graphite powders, and, for comparison, two mixtures of alloy steel composition. Compacts of suitable test specimen shape were pressed at 25 and 50 tsi, and sintered at 700°C. (1300°F.) and 1090°C. (2000°F.) for 15 minutes each. The graphite-

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[29] W. Rostoker, *Trans. Can. Inst. Mining Met., 50,* 497 (1947).

[30] O. Kantorowicz, *Ann. Physik, 12,* 1 (1932) .

[31] F. Skaupy and O. Kantorowicz, *Metallwirtschaft, 10,* 45 (1931); *Z. Elektrochem., 37,* 482 (1931).

[32] R. Steinitz, *Powder Met. Bull., 1,* No. 1, 6 (1946).

containing mixtures were also measured after coining to approximately 97% density. As shown in Table 159, the resistivities of the two different iron powders are of the same order of magnitude in the pressed state, but about 500–1000 times that of ordinary iron. The somewhat higher resistivity of the electrolytic iron is explained by inferior compactibility—with ensuing lack of contact areas, excessive straining of the more solid electrolytic particles, or heavier oxide films around the electrolytic particles. In both powders, however, the higher pressure reduces resistivity appreciably. After a short presintering at 700°C. (1300°F.) the resistivities drop to about 1% of the previous values, thus falling in the order of magnitude of ordinary iron. The now lower value for the electrolytic powder is attributed to a higher density of the compact. Sintering at the higher temperature causes a further reduction in resistivity values, but still leaves them above the normal figures in accordance with the incomplete density. As expected, mixing graphite with iron increases the resistivity of the pressed compacts considerably because of the poor conductivity of the contact-inhibiting nonmetallic phase. Upon sintering, however, these conditions are completely changed and resistivity values similar to those observed for pure iron ensue. The general trend is the same for alloy steel mixtures for it is evident that even a short sintering period rapidly reduces the resistivity of an unsintered iron compact, permitting the conclusion that the formation of gross metallic bonding between the particles commences even in the earliest stages of the sintering operation.

TABLE 159

Electrical Resistivities[a] of Compressed and Sintered Iron and Steel Compacts (Steinitz[32])

Powder	After pressing		Pressed at 50 tsi and sintered for 15 minutes		Sintered and coined to about 97% density
	25 tsi	50 tsi	700°C. (1300°F.)	1090°C. (2000°F.)	
Reduced iron	2,290	716	8 4	6 8	—
Electrolytic iron	3,820	1115	6 8	4 9	—
Iron + 0.4% graphite	50,000	3350	About 15	5 3	4.7
Iron + 0.85% graphite	290,000	7600	About 20	About 7	5.3
18% Cr + 8% Ni + Fe	—	2160	—	27 0	—
18% W + 4% Cr + 1% V + Fe	—	3065	—	35 1	—
Resistivity of cast and wrought iron					*3 95*

[a] In ohm × inch × 10^6.

Extending his experimental work with different iron powders, Steinitz[33] also investigated the effect of various processing conditions on density with a view to establishing optimum conditions for magnetic permeability.

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[33] R. Steinitz, *Powder Met. Bull., 1,* No. 5, 70 (1946).

TABLE 160

Densities of Sintered Iron Powder Compacts as Affected by Raw Material and Processing Variables (Steinitz[33])

Density		Powder	Compacting pressure, tsi	Sintering temperature		Coining pressure, tsi
%	g./cc.			°C.	°F.	
96	7 55	Electrolytic A	25	1150	2100[a]	50[a]
95	7 45	Electrolytic B	20–30	1100	2000	50
90	7.05	Reduced A	25	1100	2000[a]	50[a]
90	7.05	Reduced C	25	1100	2000	50
88	6.9	Reduced A	25	1100	2000	50
82	6.45	Reduced B	40	1100	2000	—
80	6 3	Reduced A	35	1100	2000	—
80	6 3	Electrolytic B	28	1100	2000	—
78	6.1	Reduced C	30	1100	2000	—
75	5 9	Reduced B	25	1100	2000	—
75	5 9	Reduced C	25	1100	2000	—
74	5.8	Reduced A	25	1100	2000	—
70	5 5	Reduced A	20	1100	2000	—
70	5 5	Electrolytic B	15	1100	2000	—
60	4 7	Reduced A	10	1100	2000	—

Powder specifications

Powder	Apparent density, g./cc.	Approximate screen analysis, mesh					
		+100	−100 +150	−150 +200	−200 +250	−250 +325	−325
Electrolytic A	3 1	0	11.0	29.5	7.5	17.5	34.5
Electrolytic B	2 3	1 5	10.0	33 0	15 0	13.5	27.0
Reduced A	2 0	2 5	22 0	26.5	9.0	17.0	23.0
Reduced B	2 7	4 5	19 0	23 0	10.5	12.5	30.5
Reduced C	2 4	0	27 0	25 0	12.0	13 0	23.0

[a] Sintered and coined twice.

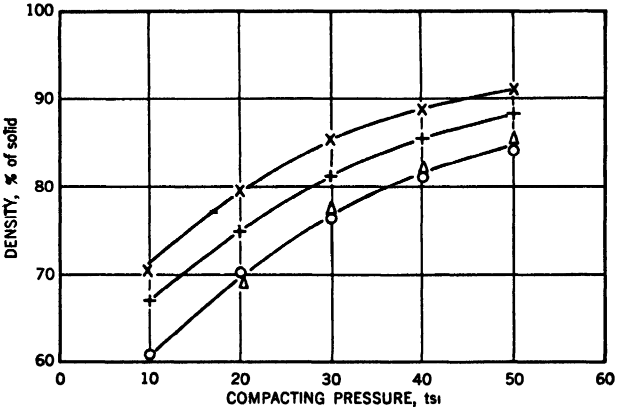

Fig. 433. Effect of initial compacting pressure on the density after sintering at 1100°C. (2010°F.); and coining at 50 tsi of compacts from different iron powders (according to Steinitz[33]): ○, reduced powder A; △, reduced powder B; ×, electrolytic powder A; +, electrolytic powder B; 0.5% Sterotex lubricant added to all powders.

The results of this work are summarized in Table 160 and in Figure 433. The powder specifications of the two electrolytic types and three reduced types of iron powder are also shown in Table 160. It is evident that a comparatively large range of densities (96 to 60%) can be easily produced by using different powders and compacting pressures without changing the sintering conditions. It is interesting to note that the reduced iron powders could be substituted for each other with only slight deviations, although the apparent densities of the powders ranged from 2.0 to 2.7 g./cc. A different behavior was observed for the electrolytic powders, where the powder with the lower apparent density resulted in a higher final density regardless of the compacting pressure used; this is explained by better compactibility.

TABLE 161

Engineering Properties of Sintered Iron Parts Prepared from Iron Powder as Compared with Low-Carbon Steel (Kieffer, Benesovsky, and Bartels[34])

Material	Compacting pressure, tsi	Density, g./cc.	Porosity, %	Hardness, Vickers	Tensile strength, psi	Elongation, %
Sintered iron from DPG atomized powder (particle size < 0.3 mm.)	14[a]	5.50	30	32	10,800	1.8
	28[a]	6.36	19	50	14,800	3.4
	42[a]	6.69	15	60	22,000	5.8
	56[a]	6.90	12	70	29,000	9.5
	42 and 42[b]	7.15	9	90	35,000	13.2
Sintered iron from Hametag eddy mill powder (particle size < 0.3 mm.)	14[a]	5.75	27	32	9,000	1.3
	28[a]	6.59	16	58	19,200	3.8
	42[a]	7.02	10.5	66	24,200	6.7
	56[a]	7.20	8.2	75	32,000	10.6
	42 and 42[b]	7.28	7.2	89	35,200	14.5
Low-carbon steel	—	7.85	—	80–100	35,500–42,500	30–40

[a] Single-pressed and sintered at 1250–1300 °C. (2280–2370 °F.).

[b] Double-pressed (both steps at 42 tsi); presintering at 850 °C. (1560 °F.) and final sintering at 1250–1300 °C. (2280–2370 °F.).

The physical properties of sintered iron from the centrifugally disintegrated and eddy-milled powders are compared with hot-rolled steel (0.15% maximum) in Table 161.[34] It is interesting to note that despite the less equiaxed particle shape, the eddy-milled powder yields slightly superior physical properties, especially when higher molding or coining pressures are employed. Apparently, a slightly higher density for the eddy-milled powder products is responsible for this effect. In this connection, it would have been interesting to learn more about the isotropic behavior of these materials, since the compacts from the flaky eddy-milled powder are likely to possess strongly directional properties.

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[34] R. Kieffer, F. Benesovsky, and H. J. Bartels, *Powder Met. Bull.*, *2*, No. 3, 54 (1947).

TABLE 162

Physical and Chemical Characteristics of German Iron Powders Used for Systematic Investigation of Iron Powder Technology (Wiemer[35])

Powder	Tap volume, cc./100 g.	Sieve analysis, weight per cent					Chemical analysis, weight per cent					
		0.4 mm.	0.3 mm.	0.15 mm.	0.06 mm.	0.05 mm.	O	C	Si	P	S	Mn
I	28	4.3	12.0	38.6	31.4	13.6	0.19	0.03	0.05	0.052	0.051	0.27
II	42	—	—	—	55.0	45.0	0.23	0.00	0.03	0.021	0.007	0.05
II	41	—	—	—	—	100	0.29	0.00	0.03	0.002	0.008	0.05
III	35	45.6	13.9	27.5	11.3	1.7	0.50	0.03	0.01	0.022	0.016	0.27
IV[a]	39	—	—	40.1	47.1	12.8	0.59	0.07	0.07	0.010	—	0.02
V[b]	43	2.9	9.6	58.7	25.8	3.0	1.05	0.07	0.18	0.022	0.36	0.24

[a] Powder IV contained 0.068% Al_2O_3, 0.20% V_2O_5, and 0.25% TiO_2; the S content was not determined.
[b] Powder V contained 0.37% of an insoluble residue.

TABLE 163

Average Mechanical Characteristics of Cold-Pressed and Sintered Soft Iron Compacts Representing All Powders Investigated (Wiemer[35])

Sintering conditions	C content, %		Density, g. cc.	Tensile strength, psi	Elongation, %	Hardness, Brinell	Structure
	Bound	Free					
1000–1100°C. (1830–2010°F.), neutral or reducing atmosphere or vacuum	0.05	—	4.5–5	5,500–8,500	1–3	25–30	Ferritic
	0.05	—	5.5–6	8,500–14,000	2–5	35–45	
	0.05	—	6–6.5	14,000–21,000	5–7	45–55	
	0.05	—	6.5–7	21,000–25,500	7–10	55–65	
Preoxidized at 400–500°C. (750–930°F.) and sintered in H_2 at 1000–1100°C.	0.05	—	6–6.5	18,500–21,000	6–9	45–55	
	0.05	—	6.5–7	23,000–25,500	8–12	55–65	
1000°C. (1830°F.), vacuum, carbon added in form of graphite powder	0.1	0.8–1	5.5	3,000–3,500	1–1.5	30	Graphitic-ferritic
	0.1	0.8–1	7	15,500–17,000	2–3	65	
	0.1–0.2	2.5	5.5	2,000–3,000	1.5–2	30	
	0.1–0.2	2.5	7	10,000–11,500	2–3	40–60	
1050°C. (1920°F.), vacuum, carbon added in form of graphite power	0.5	0.5	5.5	4,000–5,500	1–1.5	35–40	Graphitic-ferritic-pearlitic
	0.5	0.5	7	21,000–24,000	2–3	75	
1100°C. (2010°F.), vacuum, carbon added in form of graphite power	0.5–1	2–2.5	5.5	4,000–5,500	1–2	40–55	Graphitic-ferritic-pearlitic
	0.5–1	2–2.5	7	21,000–28,000	1–2	90–110	
1200–1300°C. (2190–2370°F.), neutral or slightly carburizing atmsophere or vacuum	0.4–0.6	—	6	28,000–35,000	2–3	50–70	Ferritic-pearlitic
	0.4–0.6	—	7	43,000–70,000	5–3	100–110	
	0.7–0.9	—	6	35,000–55,000	2.5–1.5	70–120	
	0.7–0.9	—	7	55,000–85,000	5–3	130–160	

In a summarizing report on a careful investigation of German iron powders used during the war,[35] the chemical and physical characteristics of the different powders are described as being chiefly responsible for the physical properties of the cold-pressed and sintered soft iron compacts. In Table 162, the physical and chemical characteristics of five principal types of powders are summarized: (I) Hametag powder, obtained by pulverizing small pieces of iron wire; (II) DPG powder[36] (rotating disk type); (III) RZ Mannesmann powder,[37] obtained by impinging a jet of compressed air against a jet of molten pig iron; (IV) Vogt powder (reduced Swedish Höganas powder)[38]; and (V) Linz powder (reduced rolling mill scale), obtained by briquetting the scale with coke and sulfite lye and reducing with blast furnace gas. The average mechanical characteristics of soft iron compacts obtained under different sintering conditions from these powders are summarized in Table 163; the properties are arranged in the order of increasing densities, regardless of the type of iron powder or mixture of two or more powders used. Not included in this investigation, however, were powders obtained in large-scale tests by the so-called "tunnel-furnace" reduction process,[39] which employed a typical tunnel furnace as used in the ceramic industry for the reduction—with producer gas--of mill scale and iron oxide from iron sulfate slag, and of DPG powder of high oxygen content.

The technological evaluation of German iron powders in the postwar era was recently discussed by Eisenkolb,[40] who investigated the compacting properties of Hametag powders under various conditions. The usual density and tensile strength tests on sintered specimens were augmented by tensile tests of green compacts. Among the factors considered were particle size and annealing temperature of the powder, pressing lubricants, and length of storage of the powder. It is interesting to note that Eisenkolb defined the compactibility of the powder by the minimum pressure that gives pressings which can be used, analogous to the author's own concept of a "minimum briquetting pressure," as a criterion of the powder's com-

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[35] H. Wiemer, *Powder Met. Bull.*, *2*, No. 1, 16 (1947); U. S. Dept. of Commerce, Office of Publ. Board, P.B. 6787 and 14760; *Met. Powder Rept.*, *1*, No. 4, 61 (1946); British Intelligence Objectives Sub-committee Final Report No. 676, Item No. 21 (Sept. 1956). Also *Met. Powder Rept.*, *2*, No. 1, 3 (1947); British Intelligence Objectives Sub-committee Final Report No. 1223 (June 1947).

[36] British Intelligence Objectives Sub-committee, Final Report Nos. 729 and 860, Item No. 21 (Jan. 1947); *Met. Powd. Rept.*, *1*, No. 7, 103 (1947).

[37] D. I. Scholz, *Powder Met. Bull.*, *2*, No. 2, 30 (1947);U. S. Dept. of Commerce, Office of Publ. Board, P.B. 17380.

[38] W. Luyken and H. Kirchberg, *Powder Met. Bull.*, *2*, No. 2, 38 (1947); U. S. Dept. of Commerce, Office of Publ. Board, P.B. 6789.

[39] British Intelligence Objectives Sub-committee, Doc. F.D 1765/46; *Met. Powd. Rept.*, *1*, No. 5, 69 (1947).

[40] F. Eisenkolb, *Stahl u. Eisen*, *66–67*, 78 (1947).

paction capacity (see also Volume I, Chapter V). The specific gravity of the compact divided by the compacting pressure is defined by Eisenkolb as the "coefficient of pressing" and serves as an additional characterization of the powder.

The effect of particle size distribution on the relation between the tensile properties and sintering temperature and time, respectively, for liquid-disintegrated DPG powder has also been studied recently,[40a] and it was found that the centrifugally atomized powder was in a far more stable (less activated) state than, for instance, a mechanically disintegrated powder. Accordingly, sinter bonds and ultimate physical properties were generally of a lower order, although a finer powder grade indicated a distinctly superior sintering performance.

TABLE 164

Physical Properties of Electrolytic Iron Powder Used by Balke[42]

Properties	Powder			
	A	B	C	D
Sieve analysis, %				
Passing No. 100 sieve, retained on No. 150 sieve	15 0	11 9	3.9	—
Passing No. 150 sieve, retained on No. 200 sieve	26 2	30 0	11.0	—
Passing No. 200 sieve, retained on No. 270 sieve	14 0	15 1	12 2	—
Passing No. 270 sieve, retained on No. 325 sieve	12 6	12 0	19 0	—
Passing No. 325 sieve, retained on No. 400 sieve	12 9	12 7	25.8	100 0
Passing No. 400 sieve	19.3	18 3	28 1	—
Total	*100 0*	*100 0*	*100 0*	*100 0*
Flow, seconds[a]	37 2	42.0	33.0	25 2
Weight,[b] g./in.^{3}	37 5	37 3	41.5	47.3
Loss in hydrogen, %	0 54	0 022	0.123	0.006

[a] Seconds required for 50 g. to pass through a Hall flow meter.
[b] Corresponding values for apparent density in g./cc.: Powder A, 2.29; B, 2.28; C, 2.53; D, 2.89.

EFFECTS CAUSED BY PROCESSING VARIABLES

The effect of compacting and sintering upon density of an iron powder all passing through a 250-mesh sieve, and one-half passing through a 325-mesh sieve, was investigated by Kelley.[41] For a definite sintering cycle—involving a temperature of 1425–1450°C. (2600–2640°F.), a sintering time of 32 hours, and an atmosphere of pure hydrogen—a variation

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[40a] H. Bernstorff, *Metal Treatment, 15*, No. 54, 85 (1948).

[41] F. C. Kelley, in J. Wulff, *Powder Metallurgy*. Am. Soc. Metals, Cleveland, 1942, p. 60.

in compacting pressure between 20 and 70 tsi was of little consequence, for the density was found to be 7.81 g./cc. (99.2% of theoretical) for any pressure within these limits. However, when varying the sintering temperature between 800 and 1425–1450°C. (1475 and 2600–2640°F.), with the compacting pressure kept at 30 tsi, and the sintering kept to 32 hours, a maximum density was obtained at 1400°C. (2550°F.). The effect of time on density follows a similar trend: for a constant molding pressure of 30 tsi and a sintering temperature of 1425–1450°C. (2600–2640°F.), a continuous increase in density was effected by an increase in time, and a value of 7.859 g./cc. (practically identical with the theoretical density) was recorded for 64 hours sintering time.

TABLE 165

Physical Properties of Pressed and Sintered Electrolytic Iron (Balke[42])

Pressure, tsi	Density g./cc.				Hardness, Rockwell			
	Pressed	Sintered at 1100°C. (2010°F.) 1 hr.		Sintered 1 hr. at 1400°C. (2550°F.)	Pressed	Sintered at 1100°C. (2010°F.) 1 hr.		Sintered 1 hr. at 1400°C (2550°F)
	Powder B	Powder A	Powder B	Powder B	Powder C	Powder C (A)	Powder B	Powder B
5	4.38	4.19	4.47	—	Soft	Soft	Soft	—
10	5.31	4.99	5.46	—	Soft	Soft	H-22	—
20	6.22	5.89	6.26	6.95	H-60	H-57	H-63	H-81
40	6.93	6.75	7.11	7.33	H-90	H-80	H-89	H-89
60	7.35	6.95	7.46	7.51	B-56	B-31	B-40	B-17
80	7.46	7.18	7.52	7.55	B-65	B-39	B-40	B-15
100	7.68	7.34	7.65	7.65	B-72	B-45	B-47	B-21
130	7.77	7.60	7.81	7.76	B-82	B-49	B-50	B-24
160	7.83	7.66	7.79	7.84	B-86	B-50	B-50	B-24

Pressure, tsi	Tensile strength, psi				Elongation in 2 in., %		Reduction of area, %, sintered at 1400°C. (2550°F.) 1 hr.
	Pressed		Sintered at 1100°C. (2010°F.) 1 hr.	Sintered at 1400°C. (2550°F.) 1 hr.	Sintered at 1100°C. (2010°F.) 1 hr.	Sintered at 1400°C. (2550°F.) 1 hr.	
	Powder A	Powder B	Average of Powders A + B + C	Powder B	Powder B	Powder B	Powder B
5	—	—	6,100	—	3.1	—	—
10	—	—	11,800	—	4.7	—	—
20	—	1130	24,500	35,900	4.7	18.8	20
40	1530	2800	38,000	38,300	5.9	20.3	35
60	2480	3570	46,400	40,800	10.9	34.4	48
80	3130	4980	51,800	40,500	16.8	36.0	52
100	4280	6600	52,500	40,400	24.2	36.0	51
130	6550	9100	54,100	41,200	21.0	31.0	61
160	7900	9500	55,200	41,600	30.5	34.4	68

The effect of the initial molding pressure and the subsequent coining pressure on the density, hardness, and tensile properties of very pure electrolytic iron powder was investigated over a pressure range of 5 to 160 tsi by Balke.[42] Table 164 gives the physical properties of the four types of soft-annealed electrolytic iron powders used, and Table 165 gives data for density and hardness of bars after pressing and after sintering for one hour at 1100°C. (2010°F.) or 1400°C. (2550°F.). Figure 434 shows graphically the effect of pressure on the density of the green compacts. The powder with a very low oxygen content had a green density of 7.79 to 7.83 g./cc. when pressed at 160 tsi, while powders of higher oxygen content gave bars of appreciably lower density. A similar trend was noticeable after sintering at 1100°C. (2010°F.) for one hour. A density of 7.85 g./cc. was obtained by pressing the pure powder at 160 tsi and

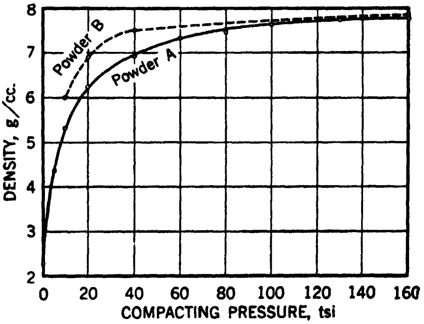

Fig. 434. Relation between compacting pressure and resulting densities of unsintered iron briquettes (according to Balke[42]): powder A molded into bars having a ratio of width to thickness of 8:1.0; powder B molded into disks having a ratio of diameter to thickness of 6:1.

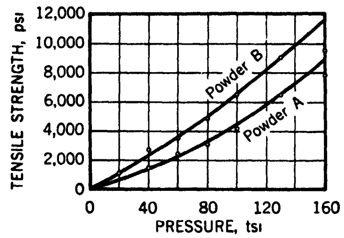

Fig. 435. Relation between compacting pressure and tensile strength for unsintered iron briquettes from powders A and B (according to Balke[42]).

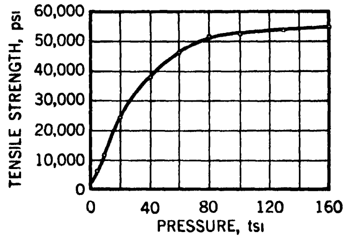

Fig. 436. Relation between compacting pressure and tensile strength for iron bars sintered at 1100°C. (2010°F.) for 1 hour (average of results for powders A, B, and C).[42]

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[42] C. W. Balke, in *Symposium on Powder Metallurgy,* ASTM, Philadelphia, Pa., 1943, p. 11.

sintering at 1400°C. (2550°F.) for one hour. The hardness figures in Table 165 indicate that considerable strain hardening took place during compaction, which was a factor in limiting the density that could be obtained in a single compression. After removal of the strain hardness by annealing (sintering) the compacts could be repressed to a substantially higher density without increase of pressure. When pressing very pure and fine powder at 160 tsi, sintering at 1100°C. (2010°F.) for one hour, and repressing and resintering the compact under identical conditions, the theoretical density of 7.87 g./cc. could be recorded.

TABLE 166

Properties of Sintered Electrolytic Iron as Compared with Ingot Iron (Balke[42])

Metal	Operation	Density g /cc	Hardness, Rockwell "B"	Tensile strength, psi	Elongation in 2 in., %	Reduction of area, %	Carbon, %	Grains per mm.^{2}
Ingot iron...	—	7.87	30	39,200	35.2	62	0.072	70
Powder D.....	Pressed 160 tsi; sintered at 1100°C. (2010°F.) 1 hr.	7.81	44	58,500	42.2	67	0.043	405
	Pressed 160 tsi; sintered at 1400°C. (2550°F.) 1 hr.	7.85	23	41,300	37.5	68	—	15
	Pressed 160 tsi; sintered at 1100°C. (2010°F.) 1 hr.; repressed 160 tsi; and resintered at 1100°C. (2010°F.) 1 hr.	7.87	37	50,200	40.6	77	—	430
Powder B.......	Pressed 160 tsi; sintered at 1100°C. (2010°F.) 1 hr.	7.79	44	47,700	37.5	68	0.014	440
	Pressed 160 tons; sintered at 1400°C. (2550°F.) 1 hr.	7.84	24	41,600	34.4	68	—	22
Powder like B...	Pressed 100 tsi; sintered at 1350°C. (2460°F.) 1 hr.; repressed 100 tsi; resintered at 1350°C. (2460°F.) 1 hr.	7.85	54	50,700	37.5	68	0.071	440

The beneficial effect of the high purity of the powder on interparticle bonding during compaction is best demonstrated by the remarkable cohesive strength of the green compacts, as shown in Figure 435, where the tensile strength is plotted against compacting pressure for unsintered bars, and where values approach 12,000 psi. The tensile strength, however, increases nearly fivefold after sintering the bars at 1100°C. (2010°F.), as shown in the graph of Figure 436. The complete data of the physical properties of pressed and sintered powders are given in Table 165, and some of the results obtained by Balke are compared with the properties of ingot iron in Table 166. It is evident from these data that it is possible by repeated cold pressing and sintering not only to reach the density of fused ingot iron, but also to *surpass* its hardness, tensile strength, elongation, and reduction of area, with the finer grain structure of the sintered iron undoubtedly being chiefly responsible for this fact.

The effects of small amounts of elements commonly present in steel on the properties of sintered soft iron, with special attention given to the effects of the sintering furnace atmosphere, may be summarized as follows.[43] Preoxidation of green compacts at 400–500°C. (750–930°F.) followed by sintering in hydrogen has been found to result in improvements in tensile strength and particularly in impact strength, probably due to an increase in grain size. Additions of sulfur up to 0.9% can improve the strength without changes in hardness and with only slight loss in elongation. If specimens of different sulfur content are sintered simultaneously in vacuum or hydrogen, an equalization of sulfur concentration takes place; however, in the case of hydrogen atmosphere, this is accompanied by considerable sulfur losses. Whether the observed increases in strength are maintained after complete elimination of the added sulfur, as in the case with oxygen, has not yet been determined. Up to about 0.5% of phosphorus addition (in the form of powdered ferrophosphorus containing 27% P) also results—after sintering in hydrogen—in a noticeable increase in tensile strength. However, this effect is accompanied by a substantial decrease in elongation, with a corresponding increase in hardness. Experiments in an ammonia atmosphere indicated the introduction of nitrogen in uniform distribution. A variation in nitrogen content over wide limits may be achieved by the proper selection of sintering conditions.

Rostoker[43a] recently reported truly remarkable density values with iron compacts that were investigated for their magnetic properties (see also Chapter XXIV). Density values of 7.850 and 7.895 g./cc., respec-

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[43] H. Wiemer, *Powder Met. Bull., 1,* No. 6, 92 (1946); U. S. Dept. of Commerce, Office of Publ. Board, P.B. 14761.

[43a] W. Rostoker, *Trans. Am. Inst. Mining Met. Engrs., 180,* 672 (1949).

tively, were obtained in compacts from pure electrolytic and carbonyl iron powders by subjecting them to the following processing cycle: after initial compaction at 30 tsi, the specimens were given a short-time, low-temperature hydrogen annealing treatment, followed by repressing at 75 tsi, and sintering in hydrogen first at 1420°C. (2590°F.) for 24 hours, and then at 800°C. (1470°F.) for 16 hours. The unusually high figure for the carbonyl iron—the Critical Tables record a value of 7.90 g./cc. for the density of pure iron—was checked by x-ray diffraction measurements, and the value calculated from the lattice parameter was 7.882 g./cc.

TABLE 167

Effects of Repeated Pressing and Sintering Cycles on the Properties of Pure Iron Compacts[a] (Kieffer and Hotop[43b])

Property	Pressure,[b] tsi	Number of cycles[c] 1	2	3	4	5
Density, g/cc.						
Before final sintering	14.3	5.21	5.69	5.88	6.08	6.18
	28.5	6.04	6.59	6.79	7.02	7.04
	43.0	6.46	6.98	7.30	7.40	7.42
After final sintering	14.3	5.60	6.00	6.22	6.41	6.40
	28.5	6.38	6.81	7.02	7.20	7.21
	43.0	6.70	7.17	7.37	7.45	7.47
Vickers hardness,[d] kg./mm.^{2}	28.5	52	80	90	94	97
	43.0	58	90	107	110	112
Tensile strength, psi[d]	28.5	15,000	24,000	32,000	33,500	34,500
	43.0	25,000	34,000	39,000	40,000	41,000
Elongation, %[d]	28.5	3.4	7.8	12.8	13.5	15.0
	43.0	5.8	13.2	16.4	19.0	20.4

[a] From soft liquid disintegrated powder (type DPG), $< 150\ \mu$.

[b] Same pressure for all cycles.

[c] Sintering conditions: presintering and intermediate sintering 1 hour at 900°C. (1650°F.), final sintering 2 hours at 1250°C. (2280°F.), all in hydrogen.

[d] Values taken after final sintering.

Kieffer and Hotop[43b] in their recent book on sintered iron and steel have for the first time reported test results of pure iron powder compacts that were subjected to more than one repeated pressing and sintering cycle. Table 167 indicates the effects of a number of repetitions of the compression-plus-sintering cycle on density, hardness, and tensile properties of iron compacts produced from DPG-rotating disk liquid disintegrated powder of —100 mesh size. The identical pressures of 28.5 and 43 tsi, respectively, were used in all cycles; sintering, always conducted in hydrogen, was performed at two different temperatures (and times): 1250°C. (2280°F.) for 2 hours for the last cycle, and 900°C. (1650°F.) for 1 hour for all preceding cycles. Apparently, the density is substantially

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[43b] R. Kieffer and W. Hotop, *Sintereisen und Sinterstahl.* Springer, Vienna, 1948, pp. 232 ff.

increased by a third pressing and sintering cycle, while a fourth cycle causes only a comparatively small increment, and a fifth cycle results in virtually no further increase at all. Hardness and tensile strength follow closely the pattern set by the density values, but elongation figures increase progressively with the number of cycles, and show sudden drastic increases after the second cycle for the specimens pressed at the higher pressure, and after the third cycle for the specimens pressed at the lower pressure.

Wiemer and Hanebuth[43c] were able to increase the tensile properties of sintered iron to a remarkable extent by subjecting the compacts to a presintering treatment in air for the purpose of preoxidation to be followed by hydrogen-reduction during subsequent sintering. When using a presintering treatment of 30 minutes in air at 400–500°C. (750–930°F.), followed by cooling and then sintering in hydrogen for 2 hours at 1100°C. (2010°F.), tensile strength values, for some powders and certain specific pressures, could be increased 25%, and elongation values in other instances increased as much as 50%. For example, a liquid disintegrated —100-mesh powder compacted at 43 tsi had a tensile strength of 17,700 psi without, and 24,200 psi with the preoxidation treatment; the corresponding elongation values were 4.8 and 7.2%, respectively. According to Vogt[43d] a preliminary treatment with oxidizing acids or salts has an effect similar to the preoxidation by heating in air.

In addition to the different methods just elaborated on—obtaining optimum physical properties by producing material of highest possible density with the aid of high sintering temperatures, long sintering times, extremely pure powders, and repeated application of very high pressures, respectively—there exist two other procedures which give similar results: hot pressing and subsequent metal working. Hot-press experiments made on iron powders by Sauerwald and Hunczek,[44] Schwarzkopf and Goetzel,[45] and Henry and Cordiano[46] (see Vol. I, Chap. XII) have shown that density and physical properties similar to those obtainable with fused electrolytic iron are secured readily if the proper technique is used, and if adequately high temperatures and pressures are selected. Analogous to the experiences with fused ductile metals and with sintered refractory metals, metal-working operations have also produced very favorable effects on density and physical properties of sintered iron compacts. The

[43c] H. Wiemer and R. Hanebuth, cited in R. Kieffer and W. Hotop, *Sintereisen und Sinterstahl.* Springer, Vienna, 1948, p. 533.

[43d] German Pat. 745,806.

[44] F. Sauerwald and J. Hunczek, *Z. Metallkunde, 21,* 22 (1929).

[45] P. Schwarzkopf and C. G. Goetzel, *Iron Age, 148,* No. 10, 37 (1941).

[46] O. H. Henry and J. J. Cordiano, *Trans. Am. Inst. Mining Met. Engrs., 166,* 520 (1946).

TABLE 168

Characteristics of Hot-Extruded Sintered Iron as Compared with Cast and Sintered Iron (Kieffer and Hotop[48b])

Material	Treatment	Density, %	Vickers hardness, kg./mm.	Tensile strength, psi	Elongation, %
Electrolytic iron	Cast, rolled, normalized	100	45–60	35,000–40,000	40–60
Commercial powder	Cold pressed at 43–57 tsi, sintered at 1000 °C. (1830 ° F.)	83–88	60–70	25,000–30,000	8–12
	Cold pressed, sintered, repressed, resintered	90–93	85–95	32,000–37,000	15–20
	Hot pressed at 810 °C. (1490 °F.) and 25 tsi	95–98	90–120	45,000–52,500	17–23
Carbonyl powder	Pressed, sintered, hot rolled to 0.5 mm. sheet	100	170–180	89,500–92,500	1–2
	Pressed, sintered, hot rolled and annealed	100	56–80	25,500–35,500	30–40
	Extruded	94	113	47,000–55,000	12–16
	Extruded, annealed for 1 hr. at 1300 °C. (2370 °F.)	92	113	47,000–55,000	37–39
	Extruded, cold worked (50%)	99	182	75,000–86,000	9–11
	Extruded, cold worked, annealed	99	100	47,000–48,000	20–23
Sponge powder	Extruded	91.5	112	48,000–51,000	10–12
	Extruded, annealed	91	120	47,000–49,500	21–23
	Extruded, cold worked	95	182	78,000–79,500	1–3
	Extruded, cold worked, annealed	94	109	47,000–48.000	20–23
Eddy-milled powder	Extruded	92	127	57,000–60,000	14–21
	Extruded, cold worked, annealed	98 5	135	55,000–59,500	25–31

results of experimental work with various types of iron powder by Goetzel[47] and Koehring[48] (see Volume I, Chapter XVIII) clearly indicate the improvements of physical properties (especially yield point and tensile strength) with increasing density. This has been confirmed by Kieffer

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[47] C. G. Goetzel, *Iron Age, 150,* No. 14, 82 (1942).

[48] R. P. Koehring, in J. Wulff, *Powder Metallurgy.* Am. Soc. Metals, Cleveland, 1942, p. 304.

and Hotop[48a] who demonstrated the favorable effects of hot repressing (die forging) on these properties.

Of particular interest, however, appears to be the work done on extrusion of sintered iron by the same investigators.[48b] Following compaction of the iron powder at about 18 tsi to 1.6-in. diameter, 8-in. long cylinders, the compacts were first sintered in hydrogen at 1250°C. (2280°F.) for 2 hours, and then immediately extruded in a press developed by Krall,[48c] and equipped with a cemented carbide die of about $^3/_8$-in. orifice diameter. The cylinders entered the extrusion press while at a temperature of about 1150°C. (2100°F.), and left the extrusion die at about 600°C. (1100°F.). The required extrusion pressures were comparatively high, and varied for the different types of iron powders tested: for carbonyl iron and eddy-milled powder the pressures were 92–107 tsi, and for the less pure sponge iron powder 125–130 tsi. The results of this work are summarized in Table 168, which also gives data for material processed by other methods, or for extruded metal subjected to additional thermal or mechanical treatments.

In analyzing the foregoing, it appears to the author that neither the procedures employed by Kelley, Balke, Rostoker, or Kieffer and Hotop, nor the hot pressing, hot repressing or extrusion methods with their drastic requirements for materials of construction and their inherent slow production rates appear practical from an economic and a technical point of view. Cold and hot working subsequent to the sintering operation can also be expected to remain limited in application because of the reduced production rates and the undesirable loss in dimensional accuracy of the part.

The close relationship between density and physical properties is already apparent in iron compacts produced with moderate pressures and sintering cycles. The properties of compacts prepared in this manner are given in Table 169.[47] Values for electrolytic fused and annealed iron given for the sake of comparison in the same table are, in the case of hardness and strength, reached or sometimes even surpassed by the sintered iron; ductility values, however, remain appreciably lower in every instance. In Figure 437, the increase of density, yield point, tensile strength, and elongation with increasing compacting pressure is shown for mechanically comminuted pure iron sintered at 800°C. (1475°F.) in hydro-

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[48a] R. Kieffer and W. Hotop, *Sintereisen und Sinterstahl.* Springer, Vienna, 1948, pp. 249, 250.

[48b] R. Kieffer and W. Hotop, *loc. cit.*, pp. 257 ff.

[48c] German Pat. 738,536.

TABLE 169

Physical Properties of Sintered Pure Iron from Powders of Different Origin

Material	Treatment					Product					
	Operation[a]	Pressure, tsi	Sintering temperature		Sintering time, hr.	Density, % (7.87 = 100)	Brinell hardness	Yield point, psi	Tensile strength, psi	Elongation (2 in.) %	Reduction in area, %
			°C.	°F.							
H_2-reduced	S	25	1200	2190	1	78.6	36	8,600	17,900	6.5	7.6
	S	50	1200	2190	1	87.4	64	21,300	34,600	14.5	18.3
	S, RP	50	1200	2190	1	95.6	96	52,500	54,700	1.5[b]	11.0
	S, RP, RS (1 hr.)	50	1200	2190	1	97.0	74	19,400	37,600	25.0	18.4
Coarse, electrolytic	S	25	1200	2190	1	88.2	40	12,400	20,000	10.5[b]	9.8
	S, RP, RS	50	1200	2190	1	98.5	67	15,700	30,500	27.5	32.0
Fine, electrolytic	S	25	1200	2190	1	86.3	44	13,700	24,100	10.5[b]	20.7
	S, RP, RS	50	1200	2190	1	97.2	67	15,000	30,200	17.5	28.4

[a] S, sintered; RP, repressed at indicated pressure; RS, resintered at indicated sintering temperature and time.

[b] Fractured outside gage length.

gen for thirty minutes.[49] In contrast to the findings of Kelley[50] at the higher sintering temperatures, Eilender and Schwalbe[49] found no improvement in mechanical properties when sintering at 800°C. (1475°F.) was extended beyond three hours. According to an investigation by Libsch, Volterra, and Wulff,[51] the density and tensile strength of electrolytic iron compacts after four hours at temperatures around 850°C. (1560°F.) remain essentially constant, although the elongation continues to increase slightly. The same trend prevails at temperatures above 1100°C. (2010°F.), but saturation values for density and tensile strength are reached in a shorter time. Compacts pressed cold and sintered above 400°C. (750°F.) show a distinct improvement in physical properties with rising temperature up to about 850°C. (1560°F.); at higher temperatures a decreasing trend for the same properties is perceptible, which may be attributed to the alpha–gamma transformation or the evolution of entrapped gases; above 1100°C. (2010°F.) the physical properties again increase in value with increasing temperature, but this effect is accompanied by excessive grain growth. The physical properties of electrolytic iron powder compacts pressed at 33 tsi and sintered in dry hydrogen at 825°C. (1515°F.) for four hours are reproduced in Table 170.[51]

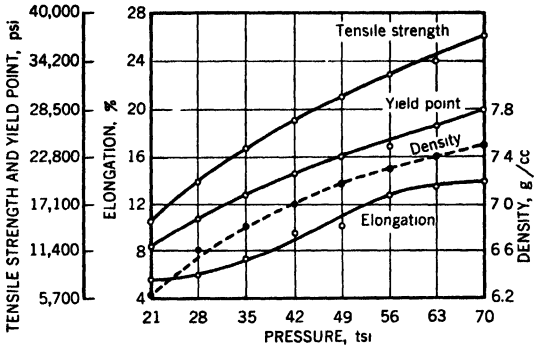

Fig. 437. Effect of compacting pressure on density, yield point, tensile strength, and elongation of iron compacts from Hametag powder of 75–100 μ size, sintered in hydrogen at 800°C. (1470°F.) for $^1/_2$ hour (according to Eilender and Schwalbe[49]).

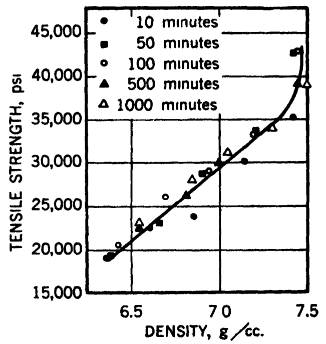

Fig. 438. Effect of sintering time on the relation between tensile strength and density for electrolytic iron powder compacts sintered at 925°C. (1700°F.) (after Squire[52]).

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[49] W. Eilender and R. Schwalbe, *Arch. Eisenhüttenw.*, *13*, 267 (1939–40).

[50] F. C. Kelley, in J. Wulff, *Powder Metallurgy*. Am. Soc. Metals, Cleveland, 1942, p. 60.

[51] J. Libsch, R. Volterra, and J. Wulff, in J. Wulff, *Powder Metallurgy*. Am. Soc. Metals, Cleveland, 1942, p. 379.

The effect of processing conditions upon the density-property relationship of compacts prepared from various iron powders has been investigated by Squire,[52-54] and the density has been established in this excellent piece of work as the primary criterion of the mechanical properties. This becomes apparent from Figure 438, which shows a nearly linear relationship between tensile strength and density for electrolytic iron powder compacts sintered at 925°C. (1700°F.), with only insignificant deviations caused by an increase in sintering time from 10 to 1000 minutes. A similar relationship between tensile strength and density is shown in the case of compacts prepared from graded electrolytic and reduced iron powders and sintered for one hour at 1100°C. (2010°F.). As shown in the diagrams of Figures 439*A–D* and 440*A–E*, the effect of increasing density is equally pronounced on such physical properties as tensile strength (Figs. 439*A*, 440*A*); elongation (Figs. 439*B*, 440*B*); hardness (Figs. 439*C*, 440*C*); impact strength (Figs. 439*D*, 440*D*); and modulus of elasticity (Fig. 440*E*). The relation is, however, not always strictly linear, especially as far as elongation and impact resistance are concerned. (Incidentally, some of the impact values found by Squire are extraordinarily high, but duplicate measurements exclude the possibility of experimental error.) The graphs of Figures 439 and 440 clearly indicate that the exact relation between density and respective physical property (*i.e.*, the position of the curve in the diagram) is dependent only upon the particle size of the powder used, but is independent of the type or history of the powder used. Furthermore, this relation is apparently independent of the method of attaining any given density value up to about 95% of

TABLE 170

Physical Properties of Electrolytic Iron Powder Compacts Pressed at 33 Tsi and Heat-Treated in Dry Hydrogen at 825°C. (1520°F.) for 4 Hours (Libsch, Volterra, and Wulff[51])

Powder size, in mesh	Brinell hardness	Tensile strength, psi	Elongation, %	Density, g./cc.
100 to 200 (coarse)	40.3	28,600	15.2	7.20
200 to 325 (medium)	41.5	26,400	13.5	7.06
325 to 500 (fine)	45.4	30,000	13.0	6.90
Mixed (66% coarse, 17% medium, 17% fine)	39.4	31,000	16.5	7.27

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[52] A. Squire, *Trans. Am. Inst. Mining Met. Engrs.*, *171*, 473, 485 (1947).

[53] A. Squire, *Watertown Arsenal Lab. Repts. WAL 671/8, 671/12, 671/16, 671/23, 671/31, 671/32* (1946).

[54] A. Squire, U. S. Dept. of Commerce, Office of Technical Services Repts. P.B. 4416, June 17, 1944; P.B. 4417, Oct. 31, 1944.

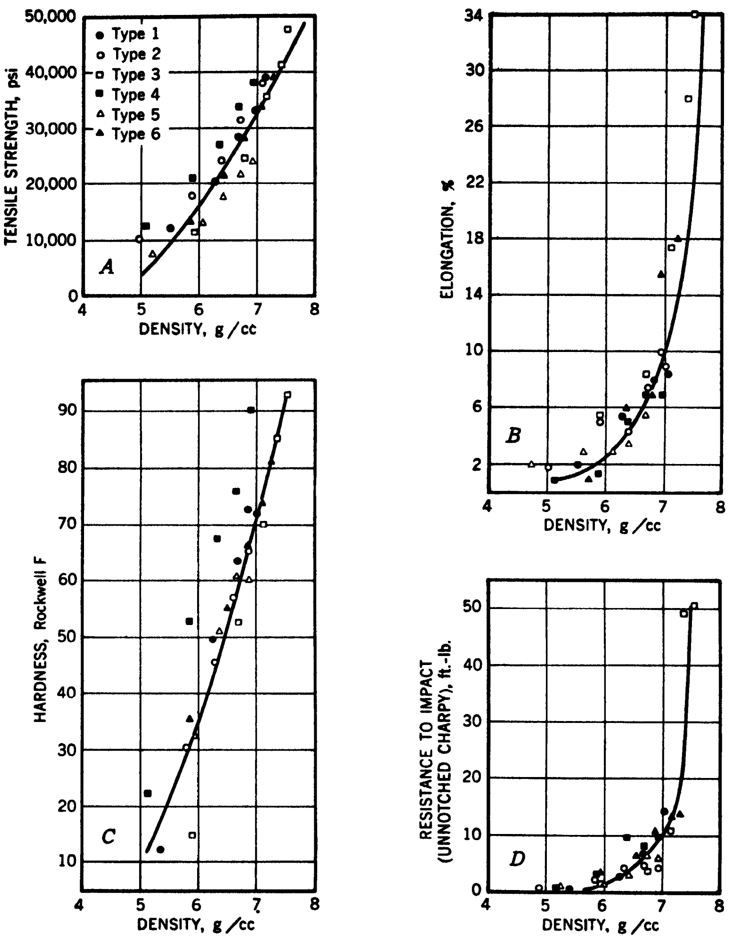

Fig. 439. Influence of the type of iron powder used on the physical properties of compacts after sintering in hydrogen for 1 hour at 1100°C. (2010°F.) (according to Squire[52]). *A*, relation between tensile strength and density; *B*, relation between elongation and density; *C*, relation between hardness and density; *D*, relation between impact strength and density. Points designate the following types of iron powder: 1, carbon monoxide-reduced mill scale; 2, hydrogen-reduced iron oxide; 3, hydrogen-reduced mill scale; 4–6, electrolytic iron.

the theoretical value, as proved by diagrams *A–F* of Figure 441, which are graphs for a number of physical properties of compacts treated in different ways, *i.e.*, either sintered or sintered, repressed, and resintered. The characteristics of the powders used by Squire in his comprehensive study are given in Table 171.

The effect of specimen length on the density of electrolytic iron powders compacted under various pressures, and the effect of the addition of lubricants on the tensile properties of sintered electrolytic iron powder compacts have been determined by J. P. Burr and W. Clarke[55] in Eng-

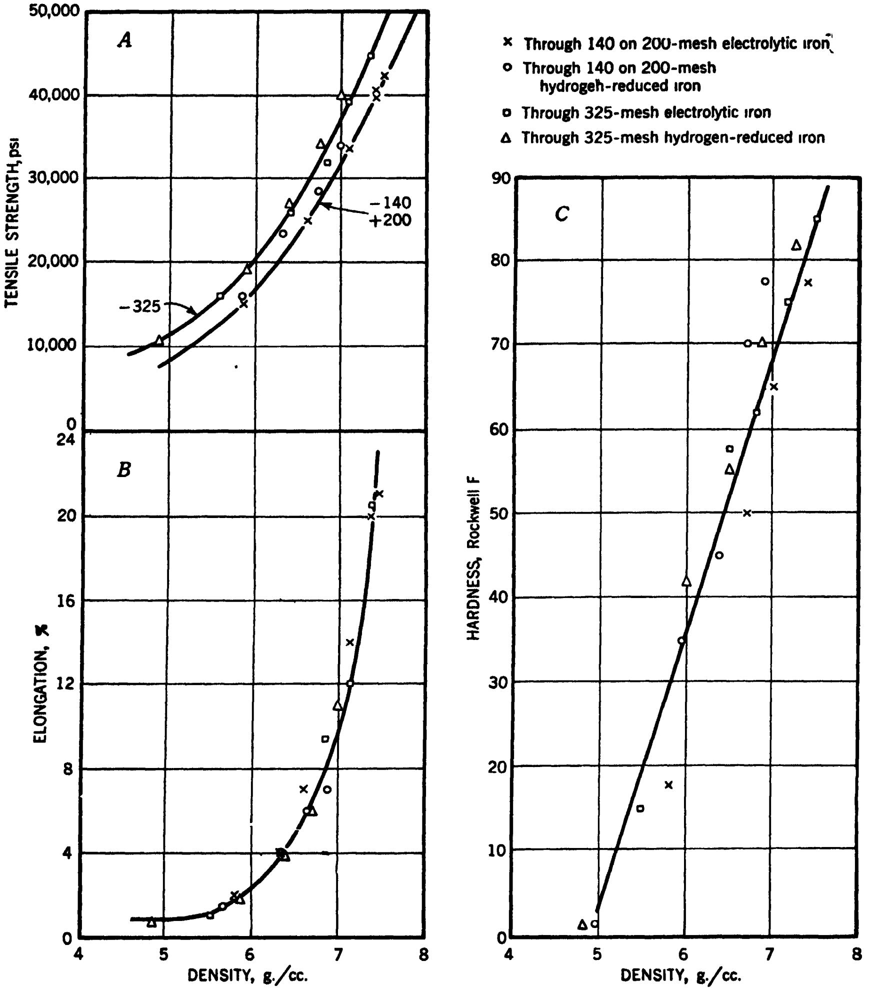

Fig. 440. Influence of the particle size of the iron powder on the physical properties of compacts after sintering in hydrogen for 1 hour at 1100°C. (2010°F.) (according to Squire[52]): *A*, relation between tensile strength and density; *B*, relation between elongation and density; *C*, relation between hardness and density.

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[55] J. P. Burr and W. Clarke, *Symposium on Powder Metallurgy*. The Iron and Steel Institute, Special Report No. 38, London, 1947, p. 113.

land, and the same authors have also made an attempt to calculate pressure losses at the centers of the compacts.

Methods for the evaluation of the molding, coining, and sintering properties of commercial iron powders, with special reference to Swedish iron powder, have recently been given by Kuzmick.[55a]

The physical properties actually obtainable in commercial production of pure iron powder components closely resemble the values given in Tables 169 and 170. Practical density figures of so-called "dense" iron parts usually lie in the range of 80 to 90% of the true density, and can be obtained with plastic powders (*e.g.*, reduced or electrolytic) by pressing at 20 to 30 tsi, sintering for 30 minutes at a peak temperature of 1100°C. (2010°F.), coining at 50 tsi, and annealing at about 700–900°C. (1300–1650°F.). Parts of simple shape can be produced commercially to 95% of theoretical density without sacrificing accuracy of dimensions.[56]

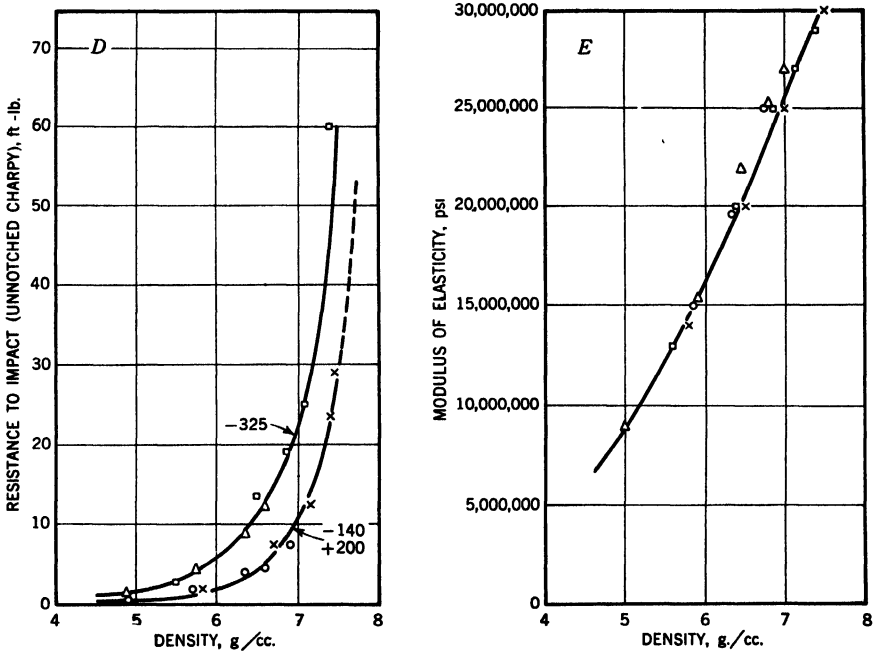

Fig. 440. (Continued) Influence of the particle size of the iron powder on the physical properties of compacts after sintering in hydrogen for 1 hour at 1100°C. (2010°F.) (according to Squire[52]): *D*, relation between impact strength and density; *E*, relation between modulus of elasticity and density.

[55a] J. F. Kuzmick, *Trans. Am. Inst. Mining Met. Engrs.*, *175*, 813 (1948).

[56] R. P. Seelig, discussion of F. V. Lenel, *Trans. Am. Inst. Mining Met. Engrs.*, *161*, 541 (1945).

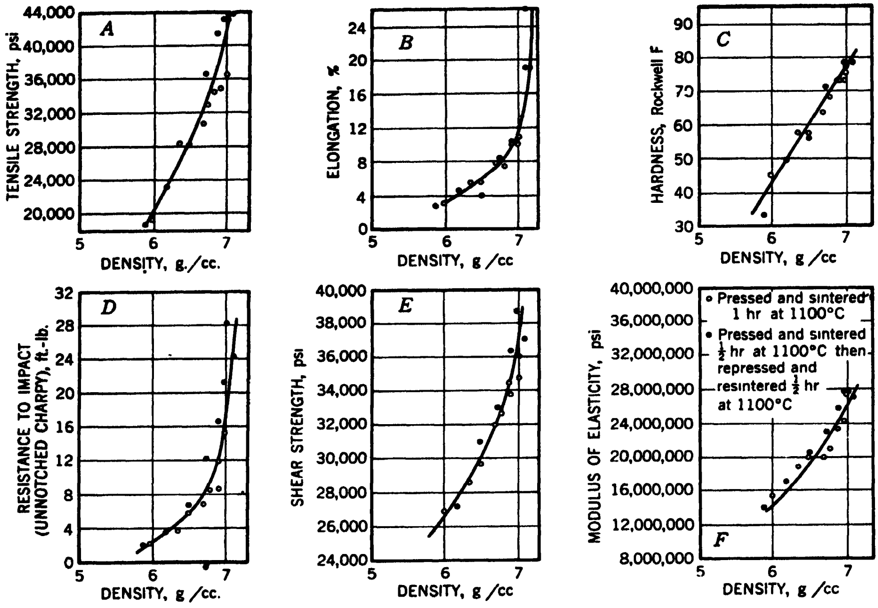

Fig. 441. Effect of repressing and resintering on the physical properties of iron powder compacts (according to Squire[52]): *A*, relation between tensile strength and density; *B*, relation between elongation and density; *C*, relation between hardness and density; *D*, relation between impact strength and density; *E*, relation between shear strength and density; and *F*, relation between modulus of elasticity and density.

TABLE 171

Characteristics of Iron Powders Used by Squire[52]

Powder No.	1	2	3	4	5	6
Chemical analysis, %						
Carbon	0.19–0.18	0.02	0.04	0.04	0.08	0.02
Manganese	0.18	0.34	0.0	0.14	0.25	0
Silicon	0.075	0.20	0.01	0.17	0.10	0
Sulfur	0.022	0.009	0.012	0.009	0.23	0.008
Phosphorus	0.005	0.007	0.003	0.019	0.007	0.002
Nickel	0.09	0.06	0	0	0.045	Trace
Chromium	0.03	0.04	0	0.03	0.03	0.03
Screen analysis, %						
+100	0.05	0.35	1.2	0	1.8	1.5
−100 +140	7.40	4.2	15.4	0	5.9	8.5
−140 +200	23.25	29.6	39.5	0	34.25	24.8
−200 +270	9.75	9.9	10.4	0.05	10.65	9.8
−270 +325	12.35	13.5	11.8	0.15	14.15	14.0
−325	46.80	43.0	22.0	99.45	32.75	41.2
Apparent density, g./cc.	1.71	2.27	2.88	2.79	2.67	2.52
Tap density, g./cc.	2.55	2.75	3.30	4.28	3.05	3.52
Specific surface, cm.^{2}/g.	1059	522	235	1460	488	530
Flow rate, g./sec.	0	0	1.50	0	1.86	1.06

Applications of Sintered Iron

At first glance the number of small parts that can be manufactured from iron powder appears to be almost unlimited; even if the limitations imposed on the process and products by presently available equipment and shortcomings in the performance of the powder as set forth in Volume I, Chapter IX, as well as those inherent in their economy, are considered fully, a very considerable number of shapes can be produced on the basis of our present experience. In fact, it must be borne in mind that any part up to about ten pounds that requires machining or other

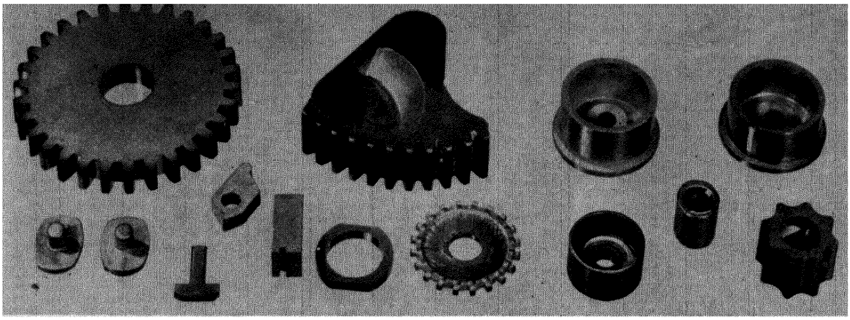

Fig. 442. Assortment of structural parts from sintered iron (courtesy of American Electro Metal Corp.).

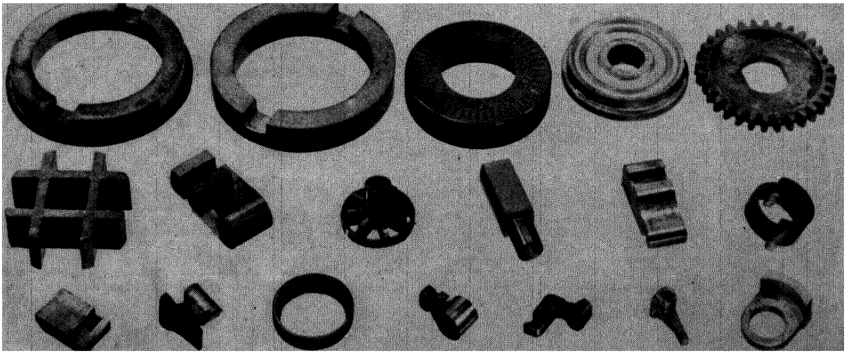

Fig. 443. Variety of structural components from sintered iron (courtesy of R. P. Seelig).

expensive working and is of such symmetric design that it can be molded in and ejected from a die is a potential iron powder product.

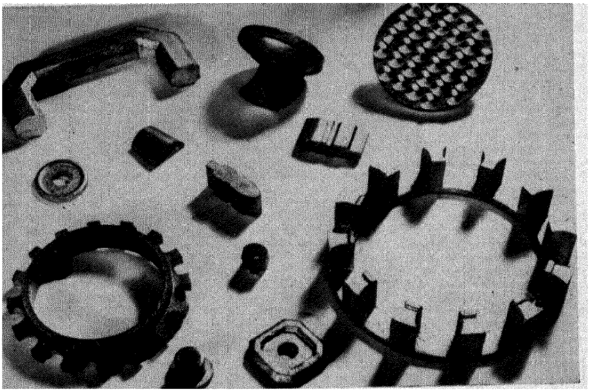

Fig. 444. Assortment of sintered iron parts used in European machine and apparatus constructions (according to Kieffer, Benesovsky, and Bartels[57]).

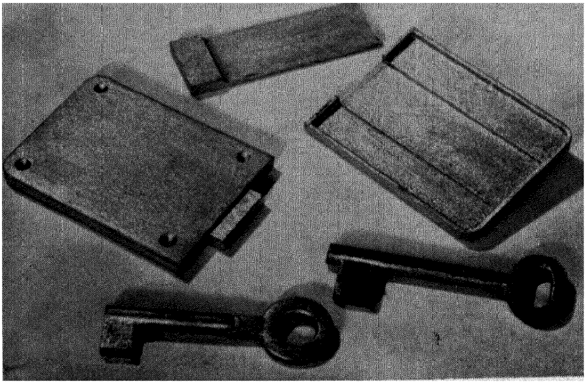

Fig. 445. Assortment of key blanks, latches, and lock boxes produced economically in post-war Austria from sintered iron (according to Kieffer, Benesovsky, and Bartels[57]).

The comparatively poor physical properties obtainable in sintered pure iron parts restrict their applications principally to mild steel machine elements which are normally machined from iron and steel foundry products. Assortments of domestic sintered iron parts are shown in Figures 442 and 443, and European sintered iron products in Figures 444 and 445.[57]

Equipment containing small integral parts, both moving and stationary, that constitutes potential applications for sintered iron products is listed by Firth.[58] The list, somewhat enlarged, includes agricultural machinery, air-conditioning equipment, automobiles, construction machinery, electrical control and signal apparatus, engines and turbines, hearing aids, heating and cooking apparatus and controls, laundry equipment, office and store machines, professional and scientific instruments, radio and television equipment, refrigerators, service industry machines, surgical, medical and dental instruments, tools and general hardware, textile machines, toy trains, and x-ray apparatus.

SINTERED CARBON STEELS

Industrial Developments

The demand for parts possessing greater strength and, particularly, increased hardness and wear resistance than found in sintered iron has led to the development of iron–carbon alloys, which are conveniently referred to as "sintered steels." The term "pseudosteels" would undoubtedly be more correct, since the structure of these materials is generally abnormal in a number of ways. Primarily, the presence of pores obscures the grain structure; also, upon slow cooling, the pearlitic structure is usually coarser than found in normal steels. Upon quenching—even in water or brine—the structure does not usually transform into martensite but only into very fine pearlite. This peculiar phenomenon is accompanied by only a limited ability of the material to harden, which may be attributed to the absence in the structure of such beneficial elements as manganese or silicon (for further details, see Volume I, Chapter XIX).

During the past decade the powder metallurgy of steel has gone through many development phases, and several fundamentally different approaches have crystallized. The principal ones include:

(*1*) Production of sintered steel parts by mixing the elemental constituents and diffusion-sintering the compacted powder mixture.

(*2*) Prealloying the powder by gas-carburization and sintering the cold-pressed powder compacts.

(*3*) Production of steel powders by mechanical comminution of bulk steel, or by atomization of cast iron, followed by decarburization and either hot-pressing or cold-pressing and sintering the steel powder.

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[57] R. Kieffer, F. Benesovsky, and H. J. Bartels, *Powder Met. Bull.*, *2*, No. 3, 54 (1947).

[58] C. V. Firth, *Information Circ. No. 3*, Univ. Minnesota, Mines Experiment Station, Minneapolis, Minn., May, 1943.

Offermann, Buchholtz, and Schulz[59] first proved conclusively that sintered steels can be produced synthetically by mixing iron and carbon powders. They treated powder mixtures of carbonyl iron and lampblack for several hours at 1000–1100°C. (1830–2010°F.) and forged the sintered porous ingot masses into bars weighing up to five tons. Up to a combined C content of about 0.9% the resulting steels displayed a relatively homogeneous and normal microstructure. Abnormal structures with correspondingly poor mechanical properties were obtained at higher carbon contents. A partial elimination of these anomalies was achieved by the addition of phosphorus and sulfur, by the use of graphite instead of lampblack, and by the addition of suitable alloying elements such as manganese, all incorporated in the iron powder through prolonged milling. Compaction of the powder mixtures prior to sintering also contributed toward a more normal structure, since the pressing operation tends to dislodge absorbed gas films and to increase the diffusion rate of carbon into the iron. These test results have been confirmed with domestic carbonyl iron powders by Kahles.[60] Comstock[61] was the first to report very good results with mixtures of fine graphite powder and electrolytic iron powders. The distinct superiority of electrolytic iron as compared with hydrogen-reduced iron as raw material for compacts containing 0.5% C has been reported by Trail,[62] and Stern[63,63a] has confirmed these findings for a wider range of carbon contents. While the procedure employing the mixed constituents in elemental form has the great practical advantage of yielding comparatively high densities without the need for excessive molding pressures, the physical properties and the susceptibility to heat treatment are inferior to normal steels, unless essential addition elements are added (*e.g.*, manganese, silicon, etc.) and well diffused into the structure during extensive sintering treatments.

The second procedure is designed to reduce the long diffusion-sintering periods by placing part of the alloying into the powder production stage. In one process[64] a pseudosteel powder is obtained by gas-carburizing electrolytic or reduced iron powder to such a degree that each particle has eutectoid or hypereutectoid structure. This treatment is immediately

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[59] E. K. Offermann, H. Bucholtz, and E. H. Schulz, *Stahl u. Eisen, 56,* 1132 (1936) (in English).

[60] J. F. Kahles, *Trans. Am. Soc. Metals, 38,* 618 (1947).

[61] G. J. Comstock, *Communication at First Ann. Spring Meeting of Metal Powder Association,* New York, May 5, 1944.

[62] R. J. Trail, *Trans. Can. Inst. Mining Met., 47,* 490 (1944).

[63] G. Stern, *Trans. Am. Inst. Mining Met. Engrs., 166,* 556 (1946).

[63a] G. Stern, *Proc. International Powder Metallurgy Conference,* Graz, July 12–17, 1948, Referate No. 57; *Iron Age, 163,* No. 12, 81 (1949).

[64] U. S. Pat. 2,175,850.

followed by controlled surface decarburization in moist hydrogen or in steam to render the particles more plastic and adaptable for cold-molding to fairly high density (see also Volume I, Chapter III, Fig. 13). Sintering of the compacts requires only short periods for purposes of consolidation, since diffusion treatment has already taken place initially to a large extent. While the resulting material exhibits comparatively good physical properties, its ability to harden remains inferior to ordinary steels because of the absence of beneficial alloying constituents.

The third procedure derives its chief advantage from the fact that all necessary alloying ingredients are incorporated and distributed homogeneously in the raw material. If, for example, a steel powder of well-defined high-carbon content is mixed with pure, plastic iron powder, a homogeneous steel structure of normal texture can be produced during sintering[65] (see Volume I, Chapter XIV, Fig. 224*B*). Similarly, such a structure is obtainable by compacting steel powder after mixing with iron oxide and pure iron powders.[66] In these procedures, layers of the relatively plastic iron are placed on the surfaces of the hard steel particles which facilitate the production of coherent bodies during cold pressing at high pressures. The beneficial effect on the final sintered steel structure of a combined carbon in the initial powder is also apparent when cast iron powder is employed (Volume I, Chapter XIV, Fig. 224*C*). Bal'shin and Korolenko[67] and Harder[68] have produced steel powders of a malleable iron type by mechanically grinding white cast iron and annealing the grindings between 750 and 950°C. (1400 and 1700°F.). During this treatment the cementite is decomposed, and the major part of the combined carbon either converted into highly dispersed temper carbon or removed by reaction with the furnace atmosphere or oxide films surrounding the particles. The graphitic carbon can be entirely eliminated by a process which involves the comminution of the carbon-containing iron in the liquid state by atomizing, followed by pulverization after solidification and complete decarburization by treatment in a suitable atmosphere at elevated temperatures.[69] The solid and comparatively hard powder particles suggest use of the hot-press method for dense compacts. The economically preferable cold-press method results in porous compacts of but moderate physical properties. However, because of the presence of elements such as manganese and silicon in the normal steel structure (within each particle), the sintered compacts are generally more susceptible to drastic quench hardening than their counterparts produced

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[65] U. S. Pats. 2,342,799; 2,352,316.

[66] U. S. Pat. 2,315,302.

[67] M. Yu. Bal'shin and N. G. Korolenko, *Metallurgia*, *22*, No. 128, 59 (1940).

[68] U. S. Pat. 2,301,805.

[69] U. S. Pat. 2,366,371.

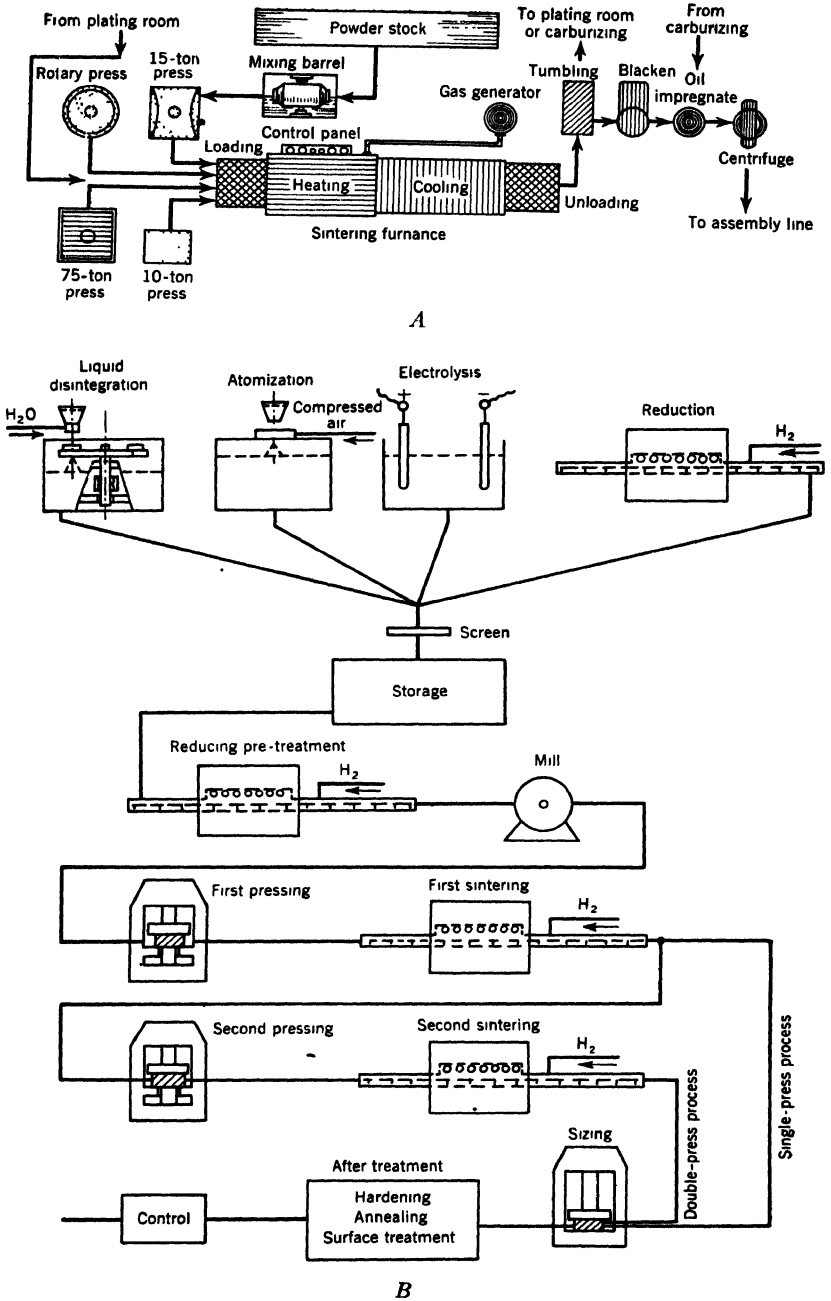

Fig. 446. Schematic representation of production of sintered steel parts *A*, by the Lionel Corporation (according to Bonanno[69a]), and *B*, by Metallwerk Plansee in Reutte, Austria (according to Kieffer, Benesovsky, and Bartels[70]).

synthetically from the elemental powders. Accordingly, hardness and wear resistance in parts from steel powder have been considerably improved.

Manufacture of Steel Parts

The manufacture of sintered steel parts resembles that of sintered pure iron parts except for two important details. Very close control of atmospheric conditions must be maintained during sintering in order to control or prevent decarburization, and the rate of cooling after sintering must be regulated to keep the steel structure soft enough to permit further plastic deformation during coining; this is usually necessary to obtain a product of satisfactory density. Of course, subsequent heat treatment to improve physical properties constitutes an additional step not included in the production of pure iron parts. Figure 446*A* gives a flow diagram of the various operations in the production of sintered steel components, as used by the Lionel Corporation[69a]; Figure 446*B* gives a similar chart of operations as used by the Metallwerk Plansee in Austria.[70]

RAW MATERIAL

The raw materials used in the production of steel parts are selected according to the method of production. When the production is based on a mixture of the elemental powders, iron powders are of the same type as used for pure iron parts. In order of importance, they are: (*1*) reduced domestic iron powder; (*2*) reduced Swedish sponge iron; (*3*) completely decarburized shotted, atomized, or disintegrated steel and cast iron; (*4*) shotted, atomized, or disintegrated steel and cast iron mixed with a large proportion of soft, pure iron; (*5*) electrolytic iron powder; and (*6*) carbonyl iron powder. (For details of production of these powders see Volume I, Chapters III and VI.)

The powdered carbon addition is preferably in the form of the finest grade of graphite. A thorough study by Glauch[71] on the adaptability of various types of natural and synthetic graphite powders in iron compacts has shown that natural graphite types give superior results, and that, of these, the crystalline types are more suitable than the amorphous; certain types of flake graphite are apparently also suitable for pressing and sintering of steel compacts. It is very important to mix the iron and graphite thoroughly, but it is not always easily accomplished. Segregation

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[69a] J. L. Bonanno, *Proc. Fifth Annual Spring Meeting of Metal Powder Association,* Chicago, April 5–6, 1949, p. 74.

[70] R. Kieffer, F. Benesovsky, and H. J. Bartels, *Powder Met. Bull., 2,* No. 3. 54 (1947).

[71] E. S. Glauch, *Proc. Second Annual Spring Meeting of Metal Powder Association,* New York, June 13, 1946, p. 2.

due to differences in specific gravity of the two components is common and must be curtailed by screening, ball milling, or adding fluids that glue the graphite particles to the surface of the iron particles. (See also Volume I, Chapter VII.)

In allotting the proper proportion of graphite to the mix, it must be borne in mind that not all of the graphite will be converted to combined carbon during later treatments. Even if very pure iron powders are used, some portion of the graphite is lost in the reaction with oxygen contained in the air volume trapped during compaction of the particles. Less pure iron powders cause additional consumption of graphite during reaction to carbon dioxide with the oxygen of the surface films or inclusions. In practice it has been found possible to closely estimate the extra amount of graphite necessary to balance these losses, and an empirical formula which takes the oxygen content as well as the particle shape into account may prove applicable in a majority of cases. In the equation:

$$G = C + 3L_hS/8$$

G is the percentage graphite to be added to the mix, C is the desired final percentage carbon content of the sintered steel, L_h is the hydrogen-loss percentage determined on the iron powder according to standard procedure,[72] and S is a shape factor which may vary from 1 for completely spherical particles (*e.g.*, carbonyl powder) to 2 for very spongy and fluffy particles (*e.g.*, hydrogen-reduced, high purity, low density powders). Thus, *e.g.*, a sintered steel compact of eutectoid composition (0.87% C)—to be produced from an electrolytic powder of 0.25% hydrogen loss and comparatively compact particle shape suggesting a shape factor of 1.5—would require a graphite addition of:

$$G = 0.87 + (3)\ (0.25)\ (1.5)/8 = 1.01\%$$

If the same steel composition is to be produced from reduced Swedish sponge iron of 0.8% hydrogen loss, to which a shape factor of 1.8 may be attributed, the graphite addition would have to be increased to 1.41%.

Any one of the commercial grades (*e.g.*, —100 mesh) of iron powders is also suitable for prealloying by gas carburization, although the reduced and electrolytic brands appear preferable. A number of techniques apply to the process; the powder may be heated and activated in rotary kiln furnaces, or it may be transported through horizontal tube furnaces, or it may fall through a vertical shaft furnace. The carburizing gas, consisting either of manufactured or natural gas, or of partially combusted hydrocarbons, is passed through the powder mass in counter-

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[72] Metal Powder Assoc. Standard, 2–48T, 1948.

stream, where possible. Immediately connecting with the carburizing cycle is a decarburizing cycle; both cycles being closely controlled as to temperature, time, and gas flow rate. The microstructure of particles of a powder, before and after the decarburization, has been illustrated in Figure 13 (Volume I, Chapter III).

Several principal types of powder are suitable for the third method of producing sintered steel: (*1*) crushed steel grit or shot; (*2*) crushed white cast iron grit or shot; and (*3*) atomized or liquid-disintegrated cast iron, or pig iron. The steel powders are produced exclusively by mechanical comminution of heat-treated and hardened high-carbon steel scrap. One type used widely for sand-blasting purposes is obtained by crushing to various grades water-quenched sheet scrap left over from the production of plow shares and similar products (see also Volume I, Chapter VI). The combined carbon content of the powder is about 1%. In the crushed condition the powder is too brittle for compaction; after annealing it becomes compressible, although high pressures are required in order to obtain moderately dense and strong compacts. A surface decarburization treatment coupled with the annealing process improves the compactibility to a marked degree, and at 50 tsi a powder decarburized to about 0.4% C becomes compressible to a density of about 75% of that of bulk steel.

Powdered cast iron is obtained either by shotting the metal to granular size, or by atomizing or centrifugally disintegrating remolten scrap. The particle size is usually coarse after shotting, and further comminution of the shot by crushing and milling is indicated. This is not required for the finer grades produced by atomization or liquid disintegration. In contrast to the crushed steels, annealing is not a practical procedure for insuring improved compactibility, since only lengthy annealing would result in graphitization of the cementite. For this reason, cast iron powders are most effectively softened by thorough decarburization. Through adequate control of the heating and cooling cycles and the proper choice of atmosphere, a uniformly decarburized powder is obtainable, and the bulk of the cementite is converted into ferrite plus pearlite. However, traces of free graphite usually cannot be avoided, and will remain inside the particles as potential regions of weakness. Only complete decarburization followed by controlled carburization will completely eliminate the free graphite.

The same types of steel and cast iron powders are also suitable for the fourth method of producing sintered steel. In this case, however, the powders are used in the nondecarburized state as originally produced.

Their proportion is usually in the order of 15–25% of the total mixture, and free graphite may be added to improve the compactibility.[72a]

When comparing the last group of powders with the one previously described, it must be realized that the greater molding difficulties are not caused entirely by the combined carbon in the structure. Even completely decarburized powders resist compaction to a greater extent than electrolytic or reduced iron powders; not only is the greater rigidity of the individual particles caused by their compactness, but the very alloying ingredients, manganese, silicon, etc., that make the powder desirable from the standpoint of ability to harden cause increased resistance to deformation during compaction.

In selecting the correct type and composition of the powder, its oxygen content must definitely be taken into account. Especially, if the material has been produced by mechanical pulverization or atomization, the particles are surrounded by heavy oxide films which will react with the carbon contained in the steel during the early stages of the sintering treatment.

MOLDING

The molding technique applicable to steel parts depends largely on the type of raw material to be processed. As long as basically soft iron powder constitutes the major constituent, the procedure is not different from that outlined before for pure iron parts. Automatic tableting presses giving high production rates are suitable, and pressures need not exceed 50 tsi. In fact, molding and particularly ejection are facilitated by the lubricating properties of the graphite powder necessary for the formation of the steel structure during sintering, and it may often be possible to employ lower molding and ejection pressures than required for pure iron parts. However, care must be exercised to avoid segregation of the much lighter graphite powder from the mix during feeding into the die cavity; this can be accomplished by appropriate particle size control, proper mixing technique, or by adding a small proportion of an organic fluid (*e.g.*, a high molecular alcohol) which acts as a segregation inhibitor (see also Volume I, Chapter VII).

When basically hard and nonplastic powders are involved (annealed steel or decarburized cast iron powders), the comparatively poor compactibility makes industrial molding extremely difficult. Specific pressures similar to those used for iron-graphite mixtures would result in

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[72a] J. A. Judd, *Symposium on Powder Metallurgy,* The Iron and Steel Institute, Special Report No. 38, London, 1947, p. 117.

compacts of low green strength unsuitable for further handling. Usable compacts would be formed only at higher pressures, *e.g.*, 50 to 100 tsi, entailing slow-acting, strongly constructed press and die equipment, with the accent on hydraulic machines and die liners from cemented carbides or similar wear-resistant materials.

The use of hot-press equipment has been suggested by Jones[73] in connection with the industrial molding of cast iron powder to which a small percentage of liquid-phase-forming iron–carbon–phosphorus master alloy is added ("Pacteron"), but the process has so far failed to develop to a significant stage (for details, see Volume I, Chapters XII and XIII).

SINTERING

The sintering procedure—like the molding technique—is largely dependent on the kind of raw material employed. The great advantage of the iron–graphite mixtures is brought about by their inherent plasticity. This desirable property can be utilized not only in compaction, but can, at least in part, be retained by a sintering operation which results in steel compacts that are susceptible to further densification and plastic deformation during a subsequent coining step. If, for instance, a sintering cycle is chosen that allows only a *limited* degree of diffusion of the carbon into the iron, but at the same time causes intimate sinter bonds to be formed between the ferritic particles, a heterogeneous structure results that consists of a basically soft ferritic network and numerous regions rich in cementite or graphite areas. (A theoretical discussion of the role of the diffusion of carbon in the production of sintered steel was recently advanced by Seith.[73a]) A treatment of iron–graphite compacts at 1000–1100°C. (1830–2010°F.) for five to twenty-five minutes in a protective atmosphere tends to create such a structure. Diffusion into a homogeneous structure is readily obtained by resintering at a longer cycle after coining; the diffusion is thereby aided by the cold work applied. Complete homogenization during the first sintering operation precludes coining at reasonable pressures; it is desirable only where comparatively dense compacts can be produced during molding at high pressures, or where an intense sintering treatment at high temperatures for extended times causes densification through shrinkage. From a practical point of view, neither approach is as good as the one that divides sintering into two steps and provides for an intermediate coining.

The sintering operation may be combined with a carburizing operation which is controlled through the action of the furnace atmosphere

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[73] W. D. Jones, *Foundry Trade J.*, *59*, 40 (1938).

[73a] W. Seith, *Proc. International Powder Metallurgy Conference*, **Graz, July 12–17, 1948, Referate No. 7.**

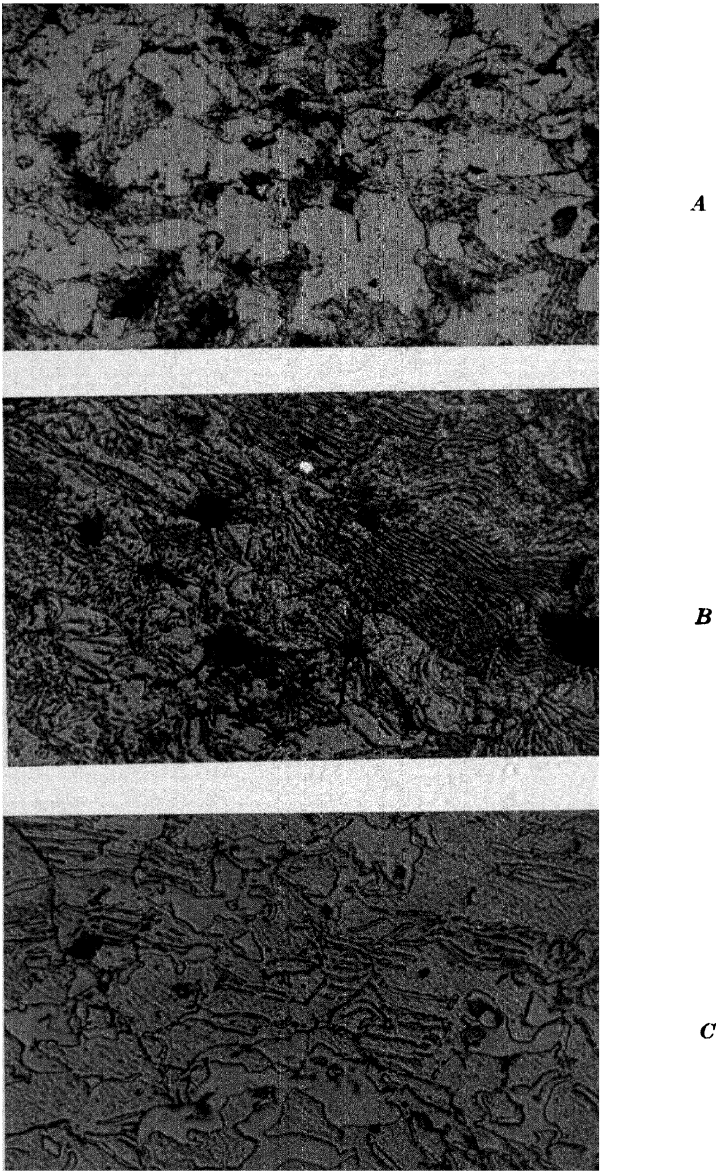

Fig. 447. Microstructure (×650) of carbon–steel compacts from gas-carburized steel powders. All compacts produced by compression at 60 tsi followed by sintering in hydrogen for 4 hours at 1000°C. (1830°F.) (courtesy of Charles Hardy, Inc.): *A*, initial powder containing 0.6% combined carbon; *B*, initial powder containing 0.9% combined carbon; *C*, initial powder containing 2.0% combined carbon.

("carbusintering").[74] Either pure iron powder or a mixture of iron powder and a small proportion of graphite can be compacted to fairly high density (80%) at 50 tsi and sintered at 1150 to 1200°C. (2100 to 2200°F.) in a carburizing atmosphere into a homogeneous structure containing 0.4% C after treatment for one hour. Coining for the purpose of further densification requires, however, a pressure of 75 to 100 tsi.

Where homogeneous steel particles serve as raw material, a *partial* carbon diffusion during sintering is not possible, and the sole function of the sintering treatment is to strengthen the sinter bonds through grain growth and homogenization of the steel structure in the austenitic state. The rigidity of the sintered structure makes subsequent coining impractical and necessitates high molding pressures as well as intensive sintering to produce reasonably high densities and physical properties. Depending on the history of the steel powder, the sintering cycle varies in temperature from 1000 to 1400°C. (1830 to 2550°F.) and in time from one to four hours. The photomicrographs in Figure 447 show the microstructures of compacts produced from gas-carburized steel powders by sintering at 1000°C. (1830°F.) for four hours; the structure of compacts produced from mechanically comminuted crushed steel scrap by sintering at 1250°C. (2280°F.) for one hour is shown in Figure 224 (Volume I, Chapter XIV).

A sintering procedure for compacts pressed from mixtures of soft or pure iron powders with a small percentage of an alloy powder with combined carbon content, *e.g.* white cast iron powder, has been outlined by Judd.[72a] The addition of about 1% graphite permits compaction at about 50 tsi; sintering is best performed at a temperature of 1120°C. (2050°F.) in dissociated ammonia for about 40 minutes, followed directly by a hot-quenching step consisting of moving the material into a furnace zone held at 700–750°C. (1290–1380°F.). This treatment results in a much stronger structure, due to spheroidization of the iron carbide in the structure. The main advantage of the sintering procedure developed by Judd apparently lies in the fact that sintering takes place in the presence of the liquid iron–iron carbide eutectic phase which produces a highly consolidated and homogenized steel structure.

The degree of diffusion and homogenization of the structure is greatly affected by the reaction of the carbon with oxygen present either in the material or in the furnace atmosphere. The necessity of compensating for the oxygen contained in the powder has been stressed. The establishment of atmosphere conditions *truly inert* to the carbon contained in the steel compact at *any* temperature level through which the compact passes during the sintering treatment constitutes one of the

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[74] A. S. Margolis, *Iron Age, 157,* No. 9, 61 (1946).

major difficulties in producing sintered steel parts. The decarburization or carburization effects of the gas-steel reactions are considerably more aggravated during sintering or combined gas carburizing and sintering (carbusintering) on account of the continuous pore structure of the compacts which increases the exposed surface area considerably. (For a more detailed discussion of furnace atmospheres suitable for the sintering of steel, see Volume I, Chapter XVII.)

SUBSEQUENT OPERATIONS

Cold coining improves the density and other physical properties in compacts produced from mixtures of iron and graphite powders which have been subjected to only a brief sintering treatment accompanied by incomplete diffusion of the carbon-rich areas into the structure. Coining with pressures of about 50 tsi can produce densities up to about 90% of theoretical in such materials,[75] and the problems of die wear and load application connected with such a procedure appear to be tolerable for industrial uses, involving comparatively simple shapes. In the case of higher density requirements, or where complicated shapes—in particular those having curves or great sectional differences—are involved, the feasibility of cold coining of sintered steel parts must yet be proved.

Hot-coining or hot-forging tends to improve plasticity and deformability of the steel compact and results in greater densification and better physical properties, especially in compacts produced from steel powders, as shown by the experiments conducted by Koehring,[76] or from mixtures containing steel or cast iron powder, as well as pure iron powder and graphite, as shown by the work of Kieffer and Hotop.[76a] According to Allen,[77] sintered steel has been forged successfully on an industrial scale for the production of bearing lock sleeves 3 inches in diameter and $^5/_8$ inch thick, and weighing 8 oz. (the part supplanting gray cast iron sleeves which had to be machined completely). The powder was produced by hammer-milling SAE 1112X steel trimmings; it was pressed at 30 tsi and sintered at 1025°C. (1875°F.) for 15 minutes and then hot-forged. Cold-trimming and cold-coining operations were required afterward.

The applicability and effects of conventional steel heat treatments,[78] such as normalizing, quench hardening, case hardening, etc.,[79,80] to sin-

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[75] G. Stern, *Trans. Am. Inst. Mining Met. Engrs., 166,* 556 (1946).

[76] R. P. Koehring, in J. Wulff, *Powder Metallurgy.* Am. Soc. Metals, Cleveland, 1942, p. 304.

[76a] R. Kieffer and W. Hotop, *Sintereisen und Sinterstahl.* Springer, Vienna, 1948, pp. 251 ff.

[77] A. H. Allen, *Steel, 108,* No. 21, 74 (1941).

[78] G. Stern and J. Greenberg, *Iron Age, 157,* No. 17, 56 (1946).

[79] G. Stern and J. Greenberg, *Powder Met. Bull., 1,* 18 (1946).

[80] G. Stern and J. Greenberg, *Powder Met. Bull., 2,* 85 (1947).

TABLE 172
Relative Efficiency of Oil and Water as Quenching Media (Chadwick and Broadfield[81])[a]

Powder	Compacting pressure, tsi	Condition	Quenching medium	Diamond pyramid hardness	Microstructure
Grade M electrolytic powder + 2% graphite	40	Hardened	Oil	437	Martensitic matrix and cementite network
	40	Hardened	Water	478	Martensitic matrix and cementite network
	40	Hardened, and tempered[b]	Oil	296	Troostite and cementite network
	40	Hardened, and tempered[b]	Water	340	Troostite and cementite network
Grade M electrolytic powder + 1% graphite	40	Hardened	Oil	437	Martensite
	40	Hardened	Water	470	Martensite
	40	Hardened and tempered[b]	Oil	269	Troostite
	40	Hardened and tempered[b]	Water	296	Troostite
Grade N electrolytic powder + 2% graphite	75	Hardened	Oil	280	Sorbitic-pearlitic matrix and cementite network
	75	Hardened	Water	576	Martensitic matrix and cementite network
	60	Hardened	Oil	540	Martensitic matrix and cementite network
Grade N electrolytic powder + 1% graphite	75	Hardened	Oil	367	Martensite and troostite
	75	Hardened	Water	622	Martensite
	60	Hardened	Oil	502	Martensite
Grade N charcoal-reduced powder + 1% graphite	60	Hardened	Oil	240	Sorbitic pearlite and ferrite
	60	Hardened	Water	509	Martensite
	20	Hardened	Oil	222	Martensite and a little troostite

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[a] Compacts previously sintered for 1 hour at 1125°C. (2060°F.).

[b] At 250°C. (480°F.).

tered steel parts have been discussed in detail in Volume I, Chapter XIX. In a recent investigation in England, Chadwick and Broadfield[81] examined the relative efficiencies of oil and water as quenching media within a broader study of sintered steel metallurgy phenomena. The results of this work are summarized in Table 172, and the specifications for the raw materials are reproduced in Table 173.

TABLE 173
Chemical and Physical Characteristics of Annealed Iron Powders Used by Chadwick and Broadfield[81]

Characteristics	Electrolytic		Charcoal-reduced[a]	Comminuted[a]	
	Grade M	Grade N	Grade N	Grade M	Grade P
Chemical composition, %					
Carbon	0.04	0.02	0.10 (0.19)	0.25 (0.41)	0.20 (0.43)
Sulfur	0.06	0.04	0.01 (0.01)	0.04 (0.06)	0.04 (0.06)
Phosphorus	0.01	0.01	Nil (nil)	0.03 (0.07)	0.04 (0.09)
Silicon	0.006	0.02	0.06	0.27	0.23
Oxygen (reduced by hydrogen)	0.20	0.15	0.22 (1.36)	0.10 (1.11)	0.14 (1.58)
Oxygen (nonreducible oxides)	Nil	Nil	0.52	Nil	Nil
Particle-size distribution, %					
Resting on 100 B.S.S. mesh (>152 μ)	18	7	1	26	Nil
150 (104–152 μ)	22	14	19	22	6
200 (76–104 μ)	13	12	21	19	9
240 (66–76 μ)	14	16	3	2	2
Passing 240 (<66 μ)	33	51	56	31	83
Apparent density, g./cc.					
Without consolidation by tapping	3.0	3.6	2.2	3.2	2.6
With consolidation by tapping	3.8	4.3	3.3	3.7	3.3
Flow time, sec.					
Standard test	26	28	36	—[b]	—[b]

[a] Values in parentheses refer to the unannealed powders.

[b] These powders flowed readily but material was insufficient to obtain comparative values.

Properties of Sintered Steel

The physical properties of sintered steels are closely linked with their history. Compacts prepared from a mixture of the plastic ingredients (iron and carbon) are usually denser and stronger than those produced from steel powders. The superior compactibility of the mixture is of considerably greater consequence than the improved uniformity of the

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[81] R. Chadwick and E. R. Broadfield, *Symposium on Powder Metallurgy*. The Iron and Steel Institute, Special Report No. 38, London, 1947, p. 123.

structure attained during sintering of compacted steel powders, and, especially for very pure iron powders (electrolytic or carbonyl), remarkable physical properties can be obtained from such mixtures.

Squire,[82-84] in an extensive investigation of iron–graphite powder mixtures containing 1% graphite, has obtained the remarkable tensile strength value of 87,000 psi associated with an elongation value of 6% for plain pressed and sintered material. The effect on porosity and tensile properties of increasing compacting pressure and sintering time are reproduced in Table 174; the influence on the same properties of the particle size of graphite used in the mixture is shown for different sintering cycles in Table 175. Table 176 gives the physical and chemical characteristics of the iron and graphite powders employed in the investigation. The relation between tensile strength and sintering is shown graphically in Figure 448 for mixtures containing 1% graphite with shotted and decarburized steel powders which were compacted at three different pressures. The effect of the particle size of graphite on the tensile strength of electrolytic iron powder compacts is shown graphically in Figures 449 and 450, in which tensile strength is plotted against sintering time and temperature, respectively. In Figure 451 the tensile properties are shown as a function of the carbon content for sintered steel compacts prepared from electrolytic iron powder by pressing, presintering, coining, and final sintering, according to Stern.[85]

Recent work in Germany[85a] took the effect of vacuum-sintering on the formation of the steel structure into account. Mixtures of different types of iron powders and carbon were pressed at 43 to 57 tsi, and then sintered for 2 to 8 hours at 1200–1300°C. (2190–2370°F.). The structures produced were either ferritic-graphitic, or ferritic-graphitic-pearlitic, or entirely pearlitic, depending on the type of iron and the proportion of carbon used in the initial mixture. However, vacuum-sintering was found to have no noticeable effect on the physical properties of the final products. The highest tensile strength value reported was 85,000 psi as sintered, and 142,000 psi as quench hardened.

The effect of subsequent heat treatments is presented graphically in Figures 452–454.[85] For a comparison with standard values of SAE steels of similar carbon content after various heat treatments, see also Chapter XXXI. In Figures 455 and 456, tensile property changes with carbon content are shown for electrolytic as well as for reduced iron powder

[82] A. Squire, *Trans. Am. Inst. Mining Met. Engrs., 171,* 473 (1947).

[83] A. Squire, *Watertown Arsenal Lab. Repts. WAL 671/14 and 671/18* (1946).

[84] A. Squire, U. S. Dept. of Commerce, Office of Technical Services Repts., P.B. 4418, 4419, 4420, July 20, 1944.

[85] G. Stern, *Trans. Am. Inst. Mining Met. Engrs., 166,* 556 (1946).

[85a] H. Wiemer and W. A. Fischer, *Arch. Eisenhüttenwesen, 19,* 125 (1948).

TABLE 174

Tensile Properties and Porosity of 99–1 Iron–Graphite Compacts as Influenced by Forming Pressure and Sintering Time[a] (Squire[82])

Conditions		Sintering time, minutes											
		15		30		45		60		90		120	
Pressure, psi	Porosity, %	Tensile strength, psi	Elongation, %	Tensile strength, psi	Elongation, %	Tensile strength, psi	Elongation, %	Tensile strength, psi	Elongation, %	Tensile strength, psi	Elongation, %	Tensile strength, psi	Elongation, %
50,000	23.5	24,350	1	32,350	1	35,650	1	37,350	1	37,350	2	45,200	2
100,000	11.8	45,400	2	60,500	4	62,450	3	65,900	4	66,600	5	72,300	5
200,000	6.0	64,700	4	77,500	6	77,500	6	84,550	7	83,200	6	87,100	6

[a] Iron powder formed by shotting and decarburizing scrap steel; average particle diameter of graphite, 2 microns; sintering temperature, 1200 °C. (2190 °F.).

TABLE 175

Tensile Properties and Porosity of 99–1 Electrolytic Iron–Graphite Compacts as Influenced by Graphite Particle Size, Sintering Temperature, and Sintering Time[a] (Squire[82])

Temperature		Time, hr.	Average diameter of graphite particles											
			16 microns			6 microns			4 microns			2 microns		
°C.	°F.		Tensile strength, psi	Elongation, %	Porosity, %	Tensile strength, psi	Elongation, %	Porosity, %	Tensile strength, psi	Elongation, %	Porosity, %	Tensile strength, psi	Elongation, %	Porosity, %
1200	2190	0.5	30,500	0	18	32,500	0	16	35,000	0	15	43,500	0	15
		1	37,500	0	16.5	40,000	0	18.5	42,000	0	14	49,500	0	14
		2	47,500	2	16	47,500	1	15	50,500	2	14	53,000	3	13
		3	48,500	2	15	50,000	2	14	51,500	4	14	54,000	3	13
1150	2100	0.5	22,000	2	18	24,000	1	17	27,500	1	16	40,000	1	15
		1	29,000	1	18	33,000	1	16	36,500	1	15	45,000	1	14
		2	39,000	0	17	41,000	1	16	45,000	1	16	48,500	2	14
		3	41,000	3	16	43,500	3	15	45,500	2	14	49,000	3	13
1100	2010	0.5	15,000	0	18	18,000	0	16	21,000	0	15	35,000	1	14
		1	22,000	0	17	26,000	0	15	30,000	1	14	41,000	1	14
		2	30,000	1	17	33,500	1	16	37,500	0	15	44,500	1	14
		3	32,500	2	16	35,500	1	15	39,500	2	14	47,000	2	14
1050	1920	0.5	14,500	2	18	17,000	2	17	20,500	2	15	27,500	1	15
		1	19,500	1	18	23,000	1	17	26,000	1	17	34,000	0	15
		2	24,500	2	17	27,500	1	15	32,000	1	14	40,000	1	14
		3	28,000	1	17	31,000	2	15	35,000	2	15	44,500	1	14
1000	1830	0.5	9,000	0	16	10,000	0	15	11,000	0	14	12,500	0	13
		1	9,000	0	17	10,000	0	16	12,000	0	17	15,500	0	15
		2	9,000	0	17	10,200	0	16	13,000	0	14	16,500	0	14
		3	9,000	0	16	10,000	0	16	12,500	0	14	14,500	0	13

[a] Pressure, 100,000 psi.

TABLE 176

Characteristics of Iron and Graphite Powders Used by Squire[82]

	Shotted, decarburized scrap-steel powder	Electrolytic iron powder	Graphite	
Chemical analysis, %				
Carbon	0.04	0.10	Ash	0.27
Manganese	0.26	0.18	SiO_2	0.02
Silicon	0.02	0.04	Fe_2O_3	0.11
Sulfur	0.03	0.02	Al_2O_3	0.02
Phosphorus	0.02	0.01	Manganese	0.001
Nickel	0.06	0.05	Chromium	Trace
Chromium	0.04	0.17	Vanadium	
Oxygen	0.43	0.59	Copper	
			Nickel	
			Calcium	
			Titanium	
Screen analysis, %				
+100	0.3	1.6		
−100 +140	0.6	10.1		
−140 +200	6.8	29.3		
−200 +270	6.7	9.7		
−270 +325	18.6	11.6		
−325	66.8	37.6		
Apparent density, g./cc.				
	2.69	2.53		0.494 (16 μ) 0.421 (6 μ) 0.432 (4 μ) 0.323 (2 μ)
Specific surface, cm.²/g.				
	409	585		1.955 (16 μ) 5.975 (6 μ) 8.535 (4 μ) 12.500 (2 μ)
Rate of flow, g./sec.				
	Would not flow	1.28		Would not flow

compacts after pressing, sintering, coining, and annealing.[86] The diagrams give evidence of the inferior quality of the reduced iron powder compacts. Stern[86] attributes this to the differences in the microstructures and densities. The structure of sintered steels obtained from electrolytic powders is characterized by a very uniform distribution of the pearlite and a comparatively small pore volume (see Fig. 298*A*, Volume I, Chapter XIX; and Fig. 461*A* and *B*, page 365). In contrast, compacts

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[86] G. Stern, *Proc. International Powder Metallurgy Conference*, Graz, July 12–17, 1948, Referate No. 57; *Iron Age, 163*, No. 12, 81 (1949).

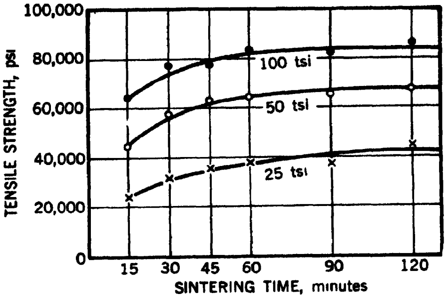

Fig. 448. Effect of sintering time on the tensile strength of shotted and decarburized steel powder compacts compressed at three different pressures and containing 1% graphite additions (according to Squire[82]).

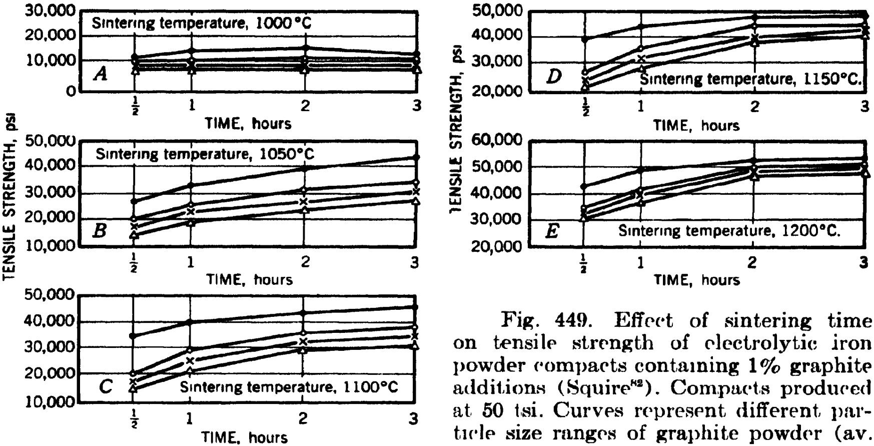

Fig. 449. Effect of sintering time on tensile strength of electrolytic iron powder compacts containing 1% graphite additions (Squire[82]). Compacts produced at 50 tsi. Curves represent different particle size ranges of graphite powder (av. diam. of carbon particles): ●, 2 microns; ○, 4 microns; ×, 6 microns; △, 16 microns.

prepared from reduced powders generally display a nonuniform distribution of the pearlite, large pores and oxide inclusions, and, therefore, inferior physical properties—except if alloyed with a small percentage of copper (p. 412). The higher oxide content of the reduced powder results in a correspondingly higher loss in carbon during sintering. In some areas, the random distribution of the oxide inclusions causes complete consumption of the graphite by reaction with the oxygen and an increased pore volume at these points; in other areas, some graphite is left over, which dissolves in the iron as sintering proceeds in the austenitic temperature range. Upon cooling a nonuniform pearlite distribution results, which—together with the lower density caused by inferior compressibility of the reduced powder and the creation of "secondary" pores by the carbon-oxygen reaction—is responsible for the inferior physical properties.

Recent European work seems to be in general agreement with the findings by Stern and Squire. Bernstorff and Silbereisen[86a] produced a

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[86a] H. Bernstorff and H. Silbereisen, *Arch. Metallkunde, 2*, No. 7/8, 295 (1948).

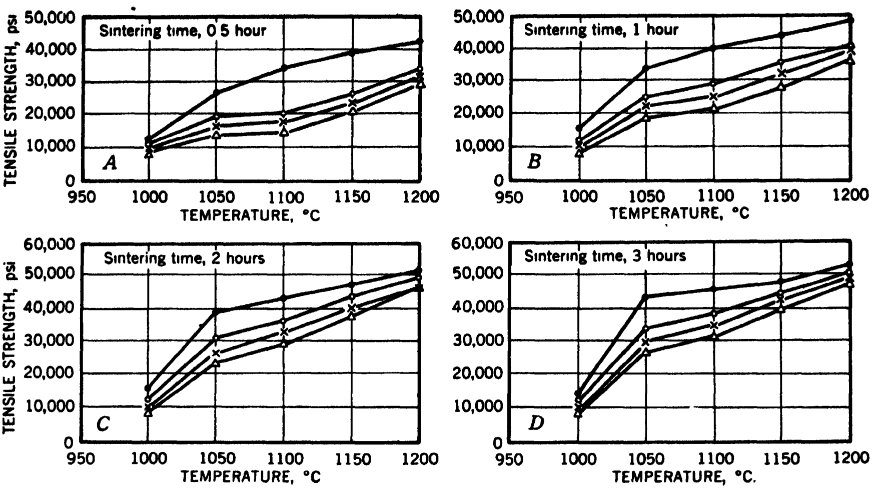

Fig. 450. Effect of sintering temperature on the tensile strength of electrolytic iron powder compacts containing 1% graphite additions (according to Squire[82]). Compacts were produced at 50 tsi. The curves in each graph represent different particle size ranges of the graphite powder (average diameter of carbon particles): ●, 2 microns; ○, 4 microns; ×, 6 microns; △, 16 microns.

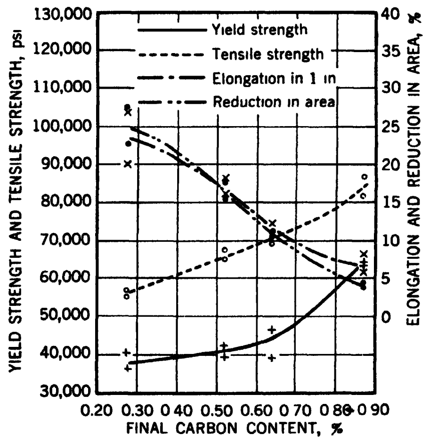

Fig. 451. Effect of the final carbon content on the physical properties of sintered carbon steel produced from mixtures of electrolytic iron and graphite powders (according to Stern[85]). Data established on compacts after furnace cooling from 1100°C. (2000°F.). Compacts were pressed at 50 tsi, presintered at 1100°C. (2000°F.) for 15 minutes, coined at 50 tsi, and sintered at 1100°C. (2000°F.) for 1 hour. Furnace atmosphere was cracked propane.

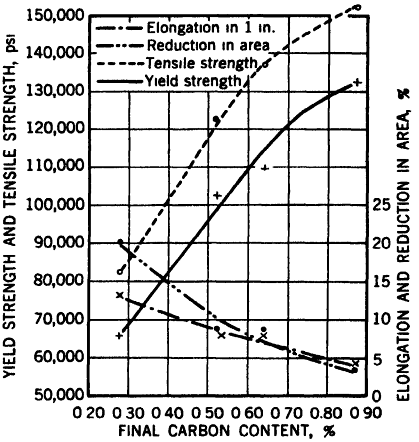

Fig. 452. Effect of the final carbon content on the physical properties of sintered carbon steel after heat treatment (according to Stern[85]). Compacts produced from mixtures of electrolytic iron and graphite powders. Processing the same as for material illustrated in Figure 451. Data established on compacts after furnace cooling from 1100°C. (2000°F.), reheating to 830°C. (1525°F.) followed by water quenching, and drawing at 315°C. (600°F.).

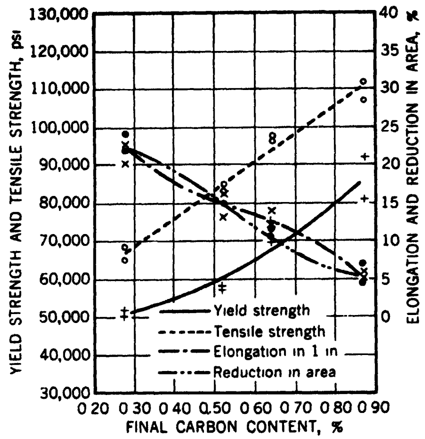

Fig. 453. Effect of the final carbon content on the physical properties of sintered carbon steel after heat treatment (according to Stern[85]). Material identical with that illustrated in Figure 452, except for a change in heat treatment involving oil quenching from 830–855°C. (1525–1575°F.) and drawing at 315–425°C. (600–800°F.).

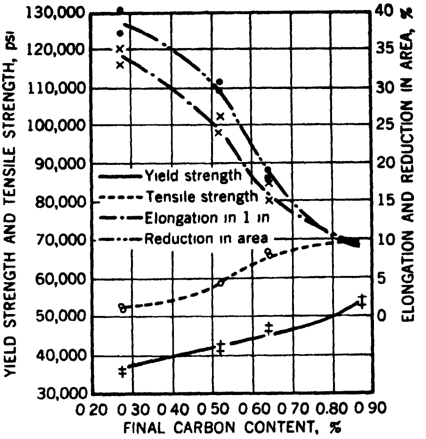

Fig. 454. Effect of the final carbon content on the physical properties of sintered carbon steel after heat treatment (according to Stern[85]). Material identical with that illustrated in Figure 453, but drawn at 705°C. (1300°F.).

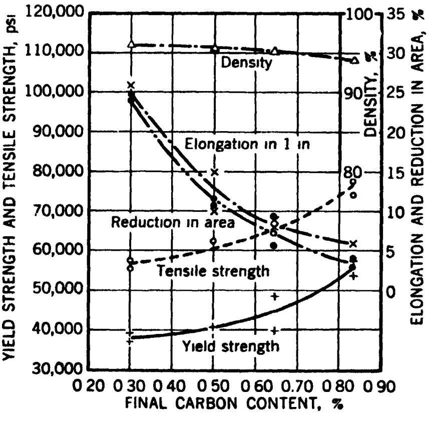

Fig. 455. Effect of the final carbon content on the physical properties of sintered carbon steel from electrolytic iron and graphite powder mixtures (according to Stern[86]). Data established on compacts after furnace cooling from annealing temperature. Compacts were pressed at 50 tsi, sintered at 1100°C. (2000°F.) for 1 hour, coined at 50 tsi, and annealed at 815°C. (1500°F.) for 30 minutes. Furnace atmosphere was cracked propane.

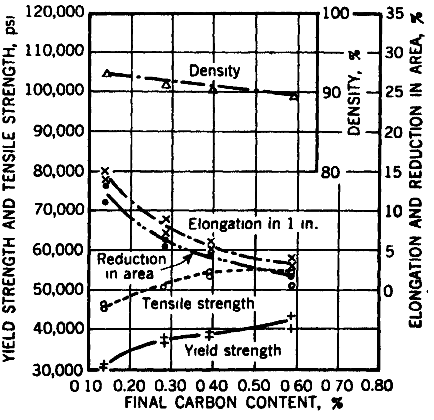

Fig. 456. Effect of the final carbon content on the physical properties of sintered carbon steel from reduced sponge iron and graphite powder mixtures (according to Stern[86]). Data established on compacts produced in the same manner as those illustrated in Figure 455.

sintered steel containing 0.67% combined carbon and displaying a tensile strength of 130,000 psi by compacting and sintering carbon-free soft iron, liquid carburizing, quenching, and final tempering at 200°C. (390°F.). They also compared sintered and cast steels of approximately equal tensile strength with regard to the necessary combined carbon content,

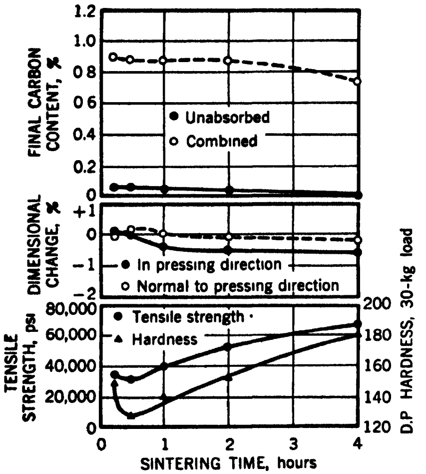

Fig. 457. Effect of sintering time at 1125°C. (2060°F.) on tensile strength, diamond pyramid hardness (D.P.), dimensional changes, and final carbon contents of sintered carbon steel compacts pressed at 40 tsi from a mixture of electrolytic iron and 1% graphite powders (according to Chadwick and Broadfield[87]).

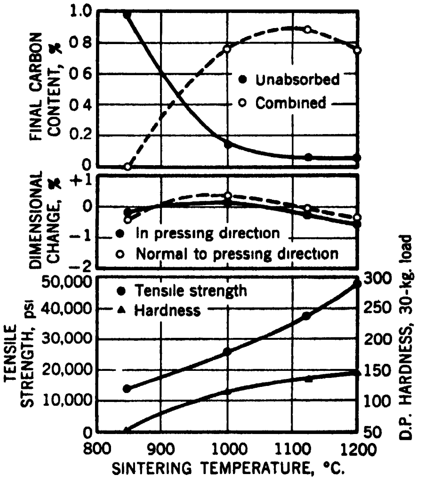

Fig. 458. Effect of sintering temperature (for 1-hour periods) on tensile strength, diamond pyramid hardness, dimensional changes, and final carbon contents of sintered carbon steel compacts pressed at 40 tsi from a mixture of electrolytic iron and 1% graphite powders (according to Chadwick and Broadfield[87])

and found that specimens from powder, pressed at about 43 tsi, and sintered in hydrogen at 1280°C. (2340°F.) required a much greater amount of carbon than the cast steel. Lipkes and Faikina[86b] produced steel from closely sized iron powder made by reduction of mill scale, by compaction at 43 tsi, sintering for 2–3 hours at 1200°C. (2190°F.), and repressing, which contained 0.32% C, and displayed a hardness of 98 Brinell and a tensile strength of 78,500 psi. Carburizing, followed by quenching and tempering, raised the hardness to 235 Brinell, and the tensile strength to 85,300 psi.

The data of Chadwick and Broadfield[87] are also essentially in agree-

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[86b] Y. M. Lipkes and L. A. Faikina, *Stal,* 7, 149 (1947).

[87] R. Chadwick and E. R. Broadfield, *Symposium on Powder Metallurgy.* The Iron and Steel Institute, Special Report No. 38, London, 1947, p. 123.

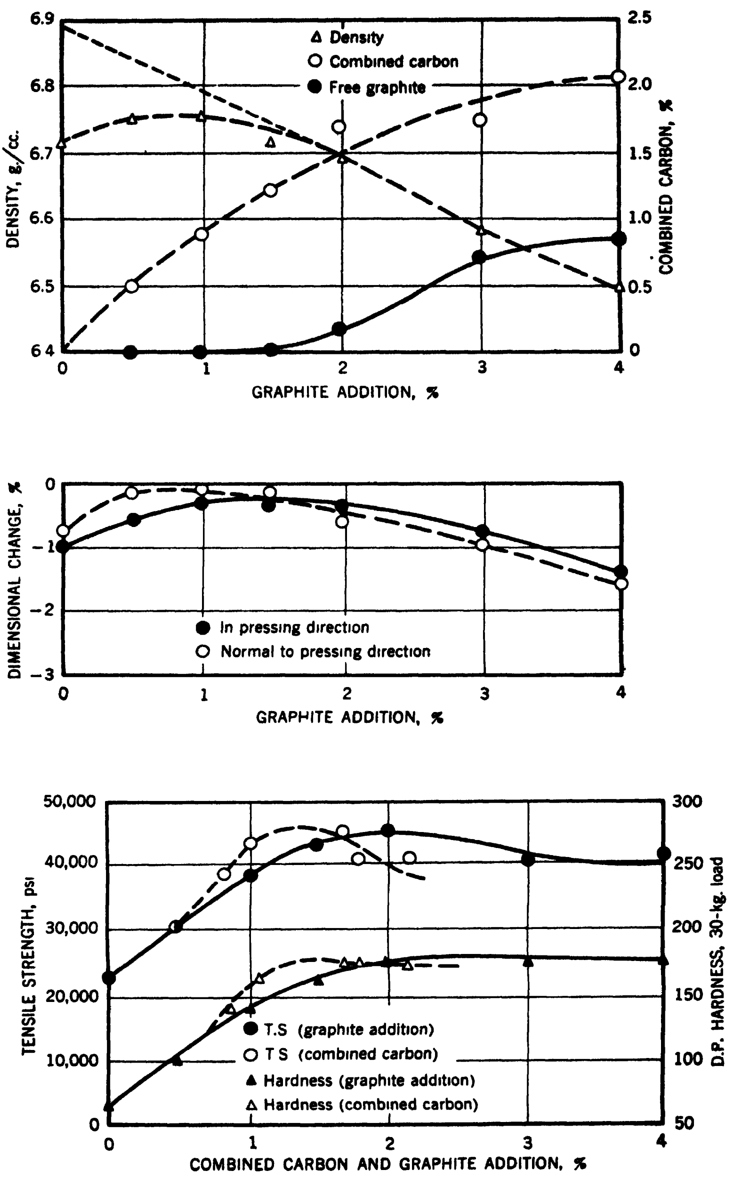


Fig. 459. Effect of graphite addition on tensile strength (T.S.), diamond pyramid hardness, dimensional changes, density, and final carbon contents, and of the final combined carbon content on tensile strength and diamond pyramid hardness of compacts pressed from mixtures of electrolytic iron and graphite powders at 40 tsi and sintered at 1125°C. (2060°F.) for 1 hour (according to Chadwick and Broadfield[87]).

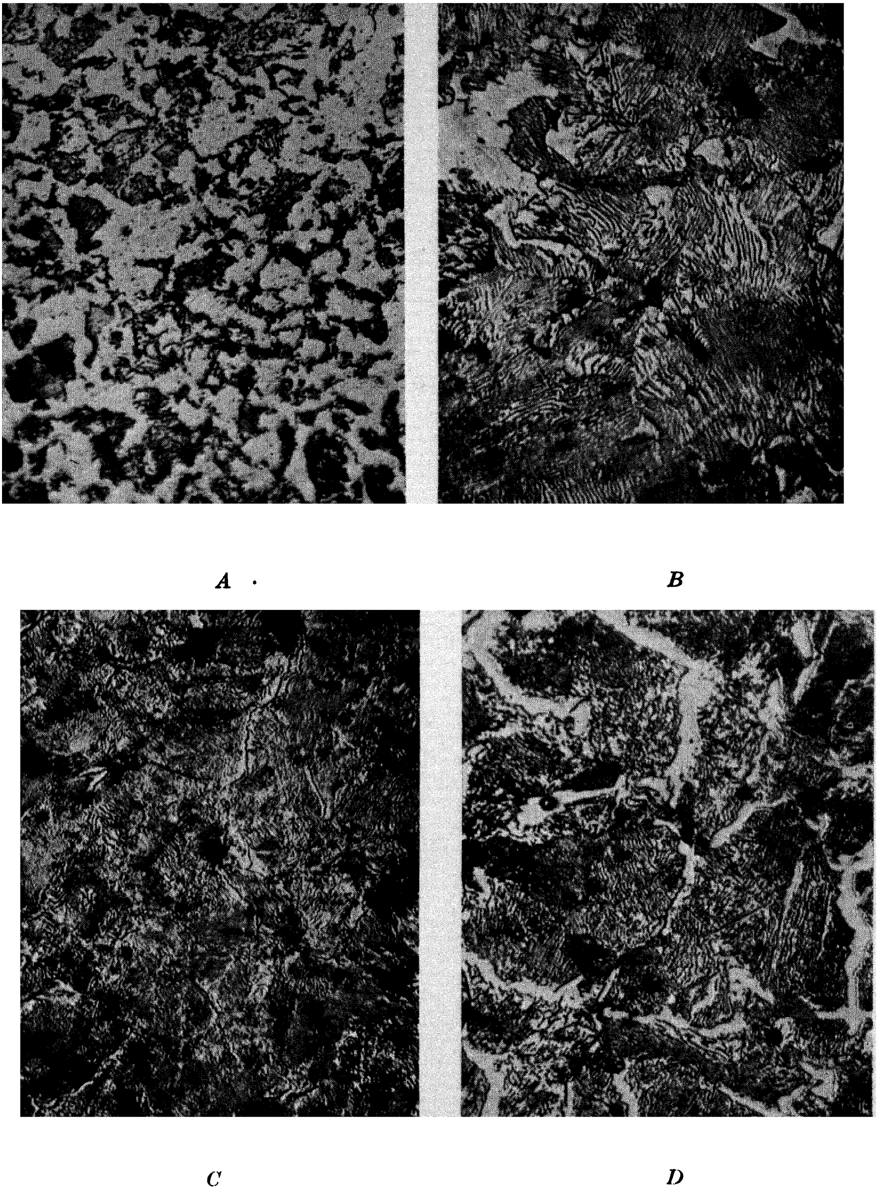


Fig. 460. Effect of graphite additions on the microstructure (×500) of compacts from mixtures of electrolytic iron and graphite powders (according to Chadwick and Broadfield[87]). All compacts were compressed at 40 tsi and sintered at 1125°C. (2060°F.) for 1 hour: *A,* 0.5% graphite addition, showing ferrite and pearlite; *B,* 1% graphite addition, showing ferrite and pearlite; *C,* 1.5% graphite addition, showing pearlite and cementite; and *D,* 4% graphite addition, showing pearlite and cementite.

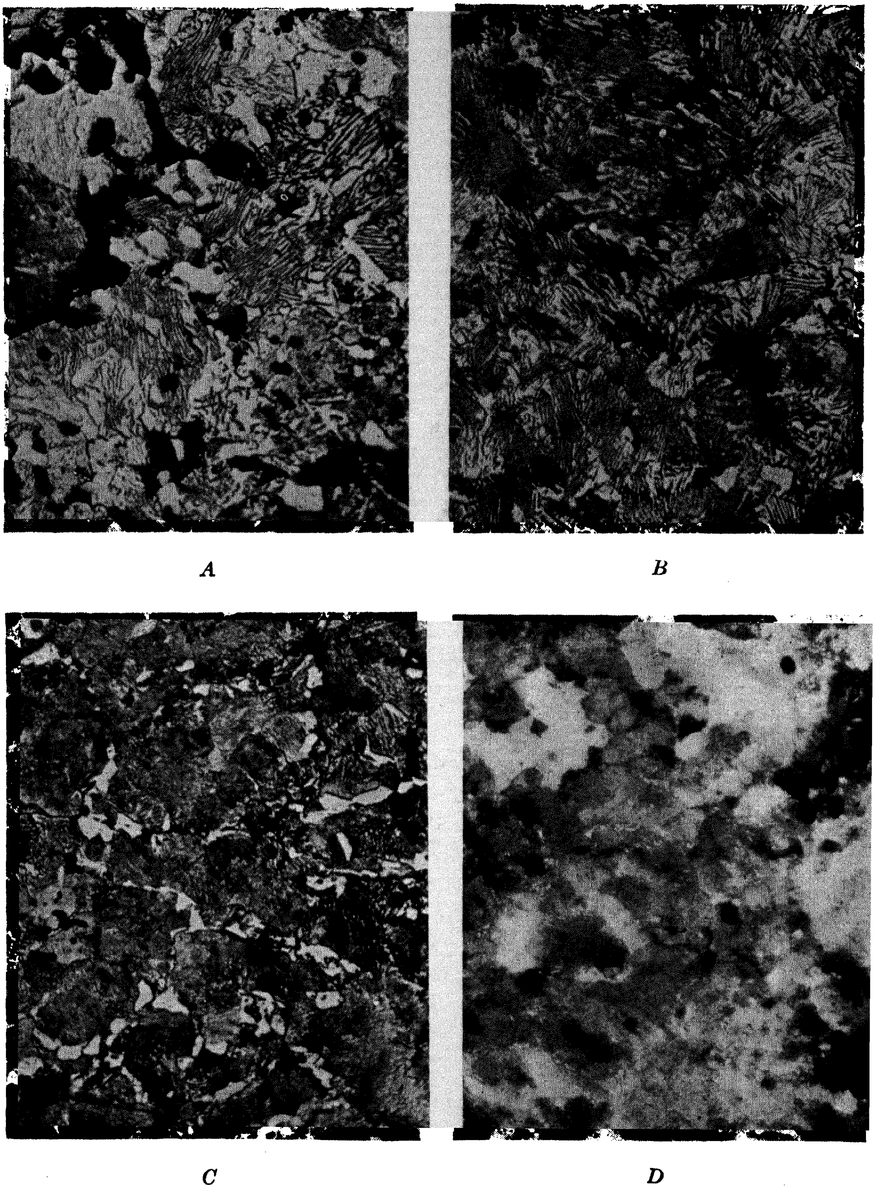
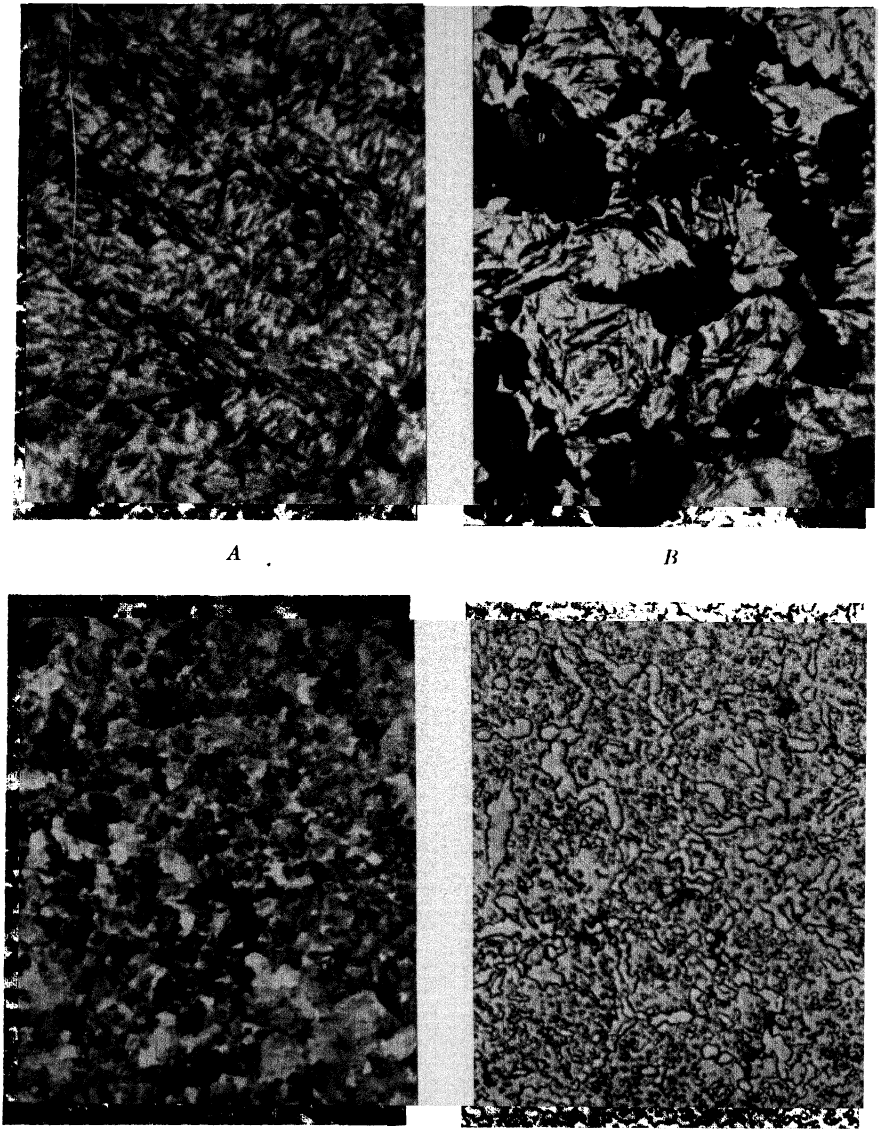


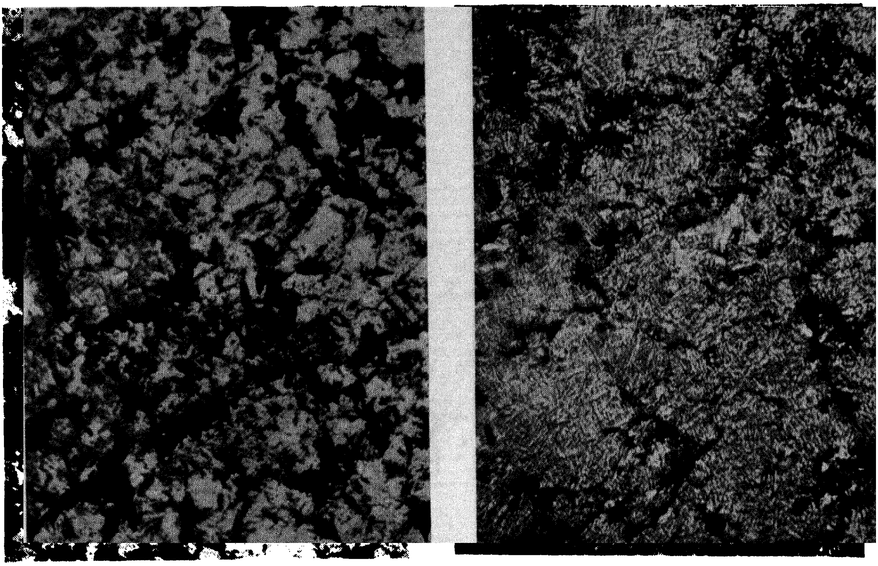
Fig. 461. Microstructure (×500) of sintered carbon steel compacts produced from mixtures of iron powders of various origins and 1% graphite powder (according to Chadwick and Broadfield[87]). All compacts were sintered at 1125°C. (2060°F.) for 1 hour: *A*, electrolytic iron powder, pressed at 20 tsi, showing ferrite and pearlite; *B*, electrolytic iron powder, pressed at 60 tsi, showing pearlite and traces of ferrite; *C*, charcoal-reduced iron powder, pressed at 40 tsi, showing ferrite and pearlite; and *D*, comminuted Degussa-type iron powder, pressed at 60 tsi, showing sorbitic pearlite.



A *B* *C* *D*

Fig. 462. Microstructure (×500) of sintered and heat treated carbon steels (according to Chadwick and Broadfield[87]). All specimens were sintered at 1125°C. (2060°F.) for 1 hour and quenched in oil: *A,* electrolytic iron powder plus 1% graphite, pressed at 60 tsi, showing martensite; *B,* electrolytic iron powder plus 1% graphite, pressed at 75 tsi, showing martensite and troostite; *C,* charcoal-reduced iron powder plus 1% graphite, pressed at 60 tsi, showing sorbitic pearlite; and *D,* electrolytic iron powder plus 2% graphite, pressed at 60 tsi, tempered at 650°C. (1200°F.), showing globular cementite in ferrite matrix.

ment with the observations of Squire and Stern. In a comparison of the properties of compacts from mixtures of (*1*) electrolytic iron powder, (*2*) Swedish sponge iron powder, and (*3*) a German powder made by the Degussa process (*cf.* Vol. I, p. 45), with 1–4% graphite, the authors found that the resulting mechanical properties and microstructures did not differ to any appreciable extent, and pearlite structures were formed with either ferrite or cementite present in accordance with the percentage of carbon contained in the compact. The powders used in the investigation were all annealed at 800°C. (1470°F.), pressed at 20–75 tsi, and sintered in cracked ammonia at 1125°C. (2060°F.) for 1 hour. Cooled specimens were then reheated at 800–820°C. (1470–1510°F.), quenched in water or oil and tempered at 200–650°C. (400–1200°F.) in cracked ammonia. Some of the test results obtained by Chadwick and Broadfield are given in Figures 457–459. Figure 457 shows the effect of increasing



A *B*

Fig. 463. Microstructure (×500) of sintered carbon steel compacts after heat treatment by water-quenching (according to Chadwick and Broadfield[87]): *A*, comminuted iron powder plus 1% graphite, pressed at 40 tsi, sintered at 1125°C. (2060°F.) for 1 hour, water-quenched structure showing white martensite; and *B*, charcoal-reduced iron powder plus 1% graphite, pressed at 20 tsi, sintered at 1125°C. (2060°F.) for 1 hour, water-quenched and tempered at 350°C. (660°F.), showing sorbite.

TABLE 177
Physical Properties of Sintered Carbon Steels Obtained from Gas-Carburized Iron Powders[a]

History of powder	Molding pressure, tsi	Sintering		Heat treatment[b]	Properties			
		Temp.	Time, hr.		Brinell hardness	Yield point, psi	Tensile strength, psi	Elongation, %
Reduced iron, carburized in 18–1 hydrogen–butane atmosphere at 900°C. for 1 hr.; decarburized in hydrogen for 1 hr.; C content of powder 0.14%	60	1000°C. (1830°F.)	4	None	54–61	—	46,600	5.0
				o.q.; t.	—	—	68,500	1.0
Reduced iron, carburized in 11–1 hydrogen–butane atmosphere at 900°C. for 1 hr.; decarburized in hydrogen at 900°C. for 1 hr.; C content of powder 0.46–0.53%	60	1000°C. (1830°F.)	4	None	57–65	—	47,200	4.0
				o.q.; t.	—	—	70,000–77,200	—
Reduced iron, carburized in 10–1 hydrogen–butane atmosphere at 900°C. for 2 hr.; decarburized in hydrogen at 900°C. for 1 hr.; C content of powder 0.75%	60	1000°C. (1830°F.)	4	None	59–70	—	47,450	4.0
				o.q; t.	—	—	69,000–70,000	—
Reduced iron, carburized in 20–1 partially combusted city gas–butane atmosphere at 900°C. for 2 hr.; decarburized in hydrogen at 900°C. for 1 hr.; C content of powder 0.2–0.5%	50	1300°C. (2370°F.)	4	None	—	29,900	57,500	6.0
				o.q; t	—	31,900–39,500	62,100–72,400	—
Electrolytic iron, carburized in 15–1 hydrogen–butane atmosphere at 900°C. for 1 hr.; decarburized in hydrogen at 900°C. for 1 hr.; C content of powder 0.45%	60	1000°C. (1830°F.)	4	None	—	21,400–28,500	42,400–46,600	8–11
				o.q; t.	—	38,800–47,700	70,800–72,500	—

[a] Results obtained with tests conducted by Hardy Metallurgical Co.; research reports Nos. 123, 127, 137, and 149.

[b] Heat treatment: reheat to 900°C. (1650°F.) for 1 hour; oil quench (o.q.); temper (t.) at 260°C. (500°F.) for 1 hour.

sintering time from 30 minutes to 4 hours on the tensile strength, diamond pyramid hardness, dimensional changes (both in the direction of pressing and normal to it), and combined and free carbon content for compacts pressed at 40 tsi from a mixture of electrolytic iron and 1% natural graphite. Figure 458 illustrates the same properties as a function of the sintering temperature between 800 and 1200°C. (1470 and 2190°F.) for a constant sintering time of 1 hour. The effect of graphite additions up to 4% is illustrated in Figure 459 on the same physical properties, as well as on density and on the final combined and free carbon content; its effect on the microstructure is shown in the photomicrographs of Figure 460. The microstructures of sintered compacts produced from different powders are reproduced in Figure 461, those of heat-treated compacts in Figures 462 and 463.

Sintered carbon steel parts prepared from gas-carburized powders have been found comparable in tensile properties with parts produced from mixtures of reduced iron and graphite powders; Table 177 gives some representative properties for various carbon contents. Steel parts produced by compacting mechanically comminuted steel scrap also have physical properties of the same order. Steels containing up to 0.5% C and with a porosity not exceeding 15% have been found to possess tensile values up to 75,000 psi and elongation values up to 10%.

The physical properties of sintered steels produced from liquid disintegrated (DPG) powder are given in Table 178[88]; the effect of subsequent heat treatment on hardness is given in Table 179. The increase in hardness and tensile strength with increased carbon content is only natural; the increase of these properties in conjunction with greater elongation as molding pressures increase is evidence of the beneficial effects of greater density. It is apparent from Table 179 that reasonably dense sintered steels can be heat-treated to surface hardness values ranging from Rockwell C-56 to C-59, *i.e.*, not appreciably below values common in hardened steel.

The effect of several repetitions of the pressing-plus-sintering cycle for steel compacts was found by Kieffer and Hotop[88a] to be similar to that established for pure iron powders (see page 328). A mixture of 75% liquid-disintegrated (DPG-type) soft iron powder and 25% liquid-disintegrated cast iron powder plus 0.4% powdered graphite was pressed at 28.5 and 43 tsi, respectively, and then sintered in carbon monoxide—containing hydrogen as follows: final sintering was in all cases performed

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[88] R. Kieffer, F. Benesovsky, and H. J. Bartels, *Powder Met. Bull.*, *2*, No. 3, 54 (1947).

[88a] R. Kieffer and W. Hotop, *Sintereisen und Sinterstahl*. Springer, Vienna, 1948, pp. 234, 235.

for 2 hours at 1220°C. (2230°F.), whereas all preceding sintering treatments were carried out for 1 hour at 800°C. (1470°F.) in order to prevent complete diffusion of the carbon and the formation of a uniform pearlitic structure (the final carbon content was about 0.7%) which would have resisted plastic deformation during repressing. Table 180 summarizes the results obtained in these experiments, and shows clearly that, as for pure iron, the optimum density is reached after the fourth cycle. On the

TABLE 178

Engineering Properties of Sintered Steel Parts with Varying Carbon Contents as Compared with Low-Carbon Steel (Kieffer, Benesovsky, and Bartels[88])

Material	Compacting pressure, tsi	Density, g./cc.	Porosity, %	Vickers hardness	Tensile strength, psi	Elongation, %
Sintered steel, 0.4% C[a]	28[c]	6.07	22.5	80–90	27,000–32,000	3.5
	42[c]	6.53	16.6	100–110	36,000–41,000	4.5
	56[c]	6.80	13.2	115–125	42,500–48,000	5.8
	42 (42)[d]	7.05	10.0	125–135	47,500–51,500	7.0
Steel C 35[b]	—	7.83	—	140–170	71,000–85,000	22
Sintered steel, 0.6% C[a]	28[c]	6.17	21.0	110–120	41,500–46,500	3.0
	42[c]	6.63	15.1	130–140	57,500–62,000	4.0
	56[c]	6.90	11.6	145–160	59,500–65,000	4.5
	42 (42)[d]	7.10	9.1	170–190	65,000–71,000	5.0
Steel C 45[b]	—	7.81	—	170–200	85,000–102,000	17
Sintered steel, 0.8% C[a]	28[c]	6.21	20.3	140–160	60,500–66,500	2.8
	42[c]	6.65	14.6	165–185	76,500–82,500	3.8
	56[c]	6.92	11.1	190–205	86,500–92,500	4.2
	42 (42)[d]	7.13	8.5	210–230	93,000–99,500	4.5
Steel with 0.8% C	—	7.79	—	240–270	121,000–135,000	5–10

[a] Prepared from DPG soft iron powder (0.3 mm.) and graphite powder.

[b] German DIN 1667 standard steel.

[c] Single-pressed and sintered at 1240°C. (2260°F.).

[d] Double-pressed (both steps at 42 tsi); presintered at 850°C. (1560°F.); and final sintering at 1250–1300°C. (2280–2370°F.).

TABLE 179

Effect of Heat Treatment on Sintered Steel (Kieffer, Benesovsky, and Bartels[88])

Material[a]	Compacting pressure, tsi	Density, g./cc.	Vickers hardness				
			Quenched in water from 850–800°C. (1560–1470°F.)	Tempered at			
				200°C. (390°F.)	300°C. (570°F.)	400°C. (750°F.)	500°C. (930°F.)
Sintered steel, 0.4% C..	42	6.53	198-232	200	190	180	150
	42 (42)[b]	7.05	387–428	400	380	320	270
Sintered steel, 0.6% C..	42	6.63	281–330	260	240	210	190
	42 (42)[b]	7.10	562–612	580	500	420	340
Sintered steel, 0.8% C .	42	6.65	402–462	380	340	300	260
	42 (42)[b]	7.13	642–698	670	600	480	380

[a] Prepared from DPG soft iron powder (0.3 mm.) and graphite powder.

[b] Double-pressed (both steps at 42 tsi); presintered at 850°C. (1560°F.); and final sintering at 1250–1300°C. (2280–2370°F.).

TABLE 180

Effects of Repeated Pressing and Sintering Cycles on the Properties of Steel Compacts[a] (Kieffer and Hotop[88a])

Property	Pressure,[b] tsi	Number of cycles[c]				
		1	2	3	4	5
Density, g/cc.						
Before final sintering......	14.3	5.10	5.50	5.70	6.10	6.20
	28.5	5.83	6.30	5.69	6.72	6.80
	43.0	6.32	6.72	6.99	7.17	7.23
After final sintering	14.3	5.79	5.82	5.90	6.00	6.04
	28.5	6.20	6.50	6.73	6.82	6.88
	43.0	6.50	6.91	7.10	7.21	7.27
Vickers hardness,[d] kg./mm.^{2}	28.5	115	160	172	182	187
	43.0	145	206	230	245	251
Tensile strength, psi[d]........	28.5	52,000	54,000	57,500	61,500	66,000
	43.0	65,000	71,000	76,000	79,000	82,500
Elongation, %[d]........... ..	28.5	2.9	3.7	4.4	4.6	4.7
	43.0	3.7	4.1	4.4	4.7	4.7

[a] From mixture of 75% soft liquid disintegrated iron powder (type DPG), $<150\mu$, 25% liquid disintegrated cast iron powder (type DPG), $<150\mu$, plus 0.4% graphite powder addition.

[b] Same pressure for all cycles.

[c] Sintering conditions: presintering and intermediate sintering 1 hour at 800°C. (1470°F.), final sintering 2 hours at 1220°C. (2230°F.), all in carbon monoxide-containing hydrogen.

[d] Values taken after final sintering.

other hand, hardness and tensile strength values are progressively increased with the number of cycles up to the fifth, while elongation figures reach saturation values after the fourth; in this respect, the steel compacts deviated somewhat from the behavior of the pure iron. In spite of the obvious improvements of the physical properties that are obtainable by such multiple repetitions of the processing cycle, practical and economic considerations will exclude anything beyond a single repetition of pressing and sintering for ordinary production work.

Koehring's[89] experiments with various types of steel powders have shown that properties approaching normal values can be reached after hot forging. Steel containing 0.3% C, produced by decarburizing finely ground (100% —100 mesh, 50% —325 mesh) iron–carbon alloy to which was added 0.6% graphite, could be forged to a density of 7.81 g./cc., and possessed a hardness of Rockwell B-74 to B-85, a yield point of 51,200 psi, a tensile strength of 73,300 psi, an elongation of 23%, and a reduction in area of 32%. Similar data for finely ground ($^1/_8$-inch average diameter) screw machine turnings of SAE 1112 steel, pressed at 30 tsi, and presintered at 1100°C. (2000°F.), were reported to have a density of 7.79 g./cc., a hardness of B-50 to B-79, a yield point of 38,100 psi, a tensile strength of 54,400 psi, an elongation of 11%, and a reduction in area of 13%.

Kieffer and Hotop[89a] could essentially confirm the findings of Koehring, although different raw materials were used, and heat treatments both before and after hot coining were more elaborate. The procedure used involved first a cold compaction at 43 tsi of the aforementioned mixture of about 75% soft iron (type DPG) and 25% cast iron to which 0.4% graphite powder was added, then sintering for 2 hours at 1220°C. (2230°F.) in carbon monoxide-containing hydrogen, then hot repressing at 43, 57, and 70 tsi and at 500, 700, and 900°C. (930, 1290, and 1650°F.), respectively, and finally annealing at 800°C. (1470°F.) for 1 hour under the same atmosphere as used for sintering (the final carbon content averaged 0.8%). It was found that the temperature of hot coining had a greater effect on the physical properties than the hot coining pressure. Hot coining at 500°C. (930°F.) at 43 tsi resulted in a tensile strength of 82,000 psi and an elongation of 5.1%; an increase in pressure to 70 tsi raised the tensile strength to 95,500 psi, but the elongation only to 6.0%. The corresponding figures for a hot coining temperature of 700°C. (1290°F.), however, were 110,000 psi and 5.3% and 112,000 psi and 7.9%, respectively, those for 900°C. (1650°F.) were 117,000 psi and 6.5%, and 122,000 psi and 8.0%, respectively. Table 181 shows a summary of the test results and permits an interesting comparison with data of cold-

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[89] R. P. Koehring, in J. Wulff, *Powder Metallurgy*. Am. Soc. Metals, Cleveland, 1942, p. 304.

[89a] R. Kieffer and W. Hotop, *Sintereisen und Sinterstahl*. Springer, Vienna, 1948, pp. 251 ff.

pressed and sintered compacts (based on one or more cycles) from the powder mixture, shown in Table 180. According to Kieffer and Hotop, a careful control of the sintering cycle is necessary to assure the high physical properties listed. Especially, excessive sintering temperatures or periods must be guarded against, lest the compacts become too hard and tough for satisfactory deformation in the hot press.

TABLE 181

Properties of Hot-Repressed Steel[a] as Function of Hot-Repressing Temperature and Pressure (according to Kieffer and Hotop[89a])

Properties	Hot-repressing pressure, psi		
	43	57	70
Density (g./cc.) at hot-repressing temperature of			
500 °C. (930 °F.)	6.72	6.86	6.96
700 °C. (1290 °F.)	7.05	7.17	7.29
900 °C. (1650 °F.)	7.20	7.33	7.42
Vickers hardness (kg./mm.²) at hot-repressing temperature of			
500 °C. (930 °F.)	201	218	240
700 °C. (1290 °F.)	228	243	254
900 °C. (1650 °F.)	242	248	275
Tensile strength (psi) at hot-repressing temperature of			
500 °C. (930 °F.)	82,000	87,000	95,500
700 °C. (1290 °F.)	110,000	109,000	112,000
900 °C. (1650 °F.)	117,000	120,000	122,000
Elongation (%) at hot-repressing temperature of			
500 °C. (930 °F.)	5.1	5.2	6.0
700 °C. (1290 °F.)	5.3	7.5	7.9
900 °C. (1650 °F.)	6.4	7.7	8.0

[a] All specimens were prepared from a mixture of 75% of liquid disintegrated soft iron powder (type DPG), $<150\mu$, 25% of liquid disintegrated cast iron power (type DPG), $<150\ \mu$, plus 0.4% graphite powder addition; they were pressed at room temperature at 43 tsi, and sintered for 2 hours at 1220 °C. (2230 °F.) in carbon monoxide-containing hydrogen atmosphere; after hot repressing, all specimens were annealed for 1 hour at 800 °C. (1470 °F.).

Kieffer and Hotop[89b] extended the work done on preoxidation of sintered iron by Wiemer and Hanebuth (see page 329) by studying the effect of such treatment on sintered carbon steel made from the same general type of powder mixture used in the repetitious cycle work. It was found that the pretreatment has no significant effect on the carbon content, provided that a carbon monoxide-containing hydrogen atmosphere is used during sintering. Analogous to the case of pure iron, the tensile strength is markedly increased by the preoxidation treatment, *i.e.*, from

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[89b] R. Kieffer and W. Hotop, *loc. cit.*, pp. 533 ff.

68,000 psi for a compact pressed at 43 tsi, presintered at 900°C. (1650°F.) for 30 minutes, repressed at 43 tsi, and sintered at 1220°C. (2230°F.) for 90 minutes, to 89,000–113,000 psi for compacts subjected to the preoxidation treatment in air at 500°C. (930°F.), with the treatment introduced at different stages of the processing cycle. A similar increase found in hardness, however, is unlike the case of pure iron, and so is the lack of an increase in elongation values, and a drastic drop in impact resistance figures (down to about one-sixth of the value for the untreated material).

Applications of Sintered Carbon Steels

During the past few years, applications for sintered carbon–steel parts have multiplied considerably, and with continued improvement of both the properties and the processing techniques, the development of further applications is indicated for machine parts that require only moderate physical properties. The list of potential applications in machinery and appliances given previously for soft iron parts refers equally to sintered steel parts, or to iron parts subjected to a surface-hardening treatment. However, the fact that the physical properties now obtainable by industrial powder metallurgy operations are inferior in almost every respect—with the possible exception of wear resistance—to corresponding properties found in ordinary engineering steels of similar carbon content, has so far prevented the production of ferrous powder metallurgy parts from making any appreciable inroad into the parts industries. The share of production carried by the powder technique will increase markedly only if certain important mechanical properties, such as, for instance, impact resistance, modulus of elasticity, and reduction of area, approach more closely the data exhibited by steel stock of equal carbon content. At the moment, the main field of application for sintered steel parts is in connection with wear-resistant parts that must possess certain bearing properties and must be produced in large volume to great dimensional accuracy. Gears, cams, spacers, bushings, and similar machine elements (Fig. 464) belong, generally speaking, to this class, and further developments are indicated mainly in this connection. A rather recent and very promising development is the production of hardened tool units and precision instrument parts as shown in Figure 465.

A classical application of sintered steel parts is the oil pump gears for automotive use (Figs. 466 and 467). The manufacture of these gears is explained in detail by Lenel[90] and reviewed in Volume I, Chapter IX. In spite of the very low physical properties of the material (approximately 2% graphite initially added causes formation of a hypereutectic porous structure with graphite inclusions, resulting in a tensile strength of not more than 25,000 psi) which are comparable to those of an inferior grade of cast iron, the powder metallurgy product has considerable advantages over the previously machined cast iron gears. They include (*1*) a porous structure capable of absorbing a large quantity of oil which aids in withstanding the specific pressure exerted on the teeth of the gear, (*2*) a

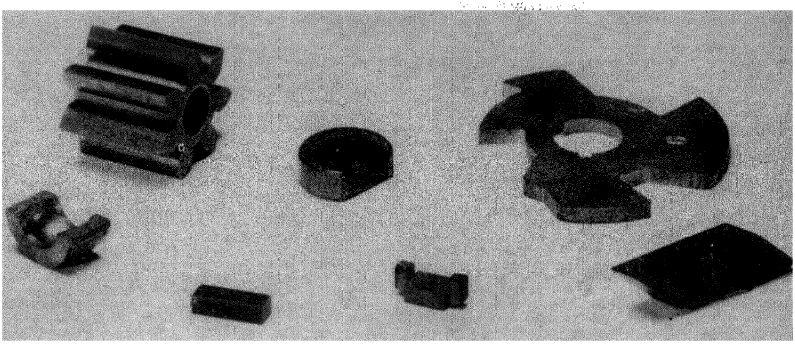

Fig. 464. Variety of machine parts from sintered steel (courtesy of Moraine Products Division, General Motors Corp.).

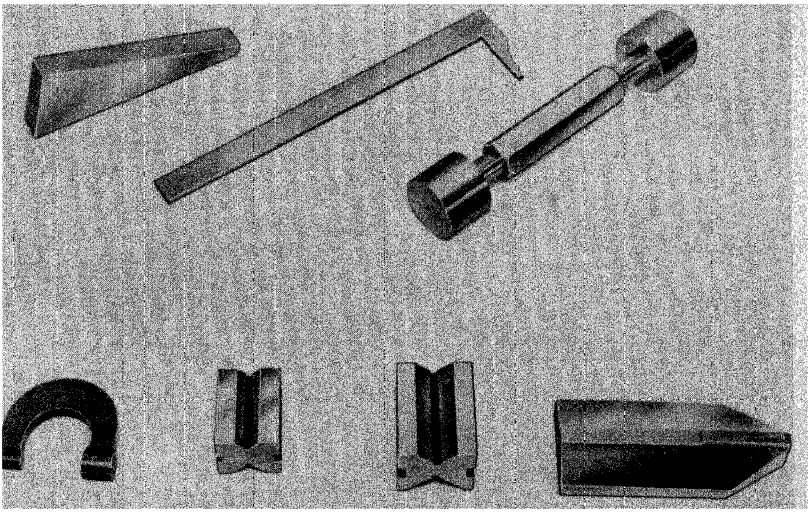

Fig. 465. Assortment of precision tool and instrument units from sintered steel. Some of these parts have been hardened up to a Rockwell hardness of C-65 (courtesy of Amplex Division, Chrysler Corp.).

more accurately formed involute tooth form than is possible by machining, and (*3*) a considerable saving in machining and material (the machined gear requiring some twenty-odd operations against four finishing operations necessary on the molded gear, and complete elimination of nearly two-thirds of the cast blank).

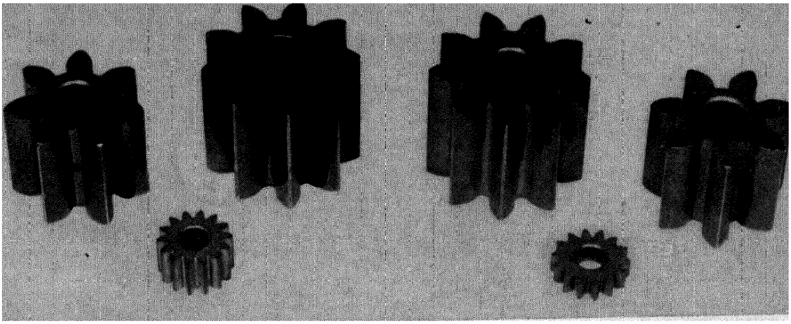

Fig. 466. Variety of oil pump gears from sintered iron–graphite powder (courtesy of Moraine Products Division, General Motors Corp.).

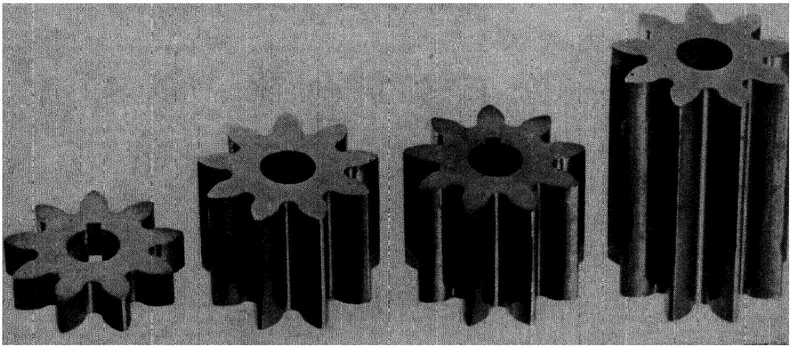

Fig. 467. Assortment of oil pump gears of different length (courtesy of American Electro Metal Corp.).

Another interesting application for sintered steel was found in England during the war, when piston rings particularly suitable for high-pressure service were developed economically according to the previously

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[90] F. V. Lenel, in J. Wulff, *Powder Metallurgy*. Am. Soc. Metals, Cleveland, 1942, p. 502.

described method (page 351) by Judd.[91,92] Like the oil pump gear, these rings are relatively porous, permitting the retention of oil, and resulting in superior bearing properties. To be quite accurate, therefore, both of these products should be classified under porous parts; as such, they are further treated in Chapter XXVII.

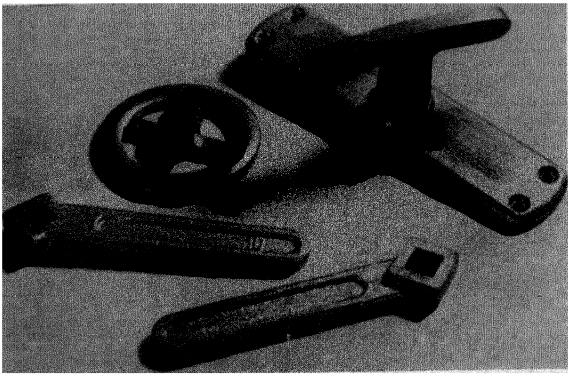

Fig. 468. Valve wheel, valve wrenches, and window latch assembly produced in Austria from sintered steel (according to Kieffer, Benesovsky, and Bartels[94]).

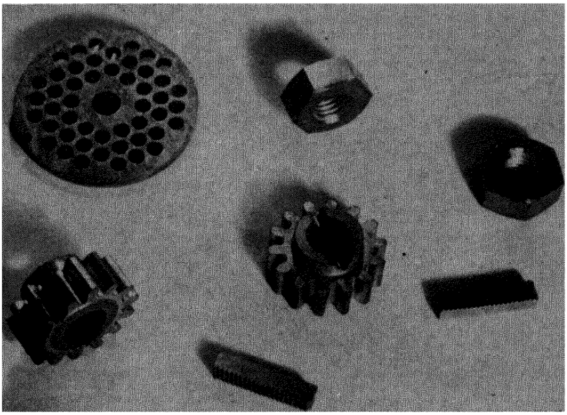

Fig. 469. Assortment of gears, racks, nuts, and a perforated plate for a meat grinder produced in Austria from sintered steel (according to Kieffer, Benesovsky, and Bartels[94]).

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[91] J. A. Judd, *Automobile Eng.*, *34*, 379 (1944).

[92] J. A. Judd, *Symposium on Powder Metallurgy.* The Iron and Steel Institute, Special Report No. 38, London, 1947, p. 117.

The uses of sintered steel parts in automobile engineering have been summarized by Judd.[93] Automotive and other applications for sintered steel parts have also been recently discussed by Langhammer,[93a] Lenel,[93b] and in the book of Kieffer and Hotop.[93c]

An assortment of sintered steel products manufactured in Austria during the postwar period[94] is reproduced in Figures 468 and 469. The gas wrench and window fitting shown in Figure 468 and the nuts shown in Figure 469 are particularly noteworthy, since they belong to a class of highly competitive articles. Only the present disruption of industry in Central Europe is a plausible explanation for the economically successful production of these parts from metal powders. The gears and racks shown in Figure 469 are also of considerable interest, since they are of the type used in power transmission, thus indicating a comparatively high quality of the sintered carbon steel used.

SINTERED ALLOY STEELS

Manufacturing Procedures

As with the plain carbon steels, sintered alloy steels can be produced from one of the following three principal types of powders: (*1*) mixtures of the elemental ingredients, *e.g.*, iron, graphite, plus nickel, chromium, manganese, etc., (*2*) mixtures of partially prealloyed powders, *e.g.*, crushed or gas-carburized steel powders, and ferroalloy powders; and (*3*) powdered alloy steels, *e.g.*, high-speed or stainless steels.

All of these materials have been used with some degree of success in the manufacture of sintered alloy steel products, but each of them presents certain difficulties. In the case of mixed powders, compaction is greatly facilitated by the major proportion of soft iron, but the formation of a true alloy steel depends largely on the extent of alloying that can be obtained during sintering. Diffusion of the individual constituents must be permitted to proceed unhampered by interfering phases (*e.g.*, oxide films) and, if necessary, such interferences must be removed by suitable action of the furnace atmosphere or addition agents (*e.g.*, metal hydrides). In any event, the sintering treatment must be carried out at sufficiently high temperatures and for long enough times to allow for

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[93] J. A. Judd, *J. Inst. Automobile Engrs. London, 15,* 83 (1946).

[93a] A. Langhammer, *Proc. International Powder Metallurgy Conference,* Graz, July 12–17, 1948, Referate No. 68.

[93b] F. V. Lenel, *ibid.,* Referate No. 64.

[93c] R. Kieffer and W. Hotop, *Sintereisen und Sinterstahl.* Springer, Vienna, 1948, pp. 376 ff.

[94] R. Kieffer, F. Benesovsky, and H. J. Bartels, *Powder Met. Bull., 2,* No. 3, 54 (1947).

complete diffusion of the individual constituents. For alloying ingredients, such as manganese, molybdenum, chromium, and nickel, sintering temperatures have to exceed 1200°C. (2200°F.) in order to arrive at reasonable sintering times, (*i.e.*, 1 to 10 hours).

If part of the diffusion is already obtained during the manufacture of the powder, the intensity of the sintering treatment can be reduced. This is particularly true where easily oxidizing alloying ingredients are added in the form of master alloys with iron. Thus, it has been found that a replacement of chromium or manganese by ferrochromium or ferromanganese has cut the sintering temperature necessary for complete diffusion by 100–200°C. (180–360°F.), while the sintering time could simultaneously be cut about one half. A less drastic reduction in sintering temperature or time can be expected if merely the iron and carbon are prealloyed to steel powder, and the other ingredients added in their elemental form. The rapid diffusion rate of carbon into iron in the austenitic range, at which sintering takes place, leaves only a small margin for reducing temperature or time. A slight advantage in using prealloyed steel powder may, however, be found in the fact that, especially for crushed and pulverized bulk steels, a more uniform structure with a finer pearlitic texture is obtainable.

Unfortunately, however, the compactibility of the mixture is further impeded with greater proportions of hard alloy powder. The lack of plasticity of the hard particles prevents formation of large contact areas in their immediate vicinity, and results in weak compacts and poor end products. The unavoidable gaps between adjacent hard particles tend to inhibit their diffusion into the matrix during sintering, counteracting the beneficial effect obtained by prealloying part of the powder.

The detrimental effects on compactibility are generally even more pronounced in the case of powdered alloys having the final composition. The methods of manufacture used conventionally for such powders (for example, mechanical comminution, atomization and rotating disk type liquid disintegration,[94a] chemical disintegration,[94b] etc.) impart substantial rigidity and hardness to the individual particles. This makes necessary the use of very high molding pressures or a hot-pressing operation in order to obtain even a limited amount of plastic deformation—this being essential for the molding of a coherent body and for sintering it into a compact metal. Poor compaction obtained by employing ordinary molding techniques produces loose interparticle bonding and, during

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[94a] G. A. Roberts and A. H. Grobe, *Iron Age, 163,* No. 13, 78 (1949); Anonymous, *Steel, 124,* No. 19, 114 (1949).

[94b] U. S. Pats, 2,381,022; 2,381,023; 2,381,024; 2,394,578; and 2,407,862.

TABLE 182

Composition, Processing, and Surface Hardness of Sintered Nickel Steels, Nickel–Chromium Steels, and High-Carbon Nickel–Chromium Steels Produced from Elemental Powders[a]

Type of alloy	Composition, %					SAE No.	Brinell hardness					
	C	Ni	Cr	Si	Fe		Pressed 65 tsi, sintered 950°C. (1740°F.) 8 hr.	Coined 65 tsi	Pack-carburized 925°C. (1680°F.) 20 hr.	Reheated 800°C. (1470°F.) 1 hr., oil quenched	Reheated 800°C. (1470°F.) 1 hr., water quenched	Tempered 400°C. (750°F.) 2 hr.
Nickel steel	0.10	3.50	—	—	Bal.	2315	93	143	200	290	—	—
							89	143	200	—	550	—
	0.20	3.50	—	—	Bal.	2315	83	134	183	305	—	—
							83	134	175	—	460	—
	0.50	3.50	—	—	Bal.	2350	89	143	205	300	—	—
							89	143	210	—	590	—
	0.20	7.00	—	—	Bal.	—	93	153	250	—	—	—
							105	156	250	—	—	—
Nickel–chromium steel	0.48	2.00	1.00	—	Bal.	3250	86	140	Not carburized	143[b]	—	—
							86	140		—	163	—
	0.20	3.50	1.50	—	Bal.	3325	89	140	233	350	—	—
							86	140	218	—	515	—
	0.35	3.65	1.25	—	Bal.	3335	89	153	Not carburized	134[b]	—	—
							86	143		—	149	—
High-carbon nickel–chromium steel	2.00	2.00	0.75	0.25	Bal.	—	77	137	Not carburized	146[c]	—	153
							77	137		—	156	163

[a] Data from tests conducted by Hardy Metallurgical Co., Research Report No. 9.

[b] Reheated at 840°C. (1545°F.) for 2 hours.

[c] Reheated at 800°C. (1470°F.) for 8 hours.

TABLE 183

Composition, Processing, and Tensile Properties of Sintered Nickel–Chromium Steels Produced from Gas-Carburized Steel, Carbonyl Nickel and Ferrochrome Powder Mixtures[a]

Composition, %				SAE No.	Type of initial iron powder[b]	C content of gas-carburized steel powder, %	Molding pressure, tsi	Sintering		Tensile strength, psi	Elongation, %	Tensile strength after hardening,[c] psi
C	Ni	Cr	Fe					Temp.	Time, hr.			
0.50	2.00	1.00	Bal.	3250	RS	0.51	60	1275 °C. (2325 °F.)	8	—	—	107,000–109,500
0.15	3.00	0.70	Bal.	3415	RS	0.20	"	" "	"	—	—	119,000–134,500
0.50	3.00	0.70	Bal.	3450	RS	0.58	"	" "	"	—	—	105,600–115,300
0.30	3.50	1.50	Bal.	3335	RS	0.30	"	" "	"	—	—	124,500–137,000
0.45	3.50	1.50	Bal.	3340	RS	0.46	"	" "	"	—	—	99,800–102,800
0.40	3.50	1.50	Bal.	3340	RS	0.45	50	1300 °C. (2375 °F.)	4	46,000	2.0	96,000–111,900
0.40	3.50	1.50	Bal.	3340	E	0.45	"	" "	3	73,100	4.5	142,300–166,000
0.15	3.50	1.50	Bal.	3312	RD	0.17	"	" "	"	70,400	3.0	88,000–104,600
0.35	3.50	1.50	Bal.	3335	RD	0.38	"	" "	4	78,600	3.0	116,500–127,300
0.45	3.50	1.50	Bal.	3340	RD	0.50	"	" "	"	77,500	4.0	116,000–129,900

[a] Data from tests conducted by Hardy Metallurgical Co., Research Reports Nos. 130, 140, and 150.

[b] RS, reduced Swedish sponge iron powder; RD, reduced domestic iron powder; E, electrolytic iron powder.

[c] Heat-treating cycle: reheated at 900 °C. (1650 °F.) for 1 hour; oil quenched; tempered at 260 °C. (500 °F.) 1 hour.

sintering, results in large intergranular spaces. These, in turn, weaken the entire structure and counteract any strengthening effects produced *within* the grains through the use of homogeneous alloy particles.

Only if the alloy powders are thoroughly annealed before use can densities of 80–85% be obtained by cold-pressing at commercially feasible pressures (*i.e.*, up to 60 tsi); for certain alloy steels (*e.g.*, nickel and nickel–chromium steels) sintering into strong and dense parts is then possible at comparatively moderate temperatures (1000–1100°C.; 1830–2010°F.) and short times (1–4 hours).

Properties

CARBON CONTAINING ALLOY STEELS

Information available to date on the development of carbon-containing sintered alloy steels is concentrated chiefly on materials produced from either of the first two classes of powder. Nickel steels, nickel–chromium steels, and corrosion and heat-resisting alloy steels of various compositions have been developed successfully from mixtures of the elemental powders, and the last two also from mixtures of prealloyed powders. Table 182 indicates surface hardness values of nickel–steel and nickel–chromium steel compacts produced from mixtures of the elemental powders and heat-treated after sintering, or coining and resintering, respectively. Tensile data of sintered and quench-hardened nickel–chromium steels from prealloyed powders are given in Table 183. The carbon was introduced by gas carburization of reduced or electrolytic iron powder, and the chromium in the form of low-carbon ferrochrome powder containing approximately 70% Cr. Only the nickel was added as virgin (carbonyl) powder. Some of the tensile strength values obtained are remarkably good in view of the fact that all specimens were compressed and sintered only once; the comparatively high sintering temperature of 1300°C. (2370°F.) and the purity of some of the iron powders used (especially the electrolytic type) may be chiefly responsible for the favorable results.

According to Judd,[94c] substantial savings in sintering time and reduction in sintering temperature are possible if the pure chromium or ferrochromium powder addition is replaced by a low-melting iron alloy which contains the chromium in larger proportion. By using the previously described method of sintering in the presence of a liquid phase (page 351), it was found possible to produce a homogeneous 1% chromium steel

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[94c] J. A. Judd, *Symposium on Powder Metallurgy,* The Iron and Steel Institute, Special Report No. 38, London, 1947, p. 117.

from a mixture of 20% of a white cast-iron powder containing 5% Cr and 80% soft iron powder.

Delisle and Knopp[95,95a] recently studied the structure and properties of sintered nickel steels from electrolytic iron powder. Two compositions, (*a*) 3.5% Ni and 0.4% C, and (*b*) 3.5% Ni, 0.40% C, 0.75% Mn (as ferromanganese), and 0.20% Si (as ferrosilicon)—the latter corresponding to the standard SAE 2330 analysis—were used, and were compared with a sintered carbon steel containing 0.40% C, balance Fe. The investigators found that diffusion of the nickel and other alloying elements takes place in the solid state to an extent sufficient to bring about a drastic change in the mechanical properties of the steel as compared to those of a plain carbon steel. For example, a 3.5% nickel steel, sintered at 1325°C. (2415°F.), and quenched in oil from 825°C. (1515°F.), and tempered for 1 hour at 400°C. (750°F.), gave a tensile strength of 142,000 psi with an elongation of 3%. For comparison, a sintered plain carbon steel having the same final carbon content (0.23%) and prepared under the same conditions (but quenched from 875°C.; 1605°F.) displayed a tensile strength of only 69,000 psi with an elongation of 8%. Even without subsequent heat treatment and at a sintering temperature of as low as 1100°C. (2010°F.) and a sintering time as short as 90 minutes, a tensile strength of 83,000 psi with an elongation of 4% was obtained for a sintered steel containing 0.40% C, and 3.5% Ni—as compared with 58,000 psi and 6% elongation for the plain carbon steel. A material increase in tensile strength up to 119,000 psi without appreciable loss in elongation (3%) was recorded when the nickel content was raised to 10%. However, even at the optimum sintering conditions employed in this work—1325°C. (2415°F.) for 3 hours, and 1280°C. (2335°F.) for 6 hours, respectively—diffusion of the metallic alloying elements was not complete. But the nonequilibrium structure (consisting of a pearlite matrix in which nickel-rich areas are uniformly distributed) offers the possibility of obtaining a hardened structure on sintering followed by slow cooling without additional heat treatment.

Increasingly complex alloys require extended sintering treatments to achieve homogeneity of structure. It has been found possible to produce corrosion and heat-resistant alloys by mixing the elemental powders and pressing them at rather high pressures, but sintering of the compacts must be conducted at comparatively high temperatures, and sintering times must be rather long, possibly several days. The evidence of complete diffusion of a chromium steel composition, containing 2.30% Cr, 0.40% C,

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[95] L. Delisle and W. V. Knopp, *Trans. Am. Inst. Mining Met. Engrs.*, *175*, 791 (1948).

[95a] L. Delisle and W. V. Knopp, *Rev. Mét.*, *44*, 245 (1947).

0.5% Mn, and 0.3% Si after sintering at 1300°C. (2375°F.) for 44 hours, can be seen from Figure 470. Although slight decarburization has taken place the ingredient elements have completely diffused into the structure, a high compacting pressure (70 tsi) having caused substantial initial densification, and the intensive sintering treatment having further consolidated the structure. On the other hand, considerable grain growth may be encountered when subjecting the alloy steel compacts to this kind of treatment and this may often be associated with an excessive porosity caused by the spontaneous release of the air compressed during compacting and the CO_2 formed by its reaction with the carbon of the mixture. This can be seen from Figure 471 which shows the completely decarburized structure of a valve and piston steel containing about 15%

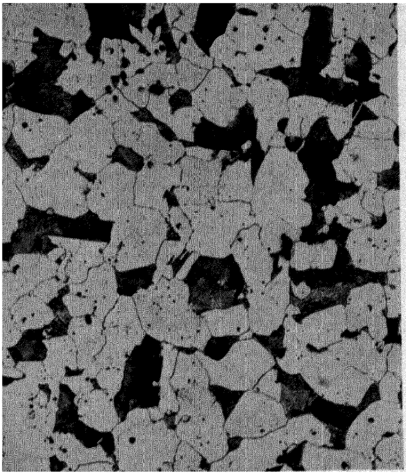

Fig. 470. Partly decarburized microstructure (×120) of chrome–carbon steel compact. Composition of mixture of elemental powders was 2.30% Cr, 0.40% C, 0.5% Mn, and 0.3% Si; mixture was compacted at 70 tsi and sintered in dry hydrogen for 44 hours at 1300°C. (2370°F.). Individual alloying ingredients have been completely dissolved by the matrix. (Courtesy of Charles Hardy, Inc.)

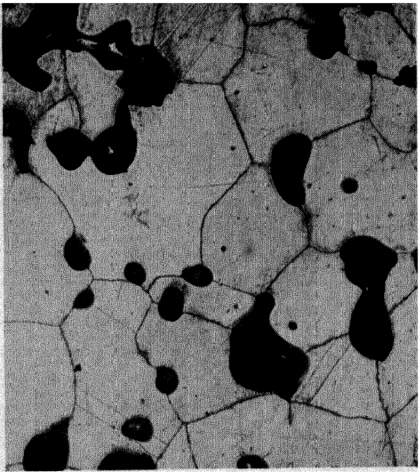

Fig. 471. Completely decarburized microstructure (×60) of high alloy nickel–chrome–tungsten steel compact. Composition of mixture of elemental powders was 15% Cr, 15% Ni, 3.0% W, 0.5% Mo, 0.8% Si, 0.7% Mn, and 0.4% C; mixture was compacted at 70 tsi and sintered in dry hydrogen for 44 hours at 1300°C. (2370°F.). Excessive porosity was caused by spontaneous release of entrapped air and its reaction products with the carbon of the mixture during rapid heating to sintering temperature. (Courtesy of Charles Hardy, Inc.)

each of Ni and Cr, 3.0% W, 0.5% Mo, 0.8% Si, 0.7% Mn, and originally, 0.4% C. The structure is homogeneous with all ingredients completely diffused; only the presence of numerous pores and inclusions distinguishes the material from a fused alloy of like composition. Other photomicrographs of similar alloys have been previously shown in Figures 225 and 226*B* (Volume I, Chapter XIV).

Balke[96] has experimented with pressures still exceeding those mentioned above in the production of a manganese–molybdenum steel. By compacting mixtures of the pure metal powders at 160 tsi before sintering (and presumably repeating the press and sintering operation at least once) the density of the standard material (*e.g.*, SAE 4650) could be approached very closely. Table 184 compares the characteristics of the sintered material with standard Mn–Mo steel of the same composition. Balke reports that the higher tensile strengths of the sintered and annealed products, as well as the higher modulus of rupture after quench hardening of the sintered compact, represent typical results obtainable when using very pure powders and high pressures.

TABLE 184

Properties of a Manganese–Molybdenum Steel from Powder versus Standard (Balke[96])

Property	Powder	Standard
Density, g./cc.	7.82	7.84
Tensile strength, psi	124,000	104,000
Rockwell hardness, "C" scale		
Annealed	27	20
Quenched	65.5	65.3
Tempered	62.8	62 8
Modulus of rupture, psi[a]	603,000	443,000

[a] After quench hardening.

An investigation of sintered manganese and chromium–manganese steels has been reported recently by Benesovsky and Kieffer.[96a] Heat-treatable manganese steels with 2–16% Mn and 0.2–1.6% C were produced from mixtures of Hametag powder and ferromanganese powder by pressing at 25–50 tsi and sintering for 4 hours in hydrogen at 1150–1200°C. (2100–2190°F.). Upon heat-treating the resulting compacts displayed pearlitic, martensitic, and austenitic structures, respectively, and the porosity averaged 12–15%. Chromium–manganese steels were pre-

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[96] C. W. Balke, in *Symposium on Powder Metallurgy.* ASTM, Philadelphia, Pa., 1943, p. 11.

[96a] F. Benesovsky and R. Kieffer, *Proc. International Powder Metallurgy Conference,* Graz, July 12–17, 1948, Referate No. 27.

pared in a similar manner, with chromium added to the mixture as electrolytic powder. However, the strong oxidizing tendencies of the chromium required special precautions during sintering, such as embedding the compacts in ferroaluminum packs. Compositions with low alloy content (1–5% Mn, 1–5% Cr, 0.5–1.5% C) could be processed

TABLE 185

Physical Properties of Sintered Manganese[a] and Chromium–Manganese[b] Steels (Benesovsky and Kieffer[96a])

Composition, %			Density, g./cc.	Vickers hardness, kg./mm.^{2}	Tensile strength, psi	Elongation, %
C	Mn	Cr				
0.2	0	—	—	—	28,000	8
	2	—	—	184[c]	50,000	6
	4	—	—	224[c]	65,000	3
	6	—	—	274[c]	75,000	0 5
	8	—	—	250[c]	82,000	2
	10	—	—	224[c]	79,000	7
	12	—	—	203[c]	71,000	9
	14	—	—	184[c]	59,000	10
	16	—	—	184[c]	57,000	—
0.8	0	—	—	—	71,000	4.5
	2	—	—	302[c]	80,000	2 5
	4	—	—	224[c]	107,000	2
	6	—	—	184[c]	94,000	0.5
	8	—	—	156[c]	81,000	2.5
	10	—	—	130[c]	70,000	5
	12	—	—	141[c]	61,000	9
	14	—	—	—	58,000	13
	16	—	—	—	56,000	17
~0 8	0	0	6 55	160	72,000	5 2
	1	1	6.52	167	75,000	6 2
	2	2	6.46	181	85,000	4 8
	3	3	6 45	205	93,000	4 1
	5	5	6 34	220	101,000	2 3
~0.4	10	10	6 15	172	78,000	11.6
	10	20	6 00	135	62,000	14.2

[a] From mixture of eddy-milled Armco iron wire (50% −100 mesh, 50% −230 mesh), 2–16% manganese in form of −230 mesh ferromanganese, and 0, 1, and 2% graphite; pressed at 43 tsi; sintered for 4 hours in carbon monoxide-containing hydrogen at 1200°C. (2190°F.) (0 and 1% graphite addition), or 1140°C. (2080°F.) (2% graphite addition).

[b] From mixtures of eddy-milled Armco iron wire (50% −100 mesh, 50% −230 mesh), 1–10% manganese in form of −230 mesh ferromanganese, 1–20% electrolytic −230 mesh chromium, and 0.5 or 1% graphite; pressed at 43 tsi; sintered in carbon monoxide-containing hydrogen for 4 hours at 1250°C. (2280°F.).

[c] Values for material after quenching from 950°C. (1740°F.).

readily by a single compaction of 50 tsi and sintering at 1200°C. (2190°F.); compositions with higher alloy contents (5–20% Mn, 10–20% Cr, 0.5–1% C) required a double pressing and sintering cycle. The high manganese–chromium alloys were found to be similar to stainless steels in structure and physical properties, but not in corrosion resistance. Table 185 shows data obtained by physical testing of these alloys. The properties could not be altered materially by attempts to impregnate the pores with molten copper (see also p. 417), and difficulties in obtaining complete penetration due to the formation of copper–manganese eutectic could only be overcome by using a special copper alloy.

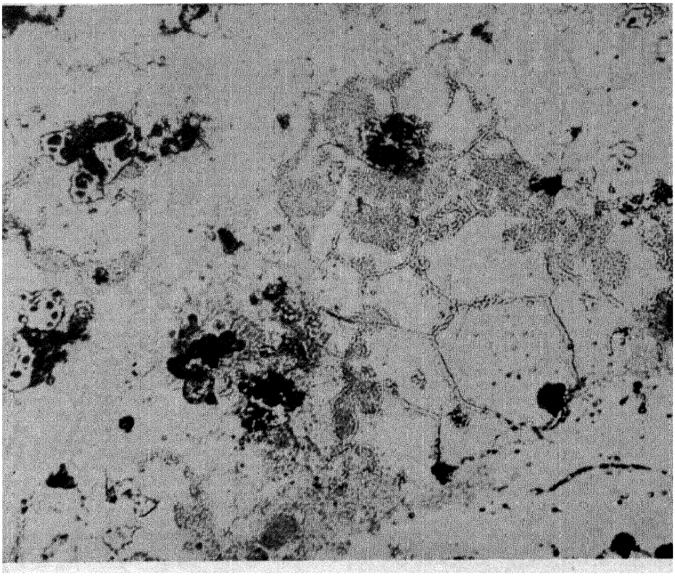

Fig. 472. Microstructure (×165) of sintered molybdenum-base high-speed steel. Composition of mixture of elemental powders was 9% Mo, 4% Cr, 3% Cu, 1% V (added as ferroalloy), 0.12% B (added as ferroalloy), and 0.8% C. Mixture was compacted at 50 tsi and sintered in dry hydrogen for 48 hours at 1200°C. (2190°F.), followed by furnace cooling. Structure lacks homogeneity and displays an austenitic matrix, a carbide network, carbide globules, pearlitic and martensitic areas, and undissolved molybdenum and chromium particles. (Courtesy of Charles Hardy, Inc.)

Alloy steels containing molybdenum or tungsten in larger proportion are less readily processed from powders. The high melting point of the refractory metal and its tendency to react with oxygen require long periods of sintering at very high temperatures for complete reduction and diffusion. A molybdenum-base high-speed steel composition having 9% Mo, 4% Cu, 1% V, 0.12% B, and 0.8% C, for example, could not be sintered into a homogeneous alloy during a 48-hour treatment at 1200°C. (2200°F.) even though the vanadium and boron were not added in elemental form but as chemically stable powdered ferroalloys. The hardness of the product was found to vary between 126 and 265 Brinell units, and the microstructure displayed molybdenum-rich and chromium-rich areas embedded in an austenitic matrix disrupted by a carbide network and pearlitic areas, as shown in Figure 472. Sintering at 1400°C. (2550°F.) improved the structure only slightly, with the molybdenum-rich constituent still being discernible after a 48-hour treatment.

Attempts to develop sintered high-speed steels by compacting homogeneous alloy powders—obtained by chemical disintegration of sensitized scrap metal (see also Volume I, Chapter III)—have not been very successful so far. The lack of plasticity of the alloy powder results in only moderate compaction, and little densification through shrinkage can be achieved during sintering unless temperatures and times are still in excess of those just mentioned for compacts from virgin powders. An alloy containing approximately 5% W, 5% Mo, 3.75% Cr, 0.5% V, and 0.5% C had, in spite of a perfectly homogeneous structure, a density of only 88% and a tensile strength of only 44,000 psi after compaction at 60 tsi and sintering at 1300°C. (2375°F.) for 8 hours. Sintering at 1400°C. (2550°F.) for 48 hours increased the density to 90% and the tensile strength to 69,000 psi, while the grain size became exceedingly large.

The approach of Wulff[97] is particularly interesting, inasmuch as he was able to produce sintered alloy steels from mixtures of partly alloyed or master alloy powders, with or without the addition of pure iron powder, with remarkable physical properties. In this work he used very fine powdered ingredients (*e.g.*, $> 5\ \mu$ ferroalloy carbides as carbon carrier) and subjected the resulting alloy steel compacts to a subsequent hot die-forging reduction of less than 30%. Physical properties which approached those of cast or wrought materials were first obtained with mixtures of —325 mesh iron powder of quite high purity and —325 mesh shotted and crushed pig iron, providing the necessary additions of carbon, sulfur, phosphorus, silicon, manganese, etc. After pressing the mixture at 33 tsi, presintering for 30 minutes at 825°C. (1515°F.), sintering for 30 minutes at 1200°C. (2190°F.) in hydrogen atmosphere (the specimens being protected by carbon covers), die forging, and annealing for 30 minutes at 1000°C. (1830°F.), the material, containing 0.48% C, had a density of 7.81 g./cc., tensile strength of 96,435 psi, and elongation of 16% for a forging reduction of 14.2%. After oil quenching from 825°C. (1515°F.) and drawing 30 minutes at 210°C. (410°F.) a hardness of Rockwell

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[97] J. Wulff, in J. Wulff, *Powder Metallurgy*. Am. Soc. Metals, Cleveland, 1942, p. 310.

C-48 to C-52 was recorded. Still more striking were the results obtained y Wulff with a composition corresponding to a standard SAE 4340 steel f the following composition: 0.38–0.43% C, 0.60–0.80% Mn, 0.20–0.35% i, 1.65–2.00% Ni, 0.70–0.90% Cr, and 0.20–0.30% Mo. Finely divided crap of this composition was first oxidized at 850°C. (1560°F.) and then ulverized to a 325-mesh size. After decarburizing in moist hydrogen, esulfurizing, and finally reducing in dry hydrogen, the powder analyzed .04% C, 0.52% Mn, 0.02% S, 0.02% P, 0.36% Si, 0.65% Cr, .84% Ni, and 0.27% Mo. This powder was then mixed with —325 mesh hotted and crushed alloy cast iron powder analyzing 3.16% C, 0.55% Ni, 1.87% Cr, 0.38% Mn, 1.21% Si, 0.18% S, 0.07%P, 0.04%Al, and .12% Cu, in a proportion given by the carbon content of the standard lloy. The processing of the mixture into test bars involved pressing t 33 tsi, presintering under a graphite cover in hydrogen for 1 hour at 25°C. (1515°F.), and then sintering for 30 minutes at 1250°C. (2280°F.). fter die forging, the bars were annealed for 30 minutes at 1000°C. 1830°F.) under the same atmospheric conditions. Hardenability was bserved by reheating the material to 825°C. (1515°F.) in a graphite oat, oil quenching and drawing for 30 minutes at 240°C. (465°F.). The sintered alloy steel analyzed 0.46% C, 0.50% Mn, 0.40% Si, 0.02% S, 0.03% P, 1.86% Ni, 0.72% Cr, and 0.19% Mo. After 18% hot reduction in the forging die, the steel had a density of 7.84 g./cc., a tensile strength of 125,450 psi, and an elongation of 16%. The hardened specimens had a Rockwell hardness of C-56 to C-61. It is noteworthy, owever, that the excellent properties listed above were obtained only after engthy experimentation to develop the right powders and proper forging technique.

CARBON-FREE STAINLESS STEELS

During the last ten years the interest in sintered alloy steels has been confined largely to austenitic stainless steels. Until recently the only approach has been to employ a mixture of the elemental powders, or of iron, nickel, and ferrochrome powders. According to Kalischer,[98] the properties of 18–8 stainless steel compacts prepared from the virgin metal powders and sintered in an extended high-temperature cycle approach those of ordinary 18–8 steel, with complete diffusion obtainable. Kieffer and Hotop[99] report that 18–8 stainless steel produced from a mixture of carbonyl iron and nickel and electrolytic chromium powders

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[98] P. R. Kalischer, in *Symposium on Powder Metallurgy*. ASTM, Philadelphia, Pa., 1943, p. 42.

[99] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe*. Springer, Berlin, 1943, p. 202.

with small additions of lampblack can be readily worked to wire and sheets after cold pressing and alternate sintering and hot working (analogous to the manufacture of refractory metals). The mechanical and chemical properties of the worked products are identical with those of the ordinary wrought material.

Figure 473 shows a completely diffused austenitic stainless steel structure of a compact produced from fine electrolytic iron, chromium, and nickel powders (other photomicrographs of this type of material have been previously shown in Figs. 226–228, Volume I, Chapter XIV). In order to obtain this homogeneous austenitic structure, the powder had to be compressed at 70 tsi and the compact sintered in an electric resistance furnace at 1300°C. (2370°F.) for 44 hours in highly purified hydrogen. The inherent porosity and precipitated carbide in the grain boundaries of the sintered compacts were found responsible for a slightly inferior resistance to corrosion as compared with the cast alloy. Even the most completely diffused material showed slight staining effects in a weak solution of 5% $CuSO_4$, and pit corrosion in a stronger solution of 20% $CuSO_4$ plus 5% H_2SO_4. The sintered product could be readily reduced to

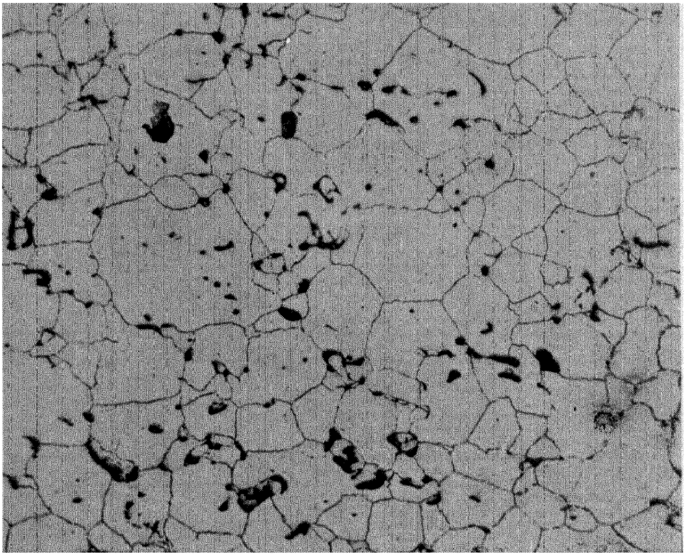

Fig. 473. Completely diffused austenitic structure (×85) of sintered 18–8 type of stainless steel. Mixture of —325-mesh electrolytic iron, nickel, and chromium powders was compacted at 70 tsi and sintered at 1300°C. (2370°F.) for 44 hours in dry hydrogen. (Courtesy of Charles Hardy, Inc.)

TABLE 186
Physical Properties of 18–8 Cr-Ni Stainless Steel Compacts and Wire from Powder versus Standard[a]

	Powder[b]	Standard[c]
Bulk test specimens		
Yield point, psi	29,000–33,000	35,000–45,000
Tensile strength, psi	63,000–66,000	80,000–90,000
Elongation, in 2 in., %	30–40	55–60
Reduction of area, %	40–50	55–65
Brinell hardness	123–133	135–185
Izod impact, ft. lb.	55–69	70–110
Hard-drawn wire, 0.012 in. Diameter		
Tensile strength, psi	303,000	300,000, min.
Soft-annealed wire, 0.012 in. Diameter		
Tensile strength, psi	107,000–109,000	100,000–130,000
Elongation in 10 in., %	33–44	38–58

[a] Data from tests conducted by Hardy Metallurgical Co., Research Report No. 99.

[b] Wire cold-rolled and drawn with two intermediate anneals at 1000°C. (1830°F.) ollowed by water quench; compacts produced from mixtures of electrolytic iron, chromium, and nickel powders, compressed at 50 tsi, sintered at 1300°C. (2375°F.) for 4 hours, repressed at 50 tsi, annealed at 1120°C. (2050°F.) for 1 hour and water quenched.

[c] Wrought material in the softened condition after water quench from 1050–150°C. (1900–2100°F.), according to *Metals Handbook*, 555 (1948). Wires produced by standard methods from cast and water-quenched alloys.

TABLE 187
Physical Properties of 18–8 Cr–Ni Stainless Steel Sintered in Electrical Resistance Furnace and in High-Frequency Induction Furnace[a]

Properties	Compacts sintered in resistance furnace[b]	Compacts sintered in induction furnace[c]
Yield point, psi	29,000–33,000	28,500–33,000
Tensile strength, psi	63,000–66,000	61,000–66,600
Elongation in 2 in., %	30–40	37–47
Reduction of area, %	40–50	39–50
Brinell hardness	123–133	112–129

[a] Data from tests conducted by Hardy Metallurgical Co., Research Reports Nos. 9 and 107.

[b] Mixture of electrolytic iron, chromium, and nickel powders compressed at 20 si, presintered at 1300°C. (2375°F.) for 2 hours, repressed at 50 tsi and sintered at 300°C. (2375°F.) for 44 hours, then water quenched from 1120°C. (2050°F.).

[c] Mixture of carbonyl iron, ferrochrome, and electrolytic nickel powders compressed at 50 tsi and sintered at 1350–1400°C. (2450–2550°F.) for 1 hour, then water quenched from 1120°C. (2050°F.).

very fine wire (0.012-in. diameter) by cold rolling and drawing, requiring only two intermediate annealing treatments at 1000°C. (1830°F.) for one hour, followed by water quench. In Table 186 the mechanical properties of the sintered stainless steel are compared with standard cast and quenched 18–8 Cr–Ni alloy; the tensile properties of the wire are compared with those of conventionally produced stainless steel wires in the same table.

The comparatively long sintering times required for complete diffusion of the ingredients could be substantially reduced when high-frequency induction heating was applied during sintering. Table 187 shows that the physical properties of 18–8 compacts, sintered in a high-frequency furnace (200,000 cycles) for one hour at 1350 to 1400°C. (2460 to 2550°F.) are comparable with those of compacts sintered in a resistance furnace for 44 hours at 1300°C. (2370°F.). Fine wires (0.012 in. in diameter) produced from the induction-sintered compacts were found to reach, in the hard drawn condition, a tensile strength of 288,000 psi, and after annealing, a tensile strength of 114,000 psi and an elongation of 44%. These values compare well with those obtained with wires from compacts sintered for the much longer time in the resistance furnace (see Table 186).

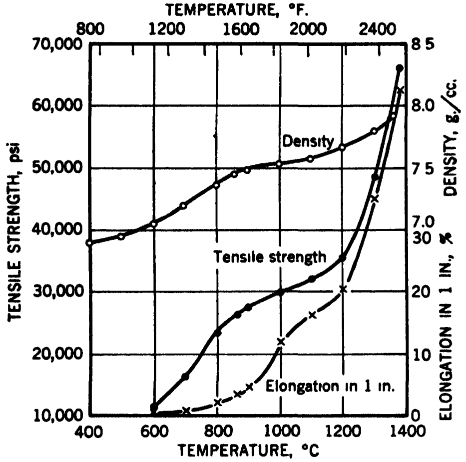

Fig. 474. Effect of sintering temperature on the physical properties of sintered stainless steel from 18–8 alloy powder (according to Wulff[101]). Compacts were pressed at 33 tsi and sintered for 4 hours in extra-pure hydrogen.

A considerable reduction in sintering time is also possible if fusion-alloyed stainless steel powder is used as starting material. The preparation of the powder by intergranular corrosion of stainless steel sheet or scrap with carbon-containing gases and chemical attack of the ensuing carbide grain boundaries[100] has been described elsewhere (Volume I, Chapter III). However, unless the powder is rendered dead soft by a special heat treatment, comparatively high pressures are necessary for molding. In the case of some commercial grades, a density of 75% re-

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[100] U. S. Pats. 2,356,807; 2,368,282.

quires a pressure of about 30–40 tsi, while a density of about 85% requires approximately 60 to 80 tsi. Wulff[101] studied the physical properties of such 18–8 stainless steel compacts after various treatments. The changes in density, tensile strength, and elongation with increasing sintering temperature for a 4-hour treatment are reproduced in Figure 474; in Figure 475 the same properties are shown as a function of time for a constant sintering temperature of 1250°C. (2280°F.). In all cases the compacts were molded at 33 tsi and sintered in extra-pure hydrogen (desiccated by passing over titanium hydride or metallic calcium). A density of close to 7 g./cc. is obtained after compression; compacts sintered at 1250°C. (2280°F.) reach a density of 7.7 g./cc., a tensile strength of over 50,000 psi, and an elongation of over 25% after treatment for 8 hours, while compacts sintered for 4 hours at 1375°C. (2500°F.) reach full density (7.85 g./cc.), a tensile strength of 66,000 psi, and an elongation of 53%.

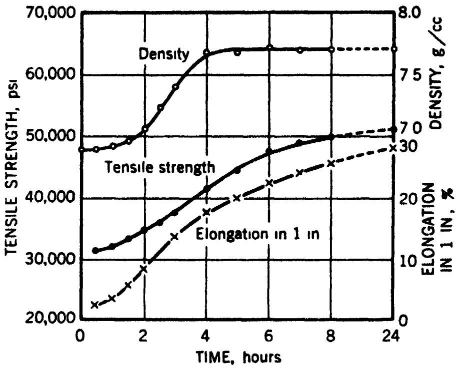

Fig. 475. Effect of sintering time on the physical properties of sintered stainless steel from 18–8 alloy powder (according to Wulff[101]). Compacts were pressed at 33 tsi and sintered at 1250°C. (2280°F.) for different lengths of time in extra-pure hydrogen.

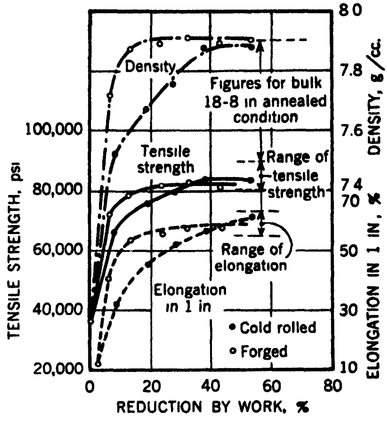

Fig. 476. Effect of subsequent working on the physical properties of sintered stainless steel from 18–8 alloy powder (according to Wulff[101]). Compacts were pressed at 33 tsi and sintered for 4 hours at 1250°C. (2280°F.) in extra-pure hydrogen. One set of specimens was die-forged immediately after withdrawal from the furnace; the other set was cold-rolled. All specimens were finally annealed 30 minutes in dry hydrogen at 1000°C. (1830°F.).

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[101] J. Wulff, in J. Wulff, *Powder Metallurgy*. Am. Soc. Metals, Cleveland, 1942, p. 137.

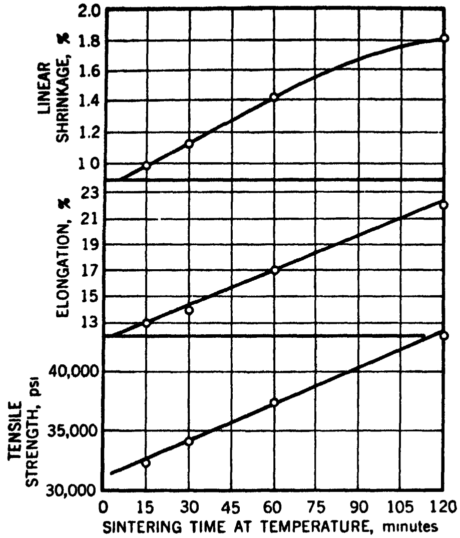

Fig. 477. Effect of sintering time on linear shrinkage and tensile properties of sintered stainless steel from 18–8 alloy powder (according to Dale[102]). Compacts were produced by pressing at 40 tsi and sintering at 1315°C. (2400°F.) for different lengths of time in dry hydrogen.

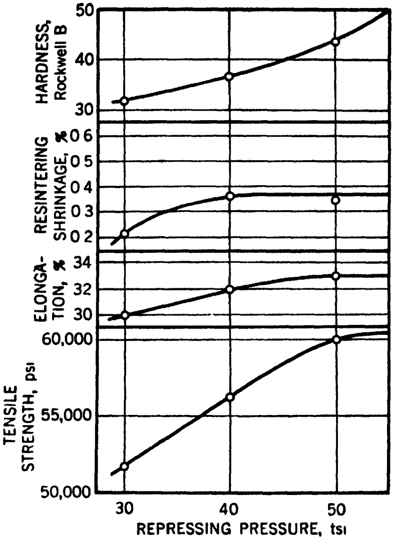

Fig. 478. Effect of repressing pressure on linear shrinkage, hardness, and tensile properties of sintered stainless steel from 18–8 alloy powder (according to Dale[102]). Compacts were produced by pressing at 40 tsi, sintering in dry hydrogen for 45 minutes at 1315°C. (2400°F.), repressing at different pressures, and resintering in dry hydrogen for 1 hour at 1315°C. (2400°F.).

The effect of subsequent working on the material is shown graphically in Figure 476, where density, tensile strength, and elongation values are plotted against percentage reduction, both for die-forged and cold-rolled specimens. The compacts were sintered for 4 hours at 1250°C. (2280°F.), and after forging or rolling, respectively, they were annealed for 30 minutes at 1000°C. (1830°F.). The die-forged material attained standard values after a reduction of only 20%, while a reduction of at least 40% was found necessary to achieve normal properties for the cold-rolled alloy.

Wulff's original work on sintered stainless steel from 18–8 chemically disintegrated alloy powder was later extended in the direction of investigating the effects of repressing and subsequent heat treating. Dale[102] established that under favorable conditions, strength, ductility,

[102] J. D. Dale, *Proc. Third Annual Spring Meeting of Metal Powder Association*, New York, May 27, 1947, p. 4.

and hardness can reach values that approach those found in the wrought alloy. The powder used by Dale had a flow rate of 18.3 sec. per 50 g.; an apparent density of 3.5 g./cc.; a green density of 6.4 g./cc. for a compacting pressure of 40 tsi; and a compression ratio of 1.7:1 for this pressure. The screen size distribution was selected as 10% —150 +200 mesh; 5% —200 +250 mesh; 20% —250 +325 mesh; and 65% —325 mesh. In preliminary tests it was found that a compacting pressure of 40 tsi resulted in optimum green strength of the compacts without undue die-wear effects. Shrinkage values obtained for a standardized sintering temperature of 1315°C. (2400°F.) were rather high, as far as their numerical values are concerned (they ranged between 1 and 2% according to the time at temperature), but they were found to be sufficiently constant to assure reproducibility on a production basis. Shrinkage values for resintering at the same temperature were considerably lower (ranging between 0.1 and 0.5%) and also fairly constant for a given time or pressure.

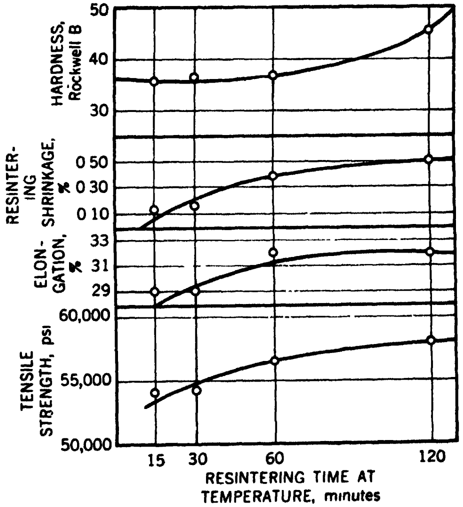

Fig. 479. Effect of resintering time on linear shrinkage, hardness, and tensile properties of sintered stainless steel from 18–8 alloy powder (according to Dale[102]). Compacts were produced by pressing at 40 tsi, sintering at 1315°C. (2400°F.) for 45 minutes in dry hydrogen, repressing at 40 tsi, and resintering at 1315°C. (2400°F.) for different lengths of time in dry hydrogen.

In the diagram of Figure 477 the effect of sintering time is shown on the linear shrinkage, and on tensile strength and elongation for compacts pressed at 40 tsi and sintered at 1315°C. (2400°F.) in dry hydrogen of a dew point of —70°C. (—94°F.). After 2 hours of sintering, saturation values were not yet attained; the shrinkage curve indicates that

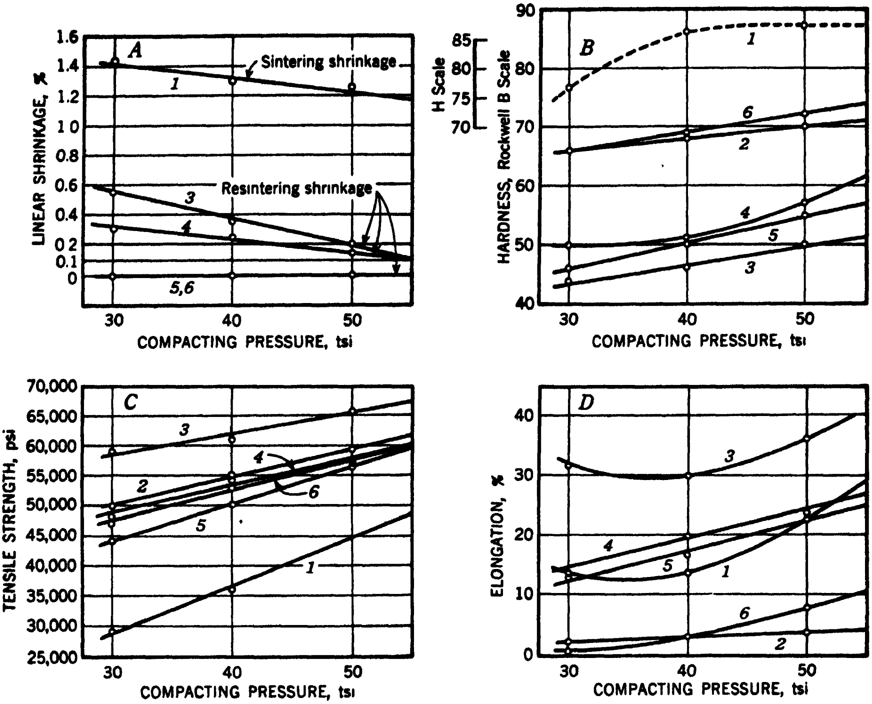

Fig. 480. Effect of initial compacting pressure on linear shrinkage, hardness, and tensile properties of sintered and subsequently treated stainless steel from 18–8 alloy powder (according to Dale[102]). All compacts were sintered for 45 minutes at 1315°C. (2400°F.) in dry hydrogen: *A*, linear shrinkage versus pressure; *B*, hardness versus pressure; *C*, tensile strength versus pressure; and *D*, elongation versus pressure, all at various conditions of resintering and cooling, as given below:

Curve	Repressing pressure, tsi	Time, min.	Resintering temperature °C.	°F.	Condition	Material
1	—	—	—	—	Cooled	Sintered
2	50	—	—	—	Cooled	Coined
3	50	60	1315	2400	Cooled	Resintered
4	50	60	1315	2400	Quenched	Resintered
5	50	30	1040	1900	Cooled	Annealed
6	50	30	400	750	Cooled	Drawn

only a slight increase in density over that measured after compaction (6.5 g./cc., *i.e.*, about 83% of theoretical) is achieved during this period, and that further time may have little effect on density—possibly in contrast to the other properties, which can be expected to increase markedly with further sintering time.

The benefit that can be derived from a repressing operation may best be seen from the diagrams of Figures 478 and 479, which show the effects of repressing pressure and resintering time, respectively, on shrinkage, hardness, and tensile properties. Apparently, saturation values of about 60,000 psi tensile strength at 30% elongation, and a shrinkage of 0.5% are reached with reasonable pressures and periods of sintering and resintering. Another interesting phase of the investigation relates to the effect of subsequent heat treatments. As shown in the composite diagram of Figure 480*A–D*, where the various properties are plotted as a function of the initial compacting pressure for different subsequent treatments, quite remarkable physical properties can be obtained by repressing and resintering, without serious sacrifice of hardness or control of shrinkage. It is somewhat surprising, however, to observe that a subsequent quench treatment had an adverse effect on the elongation values.

A summary of the results obtained by Dale is given in Table 188. It may be noticed that the data are in close agreement with the test results reported earlier by Wulff.[101]

TABLE 188

Summary of Physical Properties of Sintered Stainless Steel[a] (Dale[102])

Conditions	Compacting pressure, tsi	Repressing pressure tsi	Shrinkage, %		Hardness, Rockwell	Elongation, %	Tensile strength, psi
			Sintered	Resintered			
Minimum[b]	30	—	1.4	—	H 77	14	29,000
	30	40	1.4	0.4	H 91	28	51,000
	30	50	1.4	0.6	B 44	32	59,200
Optimum	40	—	1.3	—	H 86	14	36,000
	40	30	—	0.2	B 32	30	51,000
	40	40	—	0.4	B 37	32	56,600
	40	50	1.3	0.4	B 44	33	61,200
Maximum[c]	50	—	1.3	—	H 87	23	45,200
	50	50	1.3	0.2	B 50	36	65,600

[a] Atmosphere, dry hydrogen; temperature, sintering, and resintering, 1315 °C. (2400 °F.); time, sintering (optimum), 45 minutes at temperature; time, resintering (optimum), 60 minutes at temperature.

[b] Limited by poor green strength.

[c] Limited by die wear and press capacity.

According to Wulff,[101] the corrosion resistance—especially against attack by a 10% ferric chloride solution—was found to be superior in the case of the material prepared from the stainless steel alloy powder over that of sintered stainless steel prepared from a mixture of electrolytic iron, chromium, and nickel powders subjected to identical processing; it was found, however, to be inferior to cast and, especially, wrought 18–8 stainless steel. Kalischer,[103] on the other hand, claims that only the chemical analysis is properly retained by a short sintering treatment of alloy-powder compacts, whereas the resistance to oxidation and corrosion remains inferior to that obtainable with alloys prepared from the powdered ingredients and subjected to extended high-temperature sintering.

While 18–8 Cr–Ni alloy powders have been most in demand, other heat- and corrosion-resistant alloy powders have also been fabricated successfully into sintered bodies. Thus, for example, a powder produced from 35–15 Ni–Cr (Chromax) alloy castings is basically softer than the 18–8 alloy powder normally produced, and molding pressures of 20–30 tsi suffice for the formation of a coherent compact that can safely be handled. Sintering for 2 hours at 1200°C. (2190°F.) in cracked ammonia of a dew point of —60°C. (—76°F.), or lower, produces a 75–80% dense compact that can be coined to about 90% density at pressures in the order of 50 tsi. The procedure is not very different from that conventionally used in fabricating pure iron or carbon steel products, and should make this powder particularly interesting from the standpoint of industrial stainless steel parts production.

Applications

Since the development of high-strength alloy steel parts from metal powders is still in its earliest beginning, no commercial applications of major significance have yet materialized. The long sintering times necessary for the formation of homogeneous structures rule out for the time being the production on an industrial scale of nickel-chromium steel, tool steel, or heat-resistant alloy steel parts. Among the few specific applications known are small transmission gears and small dies for die-casting machines.[104]

Small parts from 18–8 and other stainless steels, however, can be produced by cold pressing and sintering under industrial conditions, and the quality of the products may be high enough to make the sintered parts comparable with parts machined from bar stock. For applications in the chemical and food industries, however, a high degree of densification of these parts is necessary for good corrosion resistance, and this implies high molding pressures and extended heat treatment in carefully purified atmosphere at high temperatures. The high cost of this procedure coupled with the high price of the raw material (particularly, if alloy powders are used), have so far failed to make the sintered product

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[103] P. R. Kalischer, in *Symposium on Powder Metallurgy*. ASTM, Philadelphia, Pa., 1943, p. 42.

[104] U. S. Pat. 2,413,512.

competitive with the standard material. Only where extensive machining is involved could the powder metallurgy products prove advantageous in view of the better machinability of the sintered stainless steels (for which the residual porosity and the ensuing type of short chip formation are believed largely responsible). In this case, stainless steel can be pressed and sintered to the approximate shape and then economically finished by customary machining methods.

SINTERED IRON ALLOYS

Most important among sintered ferrous alloys other than steels are iron alloys containing nickel, copper, or lead, since these alone have been developed on a commercial scale to date. Sintered compositions of iron with other metals, such as tin, zinc, or silver, have found no significant industrial applications (for a more detailed discussion of these alloys, see Chapter XXXII).

Manufacturing Procedures

The production methods for sintered iron alloys are governed strictly by the alloying ability of the components. The principal procedures are: (*1*) compaction and sintering of mixtures of the elemental metal powders; (*2*) compaction and sintering of alloy or pseudoalloy powders; (*3*) compaction and sintering of coated powders; and (*4*) infiltration of the liquid lower melting metal into loose or compacted and sintered iron powder.

The method involving compaction and sintering of a mixture of the elemental powders is applicable in all cases, regardless of the constitution of the alloy system involved; the method is of particular value when easy compactibility is essential. However, extended high-temperature sintering treatments are indicated when homogeneous solid solutions, such as between iron and nickel, are possible—and desirable. Less intensive sintering is required when the treatment need merely produce surface-bonding effects between less soluble components; in sintering iron–copper compositions it is only necessary to heat the compact above the liquefaction temperature of copper, whereupon the liquid phase will almost immediately braze the iron particles together into a coherent structure.

Homogeneous alloy powders, of course, can be used only when the constituents form a solid solution, as in iron–nickel alloys. In this case the powders are advantageously prepared by the joint decomposition of the two carbonyls of these metals, or by atomizing the liquid alloy. The use of the fusion-alloyed powder permits drastic reduction of the sintering time in the production of the homogeneous alloy.

In the case of duplex alloys of the iron–copper or iron–lead type, pseudoalloy powders can be produced satisfactorily by shotting or atomizing a liquid metal in which the nonalloyable component is kept in suspension by agitation or other means. The resulting powder particles then contain the minor phase as minute, well-dispersed metallic inclusions.

If a coarser agglomeration of the lower melting phase in the sintered structure is not objectionable, coated powders are also suitable. The coatings, produced by ball milling, electrodeposition, or displacement (for details see Volume I, Chapters III and VI), have the distinct advantage of facilitating compactibility as compared with the opposite effect obtained with fusion-alloyed powders. This is particularly valuable in those instances where the iron powder is hard or alloyed with carbon. For instance, copper-coated cast iron or steel powders containing 15–25% Cu can be compacted at a pressure of 15–20 tsi, while noncoated powders require at least 50 tsi for compaction into a coherent body. In addition. copper and lead coatings render the iron powder more resistant to oxidation. (Incidentally, the same effect can also be achieved by coating the iron particles with nickel.)

The method by which the low-melting constituent is introduced in the form of a liquid during sintering of the loose or compacted iron powder, or during a subsequent heat treatment, is radically different from the foregoing procedures. Here, an iron compact of carefully *predetermined porosity* is first produced by conventional methods, *e.g.*, by compaction at moderate pressures and sintering in a cycle that permits formation of a coherent metallic iron sponge or skeleton body. A high specific gravity for the compact is obtained after the heavier, low-melting metal has fully penetrated the porous compact in a process effected by the capillary forces acting in the interconnected pores (for further details, see pp. 415 ff.).

Properties

IRON–NICKEL ALLOYS

The importance of iron–nickel alloys stems from their magnetic and thermal expansion characteristics. The magnetic properties of the Permalloy powders and also of sintered iron–nickel alloys, as developed by Rostoker,[104a] have been discussed elsewhere (see Chapter XXIV). The thermal expansion characteristics have been investigated by Hamprecht and Schlecht,[105] and the change in expansion with temperature is shown for four sintered and annealed carbonyl iron–nickel alloys in Figure 481. Alloys containing 30–50% Ni have a small and consistent thermal expansion coefficient; in the range between 35 and 36% Ni the sintered alloys

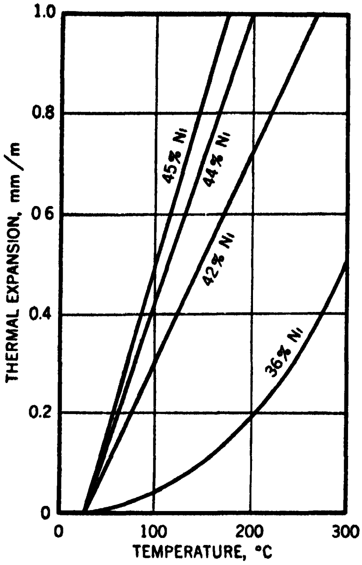

Fig. 481. Thermal expansion of sintered and annealed carbonyl nickel–iron alloys (according to Hamprecht and Schlecht[105]). 45% Ni: expansion coefficient (α) = 7.1 × 10^{-6} (constant up to 450°C.); 44% Ni: α = 5.7 × 10^{-6} (constant up to 435°C.); 42% Ni: α = 4.1 × 10^{-6} (constant up to 410°C.); 36% Ni: α = 0.5 × 10^{-6} (20–50°C.), α = 0.8 × 10^{-6} (50–100°C.), α = 1.2 × 10^{-6} (100–150°C.), α = 2.0 × 10^{-6} (150–200°C.).

prepared from very pure powders display a smaller coefficient of expansion than the corresponding alloys obtained by casting.

The structure and mechanical properties of iron–nickel alloys of the entire range have been investigated by L. Delisle and A. Finger.[106] The alloys were produced by compaction of mixtures of electrolytic iron and pulverized electrorefined nickel powders, and sintering at 1100°C. (2010°F.) for 3 hours. Figures 482 and 483 show the density, and Fig. 484 the mechanical properties, as a function of the Ni content of the alloy; the latter gives a clear indication of the excellent strength values obtainable with compositions in a nickel range of 20%. The same trend is noticeable in the compression test data presented in Figures 485 and 486. The microstructures of these alloys are reproduced in Figures 487 and 488.

IRON–NICKEL–COBALT ALLOYS

The ternary iron–nickel–cobalt alloy, with 15–19% Co, 28–30% Ni, balance Fe, known as "Kovar" or "Fernico" excels by its very low

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[104a] W. Rostoker, *Trans. Am. Inst. Mining Met. Engrs., 180,* 672 (1949).

[105] G. Hamprecht and L. Schlecht, *Metallwirtschaft, 12,* 281 (1933).

[106] L. Delisle and A. Finger, *Trans. Am. Inst. Mining Met. Engrs., 166,* 574 (1946).

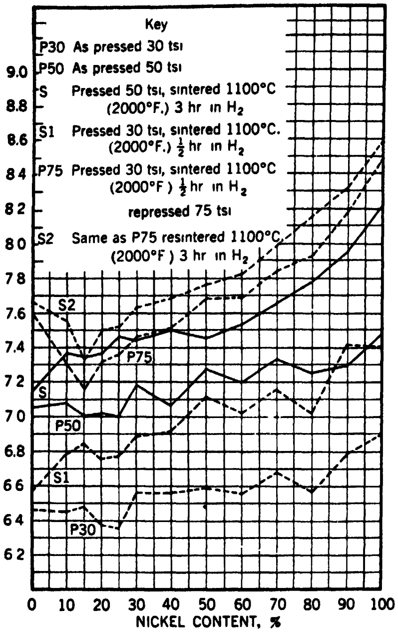

Fig. 482. Effect of the nickel content on the density of sintered iron–nickel alloy bars for different processing conditions (according to Delisle and Finger[106]).

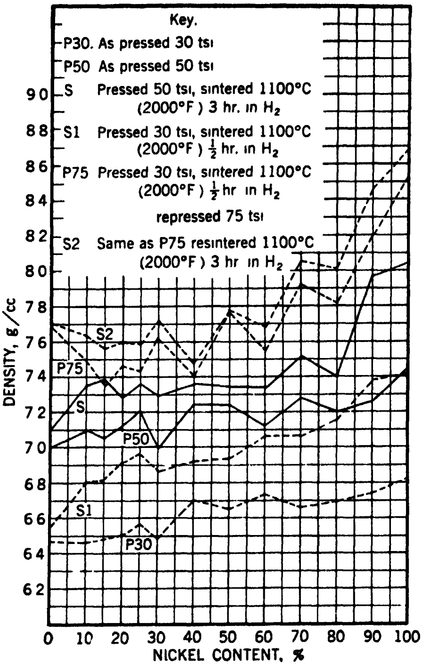

Fig. 483. Effect of the nickel content on the density of sintered iron–nickel alloy pellets for different processing conditions (according to Delisle and Finger[106]).

coefficient of expansion, making it an ideal glass-sealing material.[106a,b] The sintered product may be used to advantage in intricate shapes.[106c] Also, the possibility of employing raw materials of very high purity with the elimination of even traces of manganese and other harmful elements enables the production of a high-quality product and facilitates rolling of the alloy into strip or sheet.[107]

An investigation of the sintered alloy in France[108] was based on a mixture of hydrogen-reduced metal powders that was compacted into small cylinders at about 20 tsi and sintered either in a resistance furnace at 1050°C. (1920°F.) or in a high-frequency furnace at 1250°C.

[106a] H. Scott, *J. Franklin Inst.*, *220*, 773 (1935); U. S. Pat. 1,942,260.

[106b] A. W. Hull and E. E. Burger, *Physics*, *5*, 384 (1934).

[106c] U. S. Pat. 2,172,548.

[107] E. E. Burger, *Gen. Elec. Rev.*, *49*, No. 12, 22 (1946).

[108] N. Thienchi, *Compt. rend.*, *222*, 1046 (1946); see also *Powder Met. Bull.*, *1*, No. 5, 82 (1946).

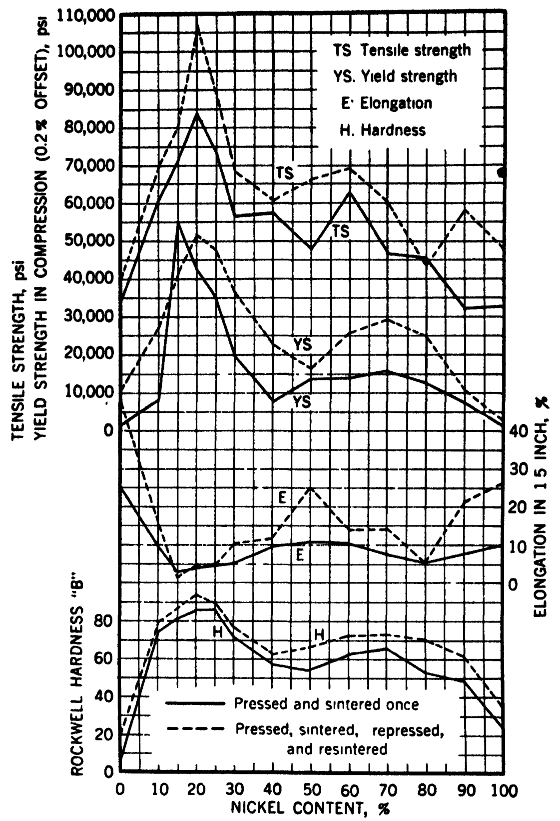

Fig. 484. Effect of the nickel content on the tensile properties and hardness of sintered and resintered iron–nickel alloy bars (according to Delisle and Finger[106]). Specimens processed only once were pressed at 50 tsi and sintered for 3 hours at 1100°C. (2010°F.); specimens processed twice were first pressed at 30 tsi and sintered for 30 minutes at 1100°C. (2010°F.), then repressed at 75 tsi and resintered for 3 hours at 1100°C. (2010°F.). All heat treatments were performed in hydrogen.

(2280°F.). Specimens sintered at the lower temperature for 10 hours had a density of 5.0 g./cc., while those sintered at the same temperature for 20 hours yielded a density of 6.5 g./cc. Sintering at the higher temperature for only one hour resulted in a density of 7.8 g./cc., or 94% of the density of the cast material. X-ray diffraction diagrams of the specimens sintered at the higher temperature were found to be identical with those of the cast alloy, whereas the patterns obtained with specimens sintered at the lower temperature were more diffuse, indicating incomplete alloying. Although all specimens welded perfectly to glass having an

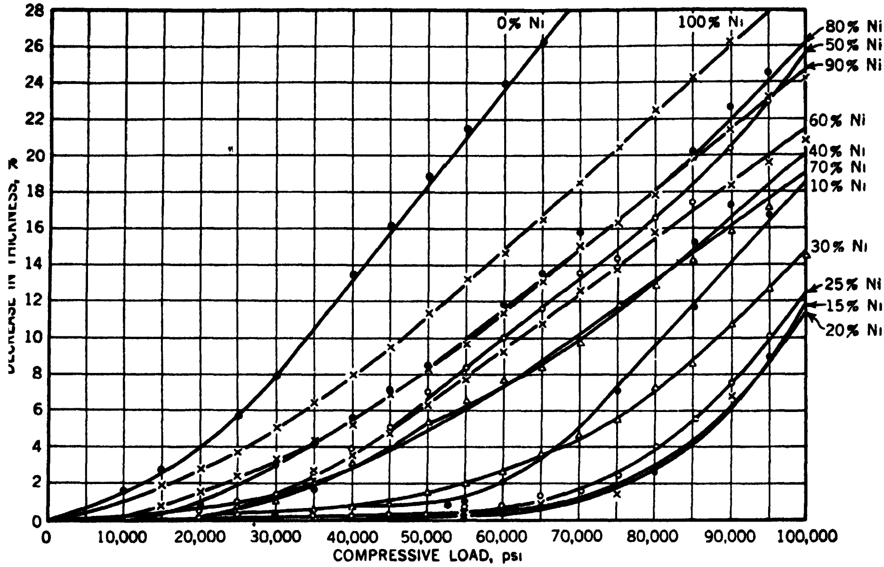

Fig. 485. Compressive properties of iron–nickel alloy compacts produced by pressing at 50 tsi and sintering for 3 hours at 1100°C. (2010°F.) in hydrogen (according to Delisle and Finger[106]).

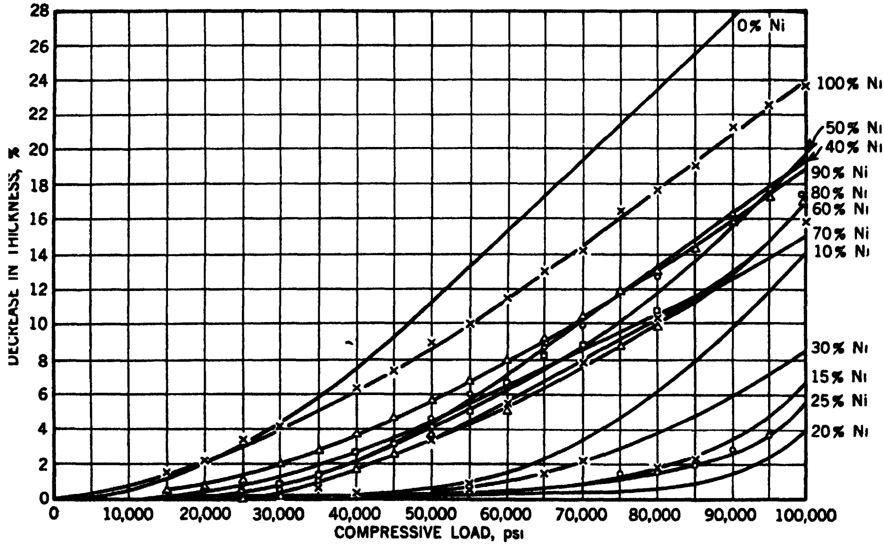

Fig. 486. Compressive properties of iron–nickel alloy compacts produced by pressing at 30 tsi, sintering for 30 minutes at 1100°C. (2010°F.) in hydrogen, repressing at 75 tsi and resintering for 3 hours at 1100°C. (2010°F.) in hydrogen (according to Delisle and Finger[106]).

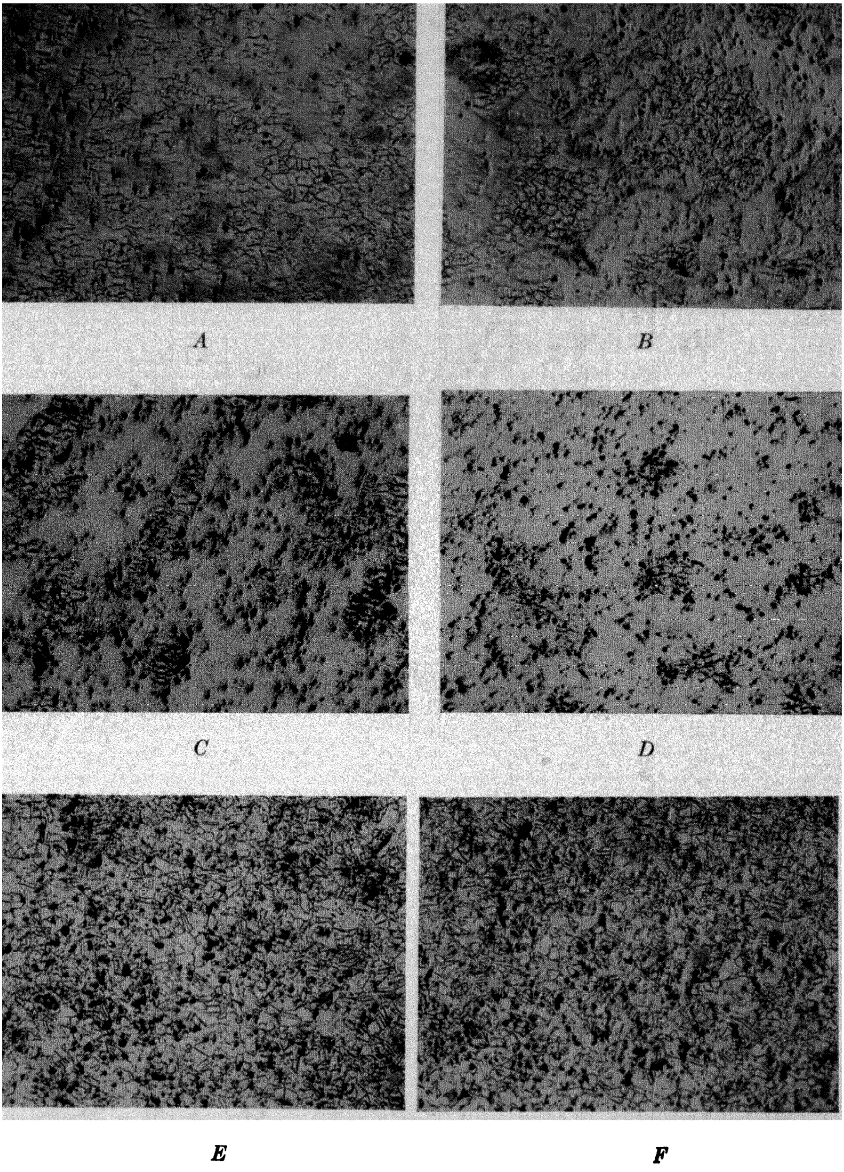

Fig. 487. Microstructure (×100) of twice-pressed and sintered iron–nickel alloys of different nickel content (according to Delisle and Finger[106]): *A*, 90–10 iron–nickel alloy, etched with 1% nital; *B*, 80–20 iron–nickel alloy, etched with 1% nital; *C*, 70–30 iron–nickel alloy, etched with 1% nital; *D*, 50–50 iron–nickel alloy, etched with 1% nital; *E*, 30–70 iron–nickel alloy, etched with 1:1:1 HNO_3:HCl:H_2O: and *F*, 10–90 iron–nickel alloy, etched with 1:1:1 HNO_3:HCl:H_2O.

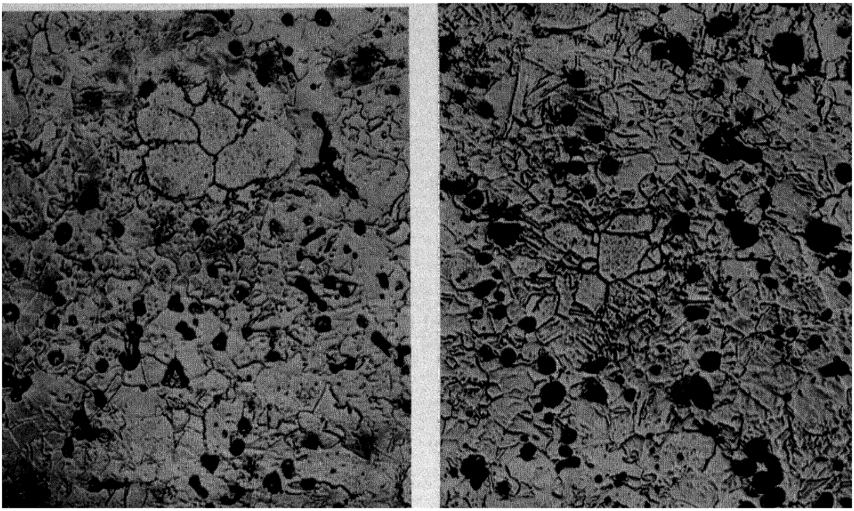

Fig. 488. Microstructure (×500) of twice-pressed and sintered iron–nickel alloys (according to Delisle and Finger[108]): *A*, 85–15 iron–nickel alloy, etched with 1:1:1 HNO_3:HCl:H_2O; and *B*, 80–20 iron–nickel alloy, etched with 1:1:1 HNO_3:HCl:H_2O.

expansion coefficient of 5×10^{-6} (per °C.), and polariscope examination revealed freedom from stresses, dilatometric studies indicated that a vacuum-tight seal would require a minimum density of 8 g./cc.

IRON–COPPER ALLOYS

The tensile properties of sintered iron–copper powder compacts have been investigated by Kelley.[109] Electrolytic iron and copper powders, as received or after annealing, were mixed in various proportions with 5 to 30% Cu, and after compacting at 30 tsi sintered in dry hydrogen at temperatures from 1100 to 1350°C. (2010 to 2460°F.) for periods from 10 minutes to 24 hours. The results obtained by varying the copper content, sintering temperature, and sintering time are summarized in Table 189. It is interesting to note that the tensile strength of a composition containing 10% Cu and sintered for 10 minutes at 1200°C. (2190°F.) is greater than that which can be attained by sintering pure iron at any temperature for any length of time. A comparison of annealed and "as-received" powders as raw material is given in Table 190 for compacts sintered at 1100°C. (2010°F.) for 30 minutes. Here, it is interesting to

TABLE 189

Physical Properties of Sintered Iron–Copper Alloys as Affected by Copper Conten and Sintering Cycle (Kelley[109])

Copper content, %	Sintering temperature °C.	°F.	Sintering time	Tensile strength, psi	Elongation, %	Reduction in area, %
5	1200	2190	10 min.	43,600	1.56	1.0
10	1200	2190	10 min.	56,100	1.56	1.5
15	1200	2190	10 min.	50,200	1.30	1.5
30	1200	2190	10 min.	35,500	0	1.0
10	1100	2010	30 min.	22,000	3.00	0
10	1100	2010	30 min.	19,100	3.00	0
10	1100	2010	2 hr.	75,800	4.00	6.9
10	1100	2010	4 hr.	80,600	2.75	5.0
10	1100	2010	8 hr.	71,400	0	3.4
10	1100	2010	24 hr.	84,000	4.00	8.0
10	1100	2010	3 hr.	83,200	2.67	1.0
10	1100	2010	3 hr.	79,500	4.00	2.5
10	1350	2460	3 hr.	79,000	5.34	2.5
10	1350	2460	3 hr.	78,200	4.00	6.0

TABLE 190

Effect of Powder Treatment on Physical Properties of Sintered Iron–Copper Alloy of Varying Copper Content (Kelley[109])

Powder treatment	Copper content, %	Tensile strength, psi	Elongation, %	Reduction, in area, %
Annealed	5	16,900	2.0	0
Annealed	5	23,400	3.0	0
As received	5	29,000	3.0	0
As received	5	35,400	2.0	0
Annealed	10	22,000	3.0	0
As received	10	40,900	1.0	0
Annealed	15	33,200	4.0	1.0
As received	15	45,600	3.0	1.5
Annealed	20	40,300	6.0	2.5
As received	20	51,400	3.0	1.0
Annealed	25	43,800	7.0	5.0
As received	25	61,900	5.0	4.0
Annealed	30	46,400	6.0	5.0
Annealed	30	48,600	6.0	4.1
As received	30	69,700	6.0	3.4
As received	30	70,000	7.0	4.9

observe that under the conditions used in this cycle, unannealed powder give superior results over annealed powders. Kelley also reports that smal compacts ($^1/_4 \times {}^1/_4 \times 2^1/_4$ in.) may be heat treated while larger compacts ($^5/_8 \times {}^5/_8 \times 7^1/_2$ in.) develop cracks on quenching. An allo containing 25% Cu—after reheating to 1000 or 1100°C. (1830 or 2010°F.

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[109] F. C. Kelley, *Iron Age, 158,* No. 7, 57 (1946).

for 30 minutes and subsequent quenching in water—reaches tensile strength values of 100,000 psi, with figures for elongation and reduction of area in the order of 1%.

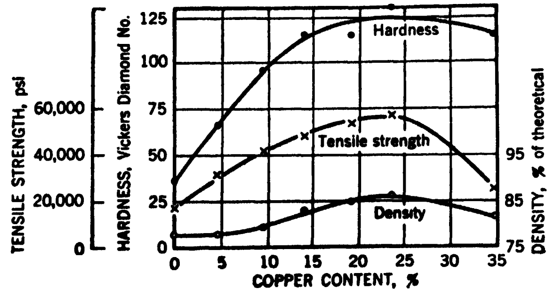

Fig. 489. Influence of the copper content on the properties of sintered iron–copper powder compacts (according to Northcott and Leadbeater[110]).

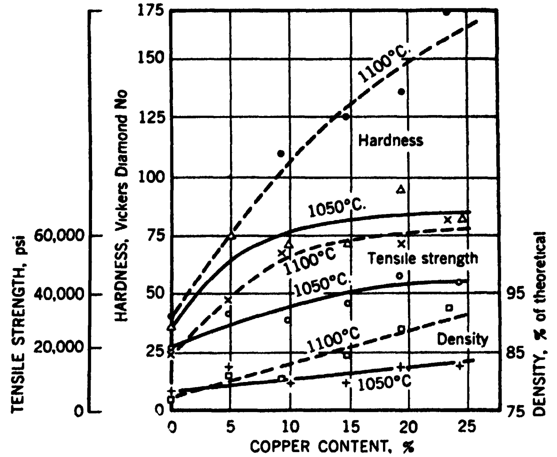

Fig. 490. Influence of the sintering temperature on the properties of iron–copper powder compacts of different copper content (according to Northcott and Leadbeater[110]).

An extensive investigation of the powder metallurgy of iron-copper mixtures has been made in England, and the contributions of Northcott and Leadbeater[110] and Chadwick, Broadfield, and Pugh[111] give a compre-

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[110] L. Northcott and C. J. Leadbeater, *Symposium on Powder Metallurgy*. The Iron and Steel Institute, Special Report No. 38, London, 1947, p. 142.

[111] R. Chadwick, E. R. Broadfield, and S. F. Pugh, *Symposium on Powder Metallurgy*. The Iron and Steel Institute, Special Report No. 38, London, 1947, p. 151.

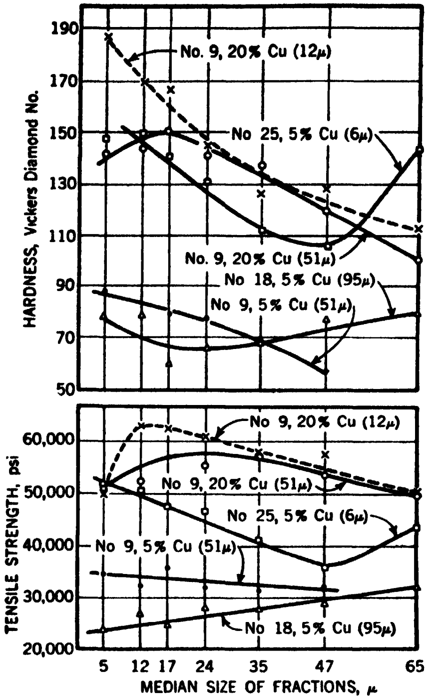

Fig. 491. Influence of particle size of iron and copper powders on the properties of sintered iron–copper compacts of different copper content (according to Northcott and Leadbeater[110]). Curves designate different iron powders and copper contents: powder No. 9, electrolytic, apparent density 2.08 g./cc., tap density 3.18 g./cc., median particle size 51 μ; powder No. 18, oxide-reduced, apparent density 2.17 g./cc., tap density 2.86 g./cc., median particle size 95 μ; powder No. 25, oxide-reduced, apparent density 0.97 g./cc., tap density 1.77 g./cc., median particle size 6 μ.

—— Iron + copper fractions; - - - Iron fractions + copper.

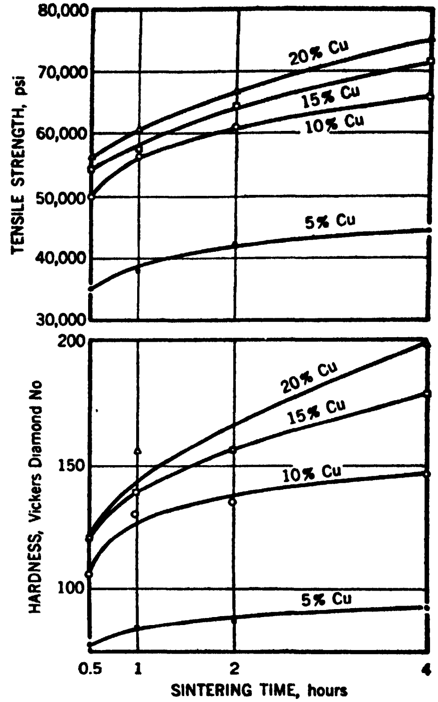

Fig. 492. Influence of sintering time on the properties of iron–copper compacts of different copper content pressed at 30 tsi and sintered in hydrogen at 1100°C. (2000°F.) for different periods of time (according to Northcott and Leadbeater[110]).

hensive picture of the properties attainable with iron–copper compacts. The investigation by Northcott and Leadbeater covers the preparation of iron–copper alloys by various methods and a study of the resulting properties and microstructures. Compacts were produced from a series of iron powders and also a series of copper powders, differing in method of production and particle characteristics (especially particle size). The powder production methods included: (*1*) simultaneous hydrogen reduction of mixed oxides; (*2*) hydrogen reduction of individual metal oxides followed by mixing; (*3*) mixing of electrolytic powders; and (*4*) coating of electrolytic iron powder with copper by chemical replacement. The procedure for mixing the powdered ingredients was standardized at 24 hours, and compacting pressures were maintained at 30 tsi. When mixing pure commercial iron and copper powders in proportions varying from 5 to 35% Cu, best physical properties and highest densities were obtained with compacts containing about 25% Cu that were sintered in hydrogen at 1100°C. (2010°F.) for 1 hour. This is presented graphically in Figure 489. Best physical properties were generally obtained with fine copper powder and sintering at 1100°C. (2010°F.) when copper in the liquid phase promoted diffusion to a clearly defined extent. With lower sintering temperatures, *e.g.*, 1050°C. (1920°F.) all physical properties were found to be appreciably lower, as indicated in Figure 490. The influence of the particle size of the iron and copper powders on the properties of compacts sintered at 1100°C. (2010°F.) can be seen from Figure 491. The sintering time used in the investigation was generally 1 hour, but improvements were obtained by increasing it to 4 hours (Fig. 492). A close relationship between tensile strength and equivalent density, irrespective of the method of manufacture of the compact, was established, and for constant porosity the maximum strength was obtained with about 10% Cu. The relation between tensile strength and porosity for different

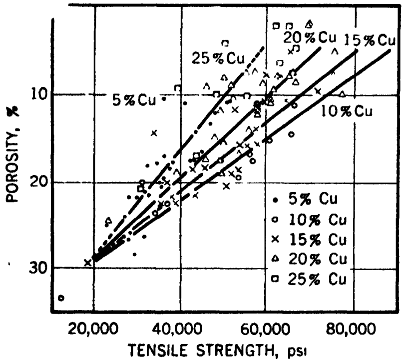

Fig. 493. Relation between tensile strength and porosity for different copper contents of iron–copper compacts (according to Northcott and Leadbeater[110]).

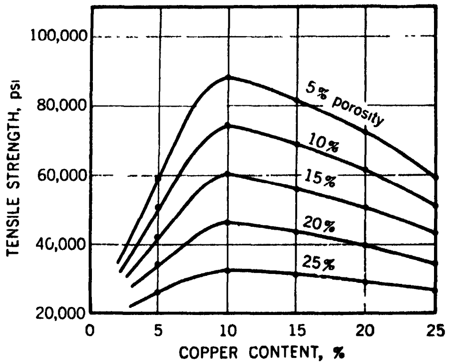

Fig. 494. Relation between tensile strength and copper content for different porosities of iron–copper compacts (according to Northcott and Leadbeater[110]).

copper contents is given in Figure 493, that between tensile strength and copper content for different porosities in Figure 494. This phase of the work includes the impregnation of pressed iron compacts with molten copper by a process described more fully in a subsequent section.

The results recorded and the conclusions drawn by Chadwick, Broadfield, and Pugh are analogous to those of Northcott and Leadbeater. In their work the former used 4 iron powders (electrolytic, reduced oxide prepared from mild steel turnings, Swedish sponge iron, and reduced mill scale from the United States) and two copper powders (electrolytic and hydrogen-reduced). The effects of variations in particle size, compacting pressure, and sintering temperature were studied, and some of the results are reproduced in the diagrams of Figures 495 and 496, showing the effect of copper content on porosity and dimensional changes, and on mechanical properties, respectively. The optimum tensile strength and elongation are obtained for 25% Cu contents, and with an iron powder of low compressibility. It is interesting to note that compacts produced from electrolytic iron which was readily compressible had a lower tensile strength and ductility than compacts prepared from the hydrogen-reduced powders. The extent of diffusion and solubility of the iron particles in the liquid copper during sintering above the melting point of the copper becomes evident from Figures 497*A* and *B*, which display photomicrographs of 75–25 iron–copper compacts after sintering at 1120°C.

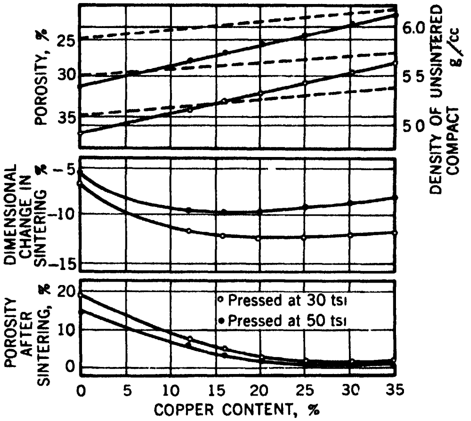

Fig. 495. Effect of copper content on porosity and dimensional changes of iron–copper powder compacts pressed at different pressures and sintered at 1120°C. (2050°F.) for 15 minutes (according to Chadwick, Broadfield, and Pugh[111]).

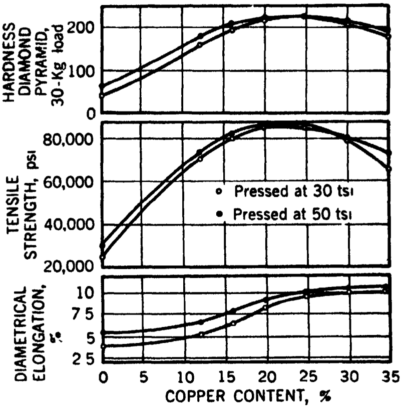

Fig. 496. Effect of copper content on the mechanical properties of iron–copper powder compacts pressed at different pressures and sintered at 1120°C. (2050°F.) for 15 minutes (according to Chadwick, Broadfield, and Pugh[111]).

(2050°F.) for 15 minutes and at 1100°C. (2010°F.) for 30 minutes, respectively.

Iron-base compositions containing copper as well as copper and manganese in a 70:30 ratio have been investigated by A. Squire.[112] An addition of 10% Cu resulted in an increase in tensile strength from about 30,000 psi (for plain sintered iron) to 85,000 psi, whereas 10% of the copper–manganese alloy raised the tensile strength up to 90,000 psi.

The physical properties of sintered alloys of iron with copper and carbon have recently been discussed by Stern.[112a] The alloys were prepared from mixtures of oxide-reduced iron powder to which 0.40–1.05% graphite was added, and 1, 2, and 5% electrolytic copper. Test specimens were prepared by pressing tensile bars at 50 tsi, sintering at 1100°C. (2010°F.) for 15 minutes in dissociated ammonia, repressing at 50 tsi, resintering at 1100°C. (2010°F.) for 1 hour in dissociated ammonia, and heat-treating by oil or water quenching from 830–850°C. (1525–1560°F.) followed by drawing at either 315°C. (600°F.) or 425°C. (800°F.). The tensile strength of the treated alloys (density between 6.84 and 7.03 g./cc.) was found to be comparable to equivalent cast carbon steel, while the ductility values were lower in spite of the lower

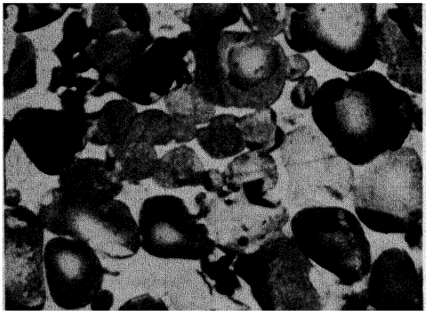

Fig. 497*A*. Microstructure (×380) of a 75–25 iron–copper compact after sintering at 1120°C. (2050°F.) for 15 minutes (according to Chadwick, Broadfield, and Pugh[111]). The spheroidized particles of various shades are the iron, and the white background is the copper phase.

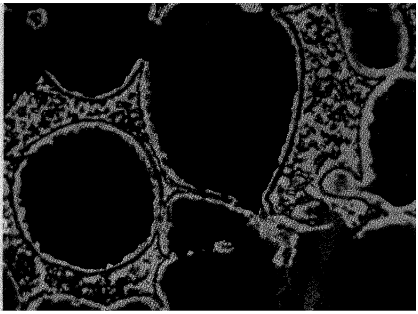

Fig. 497*B*. Microstructure (×1500) of a 75–25 iron–copper compact after sintering at 1100°C. (2010°F.) for 30 minutes (according to Northcott and Leadbeater[110]). The light copper phase is disrupted by the iron-rich precipitate and separated from the iron grains by a thin diffusion layer.

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[112] A. Squire, *Watertown Arsenal Lab. Rept. WAL 671/8* (1946).

[112a] G. Stern, *Proc. International Powder Metallurgy Conference*, Graz, July 12–17, 1948, Referate No. 57; *Iron Age, 163*, No. 12, 81 (1949).

ultimate carbon range (0.33–0.50%). The alloy containing 1% copper exhibited a tensile strength of 60,650 psi, an elongation of 8.5%, and a reduction in area of 8.0%; the corresponding values for the alloy containing 2% copper were 68,650 psi tensile strength, 6.0% elongation, and

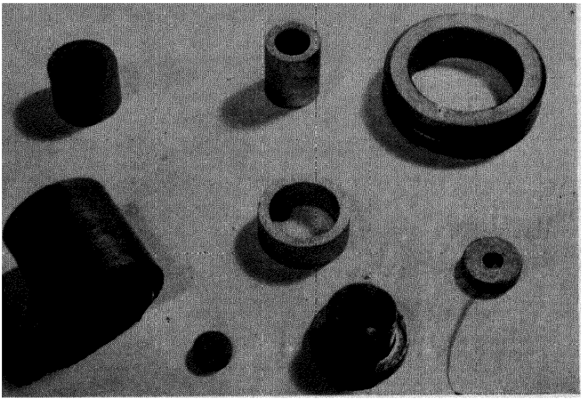

Fig. 498. Assortment of sintered iron–copper bearings, bushings, and sleeves (according to Kieffer, Benesovsky, and Bartels[112b]).

TABLE 191

Physical Properties of Pressed and Sintered Iron–Copper Alloys Used for Machine Parts[a]

Properties	98-2 Fe–Cu alloy	90–10 Fe–Cu alloy	75-25 Fe-Cu alloy
Density, g./cc.	5.6–6.1	6.2	6.9–7.2
Tensile strength, psi	25,000	30,000	35,000–45,000
Compressive strength, psi	—	140,000	190,000–250,000
Compressive strength, for			
0.001 in. set, psi	—	—	35,000–70,000
0.005 in. set, psi	—	—	60,000–90,000
0.015 in. set, psi	—	—	75,000–120,000
Elongation in 2 in., %	—	—	<2
Brinell hardness	60–90	60–90	60–90
Coefficient of thermal expansion per °C.	—	—	14.2–14.4 $\times 10^{-6}$
°F.	—	—	7.9–8.0 $\times 10^{-6}$
Electrical conductivity, % of copper	—	—	11.8–12.05

[a] Data from P. Schwarzkopf, *Powder Metallurgy*, Macmillan, New York, 1947, Table XVIII; and A. J. Langhammer, *Machinery*, *51*, No. 8, 152 (1945).

[112b] R. Kieffer, F. Benesovsky, and H. J. Bartels, *Powder Met. Bull.*, *2*, No. 3, 54 (1947).

3.7% reduction in area; those for the alloy containing 5% copper were 83,100 psi tensile strength, 2.0% elongation, and 1.6% reduction in area.

Structural parts of varying density are today produced on a commercial scale from iron–copper compositions that contain from 2 to about 25% Cu. Fig. 498[112b] displays an assortment of iron–copper bearings and bushings. The physical properties of several typical materials are given in Table 191. In all instances a mixture of the ingredients is compacted and sintered at or above the melting temperature of the copper, followed by sizing or coining. The comparatively low tensile values permit the conclusion that production of these materials makes no allowance for precipitation treatments, or that the usually quite marked effects of such treatment (see also Volume I, Chapter XIX) are depreciated by the substantial porosity in the products.

When the pore effects of the iron compact are eliminated through impregnation with liquid copper, full advantage can be taken of the limited solubility of the iron particles in the liquid copper, and of the ensuing precipitation hardening effects.[112c] Thus, mechanical properties of an entirely different order of magnitude than those of Table 191 are obtainable. In view of these implications, the subject will be treated more fully in a subsequent discussion of the recently developed "cemented" steels.

IRON—LEAD ALLOYS

The addition of lead to iron improves primarily the antifriction properties and specific gravity of the iron. The mechanical properties are generally affected adversely, since the low-melting metal phase tends to reduce the tensile strength while embrittling the entire structure.

Applications

The principal application for iron–nickel alloys is in the magnetic field, and, as such, is treated in Chapter XXIV. Alloys containing between 30 and 50% Ni have found considerable usefulness in the manufacture of bimetal thermostats and regulators for measuring instruments and furnaces, and for automatic cutouts. For lead-in wires in lamp and radio applications, glass-to-metal sealing materials of very low coefficient of expansion are used; sintered alloys of iron–nickel of the "Invar" type (64–36 Fe–Ni) as well as iron–nickel–cobalt of the "Kovar" type (54–28–18 Fe–Ni–Co) have been found well suited for this purpose.

Sintered alloys of iron with copper and lead have been applied principally in the machine parts and bearing industries, with the lower melting metal addition serving the double purpose of facilitating the

[112c] Brit. Pat. 586,895.

fabrication (*e.g.*, molding) of the part and improving the antifriction properties. The additional advantage of an improved corrosion resistance of the sintered product has been found useful for many applications in the structural parts field, and the increased weight per part, in particular in iron–lead compositions, has made the material applicable for balancing and sliding weights and similar parts. Iron alloys that contain brass (5%) in addition to copper (5%) have recently been reported[112d] as being used in the production of ball races and hub and clutch combinations for phonograph record changers. An interesting description of improved manufacturing techniques for automotive parts from iron–copper powder mixtures has recently been given by Ensign.[113]

CEMENTED STEELS

A review of the powder metallurgy of iron and steel remains incomplete without reference to the newly developed iron–copper base materials introduced under the name of "cemented steels."[114,115] The products are manufactured by infiltration of copper alloys into porous iron or steel skeleton compacts; they have high strength characteristics, for which a virtually pore-free structure, as well as the specific alloying properties of iron and copper, is believed responsible. The development of this material is a first attempt to obtain dense and strong parts on an economically and technically sound basis, that is, by *filling* the pores with the fluid lower melting metal instead of *squeezing* them together by means of excessive energy expenditure (high-pressure molding, coining, hot pressing, hot working, etc.). The flexibility of the process, coupled with such inherent advantages as the possibility of using inexpensive iron powders, and precipitation or quench-hardening treatments, and of obtaining materials that are easily machinable, platable, and brazable (to the extent of being self-brazing), makes the material particularly suitable for applications involving machine and engine parts of intricate design which require above-average strength and ductility.

Industrial Development

The historical development of infiltration methods leading to the introduction of the cemented ("cupric") steel products has been reviewed by Kopecki.[304] Based on Leiser's[115a] and Gebauer's[116] pioneer work in

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[112d] D. C. Bradley, *Prod. Eng.*, *19*, No. 10, 107 (1948).

[113] E. E. Ensign, *Proc. Third Annual Spring Meeting of Metal Powder Association*, New York, May 27, 1947, p. 14; see also *Automotive Ind.*, *97*, No. 4, 30 (Aug. 1947).

[114] F. P. Peters, *Materials & Methods*, *23*, 987 (1946).

[115] E. S. Kopecki, *Iron Age*, *157*, No. 18, 50 (1946).

[115a] German Pat. 300,699; Brit. Pat. 148,533.

[116] U. S. Pats. 1,342,801; 1,395,269.

1914–17 on impregnating porous iron with copper, and on Baumhauer's successful application of the principle to tungsten carbide–cobalt compositions in 1922,[117] the first highly dense iron–copper alloys were developed by Melchior in 1930.[118] These alloys were approximately of a 50–50 iron–copper composition (by weight); they had a density of 8.25 g./cc., a Brinell hardness between 90 and 120, and an electrical conductivity of 0.17 megmho-cm. (29.3% I.A.C.S.). Tensile properties were found to correspond closely to those of standard copper. In spite of these promising physical characteristics, the interest in the material invoked by Melchior was not strong enough to lead to a commercial product. Mainly responsible for the failure to further explore such an interesting development was the fact that the products had a poor surface appearance and could not be produced to exact size. The partial solubility of the two metals caused rough and porous surfaces, marred by deep crevices, and other erosion phenomena. Furthermore, if the composite structure was produced by immersing the iron skeleton body in a molten copper bath, the surface of the skeleton in contact with the copper dissolved rapidly in the bath, and rounded corners and "icicle-like" rejuvenated cross sections resulted before the pore volume was entirely penetrated by the liquid metal.

Only very recently has the infiltration process been modified to give products that are acceptable from the standpoint of surface appearance as well as physical properties.[114,119–121] The solubility effects, so necessary for the attainment of strong cohesive bonds between the iron and copper phase in the composite structure, were rendered harmless at the surface through the action of certain alloying additions to the copper which, functioning in getter-like fashion, tended to retard or entirely inhibit the solubility of the iron particles of the skeleton surface in the molten copper pool. Thus, perfectly smooth surfaces could be produced with a thin copper coat all over the compact—including the surfaces through which the copper alloy had entered the porous iron compact.

By enriching the ferrous component of the composite, tensile values considerably above those of pure copper could be obtained without undue loss in elongation and impact resistance. The virtually complete

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[117] German Pat. 443,911.

[118] P. Melchior, discussion of F. Sauerwald and J. Hunczek, *Z. Metallkunde*, *21*, 22 (1929).

[119] U. S. Pats. 2,401,221; 2,401,483; 2,402,120.

[120] L. Northcott and C. J. Leadbeater, *Symposium on Powder Metallurgy*. The Iron and Steel Institute, Special Report No. 38, London, 1947, p. 142.

[121] Brit. Pat. Appls. 10653/47, and 10654/47 (Apr. 23, 1946); see also *Met. Powd. Rept.*, *2*, No. 5, 70 (1948); Brit. Pat. 629,326; U. S. Pat. 2,456,779.

lack of pores permitted full exploitation of precipitation-hardening effects between the iron and copper.

During the course of this work it became apparent that the liquid copper would not only braze pure iron particles into a solid and coherent structure, but also particles of carbon steels or alloy steels, obtained either by mechanical or chemical disintegration methods, or by diffusion-sintering of iron and carbon. While the surface of the steel particles became partially dissolved by the liquid copper—effecting a true cementing bond—the interior of the particle retained a typical steel structure, suggesting conventional heat treating. As a result, hardness and strength values were produced that closely matched those of ordinary carbon steels, while ductility values were found to be small, but definitely noticeable.

On the basis of these findings an industrial manufacturing method was developed which now yields parts up to 20 pounds in weight on a mass production scale.[122,123] Latest developments of the technique have not only improved the means of controlling dimensional stability of the end products, but have also covered a considerable variety of combinations of ferrous skeleton alloys and copper-base infiltrants. Most successful so far have been composites involving austenitic stainless steel skeletons and copper–nickel-base infiltrants;[124] other materials used successfully for skeleton bodies are nickel and nickel–chromium steels, and as previously mentioned (p. 385), manganese and chromium–manganese steels.[125]

Manufacturing Method

RAW MATERIALS

Many kinds of iron and steel powders have been found suitable for the ferrous skeleton, the chief criteria apparently being a closely controlled size range (usually between 60 and 325 mesh) and a narrowly defined degree and type of particle porosity. The principal powders adaptable to the process include: (*1*) electrolytic iron powder; (*2*) reduced iron powder; (*3*) decarburized cast iron shot; (*4*) decarburized or annealed steel powder; and (*5*) chemically disintegrated alloy steel powders. The possibility of utilizing such inexpensive powders as decarburized cast

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[122] E. S. Kopecki, *Iron Age, 157,* No. 18, 50 (1946).

[123] F. P. Peters, *Materials & Methods, 23,* No. 4, 987 (1946).

[124] Brit. Pat. Appl. 11363/47 (May 1, 1946); see also *Met. Powd. Rept., 2,* No. 5, 72 (1948).

[125] F. Benesovsky and R. Kieffer, *Proc. International Powder Metallurgy Conference,* Graz, July 12–17, 1948, Referate No. 27.

iron shot or reduced Swedish sponge iron makes the process attractive from a commercial point of view.

The nonferrous infiltrant, consisting of about 90–93% Cu, 3–5% Fe, 3–5% Mn, and, optionally, minor additions of P, Ti, Si, Cr, and Ni, totalling a maximum of 15%,[126] can be employed in a variety of forms. The copper alloy is produced either by mixing the powdered ingredients in proper proportions, or by fusing the alloy and shotting or atomizing it into alloy powder. The individual allotments of infiltrant are then produced by pelleting or briquetting the powder in automatic presses.

MOLDING

Only low molding pressures are needed for the production of the porous skeleton, if soft and plastic powders are used. The addition of graphite powder for the production of steel skeletons does not materially change the required pressure, since the graphite is soft and functions as a lubricant. In the case of a soft-annealed electrolytic iron powder the pressure requirements were found to be:

Percentage pore volume of skeleton	Compacting pressure, tsi	Percentage pore volume of skeleton	Compacting pressure, tsi
35	6	20	12
30	8	15	20
25	10	10	50

Reduced iron powders require somewhat higher pressures, *e.g.*, 20–25 tsi for a 25% pore volume, and 40–45 tsi for a 15% pore volume. Decarburized cast iron or steel powders require pressures of about 30 to 40 tsi for a 25% pore volume.

Only one press operation is necessary. A conventional press and die assembly is used. As lubricants, stearates and, in the case of steel products, graphite—each up to 1.5% by weight—are employed. The comparatively high percentages of lubricants ensure the formation of an interconnected pore system, and reduce wear and tear of the dies and punches to an almost negligible factor.

INFILTRATION AND SINTERING

The iron or steel skeleton compact is heated in contact with the copper alloy to a temperature above the melting point of the copper (*e.g.*, 1100–1150°C; 2010–2100°F.). Capillary action forces the molten copper alloy into the interconnected pores of the skeleton, and, if the

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[126] Brit. Pat. 10653/47, and 10654/47 (Apr. 23, 1946); see also *Met. Powd. Rept.*, *2*, No. 5, 70 (1948); Brit. Pat. 629,326, U. S. Pat. 2,456,779.

process is controlled properly, practically the entire pore volume is filled by the infiltrant.

In order to avoid gas pockets in part of the pores which would tend to interfere with the rapid penetration of the liquid alloy throughout the skeleton, all gaseous reactions must be completed before liquefaction of the infiltrant. Whereas water-forming reactions between the furnace atmosphere (mostly hydrogen) and residual oxygen are usually completed by the time the compact has reached the temperature for infiltration, compacts containing graphite require more time for completion of diffusion and reactions producing CO and CO_2. Thus, iron–graphite skeleton compacts are advantageously presintered in the absence of the infiltrant at the temperature later to be used for infiltration. This step not only eliminates harmful effects of the carbon oxide gases in advance of the critical infiltration step, but also helps to control the final dimensions of the part.

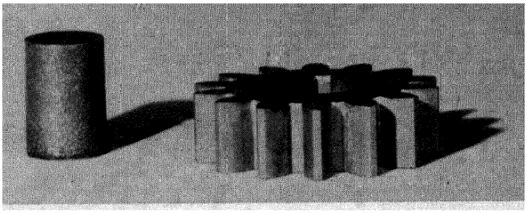

Fig. 499. Radial infiltration process applied to a gear. The slug of wrought or briquetted powdered copper or copper alloy (left) is placed into the bore of the gear (right), and both are heated in a protective atmosphere above the melting point of the copper or copper alloy, whereupon the liquid phase radially penetrates the pore system of the gear because of capillary attraction.

Infiltration can take place in both the axial and lateral or radial directions. The latter process is ideally suited for the impregnation of gears, as illustrated in Figure 499. In the former instance, the lower or upper surfaces of the compacts are contacted with the molten copper alloy held in special graphite or ceramic containers. While various furnaces have been found suitable for the infiltration work, one type especially favored is a vertical continuous furnace[127] in which the containers move downward at controlled speed, and the molten copper alloy works upward by capillary action through the interconnecting pore network (for details of the furnace, see Volume I, Chapter XVI). Irrespective of the furnace design, a very clean and dry atmosphere of controlled flow rate is essential.

[127] U. S. Pat. 2.422.439.

The infiltration cycle must allow for a sufficient period of time to assure complete penetration of the infiltrant without exposing the liquid copper alloy to the furnace gases unnecessarily long, since this would cause undesirable gas absorption and expansion effects. Small bars, approximately 3 in. long and 0.5 in. square, require an infiltration time of about 10 minutes, while larger pieces, such as cylinders 3 in. in diameter and 1 to 2 in. high, require infiltration times of 45 minutes or more.

Heating and cooling rates must also be closely controlled; precipitation hardening effects between iron and copper must be taken into account, and, in the case of steel skeletons, slow cooling is required to assure a normalized structure.

SUBSEQUENT TREATMENTS

The constitution of the binary system iron–copper[127a] permits precipitation hardening effects in fused copper-containing steels.[127b] At 1094°C. (2001°F.) (*i.e.*, the temperature of the peritectic transformation) a maximum of about 8.5% of copper is dissolved in γ-iron, whereas the solubility limit of α-iron for the metal is below 2% at about 835°C. (1535°F.); at room temperature, less than 0.04% copper is soluble in iron. Inversely, about 4% iron is dissolved in copper at 1094°C. (2001°F.), while at room temperature the solubility of copper for iron is also very small.

It is reasonable to expect that these solubility conditions allow quality improvements by heat treatment to apply equally well to copper-infiltrated iron sponges. This has been borne out in practice, although certain modifications have become apparent. Thus, it was found that, due to the special structure and the distribution of the iron and copper components on a macroscale, precipitation processes are largely confined to zones and borders. These may be comparatively thin in industrial products where only short periods of infiltration are used, as was recently shown by Northcott and Leadbeater[127c] (see Fig. 497*B*). If, however, they are allowed to form a continuous network, the effect on the physical properties may be quite pronounced.

Plain iron–copper alloy compositions can be strengthened considerably by precipitation treatment, consisting of a reheating of the material to about 835°C. (1535°F.), followed by water quenching to ascertain maximum solubility, and precipitation hardening at 500°C. (930°F.) for 1 to 2 hours. In the case of iron–carbon skeletons, heat treatment along conventional lines of hardening of steel causes changes in the

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[127a] M. Hansen, *Aufbau der Zweistofflegierungen*. Springer, Berlin, 1936, p. 557.

[127b] H. Cornelius, *Kupfer im technischen Eisen*. Springer, Berlin, 1940.

[127c] L. Northcott and C. J. Leadbeater, *Symposium on Powder Metallurgy*. The Iron and Steel Institute, Special Report No. 38, London, 1947, p. 142.

physical properties that are predominant over those obtained by the precipitation treatment of the iron–copper system. Oil as well as water quenching is applicable either immediately after infiltration or after an intermediate slow cooling and reheating to quench temperature. Stress relief is obtained by tempering after the quench treatment, but is not essential for the compositions rich in the soft copper phase.

TABLE 192

Physical Properties of Copper-Infiltrated (Cemented) Steel and Iron Compacts as Compared with Engineering Properties of Copper, Iron, and Steel Produced by Conventional Fusion or Sintering Techniques

Material	Yield point, psi	Tensile strength, psi	Elongation, %	Reduction of area %	Izod impact, ft. lb.
Cast copper........	—	33,000	40	50	50
Copper powder pressed at 50 tsi, sintered....	—	20,000	10	10	3
Copper powder pressed twice at 50 tsi, sintered............	—	28,000	20	20	5
Electrolytic fused iron	20,000	40,000	50	70	30
Armco iron	30,000	50,000	30	40	20
0.6 carbon steel	60,000	95,000	20	40	50
Iron powder pressed at 50 tsi, sintered....................	21,000	34,000	15	18	5
Iron powder pressed twice at 50 tsi, sintered...	22,000	37,000	25	25	8
80-20 cemented iron (20% Cu)...	40,000	53,000	25	32	12
80-20 cemented 0.2 carbon steel, heat-treated (water quench).	100,000	114,000	3	2	—
80-20 cemented 0.6 carbon steel, heat-treated (oil quench). ...	75,000	97,000	4	4	—
80-20 cemented 1.1 carbon steel, heat-treated (oil quench) . ..	80,000	102,000	2	2	—

Compositions low in carbon can be surface hardened by conventional pack-carburizing, gas-carburizing, or liquid-carburizing methods after the surfaces to be treated are electrolytically or chemically stripped (*e.g.*, with chromic acid) of the Cu film created during infiltration. For all other treatments the Cu film is advantageous; it prevents decarburization during heat treatment, and provides a solid anchorage for electroplating or brazing joints.

Properties

Probably the most outstanding characteristic of infiltrated and cupric cemented steel compacts is their high density, with values of about 96–99% of the composite theoretical value (obtained by the rule of mixtures in disregard of the existing limited solubility between the two metals). The almost complete absence of pores (with their detrimental effects on the internal stress distribution of the compact) causes generally im-

TABLE 193

Physical Properties of Carbon-Free Cemented Iron

Ratio Fe/Cu	Density, % of theoretical	Yield point, psi	Tensile strength, psi	Elongation in 1 in., %	Reduction in area, %	Brinell hardness
88/12	98.9	53,000	65,100	7.0	8.0	164
84/16	98.0	38,500	53,800	24.0	31.5	104
79/21	98.1	27,600	53,300	28.0	36.7	91
77/23	98.0	25,400	52,500	34.0	36.7	85
72/28	98.8	24,300	45,800	32.0	32.3	68

TABLE 194

Physical Properties of Cemented Steels

Steel, % C	Cu, %	Compacting pressure, tsi	Heat treatment[a]	Yield point, psi	Tensile strength, psi	Elongation, %	Reduction in area, %	Izod impact, ft. lb.
0.2	30	8	f.c.	80,000	92,000	3	3	3
0.2	30	8	w.q.; t.	—	102,000	—	—	—
0.2	25	10	f.c.	88,000	95,000	3	—	4
0.2	25	10	w.q.; t.	99,000	104,000	2	0	—
0.2	20	12	f.c.	94,000	96,000	3	2	3
0.2	20	12	w.q.; t.	99,000	105,000	2	—	—
0.4	30	8	f.c.	80,000	87,000	3	2	3
0.4	30	8	w.q.; t.	97,000	104,000	3	2	—
0.4	25	10	f.c.	82,000	89,000	3	—	2
0.4	25	10	w.q.; t.	85,000	104,000	3	1	—
0.4	20	12	f.c.	87,000	88,000	3	2	2
0.4	20	12	w.q.; t.	103,000	107,000	3	2	—
0.4	20	12	o.q.; t.	97,000	120,000	—	—	—
0.6	25	10	f.c.	46,000	77,000	4	4	3
0.6	25	10	o.q.; t.	66,000	83,000	3	3	—
0.6	20	12	f.c.	73,000	97,000	4	4	—
0.6	20	12	o.q.; t.	76,000	97,000	—	—	—
0.6	15	20	f.c.	78,000	96,000	4	4	—
0.6	15	20	o.q.; t.	77,000	93,000	2	2	—
0.6	10	50	f.c.	79,000	81,000	4	4	—
0.6	10	50	o.q.; t.	75,000	90,000	2	2	—
0.6	10	50	w.q.; t.	109,000	115,000	—	—	—
1.1	25	10	f.c.	64,000	76,000	4	4	3
1.1	25	10	o.q.; t.	78,000	87,000	2	2	—
1.1	20	12	f.c.	81,000	98,000	4	4	—
1.1	20	12	o.q.; t.	79,000	106,000	2	2	—
1.1	15	20	f.c.	78,000	96,000	2	2	—
1.1	15	20	o.q.; t.	84,000	100,000	—	—	—
1.1	10	50	f.c.	—	80,000	1	1	—
1.1	10	50	o.q.; t.	80,000	87,000	—	—	—
1.1	10	50	w.q.; t.	—	104,000	—	—	—

[a] f.c., furnace cooled; w.q.; t., furnace cooled, reheated, water-quenched, tempered; o.q.; t., furnace cooled, reheated, oil-quenched, tempered.

proved physical properties—in particular, yield and tensile strength, and, to a lesser degree, ductility and impact strength. Some of these properties are given in Tables 192–195 for materials made from electrolytic iron

TABLE 195

Electrical Conductivity of Cemented Iron and Steel

Material	Ratio Fe/Cu[a]	Density			Conductivity			Increase in conductivity over base metal (Fe or 0.75% C steel), %
		Calculated,[b] g./cc.	Actual, g./cc.	Actual, % of calcd.	Calculated,[b] megmho-cm.	Actual, megmho-cm.	Actual, % of calcd.	
OFHC Copper	—	—	—	—	58.2×10^{-2}	—	—	—
Iron	—	—	—	—	10.0	—	—	—
0.75% C steel	—	—	—	—	5.68	—	—	—
Fe/Cu	55/45	8.35	7.94	95.2	31.69×10^{-2}	10.62×10^{-2}	33.45	6.2
Fe/Cu	65/35	8.24	8.10	98.5	26.87	11.25	41.8	12.5
Fe/Cu	70/30	8.19	7.84	96.8	24.45	9.86	40.3	−1.4
Fe/Cu	75/25	8.14	7.96	97.7	22.05	9.94	45.0	−0.6
Fe/Cu	80/20	8.08	7.80	96.6	19.64	9.49	48.3	−5.1
Fe + C/Cu	55/45	8.35	8.04	96.3	29.30×10^{-2}	9.66×10^{-2}	32.95	70.1
Fe + C/Cu	65/35	8.24	8.04	97.7	24.06	9.46	39.3	66.6
Fe + C/Cu	70/30	8.19	8.02	98.0	21.43	9.18	42.8	61.7
Fe + C/Cu	75/25	8.14	7.84	96.3	18.81	8.46	44.95	49.0
Fe + C/Cu	80/20	8.08	7.68	95.4	16.19	7.63	47.1	34.4
Effect of Heat Treatment at 835°C. (1715°F.) Followed by Water Quench[c]								
Fe/Cu	75/25	8.14	7.82	96.1	22.05×10^{-2}	7.11×10^{-2}	32.2	−28.8
Effect of Subsequent Precipitation Hardening at 500°C. (930°F.) for 1 Hour[c]								
Fe/Cu	75/25	8.14	7.82	96.1	22.05×10^{-2}	11.67×10^{-2}	52.8	16.7

[a] By volume.

[b] In the case of the Fe/Cu and Fe + C/Cu combinations, the "calculated" values for density and electrical conductivity are based on complete nonsolubility of the components. These values are inaccurate due to the partial solubility of the components.

[c] Heat treatment and quench reduce the conductivity of the infiltrated material by 28.1%, while heat treatment and quench followed by precipitation hardening result in an increase of 17.4%.

and copper.[128] In Table 192, the principal physical properties of several iron–copper compositions are compared with the properties of the ingredient metals, both in the fused and sintered condition. The tensile strength value of plain iron–copper compositions corresponds closely to the total of the values for the individual metals after sintering; elongation, however, remains equivalent to that of either metal. The effect of the ratio of iron to copper is shown in Table 193. Only in materials very low in copper does the value for tensile strength rise noticeably—with corresponding drastic drop in elongation—which may be attributed to precipitation effects during cooling. These effects are expected to be more pronounced with smaller proportions of pure, soft copper in excess of the actual amount capable of undergoing a solution and precipitation reaction with the iron. Tensile strength values of electrolytic iron cemented with pure copper range from 40,000 to 65,000 psi, and elongation values lie between 30 and 5%; the maximum impact strength amounts to 14 ft. lb.

In Table 194, the physical properties are recorded for a number of iron–carbon–copper compositions; yield point values exceed 100,000 psi and tensile values reach 120,000 psi. However, the ductility values are very low in all carbon-containing materials, regardless of the given heat treatment; this is believed to be caused by a possible reaction of the solidifying copper with gases evolved during the solution of the graphite in the iron or with gaseous by-products (*e.g.*, hydrogen or decomposition products from salt inclusions) originating from the electrolysis of the powders.

Table 195 gives an indication of the electrical conductivity of various iron–copper and iron–carbon–copper compositions, and compares them with the "calculated" conductivity, based on the rule of mixtures for the bulk metals. The effectiveness of the solution and precipitation treatments on the iron–copper compositions is well demonstrated by the decrease in conductivity after quenching from 835° C. (1535°F.), and by the increase of the conductivity even beyond the value for the infiltrated material after precipitation hardening at 500°C. (930°F.). In this connection it may be remarked that the "calculated" conductivity as obtained by adding the conductivities of the components, according to the volume ratio of these components, is only correct if no solubility exists between the components and if no impurities are present. Other factors to be taken into consideration are the electrical resistivity at the grain boundaries and the presence of pores and interstices in the structure.

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[128] C. G. Goetzel, *Powder Met. Bull., 1,* No. 3, 37 (1946).

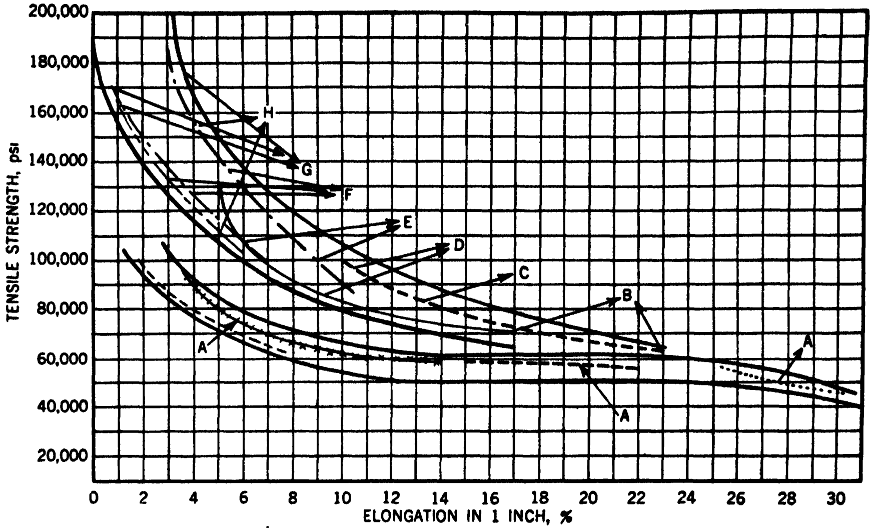

Fig. 500. Tensile properties of cemented iron and steels. Curves show relation between tensile strength and elongation for copper-impregnated iron and steel compacts before and after heat treatment. Ratio between ferrous and nonferrous components from 3:1 to 5:1. Upper band indicates range of properties obtainable by heat treatment; lower band indicates range of properties for untreated materials. Range of properties obtainable with compositions made by conventional powder metallurgy methods would fall below the lower band.

	Ferrous skeleton	Carbon, %	Nonferrous phase	Density, g./cc
—— - - ——	Domestic reduced iron	0.3	Copper alloy	Above 7.8
- - - -- -- - - -	Domestic reduced iron	None	Copper	
— - —- - —- -	Domestic reduced iron	0.7	Copper	
———- ---	Domestic reduced iron	None	Copper alloy	
—— — — -	Domestic reduced iron	0.7	Copper alloy	
- - - - - - - - -	Electrolytic iron	None	Copper	
+ + + + + +	Swedish sponge iron	0.7	Copper	7.5–7.8
× × × × × >	Swedish sponge iron	None	Copper	7.3–7.7

Heat Treatment. *A*, no heat treatment; *B*, heated to 800°C. (1470°F.), slow cooled, reheated to 500°C. (930°F.) for 4 hours; *C*, heated to 800°C. (1470°F.), slow cooled, reheated to 840°C. (1550°F.), water quenched; *D*, heated to 800°C. (1470°F.), slow cooled, reheated to 500°C. (930°F.), then reheated slowly over a period of 2 hours to 700°C. (1300°F.); *E*, heated to 800°C. (1470°F.), slow cooled, reheated to 650°C. (1200°F.), and drawn at that temperature for 18 hours; *F*, heated to 800°C. (1470°F.), slow cooled, reheated to 840°C. (1550°F.), water quenched, tempered at 500°C. (930°F.) for 2 hours; *G*, heated to 800°C. (1470°F.), slow cooled, reheated to 840°C. (1550°F.), water quenched, tempered at 315°C. (600°F.) for 1 hour; *H*, heated to 800°C. (1470°F.), slow cooled, reheated to 840°C. (1550°F.), water quenched, tempered at 600°C. (1110°F.) for 1 hour.

TABLE 196

Physical Properties Obtained with Specific Combinations of "Cemented Steel" Materials and Heat Treatment (Peters[123])

Molding Pressures 22–45 tsi; "Steel" Structures Are Approximately Eutectoid, with about 0.8% C

Material and general treatment (after infiltration)	Heat treatment (time and temperature cycles)	Physical properties		
		Tensile strength, 1000 psi	Elongation, %	Rockwell hardness
Steel–copper; no heat treatment	Presintered, infiltrated, slow- or fast-cooled	70–100	7–2	B 75–100
Steel–copper; case-carburized, quenched and tempered	Infiltrated; slow-cooled to room temp.; carburized at 1600–1750 °F. (870–955 °C.), quenched from 1500 °F. (815 °C.); tempered 1 hr. at 300 °F. (185 °C.)	120–160	5–3	Core: C 30–45 Case: C 50–60
Steel–copper; combination steel-hardening and precipitation-hardening	Infiltrated; slow-cooled to room temp.; reheated to 1475 °F. (800 °C.), water-quenched, tempered 1 hr. at 300 °F. (185 °C.)	130–185	5–3	C 30–45
Steel–copper; combination steel-hardening and precipitation-hardening	Infiltrated; slow-cooled to room temp.; reheated to 1475 °F. (800 °C.), slow-cooled to room temp.; reheated to 1550 °F. (845 °C.), water quenched, tempered 2 hr. at 930 °F. (500 °C.)	110–145	5–4	C 25–35
Steel–copper; combination steel-hardening and precipitation-hardening	Infiltrated; slow-cooled to room temp.; reheated to 1475 °F. (800 °C.) slow-cooled to room temp.; reheated to 1550 °F. (845 °C.), water quenched, tempered 1 hr. at 1100 °F. (595 °C.)	90–115	7–4	B 90–100
Steel–copper; overtempered and overaged	Infiltrated; slow-cooled to room temp.; reheated to 1475 °F. (800 °C.), slow-cooled to room temp.; reheated 18 hr. at 1200 °F. (650 °C.)	80–90	12–8	B 85–90
Iron–copper; no heat treatment	Infiltrated; slow-cooled to room temp.	50–75	12–6	B 50–80
Iron–copper; case-carburized, quenched and tempered	Infiltrated; slow-cooled to room temp.; carburized at 1600–1750 °F. (870–955 °C.); quenched from 1550 °F. (845 °C.), tempered 1 hr. at 300 °F. (185 °C.)	60–100	8–5	Core: B 70–100 Case: C 50–60

TABLE 196 (*continued*)

Material and general treatment (after infiltration)	Heat treatment (time and temperature cycles)	Physical properties		
		Tensile strength, 1000 psi	Elongation, %	Rockwell hardness
Iron–copper; precipitation-hardened	Infiltrated; slow-cooled to room temp.; reheated to 1475 °F. (800 °C.), slow-cooled to room temp.; reheated to 1550 °F. (845 °C.), water quenched, tempered 1 hr. at 600 °F. (315 °C.)	60–125	8–3	B 70–100
Iron–copper; precipitation-hardened	Infiltrated; slow-cooled to room temp.; reheated to 1475 °F. (800 °C.), slow-cooled to room temp.; reheated 2 hr. at 930–1290 °F. (500–700 °C.)	50–90	18–8	B 55–90

The comparatively low tensile values of the iron–copper materials, and the very low ductility values of the carbon-containing compositions based on electrolytic powders are improved when reduced iron powders or decarburized steel powders are employed, and when the pure copper infiltrant is replaced by certain copper alloys. As shown in Table 196 and also in Figure 500, physical properties considerably superior to those of conventionally produced ferrous powder metallurgy products are obtainable by the infiltration method, and full utilization of the heat-treating capacity of the material results in surprisingly high tensile strength and hardness values.[129,130] Iron products containing no carbon exhibit tensile strength values around 70,000 psi and elongations around 12% after infiltration with copper alloy and slow cooling, while, after precipitation hardening, tensile values around 100,000 psi and elongations of about 6% can be obtained. After infiltration and slow cooling, or after normalizing, steel–copper structures exhibit tensile values around 90,000 psi and elongations between 6 and 8%; after heat treating, the tensile strength can be increased up to about 175,000 psi at an elongation of 3%.

An interpretation of these excellent results must be based upon the understanding that the manufacturing process represents a combination of powder metallurgy and casting techniques. Because the products resemble castings, at least in part, it is obvious that high ductility and impact resistance values cannot be expected without further metal-working treatments or alloying additions. The nonferrous infiltrant fulfils a double

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[129] C. G. Goetzel, *Proc. Second Annual Spring Meeting of Metal Powder Association*, New York, June 13, 1946, p. 73.

[130] C. G. Goetzel, *Product Eng., 18*, No. 8, 115 (1947).

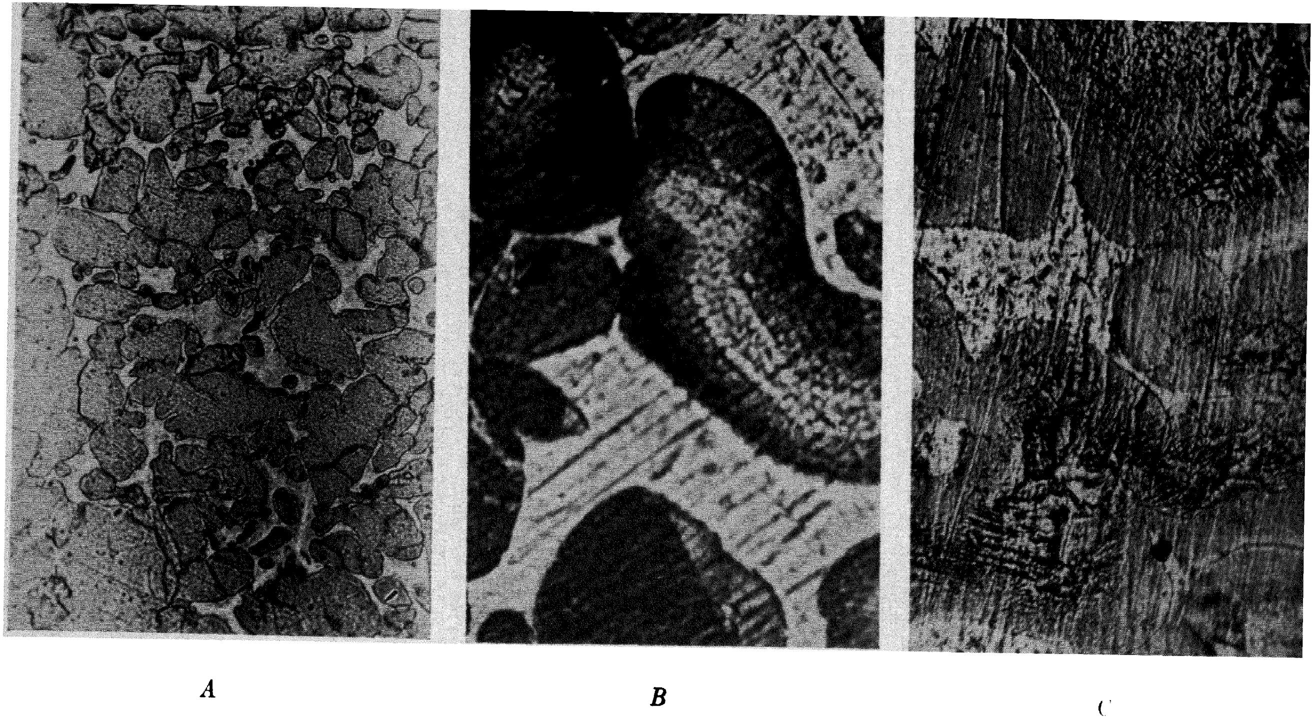

Fig. 501. Microstructures of cemented iron (copper-impregnated porous sintered iron compacts): *A*, 75–25 iron–copper composition, light etch with picral (×160); *B*, 75–25 iron–copper composition, light etch with picral (×800); and *C*, 85–15 iron–copper composition, deep etch with picral (×600).

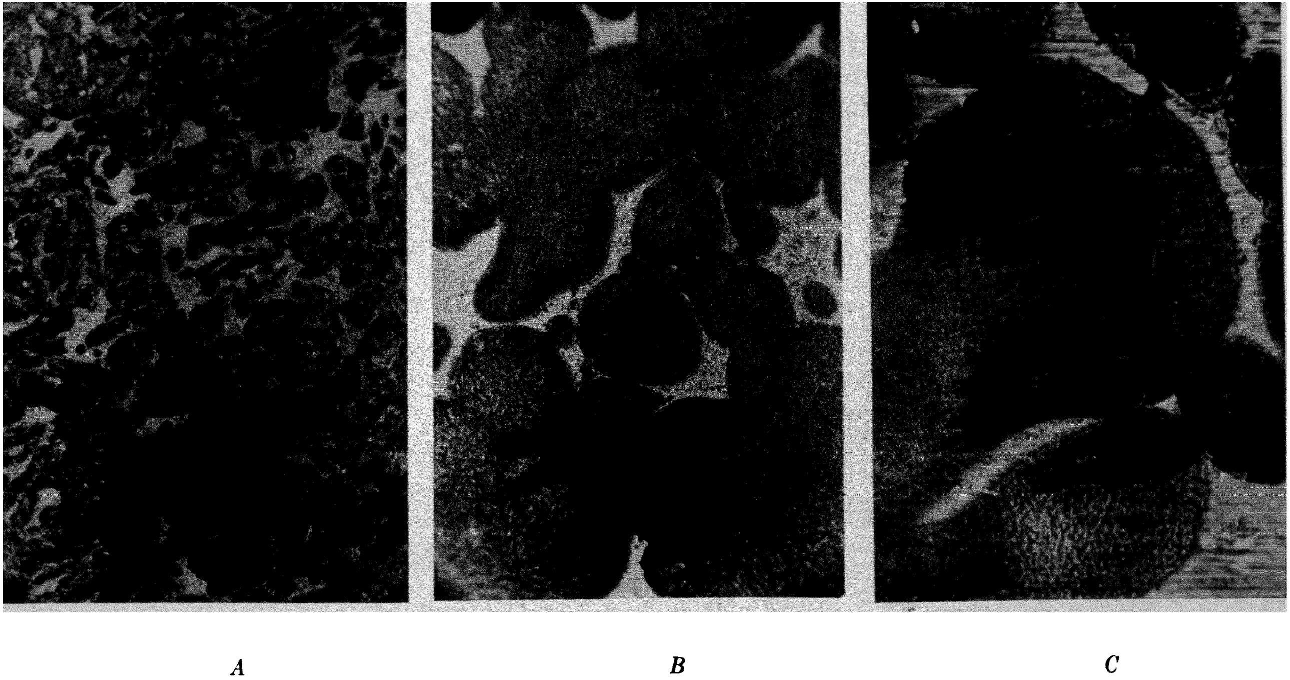

Fig. 502. Microstructures of cemented steel (copper-impregnated porous sintered carbon-steel compacts produced from iron–graphite powder mixtures): *A*, 75–25 eutectoid steel–copper composition, material as furnace cooled, etched with nital (×160); *B*, 80–20 eutectoid steel–copper composition, material cooled rapidly in furnace cooling chamber, etched with nital (×600); and *C*, 85–15 eutectoid steel–copper composition, material reheated to form spheroidized cementite, etched with nital (×800).

function: it fills virtually all pores, eliminating adverse stress concentrations; and, equally important, it performs a true cementing action which is facilitated by its affinity to the skeleton metal. In reactions comparable to those taking place in the sintering of tungsten carbides bonded by cobalt, the limited solubility of the iron in copper at infiltration temperature (about 5%), and the subsequent reprecipitation of the iron onto the larger iron particles, create very strong bonds between cementing and skeleton metals and also a considerable increase in cohesive strength of the skeleton material itself. In Figure 501*A*–*C*, photomicrographs of several iron–copper structures give evidence of the large size and rounded shape of the iron grains. The pearlitic structure of copper-cemented steel specimens (the steel of approximate eutectoid composition) before and after heat treatment is shown in Figure 502*A*–*C*.

The corrosion resistance of the cemented iron or carbon steel materials is dependent on surface conditions. Smooth copper-clad surfaces, produced with the aid of alloying additions to the copper, are slightly more resistant to corrosive attack by humidity or salt spray than steel stock, though they are inferior to nonferrous alloys or stainless steel. After removal of the copper surface film by chemical means the corrosion resistance is equivalent to that of ordinary steel. If the cupric carbon steel is electroplated with such metals as nickel, cadmium, or chromium, the same degree of corrosion resistance is obtainable that is exhibited by ordinary steels treated identically.

After removal of the copper from the surface, copper-cemented stainless steels equal ordinary stainless steel in resistance to atmospheric or salt-spray corrosion, but are, of course, much inferior in their resistance to nitric and other acids, except sulfuric acid. Compacts produced by impregnating the porous stainless steel structure with an alloy containing 85% Cu, 5% Fe, 5% Ni, and 5% Mn (*e.g.*, in form of a pressing from mixed or fusion-alloyed powders) possess after precipitation treatment (*e.g.*, heating in dissociated ammonia at 650°C. (1200°F.) for 1 hour followed by water quenching and reheating to 300°C. (570°F.) for 2 hours) a maximum tensile strength of 90,000 tsi, while the elongation after the quench treatment reaches 20%.[131] If silver is substituted for copper as infiltrant, the resistance of the composite material against acid attack becomes equal to that of bulk stainless steel, provided that all pores are filled with the silver. The structure of such material is shown in Figure 503.

In contrast to most other powder metallurgy products, the copper phase of the cemented steels in the pores accounts for good machinability

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[131] Brit. Pat. Appl. 11363/47 (May 1, 1946); see also *Met. Powd. Rept.*, *2*, No. 5, 72 (1948).

as expressed by the formation of long chips. The copper also is the main contributing factor for the excellent brazing capacity of the material. If the copper film on the surface is not removed, it functions as brazing

Fig. 503. Microstructure (×150) of composite stainless steel–silver compact produced by the infiltration technique. Material contains 15% Ag and has a density of 8.10 g./cc.

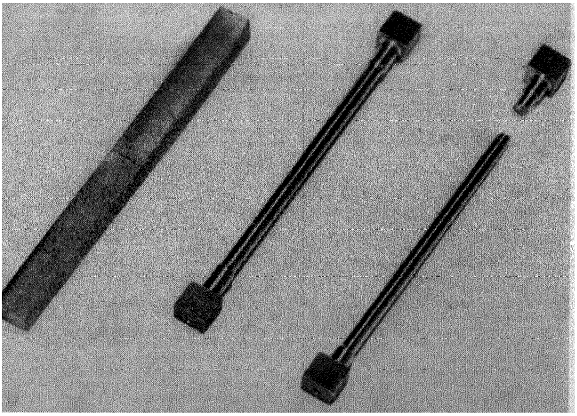

Fig. 504. Tensile test results with infiltration-brazed butted iron–copper bars. Rupture of specimen occurred in the base metal rather than at the joint, giving evidence of the high strength of the brazed bond.

element and permits direct brazing without additional material or handling. Most important in this connection are the possibilities of combining various sections into complex shapes during or after infiltration. The strength obtainable in the infiltration-brazed joints is equivalent to that of the base material, as illustrated in Figure 504, where tensile specimens machined from butted bars are shown to rupture away from the joint.

Applications

If the raw materials and infiltration practice are closely controlled dimensional tolerances can be held to about ±0.002 in. per linear inch. For closer tolerances than these, a final sizing operation is necessary which complicates the process materially. The surface appearances obtained with the cemented steels approximate those found on die castings or precision castings, and are somewhat inferior to those obtained on ordinarily sintered and coined parts. In the present stage, cemented steel parts are producible in weight ranges between about 3 ounces and 20 pounds. Even in the larger sizes the material appears to be economical, in spite of the fact that the higher cost of the infiltrant alloy (about 3 times that of iron) would favor large-scale production of small sizes. The costs of press and die would become excessively and, perhaps, prohibitively high if a dense strong part of larger proportion were to be made by conventional high-pressure powder metallurgy methods, whereas the production of the porous skeleton requires lower pressures and, there-

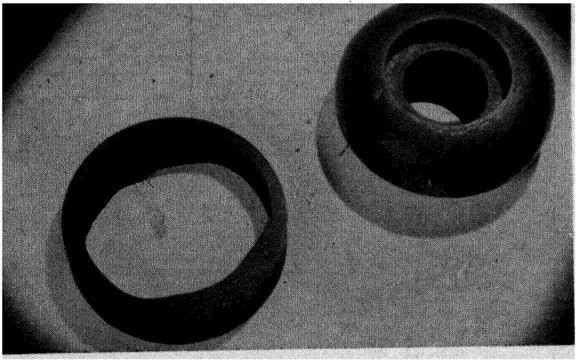

Fig. 505. High-strength wear-resistant components from cemented steel. The pump ring (left) was made from eutectoid steel with 15% copper alloy and hardened to Rockwell C-50. The roller cam (right) was made from iron with 25% copper alloy and subsequently surface-carburized and case-hardened to Rockwell C-35; it would have been impractical to make the doughnut-shaped part by conventional powder metallurgy methods. (Courtesy of American Electro Metal Corp.)

fore, smaller presses and less rigidly constructed dies. Also, because of a fairly constant cost of the infiltration operation, the ratio of infiltration cost to total piece cost becomes somewhat less favorable as the size of the piece decreases. Finally, it is important from an economic viewpoint that materials be produced from inexpensive raw materials.

With these characteristics, advantages, and limitations in mind, the general field of use for the cemented steels lies in strong iron-base parts that are difficult or impossible to make by normal powder metallurgy methods because of strength, size, or design requirements. Thus, the field of possible applications includes machine parts where fairly large quantities are required, where the mechanical properties are important, and where powder metallurgy fabrication has previously been considered to be noncompetitive. Figure 505 displays two components, each over 3 in. in diameter, that have been successfully produced by the infiltration process.

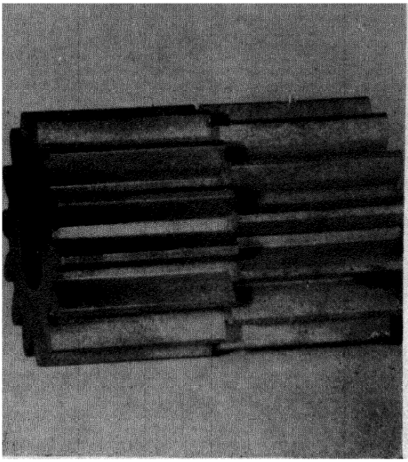

Fig. 506. Offset spur gear assembly from cemented steel. The two gears were individually molded and clamped together in a fixture before being sintered and radially infiltrated with copper alloy. During infiltration, gears were brazed into one unit. Such a gear unit cannot be produced by conventional powder metallurgy processes, since the offset teeth prevent ejection from the mold.

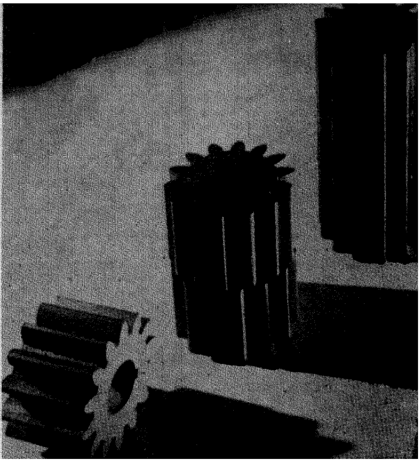

Fig. 507. Spur gears and gear combinations from cemented steel. The exceptionally long gear at the right was made by infiltration-brazing three individually pressed gears together, with the teeth in alignment. All gears were radially infiltrated as indicated in Figure 499.

Of still greater significance are those applications involving parts that are too large or too complex to be made by usual powder metallurgy methods. To these parts belong shapes with obstructions in two dimensions or parts constructed of two different, nonisometric shapes. The offset gear shown in Figure 506 is a typical example of a "self-brazed" cemented steel part that cannot be produced by normal powder metallurgy practices, because the offsetting of the gear teeth would prevent ejection of

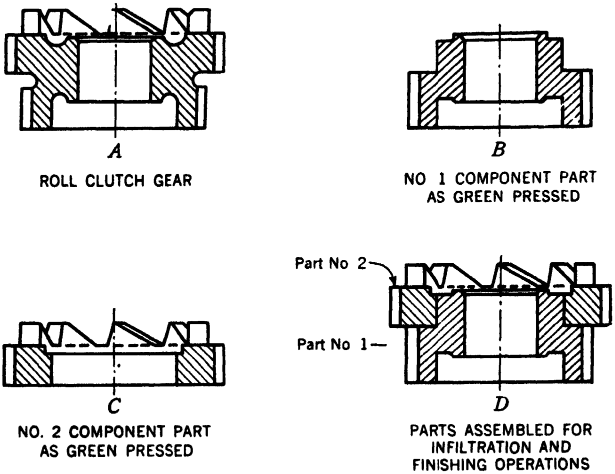

Fig. 508. Diagrammatic presentation of a roll clutch gear composed of two infiltration-brazed cemented steel sections. The original design (*A*) was broken down into two separately pressed parts (*B* and *C*) then assembled and infiltrated to give a final size, brazed unit (*D*).

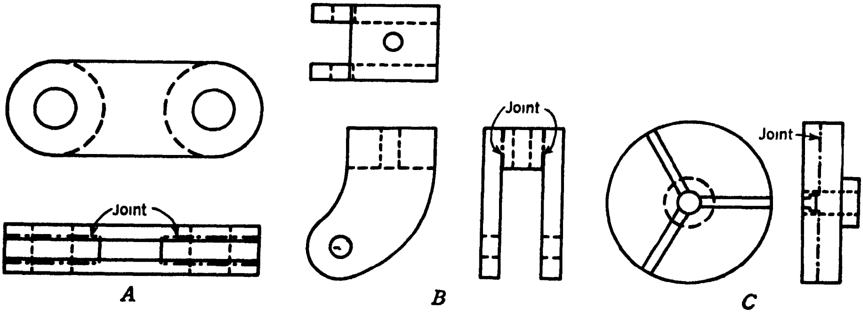

Fig. 509. Schematic presentation of compounds of complicated shape that can be produced by infiltration-brazing of cemented steel sections of symmetrical or simple contours. The components sketched represent a chain link (*A*), a bearing bracket (*B*), and a pulley (*C*). None of these components could be produced by conventional powder metallurgy techniques.

the part from the die. Figure 507 shows several gear combinations possible, with the very high spur gear hardly reproducible by ordinary powder metallurgy techniques. In combining several sections into one complex part, simple mechanical keying provides the proper location of each member. Figure 508 shows the diagram of a complicated roll clutch gear and illustrates in detail how the part is broken down into two separately pressed parts, which are then assembled and infiltrated to give a firmly joined unit. Other possible applications producible by the principle of designing symmetrically matching sections that are easy to mold and are suitable for composite construction are shown in Figure 509A–C.

The fact that the surface can be case hardened by various methods indicates the use of cemented steel parts for wear-resistant purposes. For applications requiring good antifriction properties the surface can be subjected to a prolonged electrolytic etching or chromic acid treatment, whereby the copper is attacked preferentially and minute openings are produced in the bearing surface which can be filled with lubricant.

Summary

Machine and structural parts from iron and low-carbon steels can be produced by powder metallurgy methods and have found a number of interesting applications, but primarily in cases where neither an appreciable porosity nor comparatively low physical properties are objectionable. Gears used for oil pumps in the automotive industries are a typical example of parts that can be produced in favorable competition with conventional methods of manufacture involving cast iron or bar stock steel.

There are now, however, very definite limitations to sintered ferrous parts that can be produced with industrially feasible techniques and facilities, the most important being: (*1*) low physical strength as compared with conventional fused metals; (*2*) poor corrosion resistance and machinability due to inherent porosity; (*3*) high cost of raw materials; (*4*) high initial cost of equipment and tooling up; (*5*) limitations in equipment which make it at present only suitable for comparatively small parts; (*6*) excessive tool and die wear if high-density parts are produced; (*7*) difficulties in producing complicated shapes having wide variations in cross section, eccenters, etc.; (*8*) lack of sufficient data on techniques and properties to enable design engineers to accommodate molding of complex parts.

Other factors to be considered are (*1*) because of the high initial costs, only mass production lots are practicable, and (*2*) the tooling and production costs are only lessened when sufficient man power skilled in the methods of powder metallurgical production is available.

Attempts to overcome these difficulties, at least in part, have by and large been successful only to a small extent, and the parts production from powders has so far made few inroads into the tremendous parts business. Besides certain special machine parts mostly used in the automotive industry, soft iron parts have been largely reserved for soft magnetic applications. Parts of low carbon content, or case hardened to improve their wear characteristics, have been developed for textile, printing, typewriter, automotive and similar machinery, for household appliances, and lately also for certain toys.

While alloying additions tend to improve the physical properties appreciably, such compositions have so far remained uneconomical due to higher cost in raw materials or production. The same applies to the production of such alloys as stainless steel from fusion-alloyed powders. Only in conjunction with copper are iron-base alloys by powder metallurgy now being used on an industrial scale.

Lately, an attempt has been made to improve the economy as well as the properties of ferrous powder metallurgy products by introducing a method of closing. the detrimental pore volume through filling with a lower melting metal instead of applying excessive pressures during coining or combined pressure and heat in a hot-press operation. Favored by a partial solubility of the iron in liquid copper, true cementing can take place in iron structures into whose pore volume copper is infiltrated. Iron–copper composites of this type exhibit many valuable properties, including a virtually pore-free structure, high strength, hardenability through precipitation treatments, platability, and good corrosion resistance, as well as excellent machinability. The addition of graphite transforms the ferrous component into steel without hindering the process. Copper-cemented steels are susceptible to conventional hardening treatments, thereby comparing with ordinary sintered steels, but the resulting physical properties are far superior due to the advantageous absence of the stress-raising pores. In spite of the appreciable proportion of the comparatively soft cementing metal, high surface hardness is obtainable, and good wear resistance can be achieved by alloying the ferrous or nonferrous phase, or both. The most interesting possibilities of this iron–copper base composite material lie in its self-brazing characteristics, which enable the joining of several components simply by application of heat to the assembled part in a brazing furnace possibly in conjunction with the impregnation of the pores with the liquid copper. Full realization of the far-reaching possibilities of this type of material depends on a number of factors, such as raw material costs, improvements in surface appearance and size control, parallel developments in other fabricating methods, etc. Only after considerable production experience has been gained will the field of application for this material become clearly circumscribed.

CHAPTER XXVI

Nonferrous Materials for Structural Parts

The industrial development of nonferrous powder metallurgy products of high density which are suitable for structural and machine parts has been less spectacular than that concerned with parts made by the powder metallurgy of iron and steel. Although such metals as copper, silver, and many conventional copper-base alloys are readily processed from metal powders, their high raw material cost has been largely responsible for preventing them from becoming competitive with the stamping, precision casting, die casting, and other more standard fabricating methods. Only bronzes have been used to a large extent for machine elements. Brass powder products have in general not yet been developed to a satisfactory quality at competitive cost, and it remains to be seen whether these factors can be brought into line in the near future. Nickel and cobalt powder products have found only a small number of applications, and sintered products from silver and other precious metals are used only in a few highly specialized cases. Among low melting materials, only aluminum alloys have been used with some success for the production of certain parts but here, too, the high raw material cost coupled with difficulties encountered in the molding of the parts has rendered the powder method noncompetitive with die-casting or stamping operations.

Thus, the development of dense products from powders of the commonly known nonferrous metals and alloys has, with a few exceptions, been confined to experimental and small-scale production work, and is therefore more of academic interest than of practical value. The most important exception is the manufacture of dense, heavy-duty bearings and other machine elements which benefit from certain antifriction and anticorrosion properties.

SINTERED COPPER AND COPPER ALLOYS

Manufacturing Methods

RAW MATERIALS

Granular copper powder in screen sizes varying from —100 to —325 mesh is produced by three methods: gaseous reduction, electrolysis, and atomization. While the last method has gained recently in significance, the bulk of powder consumed for metallurgical purposes is at present derived from the first two methods. Details of the manufacturing techniques and properties of the various grades of copper powder are given in Volume I, Chapter VI.

The raw materials suitable for the production of sintered copper alloys can be classified into two groups: (*1*) mixed powders, and (*2*) alloy powders. In most instances, mixtures of copper powders with powders of the component metals (*e.g.*, tin and nickel) are preferred on account of the more satisfactory compactibility obtained in the presence of the free, soft copper particles. Although the additional elements are usually present as a minor component only (*e.g.*, 5–15% Sn), their powder type is of some importance. Thus, tin is usually used as atomized powder (—100 or —200 mesh), but may also be used as very fine electrolytic powder (—325 mesh); nickel may be used in the form of fine carbonyl powder, as pulverized electrolytic powder (—100 or —200 mesh), or as reduced powder prepared from oxides or oxalate.

There are several instances in which alloy powders are preferred to mixed powders[1]; among these are brasses and copper–lead alloys. While the compactibility of these alloy powders is but slightly less than that of mixtures of the powdered ingredients (since the alloys are rather plastic in their own right), diffusion or homogenization during sintering of the alloy is helped greatly, and critical losses during the treatment of such highly volatile metals as zinc are minimized greatly or eliminated completely. Among the methods most suitable for the production of the alloy powders are atomization and liquid disintegration (Cu–Zn, Cu–Sn, Cu–Pb), diffusion sintering (Cu–Zn, Cu–Sn, Cu–Ni), and coating (Cu–Pb).

MOLDING

The molding of copper and copper-base alloy parts does not differ basically from the molding of ferrous powder parts as described in Chapter XXV. Pure copper powders and mixtures of copper and other alloying additions in the form of elemental powders behave during compaction like pure iron powders or mixtures of iron and graphite powders; on the other hand, alloy powders, especially if obtained by fusion alloying, behave less favorably during molding, although better than carbon steel and alloy steel powders. To overcome the increased rigidity of the alloy powders, it has been suggested by Jones[2] that hot-pressing techniques be

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[1] T. H. Lashar, in *Symposium on Powder Metallurgy*. ASTM, Philadelphia, Pa., 1934, p. 41.

[2] W. D. Jones, *Metal Ind. London, 56,* 69, 225 (1940).

used on an industrial scale. When employing the more customary cold-press and subsequent sintering methods, the rules laid down in Volume I, Chapter IX, apply. R. P. Seelig[3,4] reviewed these molding problems with special reference to bronzes; similarly, Kelton[5] discussed the problems connected with the molding of brass powder parts.

Although the similarity in molding performance between copper-base and iron-base powders is quite striking, there are some differences worthy of consideration. The specific molding pressures applied are generally of a somewhat lower order of magnitude for nonferrous powders, because of the greater plasticity and softness found in the particles. Copper, bronze, or brass compacts are usually molded at pressures varying between 15 and 25 tsi, as compared with pressures of 30–50 tsi for iron or iron–graphite compacts of similar green density.

In view of the lower pressures applied, friction effects on the walls are of somewhat less serious consequence, and methods of lubrication differ accordingly from those applicable in ferrous powder molding. While in the latter instance internal lubrication (*i.e.*, powdered nonmetallic lubricants mixed with the metal powder) is used successfully, it is of debatable merit in the case of copper-base pressings. It has been found that the addition of a small percentage of graphite to copper–tin and copper–tin–lead powder mixtures greatly facilitates the molding of parts and bearings by reducing briquetting and ejection pressures, thereby yielding a more uniform and reproducible product. Also, the addition of a small percentage (up to 1.5% by weight) of a nonmetallic lubricant, such as powdered stearic acid, still further reduces friction between the particles and at the die faces, while, at the same time, the volatilization of the lubricant during the early stages of the sintering operation functions as a pore-creating and regulating factor (see also Volume I, Chapter VII). However, it must be borne in mind that these effects are advantageous only in the production of intentionally *porous* parts, such as self-lubricating bearings. In the molding of substantially *dense* structures it has been found that the densification effects obtained by the increased molding pressure are counteracted by the pore-creating tendency of the volatile lubricant. Moreover, certain types of organic lubricants appear to decompose when the powder is stored for a long period of time, thus causing an undesirable reaction between the decomposition products and the copper or other nonferrous metal powders. As a consequence, external lubrication of the die walls appears preferable for the molding of dense copper or copper–alloy parts.

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[3] R. P. Seelig, *Steel, 117,* No. 21, 116 (1945).

[4] R. Hradecky and R. P. Seelig, *Iron Age, 156,* No. 13, 50 (1945).

[5] E. H. Kelton, *Machine Design, 16,* 129 (1944).

In the case of mixtures of powders of greatly differing specific gravity, the problem of segregation during feeding into the mold, or during the initial stages of molding, must also be considered. A careful selection of particle size distribution of the individual component powder, or the addition of certain segregation inhibiting agents (*e.g.*, high-molecular alcohols), may be necessary (for further details see Volume I, Chapter VII).

SINTERING

Corresponding with the lower melting temperatures of the nonferrous materials, the practical sintering temperatures for copper and copper alloys are considerably below those used in the production of ferrous powder products. Table 197 indicates the sintering temperature ranges and preferred sintering temperatures for several nonferrous compositions of general interest. In most instances, the sintering times required for the attainment of satisfactory diffusion and tensile properties need not exceed one hour at the indicated temperatures. Furnace atmosphere requirements are generally quite liberal, with the important exception in brass sintering. Hydrogen, cracked ammonia, or partially combusted natural gas or hydrocarbons (see Volume I, Chapter XVII) are all satisfactory for copper and its alloys with tin or nickel. Since these alloys are not extremely sensitive to oxidation, the dew point of the atmosphere need not be very low, thus permitting the use of a continuous conveyor-type sintering furnace with open charge and discharge doors (see Volume I, Chapters XV and XVI).

TABLE 197
Conventional Sintering Temperatures of Copper-Base Alloys

Material	Melting temperature[a]		Sintering temperature range		Preferred sintering temperature	
	°C.	°F.	°C.	°F.	°C.	°F.
Copper	1083	1981	750–1000	1380–1830	900	1650
90–5 Cu–Sn bronze	910	1670	850–885	1560–1625	870	1600
90–10 Cu–Sn bronze	850	1560	750–830	1380–1525	810	1490
88–10–2 Cu–Sn–Zn bronze	830	1525	750–815	1380–1500	800	1470
88–10–2 Cu–Sn–Pb bronze	815	1500	725–800	1335–1470	775	1425
90–10 brass	1025	1880	860–940	1580–1725	880	1615
80–20 brass	970	1780	840–920	1545–1690	870	1600
70–30 brass	910	1670	825–900	1515–1650	865	1590
90–10 Cu–Ni cupro-nickel	1120	2050	910–1060	1670–1940	1010	1850
70–30 Cu–Ni cupro-nickel	1185	2165	940–1080	1725–1975	980	1800
70–25–5 Cu–Ni–Sn cupro-nickel	1170	2140	940–1010	1725–1850	980	1800

[a] Solidus temperature.

Where alloying ingredients of high vapor pressure are involved, as in copper alloys containing an appreciable proportion of zinc or lead, losses of these elements by sweating or evaporation are unavoidable during sintering at higher temperatures and may cause substantial changes in composition of the alloy. These losses can be minimized effectively by raising the partial pressure of the element in the furnace atmosphere. A tightly closed furnace system (*e.g.*, carefully sealed retorts) through which only a small flow of protective atmosphere is passing, is therefore essential in the sintering of copper–zinc and copper–lead alloys. Other expedients often resorted to imply the use of free zinc or lead metal, or copper alloys containing these elements in major proportion, next to the charge to raise the partial pressure of the volatile metal in the atmosphere; or, a tight grouping of the compacts, if possible, inside a powder pack consisting of a mixture of lead or zinc powder with a large proportion of sand or other inert matter (see also Volume I, Chapter XV). Miller[5a]—experimenting with a 70–30 atomized brass powder—recently confirmed the fact that the *composition* of the protective atmosphere introduced into the sintering furnace also plays an important role in the dezincification process. Zinc losses appear to be lowest for atmospheres consisting of nitrogen–hydrogen mixtures, especially in the case of a high $N_2:H_2$ ratio. With dissociated ammonia, dezincification is definitely a factor, but the resulting shrinkage of the compacts gives optimum physical properties, especially if a moderate compacting pressure (30–40 tsi), an easily volatile pressing lubricant (wax or fatty acid), and sintering temperatures not in excess of 900°C. (1650°F.) are used.

When sintering pure copper in an atmosphere containing zinc vapor, a brass layer is formed at the surface.[6] Depth of penetration grows as temperature increases, but the temperature is limited by local melting or sweating to about 900°C. (1650°F.). A treatment for 3 hours has been found to yield a case of approximately 0.010-in. depth. The vapor is produced by placing small zinc castings in flat crucibles immediately adjacent to the specimens, with nitrogen the most suitable furnace atmosphere.

SUBSEQUENT OPERATIONS

Copper, brass, and bronze parts usually require additional operations after sintering. Products of pure copper change their dimensions in the sintering operations according to laws similar to those that apply to pure

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[5a] H. C. Miller, *Proc. Fourth Annual Spring Meeting of Metal Powder Association*, Chicago, April 15–16, 1948, p. 70.

[6] H. Unckel, *Z. Metallkunde, 36*, 164 (1944).

iron,[7,8] displaying a general tendency toward shrinkage. This effect, of course, is more pronounced the finer the powder, the lower the compacting pressure, or the more intensive the sintering operation (see Volume I, Chapter XIV), but it is usually possible under commercially acceptable conditions to produce parts of closely controlled dimensions (*i.e.*, within 0.5% linear shrinkage). Where closer tolerances are to be held, a subsequent low-pressure sizing operation is indicated. Since the plasticity of most pure copper powders permits direct compression to high densities (up to about 95% of theoretical), it is usually unnecessary to introduce subsequent condensing through high-pressure coining—provided that the sintering cycle is chosen so that the high initial density is retained.

The problem of size control becomes more complicated when copper alloys, and, in particular, those compositions that contain a low-melting constituent, are dealt with. In the case of copper–tin alloys, sintering causes rather complex dimensional changes[9] often involving both shrinkage and growth in the same part.[10] Caused primarily by the dezincification taking place during sintering, brass powder compacts display a very pronounced tendency toward growth, especially when the parts are compacted from mixtures of the elemental components.[11] Thus, in these alloys a subsequent compression operation has to fulfil the double purpose of giving the part its correct size and improving substantially the density and physical properties that have been impaired during the growth development in the sintering operation.

In those copper alloys that are subject to precipitation treatment the coining operation is essential for maximum density and tensile properties of the final product. Taking as an example a 70–25–5 Cu–Ni–Sn composition, the sintered alloy is first rendered dead-soft by a solution-quench treatment directly following the sintering operation; the highest practicable coining pressures (50–80 tsi) are then applied, ensuring accurate size, and high density, hardness, and strength. A precipitation treatment at about 400°C. (750°F.) for 12 hours results in a marked increase in hardness and tensile strength without detriment to dimensional accuracy.[11a]

In the less complex alloys, heat treatments following sizing or coin-

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[7] C. G. Goetzel, *The Influence of Processing Methods on the Structure and Properties of Compressed and Heat Treated Copper Powders*. Dissertation, Columbia University, New York, 1939.

[8] J. E. Drapeau, Jr., in J. Wulff, *Powder Metallurgy*. Am. Soc. Metals, Cleveland, 1942, p. 323.

[9] C. G. Goetzel, *Trans. Am. Inst. Mining Met. Engrs., 161,* 580 (1945).

[10] J. E. Drapeau, Jr., in J. Wulff, *Powder Metallurgy*. Am. Soc. Metals, Cleveland, 1942, p. 332.

[11] C. G. Goetzel, *Trans. Am. Soc. Metals, 30,* 86 (1942).

[11a] W. N. Pratt, *Powder Met. Bull., 1,* No. 3, 43 (1946).

ing usually serve to relieve stresses or promote further diffusion by annealing or resintering. Excessive dimensional changes that may be caused by these treatments often require an additional pressure-sizing operation. Conventional mechanical finishing operations can be applied to all copper-base powder alloys. Machining operations are performed most advantageously after coining, when the material is in the stressed state. Alloys containing small percentages of lead (up to 2%) are said to improve the machinability of nonferrous parts considerably.

Properties

COPPER

The sintering characteristics and properties of copper have been studied extensively during the last 25 years, particularly by Sauerwald and coworkers,[12-23] Kikuchi,[24] Trzebiatowski,[25] Goetzel,[26-30] Bier and O'Keefe,[31] and more recently by Cook and Pugh,[32] Kalpers,[32a] and Jordan and Duwez.[32b]

Bier and O'Keefe studied the effect of sintering temperature and time on the structure of compacts that were prepared by compression of reduced powders at 30 tsi, and found that the particles lost their identity entirely only at comparatively high temperatures, *i.e.*, at 900°C. (1650°F.) after 30 minutes, or at 950°C. (1750°F.) after 12 minutes.

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[12] F. Sauerwald, *Z. anorg. allgem. Chem., 122,* 277 (1922).

[13] F. Sauerwald, *Z. Elektrochem., 29,* 79 (1923).

[14] F. Sauerwald and E. Jaenichen, *Z. Elektrochem., 30,* 175 (1924).

[15] F. Sauerwald, *Z. Metallkunde, 16,* 41, (1924).

[16] F. Sauerwald and G. Elsner, *Z. Elektrochem., 31,* 15 (1925).

[17] F. Sauerwald and E. Jaenichen, *Z. Elektrochem., 31,* 18 (1925).

[18] F. Sauerwald, *Z. Metallkunde, 20,* 227 (1928).

[19] F. Sauerwald, *Metallwirtschaft, 7,* 1353 (1928).

[20] F. Sauerwald and J. Hunczek, *Z. Metallkunde, 21,* 22 (1929).

[21] F. Sauerwald and St. Kubik, *Z. Elektrochem., 38,* 33 (1932).

[22] F. Sauerwald and L. Holub, *Z. Elektrochem., 39,* 750 (1933).

[23] F. Sauerwald, *Metallwirtschaft, 20,* 649, 671 (1941).

[24] R. Kikuchi, *Science Reports Tôhoku Univ., 26,* 125 (1937).

[25] W. Trzebiatowski, *Z. physik. Chem., A169,* 91 (1934); *B24,* 75, 87 (1934).

[26] C. G. Goetzel, *Metals & Alloys, 12,* 30, 154 (1940).

[27] C. G. Goetzel, *J. Inst. Metals, 66,* 319 (1940).

[28] C. G. Goetzel and R. P. Seelig, *Trans. Am. Soc. Testing Materials, 40,* 746 (1940).

[29] C G. Goetzel, *Trans. Am. Soc. Metals, 28,* 909 (1940).

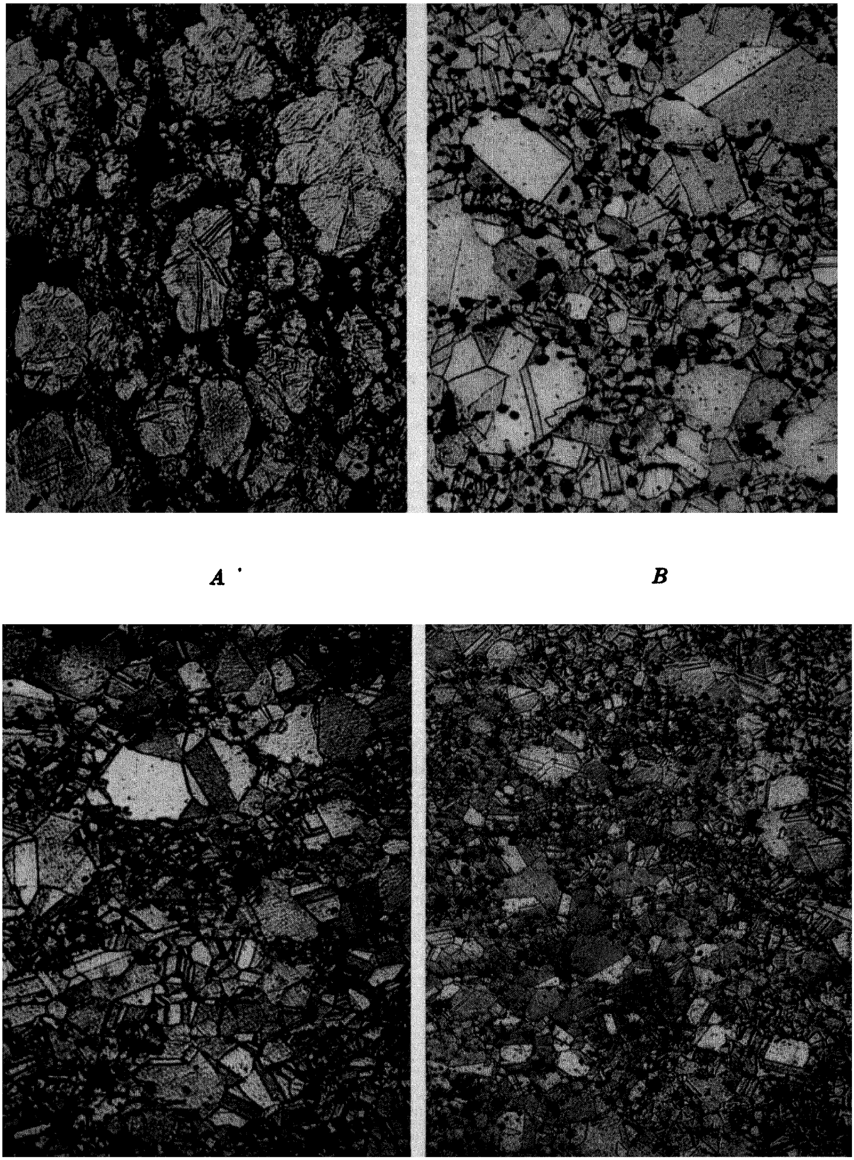
[30] C. G. Goetzel, *Wire and Wire Products, 16,* 217, 274 (1941).

[31] C. J. Bier and J. F. O'Keefe, *Trans. Am. Inst. Mining Met. Engrs., 161,* 596 (1945).

[32] M. Cook and S. F. Pugh, *Symposium on Powder Metallurgy.* The Iron and Steel Institute, Special Report No. 38, London, 1947, p. 162.

[32a] H. Kalpers, *Arch. Metallkunde, 1,* No. 7/8, 368 (1947).

[32b] C. B. Jordan and P. Duwez, *J. Metals, 1,* No. 2, 96 (1949).



A B

C D

Fig. 510. Effect of length of sintering time on the microstructure (×135) of electrolytic copper powder compacts. Compacts were pressed at 45 tsi and sintered in hydrogen at 750°C. (1380°F.): *A,* compressed powder showing nodular particle structure containing aggregates of crystallites. *B,* after sintering for 2 hours, showing agglomeration of recrystallized particles; *C,* after sintering for 10 hours, showing polyhedral grain structure with original particle boundaries still discernible; *D,* after sintering for 16 hours, showing equiaxed uniform grain structure.

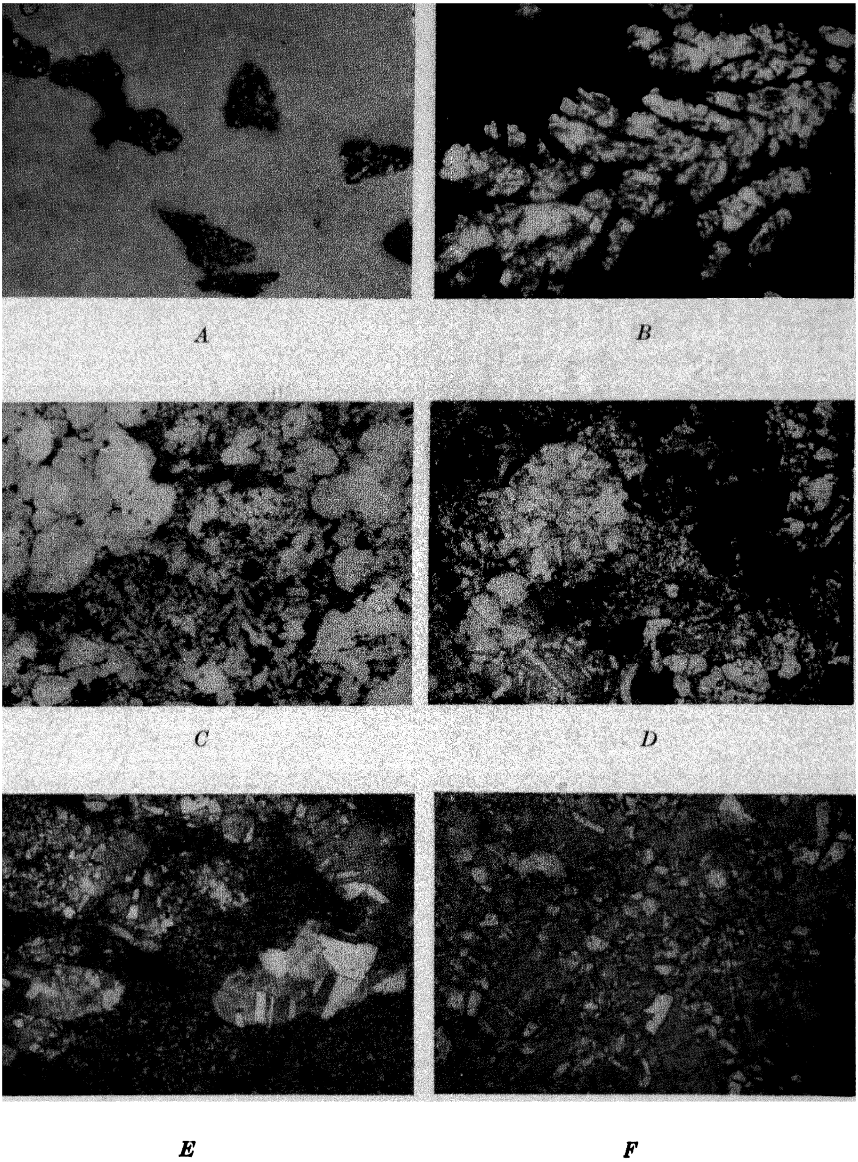


Fig. 511. Changes in microstructure resulting from sintering at progressively increasing temperatures of electrolytic copper powder compacted at 40 tsi (according to Cook and Pugh[32]): *A*, surface appearance and shape of loose powder, ×75; *B*, etched section through powder particle, ×375; *C*, unsintered powder compact, ×150; *D*, compact sintered at 400°C. (750°F.) for 10 minutes, ×150; *E*, compact sintered at 800°C. (1470°F.) for 10 minutes, ×150; *F*, compact sintered at 1000°C. (1830°F.) for 10 minutes, ×150.

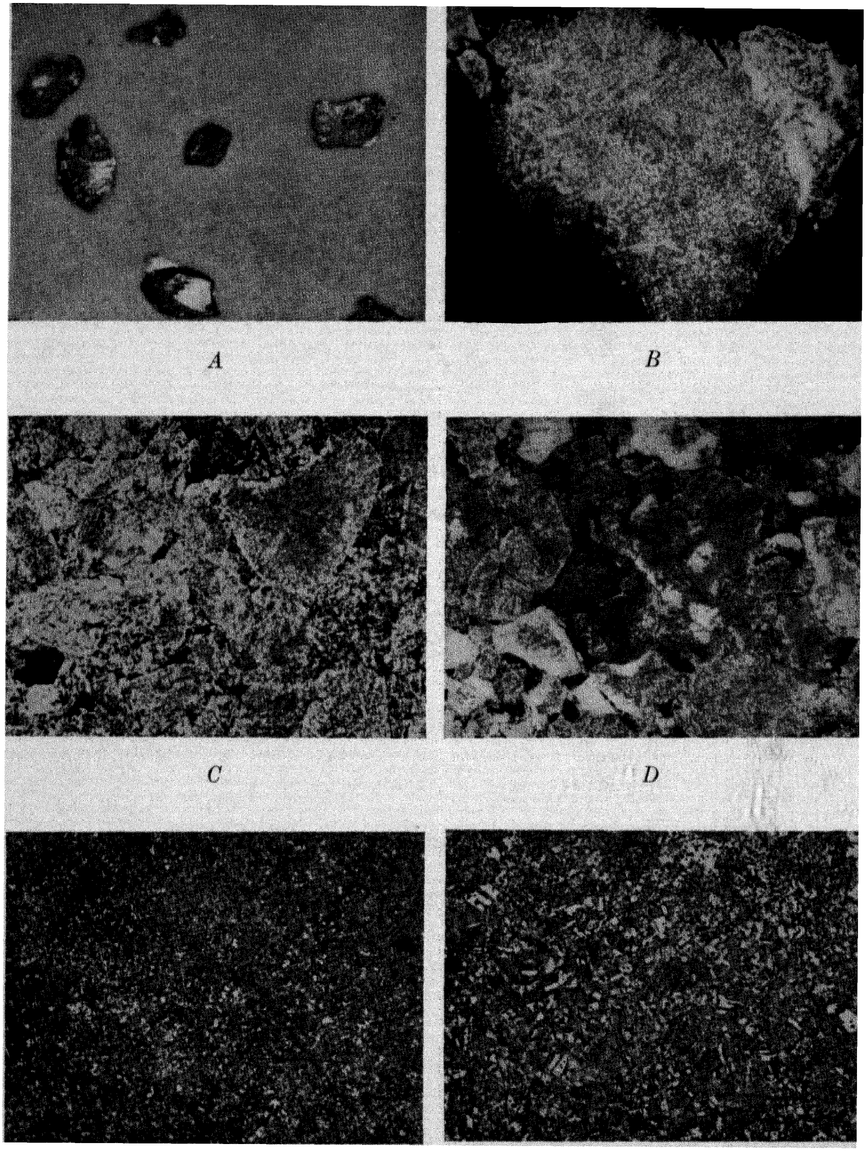


Fig. 512. Changes in microstructure resulting from sintering at progressively increasing temperatures of hydrogen-reduced copper powder compacted at 40 tsi (according to Cook and Pugh[32]). See caption of Figure 511 for identification of Parts *A–F*.

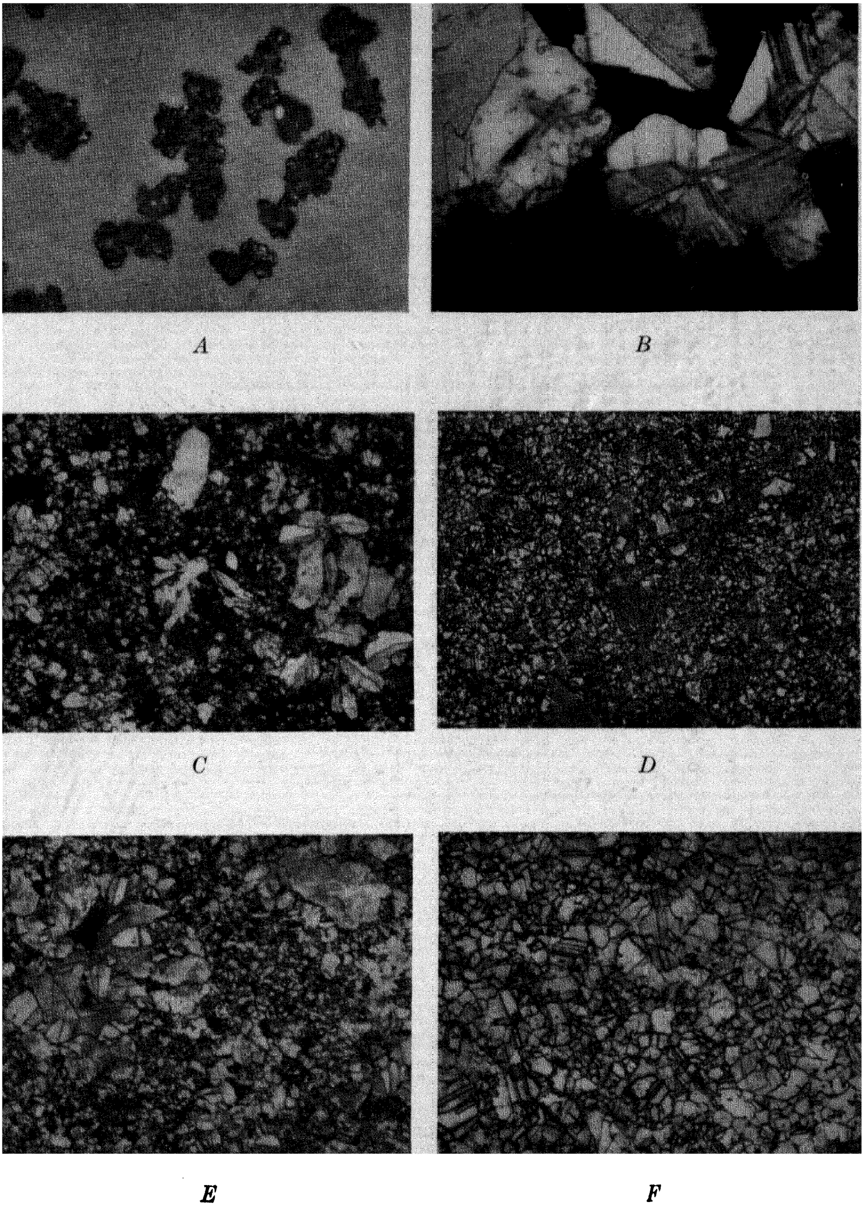


Fig. 513. Changes in microstructure resulting from sintering at progressively increasing temperatures of precipitated copper powder compacted at 40 tsi (according to Cook and Pugh[32]). See caption of Figure 511 for identification of Parts *A–F*.

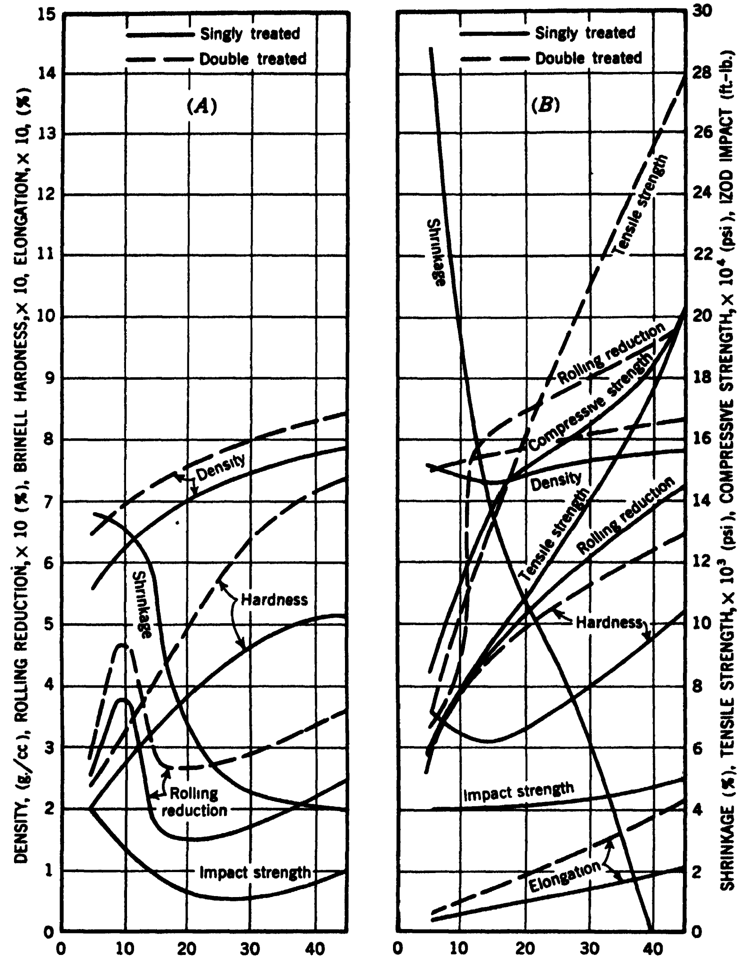


Fig 514. Effect of pressure on the properties of compacts made from fine-grade 100% —200, 97% —325 mesh electrolytic copper powder: (*A*), hydrogen-sintered specimens (at 750°C., 1380°F. for 16 hours); (*B*), vacuum-sintered specimens (at 750°C., 1380°F. for 16 hours).

For a temperature of 750°C. (1380°F.), the author found that a 16-hour treatment was necessary for complete solution of the initial particles into the polygonal copper grain structure,[33] as shown by the photomicrographs of Figure 510. Cook and Pugh, studying electrolytic, reduced.

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[33] C. G. Goetzel, *The Influence of Processing Methods on the Structure and Properties of Compressed and Heat Treated Copper Powders*. Dissertation, Columbia University, New York, 1939.

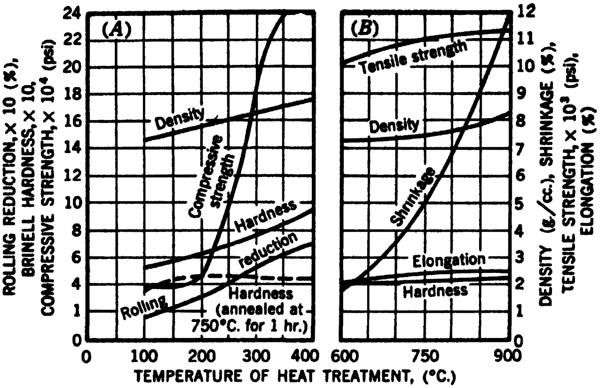
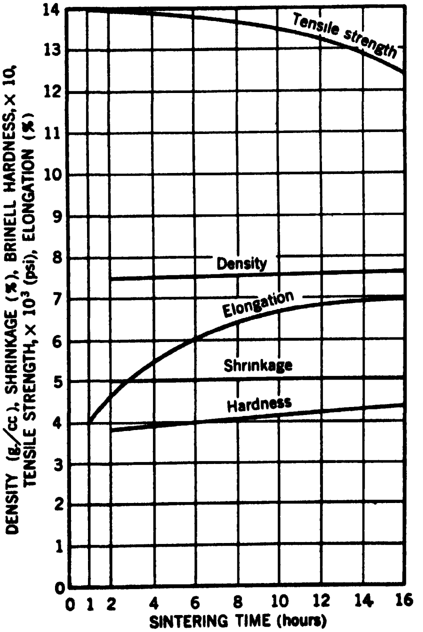


Fig. 515. Effect of temperature of treatment on the properties of hot-pressed (*A*), and of cold-pressed and sintered (*B*); compacts compressed at 25 tsi from fine-grade electrolytic copper powder.



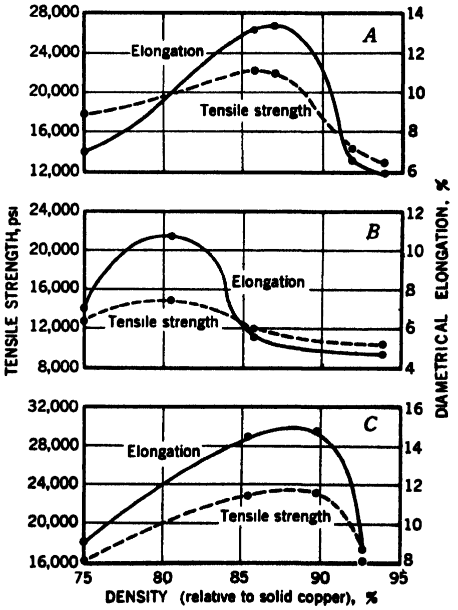


Fig. 516. Effect of sintering time on the properties of sintered compacts made from fine-grade electrolytic copper powder compacts compressed at 25 tsi and sintered at 750°C. (1380°F.).

Fig. 517. Proportional change in tensile strength and elongation values with increasing density for ring-shaped compacts prepared from (*A*) electrolytic, (*B*) oxide-reduced, and (*C*) precipitated copper powders after sintering at 1020°C. (1870°F.) for 10 minutes (according to

and precipitated powders, found that complete solution of the original particles for a sintering period of 10 minutes (at the designated temperature) is not yet achieved at 800°C. (1470°F.) in the case of the electrolytic and precipitated powders, but is accomplished with all powders at 1000°C. (1830°F.). The metamorphosis of the microstructure with rising temperatures from the loose powder state to the compacted high-temperature sintered bodies is well illustrated by a series of photomicrographs which are reproduced in Figures 511–513.[32]

TABLE 198

Properties of Copper Compacts after Pressing and Sintering, and after Coining and Resintering

Raw material	Treatment	Density, % of theoretical	Tensile strength, psi	Elongation in 2 in., %	Fatigue strength, psi	Izod impact strength, ft.-lb.
Coarse electrolytic powder (all −100 mesh, 20% −325 mesh	Pressed at 50 tsi; sintered at 750°C. (1380°F.) for 16 hr. in H_2	93.5	18,900	12	7,500	5
	Pressed at 50 tsi; sintered at 750°C. (1380°F.) for 16 hr. in H_2; coined at 50 tsi; resintered at 750°C. for 16 hr. in H_2	96.5	25,200	20	10,500	10
Fine electrolytic powder (all −325 mesh)	Pressed at 50 tsi; sintered at 750°C. (1380°F.) for 16 hr. in H_2	93	23,200	10	9,500	4
	Pressed at 50 tsi; sintered at 750°C. (1380°F.) for 16 hr. in H_2; coined at 50 tsi; resintered at 750°C. for 16 hr. in H_2	95.5	30,000	17	13,000	7

Jordan and Duwez[32b] studied the effect of the sintering atmosphere on the rate of densification, and found that sintering in vacuum causes a slower increase in density than sintering in hydrogen (for a discussion of the theoretical aspects of this work see Chapter XXXV).

The pronounced effect of the compacting and coining pressure on the properties of compacts prepared from a fine-grain electrolytic copper powder and sintered for 16 hours at 750°C. (1380°F.) in hydrogen atmosphere and in vacuum is shown in the diagram of Figure 514.[26] The less marked effect of sintering temperature on the properties of compacts obtained by compression at 25 tsi is shown in Figure 515 (part *B*), and that of sintering time for the same pressure and temperature conditions in Figure 516. Table 198 represents data showing the effect of subsequent coining at 50 tsi on compacts from coarse and fine electrolytic powders, pressed initially at 50 tsi, and sintered and resintered at 750°C. (1380°F.) for 16 hours in hydrogen. It is also apparent from these data that the finer particle size tends to increase tensile and fatigue strength at the expense of ductility. The Izod impact strength can be slightly improved to about 12 ft.-lb. by increasing the temperature for sintering and resintering to 900°C. (1650°F.). Higher temperatures cause no further improvement in impact resistance, presumably because of excessive grain growth.

Cook and Pugh established the relation between the density and the tensile properties and dimensional changes of ring-shaped compacts (Figs. 517–520). The tensile tests were carried out by expanding the rings until fracture occurred, with duplicate tests on machined cast copper rings indicating that the tensile strength values were equivalent to those obtained in the ordinary type of test, while the ductility values only amounted to about one-half. Cook and Pugh found that the dimensional changes are influenced primarily by the compacting pressure, with the sintering temperature having a corrective effect. High strength is obtained in the case of the electrolytic and precipitated powders at optimum compacting pressure and high sintering temperatures, under which conditions the dimensional changes are also at a minimum. The behavior of the oxide-reduced powder differs, however, since the increase in expansion, or increasingly reduced contraction, is more marked with increasing sintering temperature, an effect that is attributed to greater gas evolution as compared with the other powder products.

Complete density can be reached only by hot pressing, and the physical properties of material thus treated excel by far the properties obtainable by cold pressing and sintering, as can be seen from Figure 515 (part *A*) (for details see Volume I, Chapter XII). Especially noteworthy are the extremely high hardness values (up to 180 Brinell) that can be reached with very fine powders.[34] Copper powders appear to be easily suitable for hot-press operations, but so far the technique has been applied on an industrial basis only in one particular case where comparatively coarse copper granules are hot-pressed into "coalesced" copper ingots.[35,36] Further developments, especially with respect to finer powders, have not yet been realized.

The physical properties of copper powder products are summarized and compared with fused copper products elsewhere (Chapter XXXI).

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[34] W. Trzebiatowski, *Z. physik. Chem., A169,* 91 (1934).

[35] H. H. Stout, *Trans. Am. Inst. Mining Met. Engrs., 143,* 326 (1941).

[36] J. Tyssowski, *Trans. Am. Inst. Mining Met. Engrs., 143,* 335 (1941).

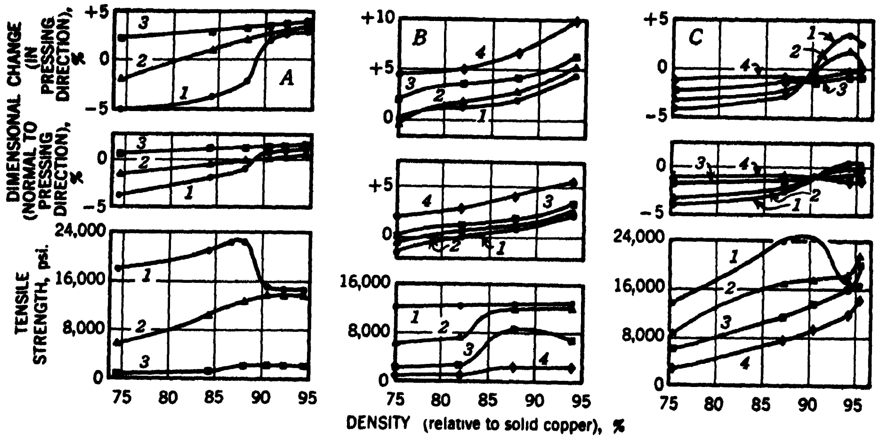

Fig. 518. Effect of density on the dimensional changes and tensile strength of ring-shaped compacts from different copper powders after sintering for 10 minutes at various temperatures (according to Cook and Pugh[32]). *A*, electrolytic powder, 23% +100 mesh, 37% −240 mesh; apparent density: 1.82 g./cc. *B*, hydrogen-reduced powder, 14% +100 mesh, 35% −240 mesh; apparent density: 2.78 g./cc. *C*, precipitated powder, 1% +100 mesh, 39% −240 mesh; apparent density: 1.59 g./cc. (Curve *1*: sintered at 1050°C., 1920°F.; *2*: sintered at 950°C., 1740°F.; *3*: sintered at 850°C., 1560°F.; *4*: sintered at 750°C., 1380°F.).

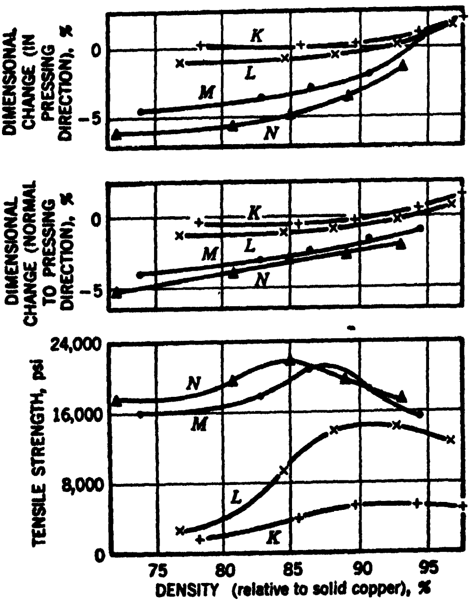

Fig. 519. Effect of density on the dimensional changes and tensile strength of compacts made from four different grades of electrolytic copper powders after sintering at 1020°C. (1870°F.) for 10 minutes (according to Cook and Pugh[32]). Grade *K*: 29% +100, 33% +150, 22% +200, 11% +240, 5% −240 mesh; *L*: 25% +100, 27% +150, 18% +200, 10% +240, 20% −240 mesh; *M*: 23% +100, 20% +150, 11% +200, 9% +240, 37% −240 mesh; *N*: 0% +100, 21% +150, 12% +200, 7% +240, 60% −240 mesh.

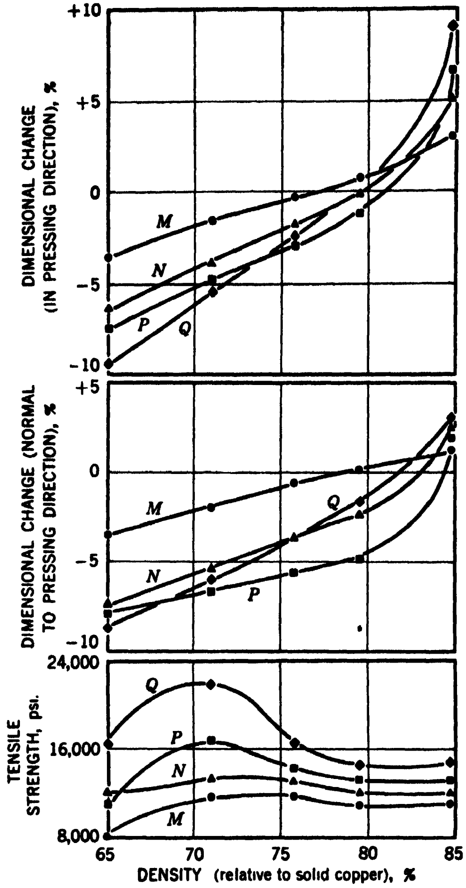

Fig. 520. Effect of density on the dimensional changes and tensile strength of compacts made from four different grades of hydrogen-reduced copper powders after sintering at 1020°C. (1870°F.) for 10 minutes (according to Cook and Pugh[32]). Grade *M*: 14% +100, 26% +150, 14% +200, 11% +240, 35% −240 mesh; *N*: 0% +100, 13% +150, 18% +200, 9% +240, 60% −240 mesh; *P*: 0% +100, 0% +150, 0% +200, 0% +240, 100% −240 mesh; *Q*: 0% +100, 0% +150, 0% +200, 0% +240, 100% −240 mesh, 100% −300 mesh.

BRASSES

The characteristics and properties of sintered and hot-pressed brass powder products have been investigated by Jones,[37] Goetzel,[38] and

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[37] W. D. Jones, *Metal Ind. London, 56,* 225 (1940).

[38] C. G. Goetzel, *Trans. Am. Soc. Metals, 30,* 86 (1942).

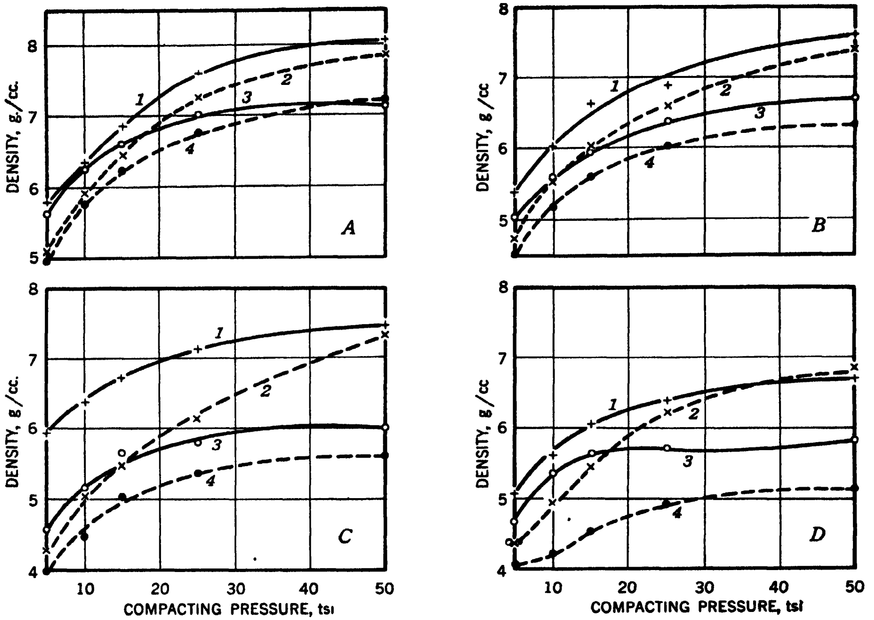

Fig. 521. Effect of increasing compacting pressure on the density of sintered brass compacts prepared from copper and zinc powder mixtures, and from prealloyed brass powders and sintered for 1 hour at 600°C. (1110°F.) and 800°C. (1470°F.), respectively: *A,* 85–15 copper–zinc compacts; *B,* 75–25 copper–zinc compacts; *C,* 65–35 copper–zinc compacts; *D,* 55–45 copper–zinc compacts. (*Curve 1*: alloy powder sintered at 800°C., 1470°F.; *2*: alloy powder sintered at 600°C., 1110°F.; *3*: powder mixture sintered at 800°C., 1470°F.; *4*: powder mixture sintered at 600°C. 1110°F.)

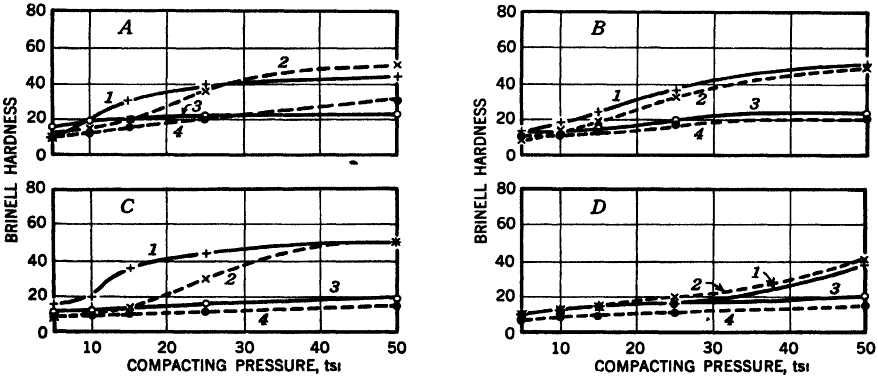

Fig. 522. Effect of increasing compacting pressure on the Brinell hardness of sintered brass compacts prepared from copper and zinc powder mixtures and from prealloyed brass powders and sintered for 1 hour at 600°C. (1110°F.) and 800°C. (1470°F.), respectively: *A,* 85–15 copper–zinc compacts; *B,* 75–25 copper–zinc compacts; *C,* 65–35 copper–zinc compacts; *D,* 55–45 copper–zinc compacts. (See Fig. 521 for identification of curves.)

Kelton.[39] In the diagrams of Figure 521*A–D*, the density is shown as a function of the initial molding pressure for compacts of various copper-zinc ratios and prepared either from mixed metal powders, or from alloy powders obtained by a preliminary diffusion-sintering treatment at 450°C. (840°F.) for 2 hours. In each diagram, curves are given for two sintering temperatures. The effect of the initial compacting pressure on hardness is shown in the diagrams of Figure 522*A–D*, and that on the compressive properties in Figure 523*A–D*. The trend of all properties to improve with increasing initial pressure is apparent, but the actual values remain disappointing over the range investigated.[38]

Kelton,[39] however, has shown that, by proper selection of processing conditions, products of satisfactory properties can be obtained from fusion-alloyed and atomized powders, especially if a small fraction of phosphorus (0.1–1%) is added to the melt as deoxidizer.[40] This is apparent from the diagrams of Figure 524*A–D*, which show, for phosphorus-containing (0.5% P) and phosphorus-free 90–10 brass powder compacts produced under different conditions, the effect of sintering temperature on tensile strength and elongation, and the relationship between sintering temperature and weight and size changes.[41] Similar relationships between sintering temperature and physical properties are plotted for a 70–30 brass powder containing 0.3% P in Figure 525*A–E*.[42] A summary of results obtained with the 70–30 and 90–10 Cu–Zn alloy powders, with and without phosphorus additions, is given in Table 199.[39,43] The phosphorus addition apparently increases the elongation, decreases the optimum sintering temperature, and permits use of a wider sintering temperature range. All data given in Table 199 are from specimens sintered at the optimum sintering temperature for not more than 30 minutes. The hydrogen and cracked gas (5% CO_2, 12% CO, 15% H_2, and 68% N_2) used in this work had a maximum moisture content of 2% by volume. The ductility of some of these alloys is quite remarkable, and elongation values of 50%, and 180° bending and 720° twisting angles, as obtained by Kelton with the phosphorized 70–30 alloy, are outstanding properties.

The physical properties of sintered high-density brass of 70–30

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[39] E. H. Kelton, *Machine Design, 16,* 129 (1944); see also *Iron Age, 155,* No. 4, 60 (1945).

[40] U. S. Pat. 2,368,943.

[41] New Jersey Zinc Co., Technical Dept. Rept. No. 783.

[42] New Jersey Zinc Co., Technical Dept. Rept. No. 671.

[43] Anonymous, *Iron Age, 155,* No. 4, 60 (1945).

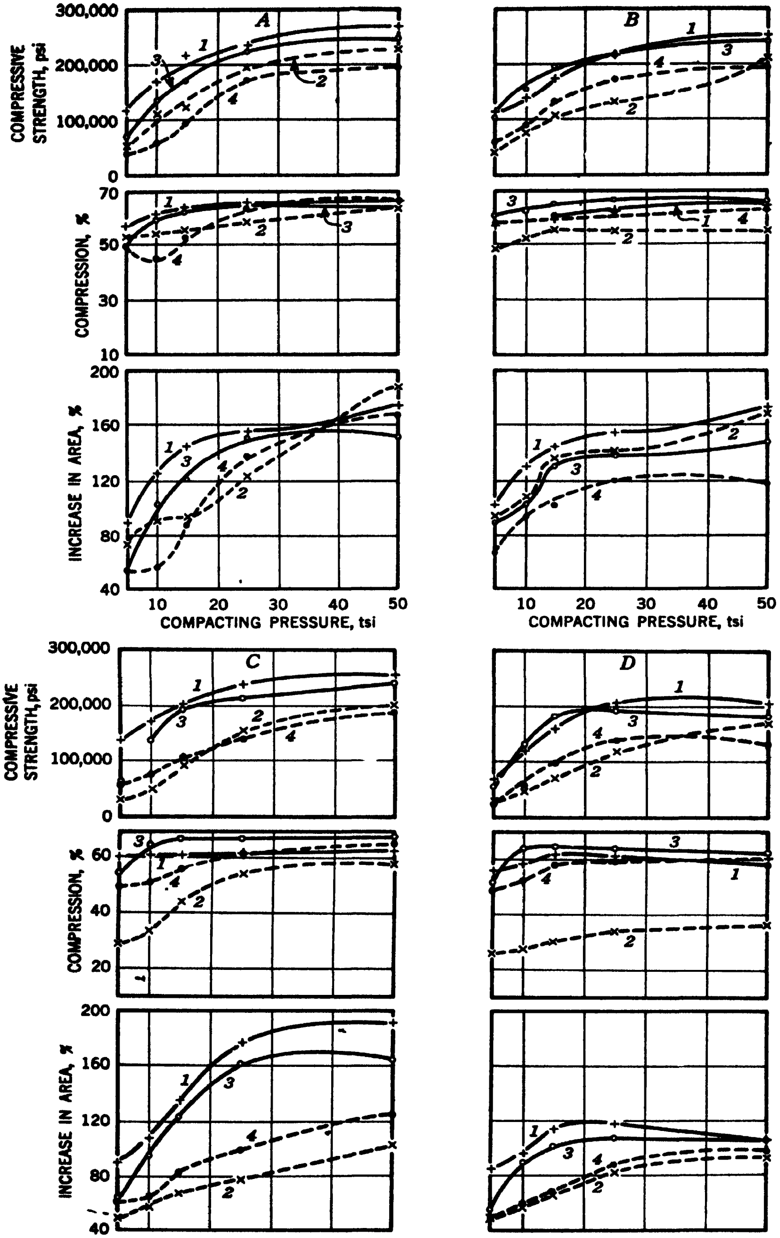

Fig. 523. Effect of increasing compacting pressure on the compressive properties of sintered brass compacts prepared from copper and zinc powder mixtures and from prealloyed brass powders and sintered for 1 hour at 600°C. (1110°F.) and 800°C. (1470°F.), respectively: *A*, 85–15 copper–zinc compacts; *B*, 75–25 copper–zinc compacts; *C*, 65–35 copper–zinc compacts; *D*, 55–45 copper–zinc compacts (See Fig. 521 for identification of curves.)

composition were also investigated by Lennox[44] in England. When producing the alloy from mixed powders, the compacts were found to distort badly during sintering because of the partial evaporation of the zinc. Compacts of higher density and substantially free of distortion were obtained from partially alloyed powders containing copper-zinc

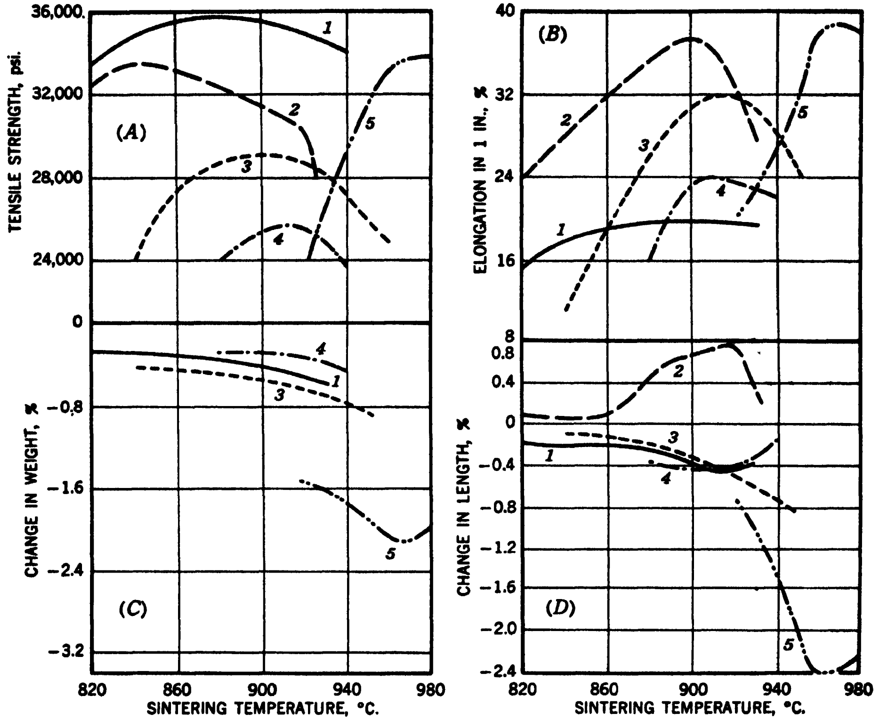

Fig. 524. Effect of sintering temperature on the tensile properties, and weight and size changes of 90–10 brass powder compacts prepared from atomized alloy powders with and without phosphorus additions. All specimens were sintered for 30 minutes at temperature; either in hydrogen atmosphere or in a synthetic cracked gas (X-gas), analyzing nominally 5% CO_2, 12% CO, 15% H_2, 68% N_2.[41] (*1*) P-free powder, pressed at 50 tsi, sintered in H_2; (*2*) 0.5%-P powder, pressed at 50 tsi, sintered in H_2; (*3*) 0.5%-P powder, pressed at 30 tsi, sintered in H_2; (*4*) 0.5%-P powder, pressed at 30 tsi, sintered in X-gas; (*5*) 0.5%-P powder, 1% stearic acid, pressed at 50 tsi, sintered in X-gas.

mixtures that had been treated in hydrogen in a rotary furnace at 450 and 550°C. (840 and 1020°F.) for either 7 or 30 minutes. A "fully" alloyed 70–30 brass powder (of undisclosed origin) was finally em-

[44] J. W. Lennox, *Symposium on Powder Metallurgy*. The Iron and Steel Institute, Special Report No. 38, London, 1947, p. 174.

ployed for the tests. Best results were obtained by cold-pressing at 30 to 35 tsi with 1% stearic acid as die lubricant, sintering at 900°C. (1650°F.) in hydrogen or dissociated ammonia for a time dependent on the size of the compact being treated, repressing at 30 to 35 tsi, and resintering under the above conditions. In the repressed state a tensile strength of 30,000 psi with an elongation of 10% was obtained in compacts having an average density of 7.69 g./cc. (approximately 10% porosity); resintering increased the elongation to 20% and reduced the tensile strength to 25,000 psi, without significant change in density. It is quite obvious from these figures that the powder and techniques used by Lennox do not constitute an improvement over the earlier art as practiced by Kelton, and it appears doubtful that the technical results recorded are of sufficient interest to warrant the costly double-treating procedure suggested.

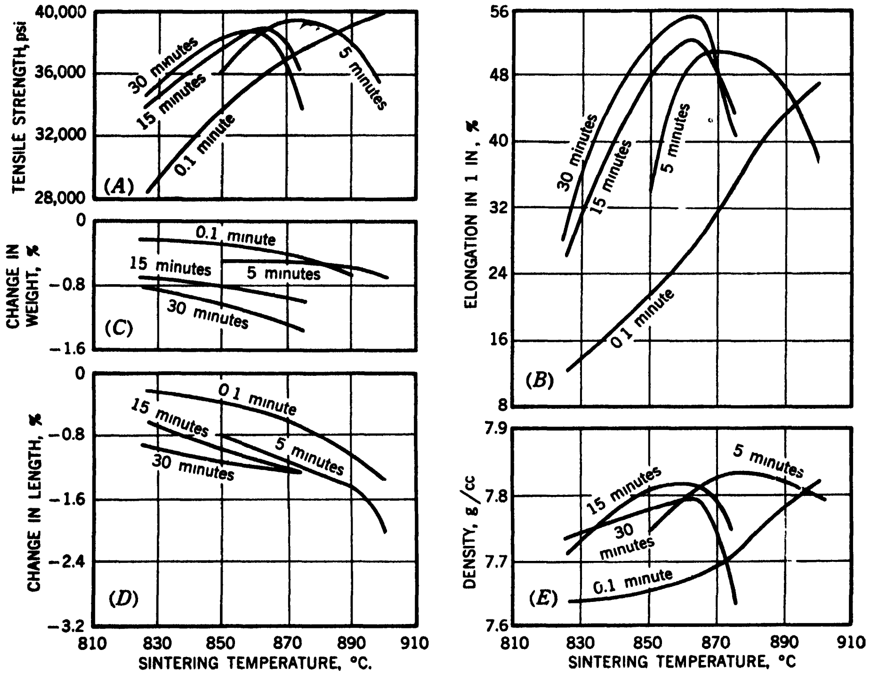

Fig. 525. Effect of sintering temperature on the tensile properties, weight and size changes, and density of 70–30 brass powder compacts prepared from atomized alloy powder containing 0.3% phosphorus. Specimens were pressed at 50 tsi and sintered in hydrogen at temperature for time indicated.[43]

Only when resorting to hot-pressing have results comparable to those reported by Kelton[39] been obtained by other investigators. The author's[38] data on hot-pressed brass compacts are given in Figure 164 (Volume I, Chapter XII). Jones[45] found that mixed elemental powders yield better results than alloy powders, but this could not be confirmed by the author when comparing mixed powders with powders prealloyed by diffusion sintering. The best properties found by Jones were 18,000 psi yield point, 37,000 psi tensile strength, and 34% elongation for 80–20 brass compacts hot-pressed at 900°C. (1650°F.). Additional data are given in Table 45 (Volume I, Chapter XII).

TABLE 199

Physical Properties of Sintered Brass Powder Compacts (Kelton[39,43])

Properties	70-30 powder				90–10 powder			
	Without phosphorus		With phosphorus		Without phosphorus		With phosphorus	
Compacting pressure, tsi	30	50	30	50	30	50	30	50
Sintering temperature, °C.	885	885	850	850	920	890	910	880
°F.	1625	1625	1560	1560	1690	1635	1670	1615
Yield point, psi (0.2% offset)	15,900	18,800	8600	8800	11,500	14,100	9200	10,300
Elastic modulus, 10^6 psi	13.2	16.3	11.9	13.9	16.0	16.7	11.4	12.9
Shear strength, psi	28,800	32,300	25,600	26,000	24,800	25,000	23,500	24,500
Tensile strength, psi	29,100	35,200	32,000	34,900	26,100	28,400	27,400	29,700
Tensile elongation, % (1 in.)	11	13	43	50	15	13	31	34
Impact strength, ft.-lb. (1/4 × 1/4-in. bars)	11	13	22[a]	25[a]	11	13	25[a]	27[a]
Brinell hardness (250 kg.)	43	51	35	39	38	49	35	41
Electric conductivity, 10^{-2} megmhos per cc. (25 °C., 77 °F.)	12.58	14.32	9.78	10.84	18.91	20.32	8.16	9.39
Thermal expansion, 10^{-6}, per °C.								
25–100 °C. (77–212° F.)	17.7	18.2	18.4	18.0	17.1	16.9	17.1	17.4
25–300 °C. (77–572° F.)	19.3	19.1	19.6	19.5	17.9	18.0	18.4	18.0
Compressive strength (10% compression), psi	38,300	43,200	29,500	31,600	34,600	39,000	31,400	32,700
Density, g./cc.	—	7.92	—	7.94	—	8.36	—	7.99
Per cent of true density[b]	—	97.0	—	97.2	—	95.0	—	90.8

[a] Pulled through without fracture.

[b] Density of bulk 70–30 brass taken as 8.17 g./cc.; density of bulk 90–10 brass taken as 8.80 g./cc.

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[45] W. D. Jones, *Metal Ind. London*, *56*, 69, 225 (1940).

The drastic increase in hardness observed in copper compacts hot-pressed at low temperatures and high pressures has also been found in hot-pressed brass compacts, with some of the values recorded exceeding by a considerable amount the hardness values customarily found for severely work-hardened brass.[38]

BRONZES

The characteristics and properties of copper–tin alloys prepared by sintering as well as hot-pressing have been studied by Jones[45] and

TABLE 200

Densities of Sintered and Hot-Pressed Bronze Compacts

	Density, g./cc.					
	Compacted at 50 tsi and sintered at 800°C. (1470°F.)		Hot-pressed at 50 tsi at			
			300°C. (570°F.)		500°C. (930°F.)	
Composition	Mixed powder	Prealloyed powder	Mixed powder	Prealloyed powder	Mixed powder	Prealloyed powder
95–5	7.4	8.25	8.85	8.45	8.9	8.25
90–10	7.85	8.5	8 8	8.65	8.85	8.6
85–15	8.0	8.45	8.8	8.25	8.85	8.5
80–20	6.9	8.0	8.85	8.45	8.83	8.0

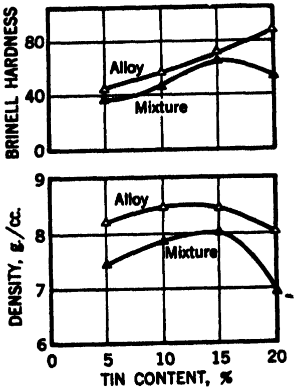

Fig. 526. Effect of composition on the density and Brinell hardness of sintered bronze compacts prepared from copper and tin powder mixtures and from prealloyed bronze powders. Specimens were pressed at 50 tsi and sintered in hydrogen for 1 hour at 800°C. (1470°F.).

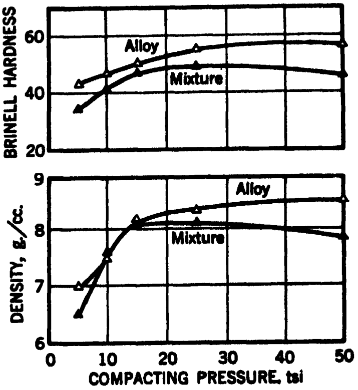

Fig. 527. Effect of increasing compacting pressure on the density and Brinell hardness of sintered 90–10 bronze compacts prepared from copper and tin powder mixtures and from prealloyed bronze powders. Specimens were pressed at the pressure indicated and sintered in hydrogen for 1 hour at 800°C. (1470°F.).

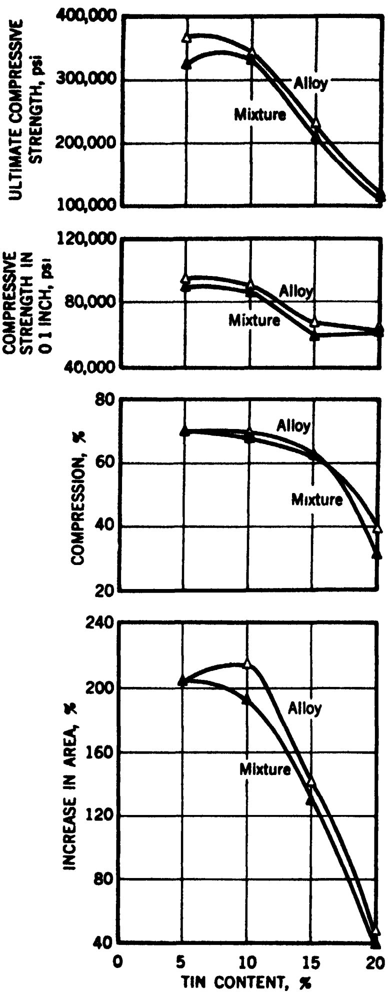

Fig. 528. Effect of composition on the compressive properties of sintered bronze compacts prepared from copper and tin powder mixtures and from prealloyed bronze powders. Specimens were pressed at 50 tsi and sintered in hydrogen for 1 hour at 800°C. (1470°F.).

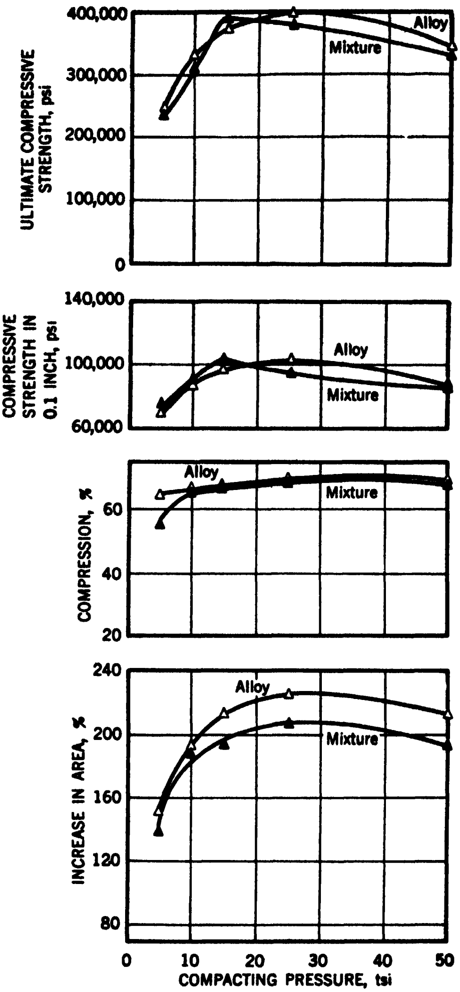

Fig. 529. Effect of increasing compacting pressure on the compressive properties of sintered 90–10 bronze compacts prepared from copper and tin powder mixtures and from prealloyed bronze powders. Specimens were pressed at the pressure indicated and sintered in hydrogen for 1 hour at 800°C. (1470°F.).

Goetzel,[46] who used mixed metal powders and fusion-alloyed or diffusion-sintered prealloyed powders, respectively. Data obtained with hot-pressed

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[46] C. G. Goetzel, *Trans. Am. Inst. Mining Met. Engrs., 161,* 580 (1945).

bronze compacts of various copper–tin ratios are given in Figure 165 and Table 45 (Volume I, Chapter XII). According to Jones, bronze compacts containing from 5 to 9% Sn, hot-pressed from mixed powders at 800°C. (1470°F.), can reach a tensile strength in excess of 50,000 psi and elongations up to 75%!

Cold-pressed and sintered bronzes show considerably lower hardness and tensile properties because of their lower density. A comparison between the densities of hot-pressed and sintered bronze compacts of different copper–tin ratios is made in Table 200 for both mixed powders and alloy powders diffusion sintered at 550°C. (1020°F.) for 1 hour. Figure 526 shows graphically the effect of the tin content on density and hardness of compacts sintered at 800°C. (1470°F.) in hydrogen for 1 hour. In Figure 527 the same properties are shown as a function of the initial molding pressures for 90–10 Cu–Sn compacts. The effect of rising tin content on the compressive properties is given graphically in Figure 528 and the same properties are plotted against initial pressure for 90–10 Cu–Sn compacts in Figure 529.

An investigation concerned with a sintered 90–10 Cu–Sn bronze has recently been reported by Lennox.[44] When employing a mixture of the powdered ingredients of commercial grades, a maximum density (in the order of 73% of the theoretical value) was obtained for a pressure of 30 tsi and a sintering temperature of 800°C. (1470°F.). This comparatively poor result was attributed to gross gas evolution as evidenced by marked expansion of the compacts during sintering. Partial alloying of the powder mixture by heating in a rotating furnace in dissociated ammonia at 250°C. (480°F.) and 650°C. (1200°F.) led to reduced densities of the pressed as well as the sintered compacts, but also to less pronounced size changes during sintering. "Fully" alloyed (atomized) powders were found to be entirely unsuitable owing to the high resilience of the particles. Best results were obtained with fine-grade powders, such as a copper powder of —240-mesh size with 70% passing through a 325-mesh screen, and a —325-mesh tin powder. The flow characteristics were improved to some extent by partial alloying or by mixing with a 90–10 or 60–40 alloy powder, but loss in density and changes in size during sintering could not be eliminated entirely. The mixture of the fine-grade elemental powders was found most suitable for the production of high-density bronze parts; compacts pressed at 30 tsi, sintered at 800°C. (1470°F.) for 30 minutes, repressed at 30 tsi, and resintered under the above conditions displayed a tensile strength of 24,000 psi, an elongation of 10%, a Brinell hardness of 61, and a density averaging 7.91 g./cc. These properties are considerably below values previously recorded for hot-pressed material by Jones.[45]

The properties of commercial copper–tin bronzes with densities ranging between 77 and 93% of theoretical are given in Table 201. The comparatively good tensile and compressive strengths, coupled with ductility and fairly high hardness, have been the reasons for the wide use of sintered bronzes for machine part applications requiring the corrosion-resistant properties of nonferrous alloys.

TABLE 201

Physical Properties of Commercial Sintered Bronze Compacts (Schwarzkopf[46a])

Material	Density, g./cc.	Ultimate strength		Elongation, %	Brinell hardness
		Tensile, psi	Compressive, psi		
90–10 heavy duty alloy[a].......	6.9	18,000	200,000	10	30
90–10 maximum duty alloy[a]...	8.3	40,000	230,000	20	60
95–5 alloy[b]........	8.0–8 1	30,000–40,000	—	5–10	65–100

[a] "Oilite" Bronze, products of Amplex Division, Chrysler Corp., Detroit, Mich.

[b] "Durex" Bronze, products of Moraine Products Division, General Motors Corp., Dayton, Ohio.

CUPRO-NICKELS

Sintered binary copper–nickel alloys have been investigated by Rhines and coworkers[47,48] in a study of the role of diffusion that takes place in the sintering of alloy compacts from mixed metal powders. The effect of an incompletely diffused structure on the physical properties has been described in Volume I, Chapter XIV, in the course of a more complete discussion of the principles of sintering, and values for hardness, tensile strength, elongation, and electrical resistivity as affected by the sintering time have been shown in Figure 223 (for additional treatment of the theoretical aspects of this subject see also Chapter XXXV).

The author, in an unpublished investigation, has extended the sintering and hot-pressing experiments reported previously for copper, brasses, and bronzes to include several cupro-nickel compositions. The equipment used in this work has been described in Volume I, Chapter XIII. In Tables 202 to 205 the test results are given for compositions containing 10, 20, 40, and 67% Ni, respectively. The investigation embraced two different raw materials, namely, mechanical mixtures of the two elemental powders in the above-indicated ratios, and prealloyed powders produced by subjecting part of the mixtures to a diffusion-sintering treatment in hydrogen atmosphere at 800°C. (1470°F.) for 2 hours. One series of

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[46a] P. Schwarzkopf, *Powder Metallurgy.* Macmillan, New York, 1947, p. 146.

[47] F. N. Rhines, in *Symposium on Powder Metallurgy.* ASTM, Philadelphia, Pa., 1943, p. 23.

[48] F. N. Rhines and R. A. Colton, in J. Wulff, *Powder Metallurgy.* Am. Soc. Metals, Cleveland, 1942, p. 67.

TABLE 202

Density, Hardness, and Compressive Properties of Sintered and Hot-Pressed 90–10 Cu–Ni Compacts

Process	Pressure, tsi	Density, g./cc.	Brinell hardness	Compressive strength, psi		Total compression, %	Increase in area, %
				Maximum stress	For 0.1 in. compression		
POWDER MIXTURE[a]							
Sintered at 800°C. (1470°F.) for 60 minutes	5	5.15	11.9	39,150	23,000	51.0	62.2
	10	6.15	15.6	65,200	50,800	48.2	65.3
	15	6.855	22.5	112,900	53,900	55.8	98.1
	25	7.575	33.9	138,200	63,000	54.8	104.6
	50	7.39	32.5	162,600	75,000	63.9	142.1
Sintered at 1000°C. (1830°F.) for 60 minutes	5	5.545	13.3	43,600	27,700	51.2	75.7
	10	6.355	16.9	66,500	53,300	48.5	79.4
	15	6.94	21.5	123,100	57,700	59.6	114.5
	25	7.60	33.0	195,100	69,600	63.9	154.4
	50	7.425	29.5	212,200	77,000	67.2	152.1
Hot-pressed at 400°C. (750°F.) for 10[b] + 1[c] minutes	5	6.57	42.75	35,700	—	22.9	9.31
	10	7.02	53.5	51,100	39,300	30.0	21.13
	15	7.525	62.5	71,300	51,100	38.1	54.1
	25	8.205	87.0	99,400	49,700	42.6	73.2
	50	8.77	110.75	114,600	47,500	44.2	83.5
Hot-pressed at 600°C. (1110°F.) for 10[b] + 1[c] minutes	5	7.51	56.5	108,400	55,500	50.8	92.1
	10	7.90	63.0	165,200	75,500	60.1	138.8
	15	8.44	74.25	222,300	88,300	65.1	191.5
	25	8.84	85.65	310,500	104,900	68.5	218.0
	50	8.90	78.25	360,100	111,100	67.5	226.0
ALLOY POWDER[d]							
Sintered at 800°C. (1470°F.) for 60 minutes	5	5.05	6.45	23,080	19,700	44.4	49.1
	10	6.095	13.50	63,100	49,700	47.4	62.0
	15	6.785	18.50	147,500	66,000	58.5	128.1
	25	7.565	31.0	184,000	73,600	62.2	151.4
	50	8.355	40.25	296,200	97,700	70.7	248.0
Sintered at 1000°C. (1830°F.) for 60 minutes	5	5.105	6.7	29,300	20,200	46.7	66.2
	10	6.205	13.0	76,500	56,000	51.8	76.4
	15	6.80	17.6	150,100	63,000	57.2	101.6
	25	7.53	24.6	194,600	75,700	62.1	142.3
	50	8.14	36.0	362,300	100,100	73.8	275.0
Hot-pressed at 400°C. (750°F.) for 10[b] + 1[c] minutes	5	6.625	34.75	19,150	—	6.38	9.31
	10	7.22	48.0	33,375	—	19.35	18.0
	15	7.625	58.5	43,500	—	11.35	20.8
	25	8.245	84.75	62,700	—	25.5	27.99
	50	8.81	112.75	81,800	—	25.6	36.99
Hot-pressed at 600°C. (1110°F.) for 10[b] + 1[c] minutes	5	7.235	44.25	57,900	47,000	32.4	36.99
	10	7.74	55.5	99,600	53,000	49.4	84.1
	15	8.265	70.75	153,100	69,300	57.7	126.3
	25	8.725	85.0	182,200	73,700	62.7	187.2
	50	8.985	96.75	310,500	99,000	70.6	254.5

[a] Electrolytic copper and nickel powders of 100-mesh grade, with 35% −325-mesh fraction.

[b] Time of drawing.

[c] Time at pressure.

[d] Powder mixture diffusion-alloyed by heating at 800°C. (1470°F.) for 2 hours in hydrogen; pulverized and annealed at 600°C. (1110°F.) for 1/2 hour in hydrogen.

TABLE 203

Density, Hardness, and Compressive Properties of Sintered and Hot-Pressed 80–20 Cu–Ni Compacts

Process	Pressure, tsi	Density, g./cc.	Brinell hardness	Compressive strength, psi: Maximum stress	Compressive strength, psi: For 0.1 in compression	Total compression, %	Increase in area, %
			Powder Mixture[a]				
Sintered at 800 °C. (1470 °F.) for 60 minutes	5	5.09	11.05	39,200	23,300	48.9	60.7
	10	6.00	19.0	66,100	49,900	46.3	58.0
	15	6.455	22.25	87,900	55,000	49.2	72.4
	25	7.24	33.75	147,600	63,900	56.1	107.8
	50	7.50	38.75	182,200	77,300	60.9	128.2
Sintered at 1000° C. (1830 °F.) for 60 minutes	5	5.36	10.6	41,600	25,500	49.3	75.5
	10	6.10	14.9	67,600	50,500	53.3	84.25
	15	6.52	17.7	90,600	57,000	52.8	85.9
	25	7.285	31.75	149,900	65,600	58.3	115.9
	50	7.435	35.25	253,800	88,800	69.2	195.3
Hot-pressed at 400 °C. (750 °F.) for 10[b] + 1[c] minutes	5	6.57	45.75	33,200	—	22.3	19.24
	10	6.815	55.0	35,150	—	23.4	24.58
	15	7.44	68.0	68,800	52,200	30.8	38.2
	25	8.045	86.0	98,900	57,100	40.3	64.6
	50	8.67	113.0	112,900	62,000	38.5	64.6
Hot-pressed at 600 °C. (1110° F.) for 10[b] + 1[c] minutes	5	7.385	52.5	100,300	55,000	69.1	129.2
	10	7.86	66.0	148,400	66,000	54.8	112.0
	15	8.19	73.25	194,800	79,900	62.2	170.1
	25	8.555	80.5	300,200	100,500	66.6	210.0
	50	8.935	90.0	318,100	107,700	67.4	210.5
			Alloy Powder[d]				
Sintered at 800 °C. (1470 °F.) for 60 minutes	5	4.88	—	20,200	14,400	42.8	—
	10	5.88	13.15	58,400	46,800	48.2	66.9
	15	6.515	18.15	95,600	54,000	53.5	83.5
	25	7.35	31.5	151,900	70,000	58.5	120.5
	50	7.63	42.75	233,400	87,000	62.9	160.7
Sintered at 1000° C. (1830 °F.) for 60 minutes	5	4.95	7.8	26,200	17,100	46.6	—
	10	5.865	12.6	65,100	48,200	50.9	71.0
	15	6.505	16.7	106,000	56,000	56.6	96.4
	25	7.365	31.75	194,100	81,100	64.8	145.7
	50	7.61	42.50	319,000	101,100	67.9	198.2
Hot-pressed at 400 °C. (750 °F.) for 10[b] + 1[c] minutes	5	6.435	31.75	15,500	—	3.75	8.07
	10	6.945	40.5	22,450	—	4.44	9.31
	15	7.475	51.75	29,800	—	5.41	10.87
	25	8.15	75.75	45,600	—	8.61	13.63
	50	8.555	109.0	70,400	—	10.55	15.21
Hot-pressed at 600 °C. (1110° F.) for 10[b] + 1[c] minutes	5	7.00	39.75	56,000	36,000	40.4	48.2
	10	7.445	47.75	76,400	56,000	40.8	86.9
	15	7.92	61.0	165,000	75,300	64.8	132.6
	25	8.51	86.0	163,900	73,500	63.4	143.4
	50	8.585	113.5	130,800	70,700	45.9	95.6

[a] Electrolytic copper and nickel powders of 100-mesh grade, with 35% −325-mesh fraction.

[b] Time of drawing.

[c] Time at pressure.

[d] Powder mixture diffusion-alloyed by heating at 800 °C. (1470 °F.) for 2 hours in hydrogen; pulverized and annealed at 600 °C. (1110 °F.) for 1/2 hour in hydrogen.

TABLE 204
Density, Hardness, and Compressive Properties of Sintered and Hot-Pressed 60–40 Cu–Ni Compacts

Process	Pressure, tsi	Density, g./cc.	Brinell hardness	Compressive strength, psi: Maximum stress	Compressive strength, psi: For 0.1 in. compression	Total compression, %	Increase in area, %
Powder Mixture[a]							
Sintered at 800°C. (1470°F.) for 60 minutes	5	4.795	11.55	24,050	14,400	44.5	55.4
	10	5.625	17.05	46,700	36,000	46.1	54.3
	15	6.02	22.25	86,500	56,600	50.8	70.5
	25	6.99	35.75	128,900	64,600	53.7	85.3
	50	7.68	47.5	183,100	75,700	54.0	108.6
Sintered at 1000° C. (1830°F.) for 60 minutes	5	4.825	10.0	28,200	16,000	46.6	63.4
	10	5.425	12.55	51,800	41,800	49.5	71.9
	15	5.92	15.75	81,500	53,000	54.8	97.6
	25	6.715	31.0	134,100	67,800	54.4	95.2
	50	7.48	42.5	232,100	87,000	62.0	138.5
Hot-pressed at 400°C. (750°F.) for 10[b] + 1[c] minutes	5	6.20	41.5	18,600	—	4.28	4.46
	10	6.575	59.25	27,310	—	9.52	10.87
	15	7.05	61.50	40,400	—	16.6	16.13
	25	7.67	79.25	63,200	—	16.3	21.75
	50	8.12	117.0	100,800	—	21.73	28.24
Hot-pressed at 600°C. (1110° F.) for 10[b] + 1[c] minutes	5	6.82	49.0	47,000	37,000	30.0	40.7
	10	6.935	59.5	77,400	50,000	36.31	51.25
	15	7.655	76.75	116,600	60,600	49.7	92.1
	25	8.335	92.25	158,600	72,000	56.0	142.4
	50	8.865	101.25	165,000	75,500	49.1	101.6
Alloy Powder[d]							
Sintered at 800°C. (1470°F.) for 60 minutes	5	4.785	—	9,600	—	25.79	—
	10	5.56	12.7	31,210	18,600	34.5	—
	15	6.025	16.05	51,400	36,600	40.8	—
	25	7.035	26.85	127,200	57,900	49.8	83.5
	50	7.64	52.25	172,000	76,000	53.7	110.4
Sintered at 1000° C. (1830°F.) for 60 minutes	5	4.445	4.2	14,000	—	34.95	—
	10	5.375	11.45	43,600	34,600	43.8	49.5
	15	5.86	14.9	63,500	48,800	44.9	57.2
	25	6.815	32.5	189,800	83,000	59.7	115.2
	50	7.68	46.5	227,100	87,500	67.0	168.7
Hot-pressed at 400°C. (750°F.) for 10[b] + 1[c] minutes	5	6.21	28.75	14,900	—	2.78	4.35
	10	6.56	39.0	19,560	—	3.60	6.84
	15	7.07	51.75	27,940	—	4.11	8.08
	25	7.695	71.0	42,100	—	6.62	11.49
	50	7.77	114.25	64,500	—	8.82	13.65
Hot-pressed at 600°C. (1110° F.) for 10[b] + 1[c] minutes	5	6.40	33.75	24,460	—	19.92	19.26
	10	6.875	44.0	43,000	—	24.79	34.8
	15	7.43	59.0	65,000	—	28.83	40.7
	25	7.97	77.25	102,200	68,600	37.49	57.8
	50	8.70	125.0	126,900	70,700	39.58	80.1

[a] Electrolytic copper and nickel powders of 100-mesh grade, with 35% −325-mesh fraction.

[b] Time of drawing.

[c] Time at pressure.

[d] Powder mixture diffusion-alloyed by heating at 800°C. (1470°F.) for 2 hours in hydrogen; pulverized and annealed at 600°C. (1110°F.) for 1/2 hour in hydrogen.

TABLE 205

Density, Hardness, and Compressive Properties of Sintered and Hot-Pressed 33–67 Cu–Ni Compacts

				Compressive strength, psi			
Process	Pressure, tsi	Density, g./cc.	Brinell hardness	Maximum stress	For 0.1 in. compression	Total compression, %	Increase in area, %
POWDER MIXTURE[a]							
Sintered at 800°C. (1470°F.) for 60 minutes	5	4.69	10.0	15,830	10,100	33.8	—
	10	5.165	13.75	28,350	18,800	33.85	39.1
	15	5.525	19.0	47,400	27,700	37.3	42.0
	25	6.14	31.0	85,500	55,500	45.3	59.4
	50	6.89	41.5	181,500	81,500	54.25	96.5
Sintered at 1000°C. (1830°F.) for 60 minutes	5	4.53	8.25	20,300	12,500	37.7	47.1
	10	4.91	10.85	29,500	19,300	38.99	48.75
	15	5.265	13.3	49,050	33,300	44.25	64.4
	25	5.775	18.8	87,800	57,500	52.4	85.9
	50	6.60	35.5	132,000	66,000	50.3	74.4
Hot-pressed at 400°C. (750°F.) for 10[b] + 1[c] minutes	5	5.83	36.75	13,900	—	1.58	1.55
	10	6.09	43.5	18,610	—	3.10	3.73
	15	6.545	54.75	27,590	—	2.97	8.08
	25	7.19	75.25	54,500	—	17.2	14.9
	50	8.10	113.25	97,400	—	16.67	19.24
Hot-pressed at 600°C. (1110°F.) for 10[b] + 1[c] minutes	5	6.515	45.5	34,590	—	17.89	19.24
	10	6.905	56.0	47,000	—	21.53	24.21
	15	7.38	69.25	66,100	—	23.81	27.31
	25	7.96	90.5	99,600	66,600	30.12	41.6
	50	8.635	120.0	137,800	77,000	37.4	64.0
ALLOY POWDER[d]							
Sintered at 800°C. (1470°F.) for 60 minutes	5	4.545	—	7,620	—	27.9	—
	10	5.295	10.95	18,500	—	24.7	—
	15	5.73	16.30	34,100	—	28.7	—
	25	6.72	45.5	50,300	40,000	30.6	29.18
	50	7.585	50.25	162,000	72,000	52.2	95.5
Sintered at 1000°C. (1830°F.) for 60 minutes	5	4.485	—	13,100	10,100	30.0	—
	10	5.135	12.15	32,700	18,600	37.1	—
	15	5.54	13.35	69,900	49,900	44.9	—
	25	6.59	33.0	187,300	77,300	61.8	186.8
	50	7.385	45.25	276,600	86,000	63.6	156.4
Hot-pressed at 400°C. (750°F.) for 10[b] + 1[c] minutes	5	5.925	18.7	13,600	—	3.54	4.66
	10	6.27	34.25	18,310	—	4.70	6.21
	15	6.75	44.75	25,500	—	2.71	8.08
	25	7.315	63.75	39,380	—	4.05	10.56
	50	8.135	103.75	67,300	—	7.39	12.71
Hot-pressed at 600°C. (1110°F.) for 10[b] + 1[c] minutes	5	6.135	32.75	19,320	—	12.93	14.9
	10	6.515	41.0	29,870	—	21.25	15.82
	15	6.96	50.5	33,200	—	8.90	15.82
	25	7.465	67.75	59,400	—	22.25	24.55
	50	8.255	10.75	91,500	—	17.3	31.69

[a] Electrolytic copper and nickel powders of 100-mesh grade with 35% −325-mesh fraction.

[b] Time of drawing.

[c] Time at pressure.

[d] Powder mixture diffusion-alloyed by heating at 800°C. (1470°F.) for 2 hours in hydrogen; pulverized and annealed at 600°C. (1110°F.) for 1/2 hour in hydrogen.

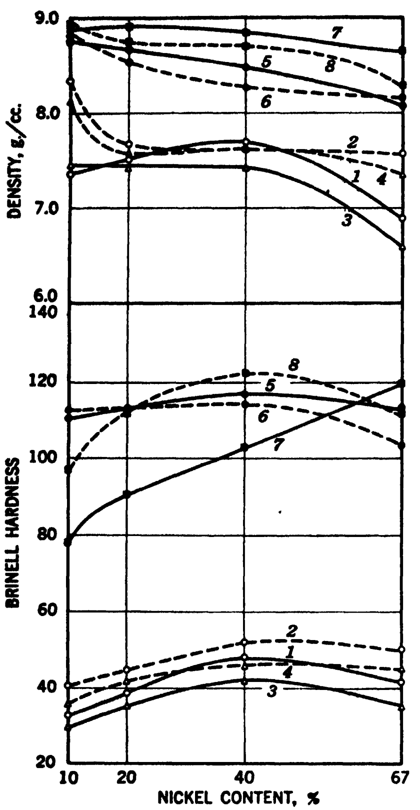

Fig. 530. Effect of composition on the density and Brinell hardness of sintered and hot-pressed cupro-nickel compacts prepared from copper and nickel powder mixtures and from prealloyed powders. Sintered specimens were pressed at 50 tsi and sintered in hydrogen for 1 hour at 800°C. (1470°F.) and 1000°C. (1830°F.), respectively; hot-pressed specimens were pressed at 50 tsi at 400°C. (750°F.) and 600°C. (1110°F.), respectively, under hydrogen atmosphere.

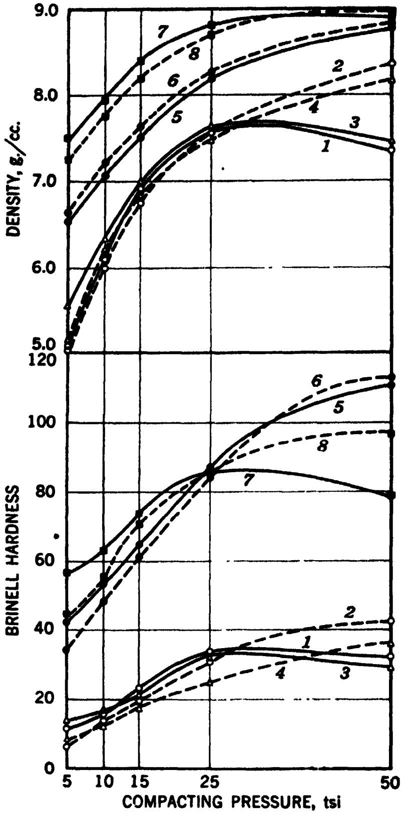

Fig. 531. Effect of increasing compacting pressure on the density and Brinell hardness of sintered and hot-pressed 90–10 cupro-nickel compacts prepared from copper and nickel powder mixtures and from prealloyed powders. Sintered specimens were pressed at the pressure indicated and sintered in hydrogen for 1 hour at 800°C. (1470°F.) and 1000°C. (1830°F.), respectively; hot-pressed specimens were pressed at the pressure indicated at 400°C. (750°F.) and 600°C. (1110°F.), respectively, under hydrogen atmosphere.

Curve (*1*) Powder mixture; compact sintered at 800°C. (1470°F.). (*2*) Alloy powder; compact sintered at 800°C. (1470°F.). (*3*) Powder mixture; compact sintered at 1000°C. (1830°F.). (*4*) Alloy powder; compact sintered at 1000°C. (1830°F.). (*5*) Powder mixture; compact hot-pressed at 400°C. (750°F.). (*6*) Alloy powder; compact hot-pressed at 400°C. (750°F.). (*7*) Powder mixture; compact hot-pressed at 600°C. (1110°F.). (*8*) Alloy powder; compact hot-pressed at 600°C. (1110°F.).

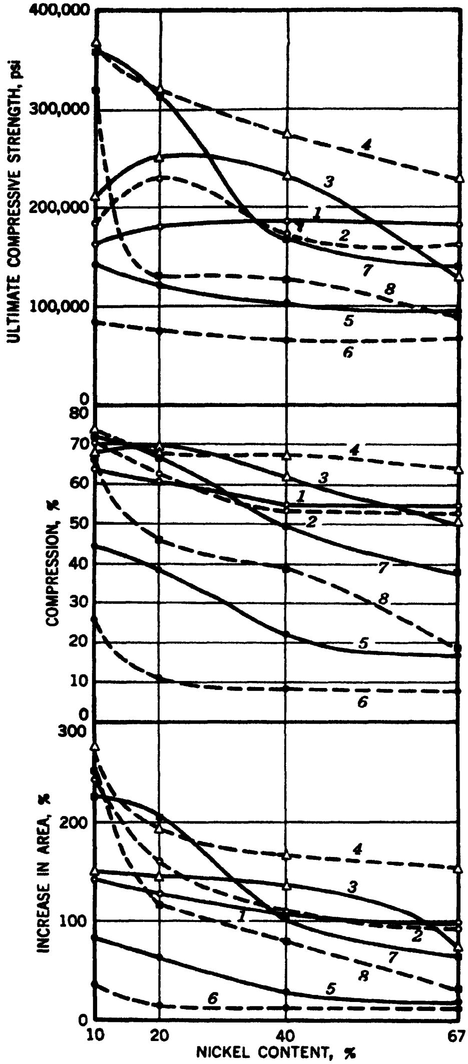

Fig. 532. Effect of composition on the compressive properties of sintered and hot-pressed cupro-nickel compacts prepared from copper and nickel powder mixtures and from prealloyed powders. Sintered specimens were pressed at 50 tsi and sintered in hydrogen for 1 hour at 800°C. (1470°F.) and 1000°C. (1830°F.), respectively; hot-pressed specimens were pressed at 50 tsi at 400°C. (750°F.) and 600°C. (1110°F.), respectively, under hydrogen atmosphere. See Figures 530 and 531 for identification of curves.

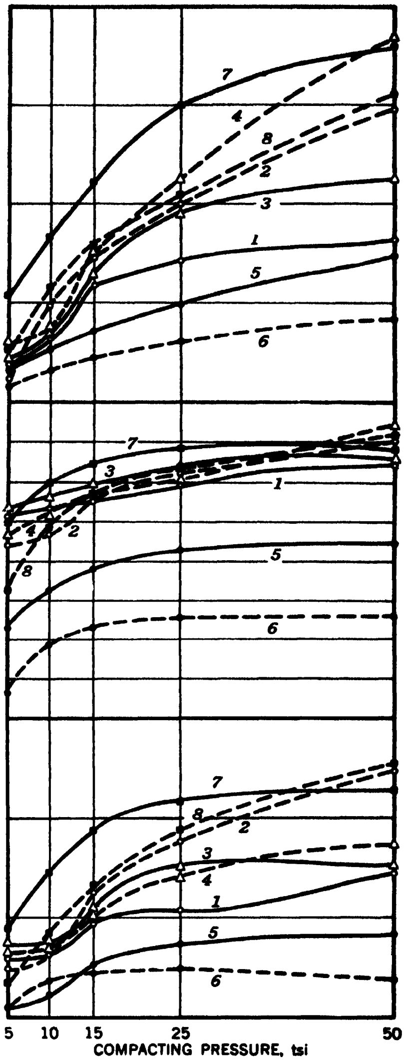

Fig. 533. Effect of increasing compacting pressure on the compressive properties of sintered and hot-pressed 90–10 cupro-nickel compacts prepared from copper and nickel powder mixtures and from prealloyed powders. Sintered specimens were pressed at the pressure indicated and sintered in hydrogen for 1 hour at 800°C. (1470°F.) and 1000°C. (1830°F.), respectively; hot-pressed specimens were pressed at the pressure indicated at 400°C. (750°F.) and 600°C. (1110°F.), respectively, under hydrogen atmosphere. See Figures 530 and 531 for

compacts was produced from these materials by cold-pressing followed by sintering for 1 hour in hydrogen at 800 and 1000°C. (1470 and 1830°F.), respectively; the other by hot-pressing in hydrogen atmosphere at 400 and 600°C. (750 and 1110°F.), respectively. In Figure 530 the effect of increasing nickel content is shown on the density and hardness of compacts pressed at 50 tsi, while in Figure 531 the same properties are shown as a function of the initial pressure for compacts of the 90–10 composition. Figure 532 shows graphically the effect of change in composition on the compressive properties of compacts compressed at 50 tsi, and Figure 533 the effect of the initial pressure on the compressive properties of compacts of the 90–10 composition. The beneficial effect on these properties of an increased molding pressure is in agreement with the results obtained with sintered brasses and bronzes; however, no apparent benefits are derived from employing the prealloyed powders. The hot-pressed compacts are generally superior as far as density and hardness are concerned; their strength and ductility, as indicated by the compression tests, are comparable with those of the sintered compacts only in the case of the materials hot pressed at the higher temperatures from the powder mixtures (the hot-pressed prealloyed powder compacts gave, in general, inferior results in the compression test).

The properties of precipitation-hardenable cupro-nickel alloys have been investigated by Pratt[49] who reports a hardness of Rockwell B-80 for a 70–25–5 Cu–Ni–Sn alloy prepared from elemental powders and fully precipitation-treated. The tensile strength of this material reaches 65,000 psi, but the elongation remains low (about 2%), though noticeable. Cupro-nickel alloys, and, in particular, the tin-containing precipitation-hardenable composition just mentioned, are especially resistant to corrosion from salt spray and sea water, which suggests their field of use in maritime machinery.

NICKEL–SILVER

An outgrowth of brass powder metallurgy has been the recent development of nickel–silver parts.[49a] These parts are generally produced from a fusion-alloyed and atomized powder analyzing 18% each of nickel and zinc, balance copper. Their processing and properties resemble those established for parts from beta-brass powders (35% Zn and above). An advantage is that the sintering range of the nickel–silver compacts is somewhat wider (940–980°C.; 1725–1800°F.). With regard to properties, nickel–silver compares well with beta-brass in tensile strength and elongation (44,000 psi and 10%, respectively), while its hardness is even

[49] W. N. Pratt, *Powder Met. Bull., 1,* No. 3, 43 (1946).

[49a] H. R. Clauser, *Material and Methods, 30,* No. 3, 85 (1949).

slightly higher (88 Rockwell "H"). Also significant is the fact that nickel-silver parts are more corrosion resistant than brass parts, and are also more easily polished.

OTHER COPPER ALLOYS

Several other sintered copper-base alloys have been investigated with a special view of improved properties through precipitation-hardening. Hensel and coworkers[50] [52] have studied ternary copper alloys containing nickel and phosphorus, nickel and tin, nickel and beryllium, cobalt and beryllium, cobalt and phosphorus, chromium and phosphorus, manganese and phosphorus, and also quaternary alloys containing nickel, phosphorus, and silicon, the latter added in the form of a prealloyed nickel silicide hardener. Very good physical and electrical properties (up to 78,000 psi tensile strength, or 33% of I.A.C.S. conductivity) are obtainable with precipitation-hardened compositions containing chromium, cobalt and beryllium, or nickel and beryllium. Some of the physical properties of these alloys are given in Tables 75 and 76 (Volume I, Chapter XIX). The silicide-hardened composition, containing 2.4% Ni, 0.8% Si, 0.3% P, balance Cu, which has been especially recommended for heavy-duty bearings, displayed in the precipitation-hardened condition a hardness of Rockwell B-75 to B-80, a tensile strength up to 61,500 psi with a corresponding elongation of 2.3%, an elastic limit up to 38,000 psi, a fatigue strength up to 17,500 psi, and an electrical conductivity up to 25% I.A.C.S.

Applications

PARTS AND SIMPLE BEARINGS

Practical applications of copper-base powder metallurgy parts have been discussed by H. Chase,[53] with special emphasis placed on structural parts for the machine, electrical, and electronics industries. Bradley[53a] has described a number of machine elements, including clock parts, speed change spur gears, brush holders, and lock bodies from brass powders; and electrical parts, such as fuse washers from brass; and saddles and spark rotors from copper powder.

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[50] F. R. Hensel, E. I. Larsen, and E. F. Swazy, *Trans. Am. Inst. Mining Met. Engrs.*, *166*, 533 (1946).

[51] F. R. Hensel, E. I. Larsen, and E. F. Swazy, *Trans. Am. Inst. Mining Met. Engrs.*, *166*, 548 (1946).

[52] U. S. Pat. 2,393,906.

[53] H. Chase, *Materials and Methods*, *24*, 1439 (1946).

[53a] D. C. Bradley, *Prod. Eng.*, *19*, No. 10, 107 (1948).

Although the experimental data clearly indicate that it is possible to produce compacts of pure copper with physical properties closely approaching those of fused copper products, the required procedures are now too cumbersome to be practicable on a commercial scale. Thus, sintered copper products are used only to a very limited extent in the electrical and electronics industries (see Chapter XXIII), and for specialties, such as watch and clock dials with embossed numerals, as shown in Figure 534.

Fig. 534. Assortment of precision parts from sintered pure copper and 80–20 brass (fastener elements on top left). Clock dial from pure copper has embossed numerals; the small circular part (center) has exceedingly close tolerances. (Courtesy of Falcon Machine and Tool Co., New Jersey Zinc Co., and H. Chase.[58])

Fig. 535. Assortment of precision parts from sintered brass. Some of these parts have been purposely distorted to demonstrate their susceptibility to deformation and abuse. The sharp knife-like edges on the smaller U-shaped parts are a particularly noteworthy molding accomplishment. (Courtesy of Merriman Bros., New Jersey Zinc Co., and H. Chase.[58])

Until very recently, sintered brass has been employed only to a limited extent. The fact that brass can be fabricated readily to intricate shapes by die casting, stamping, deep drawing, or other conventional fabricating methods has been the principal factor retarding the industrial development of the powder metallurgy of brass. Difficulties in processing brass powder compacts, which are caused chiefly by the dezincification effects encountered during the sintering operation, have added weight to the tardy progress made. While it is true that the dezincification can be curbed by the use of alloy powders, these powders offer greater difficulties in compaction. Nevertheless, brass powder parts, today, are competitive with parts from bulk brass which are used in specialized machine part applications, such as shown in Figures 534–536. Some typical applications for sintered brass include clock parts, lock bodies, small clutch mechanisms, fuse washers, brush holders, gears, and, in general, parts, requiring free machining properties and good corrosion resistance.[49a]

Sintered tin bronzes are widely used for machine parts and bearing applications. Varying over a considerable range of densities, they combine fairly high physical characteristics with desirable corrosion-resistant properties. The generally costly fabricating and machining methods necessary for the production of cast or wrought bronze products make the powder method more competitive and practical than in the case of brass parts. Some typical bronze parts are shown in Figures 537–539.

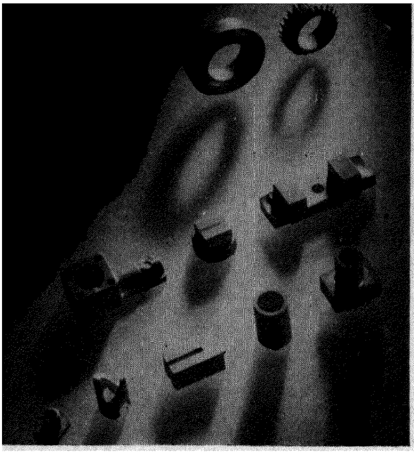

Fig. 536. Precision parts of complicated shape produced from sintered 90–10 brass. (Courtesy of New Jersey Zinc Co. and H. Chase.[58])

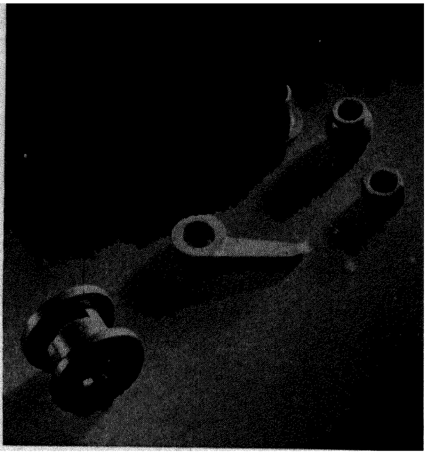

Fig. 537. Assortment of sintered brass and bronze components. Cam-like arm (center) is of brass, all other parts of (porous) bronze; the spool-like component (left, bottom) is made in two sections and then pressed together. (Courtesy of Moraine Products Division, General Motors Corp., New Jersey Zinc Co., and H. Chase.[58])

The industrial applications of sintered cupro-nickel alloys are still few in number, but increased demand for these materials, especially for the tin-containing precipitation-hardenable type, for corrosion resistant components in maritime and chemical industries may be anticipated.

Figure 540 shows an assortment of cupro-nickel parts.

Fig. 538. Machine parts produced from sintered bronze. Parts vary in density and physical properties over a certain range, but are all produced to close dimensional accuracy. (Courtesy of Amplex Division, Chrysler Corp., New Jersey Zinc Co., and H. Chase.[53])

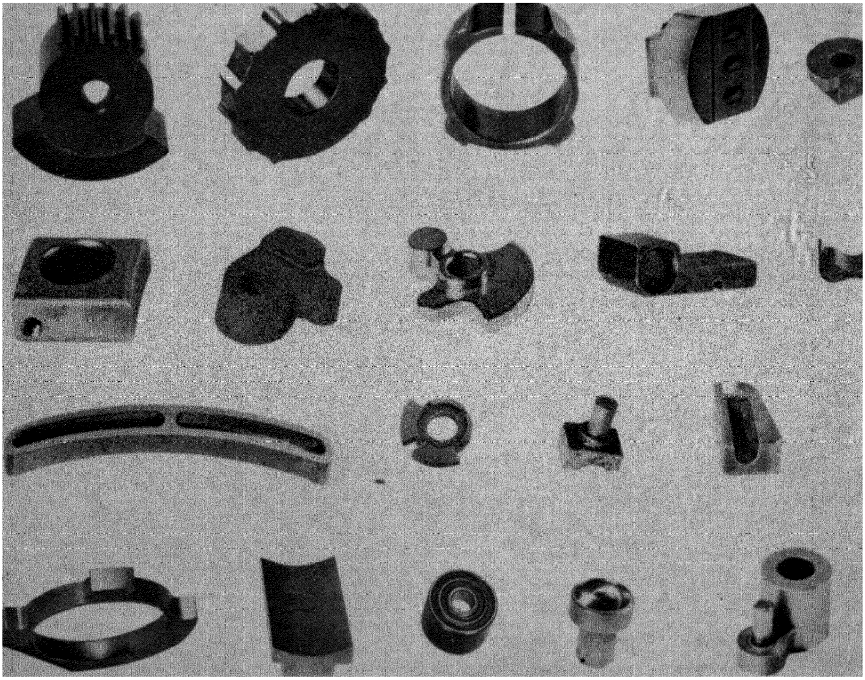

Fig. 539. Assortment of sintered bronze components of complicated shape and high degree of dimensional accuracy. (Courtesy of Amplex Division, Chrysler Corp.)

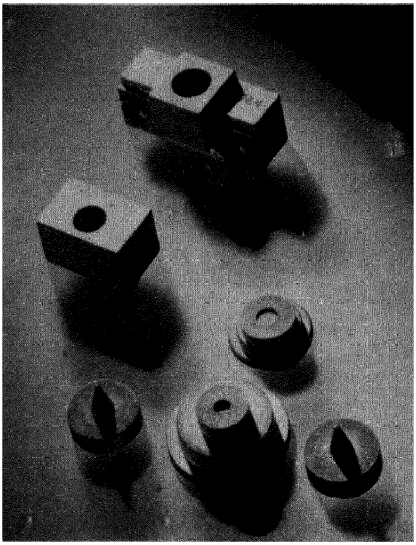

Fig. 540. Electronic components from sintered copper and 70–30 cupronickel. (Courtesy of Merriman Bros., New Jersey Zinc Co., and H. Chase.[53])

In view of the higher cost of nickel–silver powders as compared with the plain brass powders, their use is limited so far to a few specific applications where the superior characteristics of the sintered material are essential. Advance weights for magneto governors, contact lugs, and decorative medallions are typical examples.[49a]

COMPOSITE BEARINGS

Of particular importance are a number of dense copper-base alloy products which are suitable as bearing materials and are generally supported by steel reinforcements.[54] In particular, copper–lead bearings are superior in strength to cast babbitt metal bearings.[55] In a continuous process[56–58] the sintered copper–lead strip is produced by feeding the powder to a thickness of 0.085 in. onto a steel strip $4^3/_4$ in. wide and

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[54] U. S. Pat. 2,404,808.

[55] E. Fetz, *Metals & Alloys, 8,* 257 (1937).

[56] O. W. Ellis, *Trans. Can. Inst. Mining Met., 49,* 447 (1946).

[57] E. R. Darby, *Proc. Third Annual Spring Meeting of Metal Powder Association,* New York, May 27, 1947, p. 52; see also *Can. Metals and Met. Ind., 10,* No. 9, 21 (1947).

[58] Anonymous, *Autom. Inds., 97,* No. 7, 46 (1947).

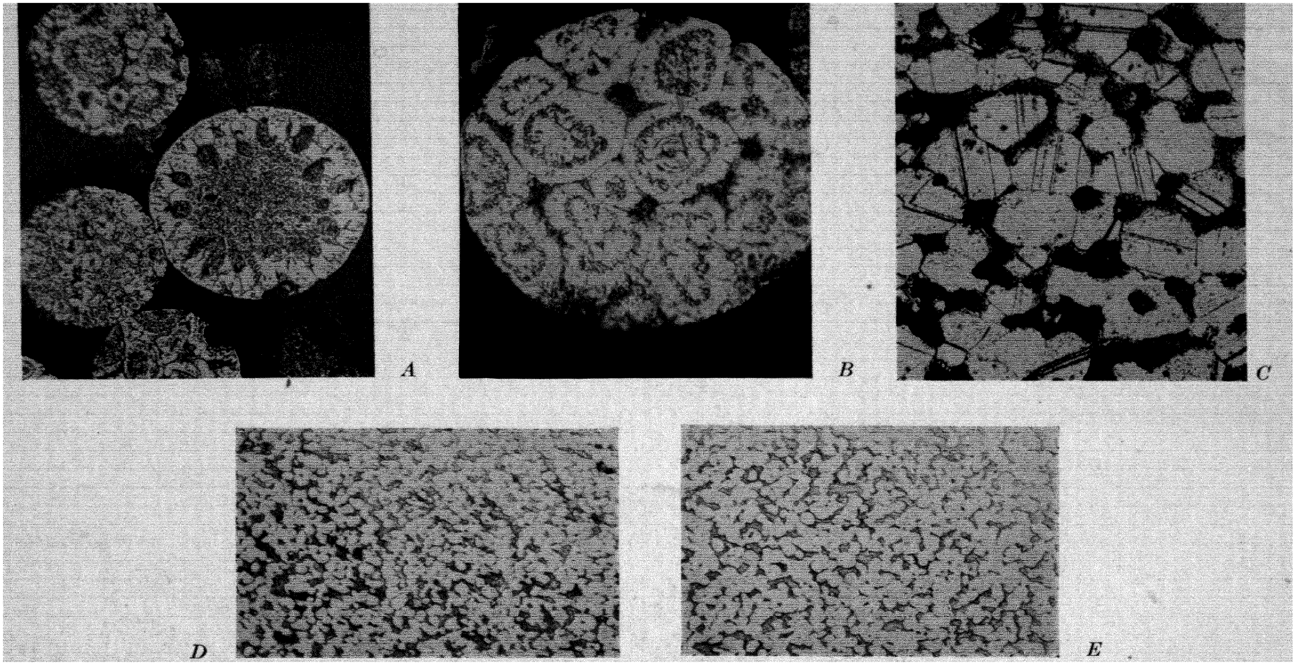

Fig. 541. Microstructure of copper–lead powder particles and sintered bearing metals. *A*, sections (×300) through particles of atomized 65–35 Cu–Pb alloy powder displaying a distribution of the lead phase in different patterns (courtesy of Federal Mogul Corp.); *B*, section (×575) through one particle of atomized 65–35 Cu–Pb alloy powder (courtesy of Federal Mogul Corp.); *C*, microstructure (×300) of sintered 60–40 Cu–Pb bearing metal produced from copper-coated lead powder by pressing at 30 tsi onto steel supports and sintering and bonding under slight spring pressure for 12 hours at 700°C. (1290°F.) in a cracked gas atmosphere (courtesy of Charles Hardy, Inc.); *D*, microstructure (×50) of 65–35 Cu–Pb bearing metal produced from the above atomized powder after cold rolling and first sintering (courtesy of Federal Mogul Corp.); *E*, microstructure (×50) of 65–35 Cu–Pb bearing metal after a second sintering treatment showing a coarsening of the copper phase by grain growth (courtesy of Federal Mogul Corp.).

0.085 in. thick, which is passed through a 70-ft. electric furnace at a rate of 66 in. per minute in an atmosphere of partially burnt natural gas. During this treatment the strip is heated to 860–870°C. (1580–1600°F.) without undue loss in lead. The strip is then uniformly rolled to a maximum density and passed back through the furnace for annealing prior to recoiling and cutting to size. Figure 541*A* and *B* shows microsections of an atomized powder suitable for this purpose, while Figure 541*C* to *E* displays the microstructure of the bearing alloy in different stages of manufacture.

A variation of this process is described in a British patent,[59] in which the bearings are produced with a lead content in excess of 35%, the maximum that can be introduced satisfactorily by prealloying the powder. The problem is solved by first sintering a 70–30 Cu–Pb powder layer onto the steel backing, rolling the layer to 30% porosity, and then knurling it to 10% porosity to cover at least 50% of the surface with indentations 0.025 in. in diameter and 0.010 in. deep. The surface layer is then coated with lead by spraying, electrodeposition, or by pouring the cast metal over it. A final machining exposes the sintered copper–lead surface and the lead-filled indentations. Alloying of the lead with indium, tin, antimony, cadmium, and other elements is possible if the surface layer is sprayed or poured. Further information about British practices in manufacturing copper–lead bimetal bearings has also been given by Tait,[60] of German practices by Eisenkolb,[60a] and of French practices by Delaplace.[60b]

With the lead content varying between 20 and 50% by weight, and preferably in the order of 35 to 40%, special techniques have been developed to overcome the nonsolubility of the components within the specified range. While mixtures of the two components can be compressed with pressures as low as 5 tsi and subsequently sized with pressures not exceeding 10 tsi, resulting in practically nonporous bearings,[61] changes in composition caused by loss of lead oozing out of the compact during sintering constitute one of the serious difficulties inherent in the method. This segregation of the lead can be curtailed considerably by using either alloy powders obtained by atomizing a molten mixture of the two metals (rapid chilling preventing segregation), or by using composite powders consisting of lead particles individually coated with copper[62] (see also

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[59] Brit. Pat. 580,660.

[60] W. H. Tait, *Symposium on Powder Metallurgy*. The Iron and Steel Institute, Special Report No. 38, London, 1947, p. 157.

[60a] F. Eisenkolb, *Arch. Metallkunde, 1,* No. 7/8, 345 (1947).

[60b] R. Delaplace, *Compt. rend., 225,* 1075 (1947).

[61] W. D. Jones, *Metallurgia, 28,* No. 168, 255 (1943).

[62] Brit. Pat 463,775; German Pat. 718,170; U. S. Pats. 2,033,240 and 2,234,371.

Vol. I; Chaps. III, VI). During sintering of the compacts made from these powders at temperatures as high as 870°C. (1600°F.), not more than 5% of the lead content is reportedly lost by sweat-out and evaporation. The microstructure of such material is shown in Figure 541*C*. The alloy powders, however, require somewhat higher molding and sizing pressures.

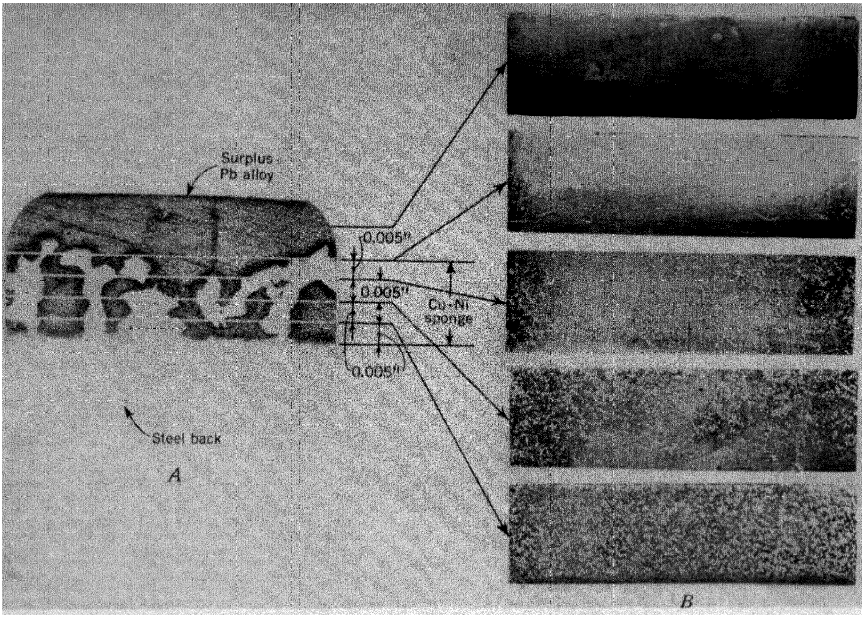

Fig. 542. Cross section (×50) and surface appearance (×3) of steel-backed bearings made of copper–nickel sponge impregnated with lead alloy (according to Boegehold[54]): *A*, cross section of bearing; *B*, surface appearance of various machined levels.

Copper–lead bearings produced by one of these methods are satisfactory for medium-heavy-duty service, *i.e.*, for shaft speeds up to 3000 r.p.m. and for oil temperatures up to 135°C. (275°F.). High speeds and temperatures cause premature scoring or corrosion failures. The necessity for overcoming these difficulties has led to the production of virtually pore-free bearing materials. Impregnation of a porous copper matrix with lead results in a superior bearing material, but the performance of the bearing is seriously impaired by unsatisfactory bonding between the copper matrix and the steel strip backing.[55] This bonding, however, is considerably improved when the matrix is made of copper–nickel mixture. Sintering of a 55–45 Cu–Ni powder mixture above the melting point of copper, compressed to the copper-plated steel backing with the aid of heavy rolls, causes solid brazing of the nickel particles to each other and to the steel back. By properly timing the sintering operation, an interconnected pore system is retained, and the pores can subsequently be impregnated with liquid babbitt metals.[63] The addition of about 3% Sn and 3% Sb to lead is sufficient to make the impregnated bearing alloy resistant to the corrosion of hot lubricating oils without endangering the antifriction properties of the lead.[64] Figure 542 shows the cross section and surface appearance of the composite bearing at low and high magnification.

During the last decade, the production of babbitt-impregnated bearings has been developed to a high degree of perfection, and the material is now produced economically in a continuous production arrangement that provides the coiled steel backing and powder feed device, pressure rolls, sintering and vacuum impregnation furnaces arranged in tandem, and stripping, cutting, and bending machinery for the finishing of the bearings.

Other solid bearing materials produced from powders include copper–graphite and iron–graphite compositions which are cold-pressed, sintered, and then directly hot-pressed to yield maximum density.[65]

SINTERED NICKEL AND NICKEL ALLOYS

Nickel

Dense products of pure nickel are produced from nickel powders on a limited scale. These products are used principally in the high-vacuum field, where sheets and wires of various size are employed. Other applications include bimetallic strips for thermoelements and nickel-clad iron and steel ingots weighing up to 1.75 tons which, after sintering, have been rolled into thin sheets.[66]

In the manufacture of sintered nickel the following types of powders can be used: (*1*) carbonyl nickel powder; (*2*) pulverized shot obtained by fusion of electrolytic nickel; and (*3*) reduced nickel powder.

Carbonyl nickel powder has been widely used in Germany, and was generally preferred before the war because of its high purity and excellent compacting and sintering characteristics. Since the war, this powder has been replaced in the United States, and also to some extent in Europe, by the other two types of powder.

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[63] R. P. Koehring, *Metal Progress, 38,* 174, 196 (1940).

[64] A. L. Boegehold, in J. Wulff, *Powder Metallurgy.* Am. Soc. Metals, Cleveland, 1942, p. 520.

[65] P. Schwarzkopf, *Powder Metallurgy.* Macmillan, New York, 1947, p. 150.

[66] L. Schlecht and G Trageser, *Metallwirtschaft, 19,* 66 (1940).

The properties of sintered nickel have been investigated extensively by Schlecht and coworkers.[66-69] Figure 543 shows the effect of sintering temperature on density.[68,70] The physical properties of sintered nickel as compared with cast nickel are tabulated elsewhere (Chapter XXXI).

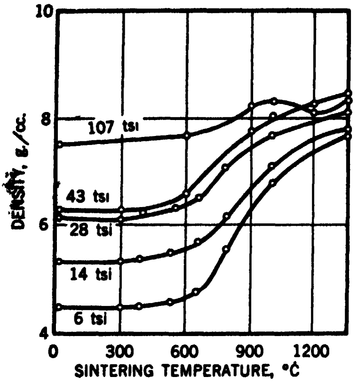

Fig. 543. Density of sintered carbonyl nickel powder compacts as a function of the sintering temperature. Compacts were pressed at different pressures as indicated (according to Grube and Schlecht,[68] and Kieffer and Hotop[70]).

Sheets produced from carbonyl nickel powder ingots are reported by Hamprecht and Schlecht[67] to possess the following mechanical properties:

Yield point, psi	17,000
Tensile strength, psi	57,000
Elongation, %	50
Reduction of area, %	80
Brinell hardness	90
Deep-drawing capacity (Ericksen test)	
For 0.5-mm. sheet	11.7 mm.
For 1.0-mm. sheet	12.7 mm.
For 1.5-mm. sheet	13.3 mm.

Fetz[71,72] has studied the recrystallization of fused nickel of different purity, and has shown the interesting fact that, due to its extraordinary high purity, sintered carbonyl compacts—subsequently fused and deformed—recrystallize at approximately 200°C. (360°F.) below the normal temperature of recrystallization found in commercial brands of the metal (about 550°C.; 1020°F.).

[67] G. Hamprecht and L. Schlecht, *Metallwirtschaft*, ***12***, 281 (1933).

[68] G. Grube and L. Schlecht, *Z. Elektrochem.*, *44*, 367, 413 (1938).

[69] L. Schlecht and G. Trageser, *Chem. Fabrik*, ***12***, 243 (1939).

[70] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe*. Springer, Berlin, 1943, p. 208.

[71] E. Fetz, *Metals & Alloys*, *8*, 339 (1937).

[72] E. Fetz, *Trans. Am. Soc. Metals*, ***25***, 1030 (1937); ***26***, 961 (1938); ***29***, 210 (1941).

The powder metallurgy of nickel has been reviewed by G. H. S. Price[73] in a broad survey of the pertinent literature. The scope of this review covers (*1*) the production of nickel powders, including the rare method of distillation of a nickel amalgam; (*2*) the effect of pressure on the density and electrical conductivity of green compacts; (*3*) the density and mechanical properties of sintered nickel; and (*4*) sintered alloys of nickel with iron, cobalt, chromium, silver, manganese, molybdenum, and tungsten. Among the applications of sintered nickel are cited master alloys; high-vacuum wires, sheets, and tubings; and certain porous nickel products, such as filters for concentrated sodium hydroxide and the sintered nickel cup in proximity fuses (see also Chapter XXVII).

Nickel Alloys

With the exception of nickel–iron alloys (see Chapters XXIV and XXV), no important nickel alloys have yet been commercially developed from powders. The sintering of alloys of the systems Ni–Cu, Ni–Cr, Ni–Co, and Ni–Mn has been studied to determine diffusion and sintering conditions. Nickel–copper alloys have been mentioned at the beginning of this chapter. The commercial production of nickel–chromium alloys has been impeded by the strong oxidizing tendencies of chromium powders. Of the nickel–cobalt alloys, only those containing a major proportion of iron (for example, 54–28–18 Fe–Ni–Co) have been developed for certain glass-to-metal sealing applications (see Chapter XXV). Nickel–manganese alloys (*e.g.*, 96–4 Ni–Mn) obtained by sintering compacted mixtures at 1100–1200°C. (2000–2200°F.) for 6–8 hours have been used successfully for spark plug electrodes.[74] Nickel–silver alloys have been reported[74a] in use as magneto weights. Nickel alloys with the refractory metals, with the exception of the "heavy alloys" (see Chapter XXI), have not yet attained commercial significance. The potential field of applications of sintered nickel alloys will be further discussed in Chapter XXXII.

SINTERED PRECIOUS METALS AND ALLOYS

Silver

The commercial uses of sintered silver products have been limited to the contact metal field and to jewelry and medallion applications; they may also develop into a useful bearing material.

The manufacture of dense silver parts is based on any one of three

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[73] G. H. S. Price, *Metal Treatment, 13,* 208 (1946).

[74] P. Schwarzkopf, *Powder Metallurgy.* Macmillan, New York, 1947, p. 150.

[74a] D. C. Bradley, *Prod. Eng., 19,* No. 10, 107 (1948).

types of powder: (*1*) electrolytic ("crystalline"); (*2*) precipitated ("amorphous"); and (*3*) atomized ("granular").

The compactibility of these powders is excellent because of the high plasticity of the metal, and almost solid densities (about 99% of theoretical) are obtainable with reasonably high pressures (50 to 70 tsi). However, this high density is generally lost during sintering, where growth phenomena caused by the evolution of entrapped and absorbed gases can be observed. The decrease in density with increasing sintering temperature is shown in Figure 544 for an atomized powder pressed at different pressures. Sintering is conducted in vacuum, but can also be carried out in air, hydrogen, or inert gases. Hydrogen, however, tends to cause excessive growth and embrittlement, presumably caused by a reaction with oxygen occluded in the particles, whereby water vapor is produced, which greatly increases the volume of gas absorbed by the metal.

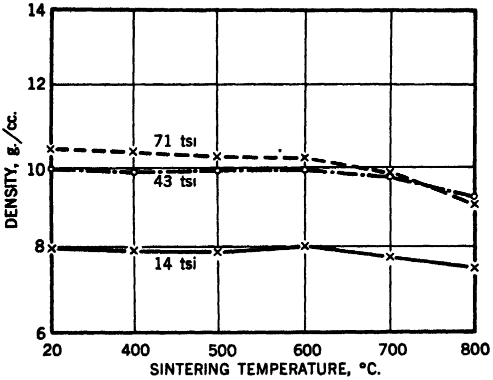

Fig 544. Density of sintered silver powder compacts as a function of the sintering temperature (according to Kieffer and Hotop[76]). Compacts were pressed at different pressures as indicated.

The properties of sintered silver have been investigated by Kikuchi,[75] Kieffer and Hotop,[76] Hensel and Larsen,[77] and Raub and Plate.[77a] The latter confirmed the earlier findings by Kikuchi that the high plasticity of silver facilitates greatly the cold-welding and bonding of the powder particles, and, in turn, permits the application of comparatively low forming pressures and sintering temperatures. After cold pressing at the comparatively low pressure range of 11 to 14 tsi, Kikuchi recorded a Brinell hardness of 150–160; after sintering at 900°C. (1650°F.) the hardness decreased to normal Brinell values of 25–30. The density, tensile

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[75] R. Kikuchi, *Science Reports Tôhoku Univ.*, *26*, 125 (1937).

[76] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe*, Springer, Berlin, 1943, pp. 163, 164.

[77] F. R. Hensel and E. I. Larsen, *Trans. Am. Inst. Mining Met. Engrs.*, *161*, 569 (1945).

[77a] E. Raub and W. Plate, *Proc. International Powder Metallurgy Conference*, Graz, July 12–17, 1948, Referate No. 4.

strength, and electrical conductivity of silver compacts sintered in air and hydrogen are given in Table 206.[77] The superiority of the air-sintered silver is apparent. (A comparison of the properties of sintered and fused silver will be found in Chapter XXXI.)

TABLE 206

Physical Properties of Fine Silver Compacts Sintered in Air and Hydrogen (Hensel and Larsen[77])

Treatment	Density, g./cc.	Tensile strength, psi	Electrical conductivity, % I.A.C.S.
Pressed at 10 tsi; sintered for 2 hours at 900 °C. (1650 °F.) in air	9.61	15,450	91
Pressed at 10 tsi; sintered for 2 hours at 900 °C. (1650 °F.) in hydrogen	7.80	7,780	69
Pressed at 10 tsi; sintered for 2 hours at 900 °C. (1650 °F.) in air; repressed at 50 tsi	10.02	31,600	97.2
Pressed at 10 tsi; sintered for 2 hours at 900 °C. (1650 °F.) in hydrogen, repressed at 50 tsi	10.01	33,500	94.4
Pressed at 10 tsi; sintered for 2 hours at 900 °C. (1650 °F.) in air, repressed at 50 tsi, annealed for 2 hours at 400 °C. (750 °F.) in air	10.02	24,200	101
Pressed at 10 tsi; sintered for 2 hours at 900 °C. (1650 °F.) in hydrogen, repressed at 50 tsi, annealed for 2 hours at 400 °C. (750 °F.) in air	10.05	24,050	101

Silver Alloys

Sintered silver alloy products have not yet found appreciable uses in industry, although several particular compositions have been investigated as possible materials for contacts, cutlery, coins, and jewelry. The most studied alloys include those of the systems Ag–Cu (coin and sterling silver), Ag–Cu–Ni, Ag–Cd, Ag–Cd–Cu, Ag–Zn–Cu, and Ag–Pb.

Silver–copper alloys have been found to be particularly suitable for the study of diffusion effects in the presence of a liquid phase (silver–copper eutectic containing 72% Ag).[75,78-81] Densities that approach closely the theoretical values of the cast alloys are obtainable if the sintering temperature exceeds the eutectic temperature of 780°C. (1435°F.), *i.e.*, if sintering is aided by the liquid phase. For lower temperatures, the density remains low, and the ultimate hardness, according to Kikuchi,[75] corresponds approximately to that of the sum of the hardness values of the components. After sintering at temperatures above the eutectic temperature, the hardness values are considerably lower, evidenc-

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[78] G. Masing, *Z. anorg. allgem. Chem.*, *62*, 265 (1909).

[79] G. Price, S. Williams, and C. J. Smithells, *J. Inst. Metals*, *62*, 239 (1938).

[80] W. D. Jones, *Metal Treatment*, *5*, 13 (1939).

[81] G. J. Comstock, *Metal Progress*, *35*, 576 (1939).

TABLE 207
Hardness of Sintered Silver–Copper Alloys (Kikuchi[76])

Composition[a]		Brinell hardness					
			Sintered at				
Ag	Cu	Pressed at 20°C. (68°F.) at 10 tsi	260°C. (500°F.)	530°C. (985°F.)	700°C. (1290°F.)	840°C. (1545°F.)	920°C. (1690°F.)
100	0	112.8	72.2	46.4	36.6	30.5	26.6
90	10	115.5	84.6	51.8	44.2	36.6	27.6
80	20	120.5	86.4	56.2	45.2	44.7	59.9
50	50	131.6	101.1	65.2	56.7	41.0	64.3
35	65	136.9	105.7	70.2	62.3	55.3	42.4
20	80	141.5	107.6	76.1	67.6	41.2	34.8
10	90	146.3	114.1	76.1	68.9	47.1	30.6
0	100	141.5	120.5	78.4	64.0	49.9	43.5

[a] Powder mixtures with average particle size range of 40–70 μ.

TABLE 208
Physical and Electrical Properties of Coin and Sterling Silver Compacts after Various Treatments (Hensel and Larsen[77])

Treatment	Properties	Coin silver[a]	Sterling silver[b]
Pressed at 10 tsi	Density, g./cc.	7.78	7.75
Sintered for 1 hour at 775°C. (1425°F.) in H_2		8.72	7.80
Repressed at 40 tsi		9.81	9.65
Quenched	Hardness, Rockwell "B"	18	15
	Ultimate strength, psi	29,900	39,800
	Elongation in 1 in., %	9.3	8.5
	Electrical conductivity, % I.A.C.S.	61.8	62.4
Aged 2 hours at 280°C. (535°F.)	Hardness, Rockwell "B"	55	58
	Ultimate strength, psi	39,800	41,000
	Elongation, in 1 in., %	5.0	6.2
	Electrical conductivity, % I.A.C.S.	62.4	68.4

[a] 90.0% Ag, 10.0% Cu.
[b] 92.5% Ag, 7.5% Cu.

TABLE 209
Physical Properties of Silver and Silver–Alloy Compacts (Hensel and Larsen[77])

Compact[a]	Density, g./cc.	Hardness, Rockwell "B"		Electrical conductivity, % IACS		Ultimate tensile strength, psi	Elongation in 1 in., %
		Before aging	After aging	Before aging	After aging		
Coin silver......	10.0	5	57	71.6	74.0	54,000	17.2
Sterling silver....	9.94	10	60	71.6	79.8	55,600	12.5

[a] (*1*) Pressed at 10 tsi; (*2*) sintered in hydrogen for 1 hour at 775°C. (1425°F.); (*3*) repressed at 40 tsi; (*4*) homogenized for 8 hours at 750°C. (1380°F.); (*5*) quenched in water from 780°C. (1435°F.); and, (*6*) aged at 280°C. (535°F.) for 2 hours.

ing advanced alloying caused by the liquid phase. Table 207 gives the hardness of silver–copper compacts of different ratios after sintering below and above the eutectic temperature.

90–10 silver–copper (coin silver) and 92.5–7.5 silver–copper (sterling silver), as well as a composition containing 85% sterling silver, balance nickel, were sintered by Hensel and Larsen,[77] who employed atomized alloy powders for this work. After sintering in hydrogen for one hour just above or below the solidus temperature of the alloys—at 825°C. (1515°F.) and 765°C. (1410°F.)—both coin silver and sterling silver compacts displayed properties comparable with those of the fused and wrought alloys. Table 208 presents the physical properties of coin silver and sterling silver compacts after various treatments. In Table 209 the physical properties of the two alloys are compared after a specific treatment, involving pressing at 10 tsi, sintering in hydrogen for one hour at 775°C. (1425°F.), repressing at 40 tsi, homogenizing for eight hours at 750°C. (1380°F.), water quenching from 780°C. (1435°F.), and aging for two hours at 280°C. (535°F.). The addition of nickel in amounts in excess of 5% was found by Hensel and Larsen to reduce increasingly the precipitation-hardening capacity of the silver–copper alloys (see Table 210).

Alloys of silver containing small percentages of cadmium and copper, zinc and copper, and antimony and copper were found by Hardy[82] to be comparable with cast alloys in hardness values after repeated cold-pressing and sintering operations.

Silver–lead alloy powders, according to Jones,[83] can be compacted readily to high densities (above 95%), and have raised considerable interest as a potential bearing material for airplane and other heavy-duty engines (see also Chapter XXXII). The use of silver–nickel and silver–cadmium oxide alloys, as well as silver compositions including tungsten and molybdenum, for contact materials has been previously described (see Chapter XXIII).

The behavior of compacted binary powder mixtures of silver with zinc, cadmium, lead, copper, iron, and nickel during sintering were recently studied by Raub and Plate,[83a] by measurements of the thermal expansion, specific resistance, and hardness, and also by microscopic and x-ray examination. In the systems of mutual insolubility (Ag–Ni, Ag–Fe) no structural or volumetric changes of significance were observed. The formation of solid solutions or intermetallic compounds, on the other hand, manifests itself by a sharp rise in thermal expansion or, in systems of

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[82] C. Hardy, *Metal Progress, 35,* 57 (1939).

[83] W. D. Jones, *Metal Treatment, 5,* 13 (1939).

[83a] E. Raub and W. Plate, *Proc. International Powder Metallurgy Conference,* Graz, July 12–17, 1948, Referate No. 4.

TABLE 210

Density and Hardness of Sintered Compacts[a] of Various Proportions of Sterling Silver and Nickel (Hensel and Larsen[77])

Sample No.	Composition, %		Pressure, tsi	Density, g./cc.			Hardness after repressing, Rockwell "F"	Density as quenched, g./cc.	Hardness as quenched, Rockwell 15 T	Hardness as aged, Rockwell "F"
	Sterling silver[b]	Nickel		Pressed	Sintered	Repressed				
1	95	5	10	7.60	6.62	9.74	84–86	8.44	22–30	35–42
			20	8.45	7.02	9.76	83–85	8.92	34–37	45–50
2	90	10	10	7.56	6.54	9.72	85–86	8.48	32–35	24–28
			20	8.35	7.11	9.72	84–85	8.74	35–39	31–32
3	85	15	10	7.51	6.28	9.55	85–86	8.38	31–41	20–23
			20	8.23	6.82	9.59	84–86	8.52	33–38	20–24
4	80	20	10	7.26	6.06	9.47	86–87	8.28	31–38	19–24
			20	8.04	6.69	9.47	85–86	8.42	31–38	22–30
5	75	25	10	7.09	6.03	9.37	86–88	8.24	34–40	28–30
			20	7.88	6.70	9.42	86–87	8.52	41–44	37–39
6	70	30	10	6.98	5.95	9.26	87–88	8.26	40–46	33–37
			20	7.76	6.60	9.22	86–88	8.48	45–49	42–43

[a] Sintered 780 to 790°C. (1435 to 1455°F.) for 1 hour in hydrogen; quenched from 780°C. (1435°F.) after soaking for 15 minutes in hydrogen atmosphere; aged at 300°C. (570°F.) for 2 hours in air; all samples repressed at 50 tsi.

[b] 92.5 Ag, 7.5 Cu.

low diffusion rates (Ag–Cu), more clearly by the change in specific resistance.

Gold

A practical application of comparatively recent date for sintered gold has been suggested in connection with carrier materials for radioactive materials.[84] For example, strips of about 2 μ thickness (*i.e.*, not exceeding the depth of penetration of alpha rays in gold) are obtained by cold-rolling slabs prepared from a mixture of 200-mesh pulverized gold powder with about 8% $RaSO_4$, after compression at about 20 tsi, sintering in air at 925°C. (1700°F.), and repressing and resintering under identical conditions. These strips, which are completely dense and contain radium in uniform distribution, are reported in use for the discharge of static electricity, for the supply of ionization current in cold cathode tubes, or for the activation of luminous paints.

TABLE 211
Density and Hardness of Sintered Gold in Relation to Sintering Temperature
(Trzebiatowski[85])

Compacting pressure, tsi	Pressed at 18°C. (65°F.)	Sintered at 100°C. (210°F.)	200°C. (390°F.)	300°C. (570°F.)	400°C. (750°F.)	500°C. (930°F.)	600°C (1110°F.)
				Density, g./cc.			
50	15.6	15.6	16.0	16.2	16.5	16.7	16.0
210	18.2	17.2	17.1	17.0	16.0	12.0	—
				Brinell hardness			
50	60	70	80	90	70	40	20
105	120	135	165	138	120	65	45
210	120	124	120	115	40	5–10	5–10

The properties of cold-pressed and sintered, as well as hot-pressed, gold compacts have been given extensive study by Trzebiatowski,[85] who used very fine powders (0.3–2 μ) prepared from $HAuCl_4$ by precipitation with alkaline H_2O_2 followed by reduction. Table 211 gives density and hardness values of gold compacts after sintering at various temperatures up to 600°C. (1110°F.) and also after hot-pressing at the same temperatures. These properties are compared with those of the fused metal in Chapter XXXI.

Gold Alloys

Alloys of gold with silver, copper, and nickel were recently studied by Raub and Plate.[83a] Compacted powder mixtures were sintered and

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[84] U. S. Pats. 1,718,899; 2,326,631; 2,462,241; 2,476,644; 2,479,882.

[85] W. Trzebiatowski, *Z. physik. Chem.*, *A169*, 91 (1934); *B24*, 75, 87 (1934).

measured for thermal expansion, specific resistance, hardness, and were also examined by x-rays and microscopically. The results showed a similar trend as those observed by the same investigator with silver alloys (p. 485): the rapid formation of solid solution in the system Au–Ag and of intermetallic compounds in the system Au–Cu was found to coincide with a marked increase of the thermal expansion, whereas for the system Au–Ni with its lower rates of diffusion the specific resistance measurements were found to be more revealing.

Platinum

The powder metallurgy of platinum has remained practically unchanged since the original procedure was developed by Wollaston[86] well over a century ago (see Volume I, Chapter II). Platinum ingots that can be rolled to sheets or drawn to wires are, according to Sivil,[87] McDonald,[88] Atkinson and Raper,[89] and Middleton, Pfeil, and Rhodes,[89a] produced in a simple manner by cold-pressing dry platinum sponge powder at low pressures (approximately 5 to 20 tsi), sintering at high temperatures in the order of 1500°C. (2730°F.), and forging at temperatures above 1000°C. (1830°F.). McDonald reports slightly superior physical and chemical properties exhibited by the sintered platinum as compared with the corresponding properties exhibited by the cast metal (see also Chapter XXXI). The density of rolled sheets produced from sintered ingots equals the theoretical density, while the hardness of the sheets after annealing ranges from 38 to 42 Brinell, as compared with 40 to 44 for the sheets produced from cast ingots. Sintered platinum is generally of slightly higher purity than the cast metal.

According to the recent findings of Middleton, Pfeil, and Rhodes, wire produced by sintering, hot-working, and finally severely cold-drawing of compacts from —90 mesh high-purity platinum powder retains its fibrous structure when heated to temperatures well above the recrystallization temperature of wire produced from melted, cast, and similarly worked pure platinum. This phenomenon is attributed by the investigators to a small but suitably dispersed pore volume, which has the effect of inhibiting recrystallization. At relatively high temperatures the fibrous structure of the sintered platinum wire was found to change to a columnar grain structure. It was also established that at the temperature of testing (corresponding to that of recrystallization of the wire

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[86] W. H. Wollaston, *Phil. Trans. Roy. Soc.*, *119*, 1 (1829).

[87] C. S. Sivil, *Trans. Am. Inst. Mining Met. Engrs.*, *93*, 246 (1931).

[88] D. McDonald, *Chemistry & Industry*, *9*, 1031 (1931).

[89] R. H. Atkinson and A. R. Raper, *J. Inst. Metals*, *59*, 207 (1936).

[89a] A. B. Middleton, L. B. Pfeil, and E. C. Rhodes, *J. Inst. Metals*, *75*, No. 7, 595 (1949).

from the melted and cast metal) the wire from the sintered metal displayed greater resistance to elongation under tensile stress and greater resistance to intergranular corrosion.

In spite of the rather advantageous set of properties obtained in these recent investigations, no important commercial applications are known to the author for sintered platinum products.

SINTERED LIGHT METALS AND ALLOYS

Aluminum

The powder metallurgy of aluminum and aluminum alloys is still in its earliest stage of development, and the commercial applications of sintered light metal parts are few in number. The main reason for the slow progress made in developing industrial applications for sintered light metals may be seen in the highly competitive field, with powder metallurgy techniques being required to match the easy machinability and workability of the cast and wrought light metals. Parts from pure aluminum are of little interest—for reasons of high powder price and because of the difficulties encountered in molding. Moreover, the properties of pure aluminum are such as to make the parts too soft and weak for most structural applications.

The manufacture of aluminum parts is based on atomized granular powders exclusively. A commercial atomization plant has been described by Birdsall.[90] Various grades from —35-mesh granules to —325-mesh fine powders are suitable. It is essential that the oxygen content is kept to a minimum, *i.e.*, the thickness of the Al_2O_3 film surrounding each particle must be kept as small as possible as in the particle shown in the photomicrograph of Figure 30 (Volume I, Chapter IV). Only very thin oxide shells are liable to be punctured effectively during the plastic deformation of the particles when subjected to the molding pressure, thereby permitting sufficient metal-to-metal contacts for a satisfactory coherence of the compact.

The molding of pure aluminum powders meets with many difficulties, primarily because of the seizing and galling effects on the die walls, the tendency of the very plastic particles to extrude between the moving and stationary parts of the die, and comparatively poor flow rates of most grades. The addition of internal lubricants to the aluminum powder is usually objectionable (they act as pore generators and also leave behind residues which would interfere with the establishment of solid sinter bonds and be the cause for inferior physical properties); therefore, careful lubrication of the die walls is most important. This implies the need for

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[90] G. W. Birdsall, *Steel*, *118*, No. 2, 82 (1946).

automatic die-wall lubrication in production work. Various lubricants have been suggested, such as flake aluminum particles suspended in stearic acid dissolved in a commercial solvent.[91] A moderately low forming pressure (not exceeding 30 tsi) is maintained in order to control the tendency of the particles to extrude. The flow rate of the powders is generally better with the coarser grades; a recently introduced minus 35, plus 100 mesh grade[91a] has a flow rate adequate for use in automatic molding presses and a compression ratio of 2.8:1 at 30 tsi, giving compacts of 2.7 g./cc. density, which, after sintering at 645°C. (1190°F.) for 45 minutes and cooling to at least 200°C. (390°F.) in a protective atmosphere, show only negligible shrinkage (0.36%) and good physical properties (12,700 tsi tensile strength, 21% elongation).

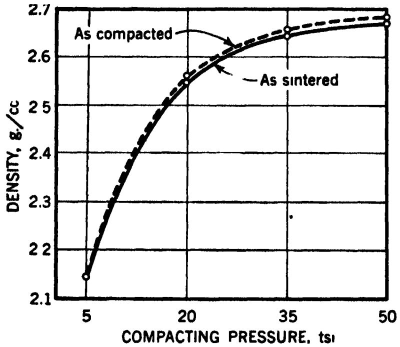

Fig. 545. Effect of the compacting pressure on the density of air-sintered aluminum (according to Cremer and Cordiano[91]).

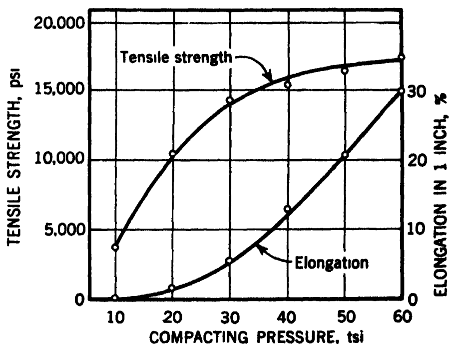

Fig. 546. Effect of the compacting pressure on the tensile properties of air-sintered aluminum (according to Cremer and Cordiano[91]).

Sintering of aluminum is usually conducted in air, nitrogen, helium, or dissociated ammonia at a temperature slightly below the fusion temperature. The properties of sintered aluminum have been investigated by Cremer and Cordiano,[91] who have also reported on successful attempts to overcome some of the molding problems just mentioned. In Figure 545 the density is shown as a function of the molding pressure, both before and after sintering. Sintering caused only an insignificant drop in density for pressures up to 50 tsi. In Figure 546 the tensile properties are plotted against the initial pressure for aluminum sintered for 30 minutes at 620°C. (1150°F.); compacts molded at 60 tsi reach a tensile strength of 17,500 psi accompanied by an elongation of 30% and a fatigue strength

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[91] G. D. Cremer and J. J. Cordiano, *Trans. Am. Inst. Mining Met. Engrs.*, ***152***, 152 (1943).

[91a] Product of Charles Hardy, Inc., New York.

of 8000 psi for 10^8 cycles of stress before rupture. These figures compare favorably with wrought aluminum as far as strength characteristics are concerned, while the value for elongation falls somewhat short of normal. The effect of compacting pressure on aluminum compacts sintered in dissociated ammonia for one hour at 615°C. (1140°F.) is given in Table 212. The value for elongation and reduction of area are comparable with the best data obtainable in fused and wrought aluminum, while yield and tensile strength values are nearer to the lower limits of the wrought metal. A tested tensile specimen of such ammonia-sintered aluminum is shown in Figure 547. Obviously, the aluminum attains complete density (2.7 g./cc.) at already moderately low molding pressures because of its excellent plasticity. If the oxide films are sufficiently thin to become disrupted during processing, maximum benefit is derived from the resulting pore-free, fine-grained structure.

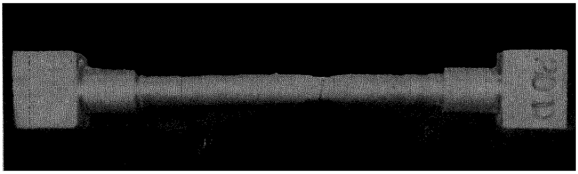

Fig. 547. Photograph of a fractured tensile test bar from sintered aluminum showing a pronounced "necking" effect as a sign of a high degree of ductility. The test bar was machined from a rectangular bar that had been pressed from a 150 mesh atomized powder at 20 tsi, and sintered in dry dissociated ammonia for 1 hour at 615°C. (1140°F.). The bar had a tensile strength of 11,810 psi, and elongation of 46.8%, and a reduction in area of 63.7%. (Courtesy of American Electro Metal Corp.)

TABLE 212

Physical Properties of Sintered Aluminum[a]

Compacting pressure, tsi	Density, g./cc.	Yield strength, psi	Tensile strength, psi	Elongation in 1 in., %	Reduction of area, %
10	2.44	6160	8,900	4.7	3.1
20	2.60	6460	11,810	46.8	63.7
30	2.69	6660	11,850	48.4	59.4
40	2.69	7600	11,780	37.5	47.7

[a] Sintering cycle: 615°C. (1140°F.) for 1 hour in dissociated ammonia.

As part of an investigation concerned with the powder metallurgy of aluminum and aluminum alloys, Bickerdike[92] recently reported some

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[92] R. L. Bickerdike, *Symposium on Powder Metallurgy*. The Iron and Steel Institute, Special Report No. 38, London, 1947, p. 185.

interesting results with hot-pressed aluminum. For these experiments a 200-mesh powder with 68% —300 mesh was used, and pressings were made first at 30 tsi at room temperature, and then at 5 tsi at temperatures of 300, 400, 500, and 600°C. (570, 750, 930, and 1110°F.). The hardness and tensile properties of these compacts are reproduced in Table 213. For the highest temperature used, a tensile strength of 15,400 psi, coupled with an elongation of 34%, constitutes a rather remarkable tensile property which is comparable with peak values found in wrought aluminum.

TABLE 213

Mechanical Properties[a] of Aluminum Compacts Hot-Pressed at 5 Tsi after Initial Cold-Compaction at 30 Tsi (Bickerdike[92])

Pressing temperature, °C.	Pressing temperature, °F.	Brinell hardness	Ultimate strength, psi	Elongation, %
300	570	33.7	12,600	1.0
400	750	30.6	12,400	2.0
500	930	28.4	12,200	4.5
600	1110	26.4	15,400	34.0

[a] The figures were obtained with 0.253-in. diameter substandard test pieces machined from bars 3 × $^3/_8$ × $^3/_8$ in.

The Brinell hardness value of 26.4 indicates, however, that the material was not in a dead-soft annealed state (wrought dead-soft aluminum usually exhibits approximately 20–24 Brinell), which may account for the higs tensile and somewhat deficient elongation values.

Aluminum Alloys

Lately, a good deal of attention has been centered around the question of manufacturing sintered aluminum alloy products,[92a] and a number of specific applications, especially in the aeronautical industries, have been reported during the war. The future of this development is dependent chiefly on whether, with low-priced alloy powders and moderate means, precision parts with physical properties superior to those obtainable today in aluminum die castings can be molded on a large scale. What makes some of the sintered alloys particularly interesting is the fact that they may be age-hardened, although these treatments may deviate to a certain extent from those conventionally employed in the production of cast and wrought material (see also Volume I, Chapter XIX).

As in the manufacture of other alloy products, mixtures of the elemental powders or fusion-alloyed powders can serve as raw materials. The former have the advantage of being more plastic and thus more

[92a] E. Nachtigall, *Proc. International Powder Metallurgy Conference,* Graz, July 12–17, 1948, Referate No. 30.

easily compressible to very high densities; but they require prolonged sintering for complete diffusion, and are also less attractive economically. The alloy powders can be obtained by atomizing or shotting fused secondary metal—making them more competitive. While they require higher molding pressures, they offer less difficulties in ejection of the compacts, since both seizing and extrusion effects are minimized. Also, they require only brief sintering cycles.

The physical properties of a number of aluminum alloys have been investigated by Kempf,[93] by Cremer and Cordiano,[91] and, more recently, by Bickerdike.[92] They refer mostly to material produced from elemental powder mixtures. In Table 214 the effect of consolidation pressure is shown for a 90–10 Al–Mg alloy prepared by mixing atomized 200-mesh powders and sintering the compacts in air at 430°C. (800°F.) for 24 hours.[93]

TABLE 214

Physical Properties of Sintered Aluminum–Magnesium Alloy Containing 10% Mg (Kempf[93])

Molding pressure, tsi	Density, g./cc.	Porosity, %	Tensile strength, psi
20.0	2.266	13 0	5,340
30.0	2.409	7.5	17,700
55.7	2.519	3 3	24,900

TABLE 215

Tensile Strength of Sintered 90–10 Al–Zn Alloy as Affected by Sintering Temperature (Kempf[93])

Temperature		Tensile strength, psi
°C.	°F.	
370	700	10,800
430	800	13,620
510	950	15,460

In Table 215 Kempf's tensile data are reproduced for an alloy containing 10% zinc, balance aluminum, which was prepared by compressing the powder mixture at 40 tsi and sintering in air for 24 hours at various temperatures, both below and above the melting point of zinc (427°C.; 787°F.), followed by water quenching.[93]

The effect of the sintering atmosphere, as well as the sintering temperature, on the physical properties of compacts of the same composition is shown in Table 216, according to a study directed by the author.[94] Mixtures of commercial grades of the elemental powders, both of which passed through a 200-mesh sieve (with two-thirds passing through a 325-mesh sieve), were uniformly compacted at 40 tsi. The good properties recorded for compacts sintered at 570°C. (1060°F.) give evidence of the consolidating effects of the liquid phase present during sintering at this

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[93] L. W. Kempf, in J. Wulff, *Powder Metallurgy.* Am. Soc. Metals, Cleveland, 1942, p. 314.

[94] M. Pepper, *unpublished data,* from Lab. Rept. of American Electro Metal Corp. (Courtesy of P. Schwarzkopf).

TABLE 216
Physical Properties of 90–10 Al-Zn Powder Compacts[a]

Sintering temperature		Sintering time, hr.	Sintering atmosphere	Yield strength, psi	Tensile strength, psi	Elongation in 1 in., %	Reduction of area, %
°C.	°F.						
370	700	2	Air	—	16,300	2	1.0
		24		—	16,500	1	1.0
		2	NH_3	—	17,800	3	1.6
		24		—	17,100	2	1.6
430	800	2	Air	16,700	17,000	4	2.3
		24		14,000	18,500	5	4.9
		2	NH_3	13,900	19,900	6	3.9
		24		13,500	19,300	4	2.4
510	950	2	Air	13,600	17,200	3	1.6
		24		11,800	19,500	6	4.5
		2	NH_3	14,900	16,600	3	1.6
		24		11,600	19,200	9	5.4
570	1060	2	Air	10,600	23,300	20	16.3
		24		14,400	25,300	17	14.1
		2	NH_3	13,300	19,200	15	12.3
		24		12,700	21,800	16	13.5

[a] After compaction of mixture of elemental powders (100% −200 mesh, 66% −325 mesh) at 40 tsi and sintering under different conditions, followed by water quench.

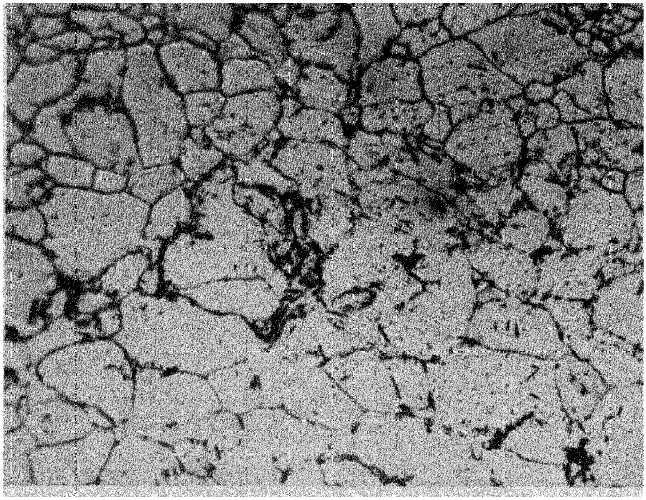

Fig. 548. Microstructure (×400) of a 90–10 aluminum-zinc compact pressed from a mixture of aluminum and zinc powders at 40 tsi, and sintered in air for 2 hours at 570°C. (1060°F.). Etched with sulfuric acid. (Courtesy of P. Schwarzkopf and American Electro Metal Corp.)

temperature. Prolongation of the sintering time from 2 to 24 hours appears in most instances to increase slightly the strength and ductility of the material. Microscopic evidence, as displayed in Figure 548, points to the fact that after 2-hour sintering, diffusion is not yet complete and that some of the pure aluminum is still retained.

If part of the zinc is replaced by magnesium, even higher strength values can be produced. In Table 217, Kempf's data are given for a more complex alloy, containing 7% Zn, 3% Mg, balance Al, which otherwise is produced in the same manner as the binary aluminum–zinc compacts (40 tsi pressure, 24-hour sintering in air, followed by water quench). When the compact, heated at 510°C. (950°F.), was reheated after quenching to 140°C. (290°F.) and aged for 20 hours, Kempf noted an increase in tensile strength from 40,000 to 45,850 psi. Table 218 shows the effect of various other sintering conditions, in addition to temperature, on the physical properties of compacts pressed at 40 tsi from the elemental powder mixture.[94] The beneficial influence of the higher temperature on diffusion and strength values is apparent, especially after the temperature has exceeded the melting point of the liquid phase.

TABLE 217

Tensile Strength of Sintered 90–7–3 Al–Zn–Mg Alloy as Affected by Sintering Temperature (Kempf[93])

Sintering temperature		Tensile strength, psi
°C.	°F.	
370	700	21,400
430	800	32,900
510	950	40,000

TABLE 218

Physical Properties of 90–7–3 Al–Zn–Mg Compacts[a]

Sintering temperature		Sintering time, hr.	Sintering atmosphere	Yield strength, psi	Tensile strength, psi	Elongation in 1 in., %	Reduction of area, %
°C.	°F.						
370	700	24	Air	—	20,100	2	2.4
430	800	2	NH_3	—	22,200	2	1.6
		24	Air	32,500	32,900	3	1.6
510	950	24	NH_3	30,100	41,500	3	1.6
			Air	34,800	41,500	3	3.2

[a] After compaction of the elemental powder mixture at 40 tsi and sintering under different conditions, followed by water quench.

Probably of greatest promise are sintered aluminum–copper alloys, both of the binary alloy type containing 4 to 5% copper, and also of the duralumin type containing about 0.5% each of magnesium and manganese in addition to 4% copper. Kempf reports for a 95–5 Al–Cu powder mixture—compacted at 40 tsi and sintered for 4 hours at 550°C. (1020°F.) —a tensile strength of 32,330 psi with an elongation of 2%. These data could still be improved considerably by the proper selection of the elemental powders (in particular a low-oxygen aluminum powder, two-thirds of which passes through 325 mesh). The figures tabulated in Table 219[94] indicate that light alloy parts with a tensile strength up to 40,000 psi and an elongation of over 15% may be produced with comparative ease.

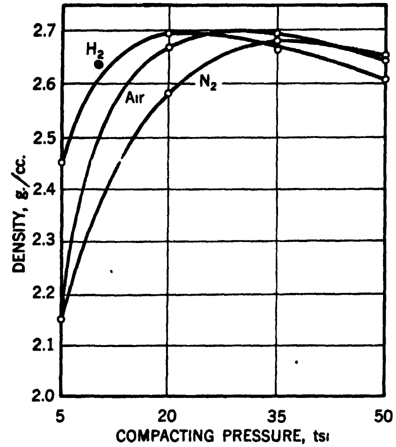

Fig. 549. Effect of the compacting pressure on the density of compacts prepared from a 96–4 aluminum–copper powder mixture and sintered under different atmospheres for 30 minutes at 600°C. (1110°F.) (according to Cremer and Cordiano[91]).

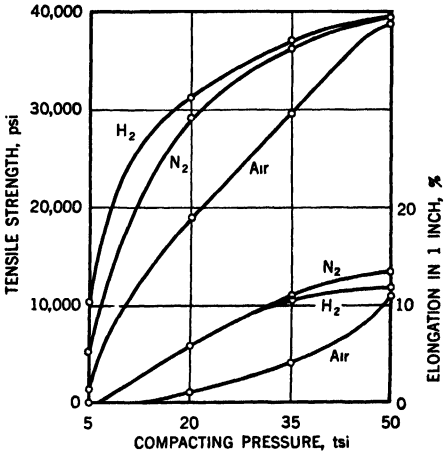

Fig. 550. Effect of the compacting pressure on the tensile properties of compacts prepared from a 96–4 aluminum–copper powder mixture and sintered under different atmospheres for 30 minutes at 600°C. (1110°F) (according to Cremer and Cordiano[91]).

TABLE 219

Physical Properties of 95-5 Al-Cu Compacts[a]

Sintering time, hr.	Sintering atmosphere	Yield strength, psi	Tensile strength, psi	Elongation in 1 in., %	Reduction of area, %
1	NH_3	15,300	19,700	4	1 6
	Air	15,600	19,100	3	1 8
4	NH_3	19,900	27,400	4	3.6
	Air	16,500	38,600	17	15.3

[a] After compaction of the elemental powder mixture at 40 tsi and sintering at 550°C. (1020°F.).

Cremer and Cordiano[91] have included 96–4 Al–Cu, 97–2.5–0.5 Al–Cu–Mg, and 95–4–0.5–0.5 Al–Cu–Mg–Mn compositions in their light alloy studies. They succeeded in sintering at 600°C. (1110°F.), *i.e.*, above the eutectic temperature of these alloys, in spite of the usually observed tendency of the alloy compacts to slump or otherwise drastically deform during such treatment. The beneficial effect of increasing the molding pressure on the density is shown in Figure 549, and the increase in tensile properties with rising initial pressure is shown in Figure 550. In both diagrams, curves are given for different atmospheres, the values being taken for compacts after quenching from 510°C. (950°F.) immediately after sintering at 600°C. (1110°F.) for 30 minutes.

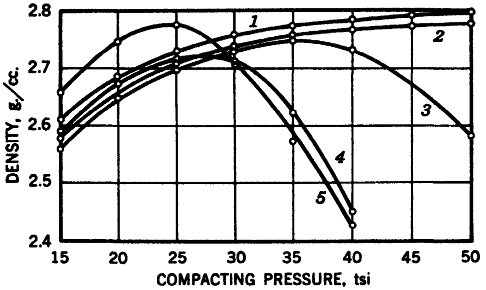

Fig. 551. Relation between compacting pressure and density as affected by the sintering temperature for 94–6 aluminum–copper compacts (according to Bickerdike[92]). All compacts were sintered in hydrogen for 2 hours at the following temperatures: *1*, 510°C. (950°F.); *2*, 528°C. (982°F.); *3*, 560°C. (1040°F.); *4*, 575°C. (1067°F.); *5*, 590°C. (1094°F.).

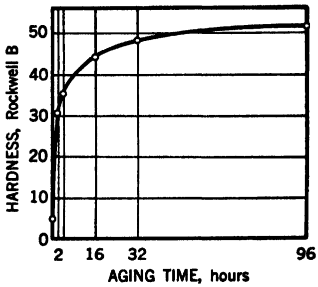

Fig. 552. Age hardening of sintered Duralumin composition prepared from mixture of 95% aluminum, 4% copper, 0.5% magnesium and 0.5% manganese powders (according to Cremer and Cordiano[91]).

Bickerdike's[92] work is essentially a confirmation of the investigations by Kempf,[93] and Cremer and Cordiano,[91] except that vacuum sintering was employed and colloidal graphite was used as a die lubricant. When sintering below the eutectic temperature, the density was found to increase steadily with the compacting pressure (see Fig. 551). Above the eutectic temperature, however, the density reached a maximum at about 25–30 tsi. Compacts pressed at 20 tsi from a 94–6 Al–Cu powder mixture and sintered at 570°C. (1060°F.) for 2 hours exhibited a tensile strength of 42,600 psi with an elongation of 4.5%. A 94–6 Al–Cu compact cold-pressed at 15 tsi and then hot-pressed at 5 tsi and 500°C. (930°F.) gave a Brinell hardness value of 49.6, a tensile strength of 22,000 psi, and an elongation of 6%. The beneficial effect on the hardness and tensile properties of sintering in vacuum as compared with sintering in air becomes

TABLE 220

Physical Properties of Aluminum–Copper Compacts Containing 6% Cu (Bickerdike[92])

Cold pressure, tsi	Sintering temperature		Furnace atmosphere	Brinell hardness	Ultimate strength, psi	Elongation, %
	°C.	°F.				
15	500	930	Air	43.6	12,000	<1.0
15	500	930	Vacuum	59.0	22,000	1.0
15	590	1090	Air	73.2	31,600	1.0
15	590	1090	Vacuum	88.7	40,200	5.0
50	500	930	Air	74.7	30,400	2.0
50	500	930	Vacuum	68.8	35,400	7.0
50	590	1090	Vacuum	91.8	48,000	7.0
5	620	1150	Vacuum	90.7	35,000	3.0
15	620	1150	Vacuum	110	36,200	3.0
50	620	1150	Vacuum	104	26,600	1.5

TABLE 221

Effect of Variation in Cold-Compacting Pressure and Sintering Temperature on Ultimate Tensile Strength and Elongation of 94–6 Al–Cu Compacts (Bickerdike[92])

Sintering temperature		Ultimate strength (in psi) for cold-compacting pressure (in tsi) of:							
°C.	°F.	15	20	25	30	35	40	45	50
510	950	—	—	16,000	21,000	27,400	27,800	31,000	32,800
528	982	—	—	19,600	35,000	38,200	(28,400)	39,200	41,000
560	1040	—	27,800	42,400	43,600	44,800	37,000	—	23,800
575	1067	23,000	42,600	39,600	36,000	13,200	—	—	—
590	1094	42,000	42,600	40,000	29,400	—	—	—	—

Sintering temperature		Elongation (in %) for cold-compacting pressure (in tsi) of:							
°C.	°F.	15	20	25	30	35	40	45	50
510	950	—	—	<1.0	1.0	2.0	3.0	3.5	5.0
528	982	—	—	<1.0	4.5	5.0	(1.5)	6.5	11.0
560	1040	—	<1.0	5.0	5.0	6.5	4.0	—	<1.0
575	1067	<1.0	4.5	7.0	4.0	1.0	—	—	—
590	1094	3.5	5.0	3.0	1.5	—	—	—	—

TABLE 222

Influence of Copper Particle Size on Hardness and Ultimate Tensile Strength of Sintered 94–6 Al–Cu Compacts (Bickerdike[92])

Copper particle size, μ	Sintering temperature		Brinell hardness	Ultimate tensile strength, psi
	°C.	°F.		
<45	520	968	71.7	26,200
45–79	520	968	64.3	19,600
79–160	520	968	51.5	14,800
<45	552	1026	76.7	39,400
45–79	552	1026	59.0	36,200
79–160	552	1026	60.3	23,000

apparent from the data of Table 220; the effect of the compacting pressure and sintering temperature on tensile strength and elongation is shown in Table 221, while the influence of the copper particle size on hardness and tensile strength is indicated in Table 222. All properties usually improve with rising sintering temperatures and with decreasing particle size of the copper component, whereas the trend with rising compacting pressure is not clearly marked, and for the higher sintering temperatures, optimum values are obtained for medium pressures.

Heat-treatable Duralumin compacts (95–4–0.5–0.5 Al–Cu–Mg–Mn) have been produced by Cremer and Cordiano[91] from a mixture of the elemental powders and 1% of a 50–50 Al–Mg powdered master alloy by pressing at 50 tsi and sintering in dry nitrogen atmosphere for 30 minutes at 580°C. (1075°F.). In Table 223, the tensile strength and elongation are shown for the material in the solution-treated and precipitation-hardened state. Increase in hardness of the alloy with time of aging is shown in Figure 552. For a 97–2.5–0.5 Al–Cu–Mg composition produced by compacting the elemental powder mixture at only 30 tsi, followed by sintering at 610°C. (1130°F.) for 30 minutes in nitrogen atmosphere, Cremer and Cordiano report a tensile strength of 40,000 psi with an elongation of 20% in the sintered (and presumably quenched) state. These values greatly surpass the values obtained by L. W. Kempf[93] in binary 95–5 Al–Cu compacts molded at 40 tsi and air-sintered for 4 hours at 550°C. (1020°F.) (see above), but compare with values obtained with a similar binary alloy produced by improved methods (see Table 219).[94]

TABLE 223

Effect of Heat Treatment on Tensile Properties of Sintered Duralumin Compacts (Cremer and Cordiano[91])

Condition of 95-4-0.5-0.5 Al-Cu-Mg-Mn alloy	Tensile strength, psi	Elongation in 1 in., %
After water quench from 510°C. (950°F.) .	33,000	10
After aging for 4 days at room temperature.......	50,000	10

An interesting approach has recently been disclosed,[95] in which a liquid alloy phase is employed during sintering as a cementing agent for the higher melting aluminum powder particles. A 200- or 325-mesh aluminum powder of a purity of at least 99.5% metallic aluminum is mixed with 2–40% Duralumin or similar aluminum alloy powder of at least 325-mesh size (but preferably of considerably greater fineness) and then compacted at 40 tsi. Sintering is then performed in air at 600°C.

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[95] Brit. Pat. Appl. 9150/47 (Apr. 16, 1946); see also *Met. Powd. Rept., 2,* No. 5, 69 (1948).

(1110°F.) for 1 hour; during this treatment the alloy powder liquefies into a continuous network and acts as binder for the aluminum particles. The temperature is sufficiently low to permit diffusion to be kept at a minimum. After quenching the compact, the properties are as follows. A mixture with 70% Al, balance Duralumin, results in a tensile strength of 24,500 psi with 18% elongation; a mixture with 80% Al, balance Duralumin, yields a tensile strength of 22,000 psi with an elongation of 20%. Compacts from a mixture with 90% Al, balance Duralumin, and sintered for only 30 minutes have a tensile strength of 30,000 psi.

Magnesium and Magnesium Alloys

The powder metallurgy production of magnesium and magnesium alloy products has not yet advanced sufficiently to become of commercial significance; the inadequacy of the now available powder supply—both with regard to chemical and physical characteristics—is generally held responsible. It has been the prevailing experience in the field that even under the most carefully controlled sintering conditions it is difficult to produce anything but low-strength, brittle magnesium or magnesium alloy compacts with the pulverized type of powder commercially available. Recent authoritative reports from Germany,[96] however, seem to indicate that in the powder metallurgy of magnesium it is not so much the powder but rather the mode of its processing that is of deciding influence on the ultimate properties of the products. On the basis of extensive research conducted during the last several years under the guidance of F. Sauerwald, the veteran powder metallurgist, some remarkable properties have been developed in magnesium alloys produced from grinding and turning chips (swarf) by using hot-pressing and extrusion techniques. When distilled magnesium powder was used, truly amazing physical properties were obtained, with yield strengths of hot-pressed and extruded magnesium lying between 12,000 and 20,000 psi, tensile strengths between 24,000 and 30,000 psi, and elongations between 7 and 8%, and these properties were still further raised to 32,000 psi yield strength, 45,000 psi tensile strength, and 8.1% elongation by alloying the magnesium with 9% Al. (For additional information on this subject, see Chapter XXXII).

Summary

Of the dense nonferrous powder metallurgy products only copper-base alloys have gained importance, and of these, copper–tin compositions are the most significant ones from a commercial standpoint, since they combine ease of manufacturing with reasonably good physical properties

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[96] F. Sauerwald, *Arch. Metallkunde, 1,* No. 7/8, 363 (1947).

of the end product. Pure copper parts are used only rarely and have been applied chiefly in the electrical industries. Brass powder metallurgy products are rarely competitive with the more conventional manufacturing methods, especially since sintering of brass requires careful control. Cupro-nickel products possess interesting properties, especially if they are of the type susceptible to precipitation treatment. Their corrosion-resistant qualities make them a potential material for salt water machinery parts. Sintered copper-lead alloys and related compositions are today successfully employed in composite, steel-backed bearings.

Nickel and nickel alloy products from powders have been developed only for special applications, such as for magnetic purposes or for materials possessing closely controlled thermal expansion properties. Alloys of nickel with chromium are not yet produced satisfactorily by powder metallurgy, and neither are nickel–copper alloys containing nickel in a major proportion.

Of the precious metal products developed by powder metallurgy methods, silver and silver alloys have secured a limited field of applications, mostly in the electrical contact field, and to a lesser degree for jewelry, cutlery, coins, and medallions, and lately also for bearings. Sintered gold has recently been reported to be in use in connection with radium-containing products. Sintered platinum is not known to be in production on any commercial scale.

Sintered light metals have moved into the foreground during the war, where numerous aluminum alloy parts have been produced for the airplane industry. Further development of aluminum powder metallurgy products depends on their competitive production. The use of low-priced alloy powders has not yet been thoroughly explored, but products produced from certain elemental powder mixtures show great promise. Those compositions that are especially susceptible to age-hardening treatments can produce physical properties superior to those displayed today by aluminum die castings. This fact, and the possibility of working to greater precision by overcoming certain difficulties inherent in the molding operation, should eventually make the powder products competitive with many die-casting products.

Thanks to its great plasticity, pure aluminum of very high quality can be produced provided the proper powder and sintering procedure is chosen. But the molding difficulties apparent in aluminum alloy mixtures are even more exaggerated for pure aluminum powders. Also, there exist no commercial applications of any significance for pure aluminum parts.

Magnesium and magnesium alloy parts are not yet produced satisfactorily by powder metallurgy because of the poor quality of the powders now available, and also for lack of experience with special processing techniques, such as those recently developed abroad.

CHAPTER XXVII

Porous Products

The production of porous metal products is a natural application of the powder metallurgy process, since all its important processing methods lead to materials which are porous *per se*. However, it must be realized that pores, in themselves, contained and distributed at random inside the metal, are not necessarily sufficient to make the product usable in a specific application. If, for example, porous products are produced by casting, the resulting porosity is usually irregular, and the individual pores or holes may be quite large and of a spongelike structure; furthermore, the pores are not usually interconnected, and may be completely separated by metal from the surface. Thus, the porosity in a casting is detrimental from a standpoint of soundness and strength of the metal, without offering the benefits of a *useful* pore structure.

The two principal uses of pores in metals are as storage space for a liquid auxiliary substance, such as oil or grease lubricants, or as separating cells for impurity-containing liquids. To fulfil these purposes, however, the pores must be intercommunicating in character, as well as of carefully controlled amount, shape, size, and distribution. Pressing and sintering methods have been found ideally suitable for producing the very same properties that are required in porous parts used in industry, and this may be the reason that, to date, powder metallurgy has found its greatest use as a process for manufacturing porous articles, particularly bearings and filters.

Obviously, the physical properties of the metal are reduced considerably by an inherent porosity. This effect is not proportional to the decrease in cross-sectional area, but is grossly exaggerated by the multitude of pores, each acting as an individual source for stress concentrations and notch effects (see also Chapter XXXIII, p. 764). Thus, such properties as ductility and impact resistance are especially impaired, while certain other properties, such as compressive strength, are below normal in proportion to the volume percentage of the metal. This fact is significant in the case of bearing materials, where a certain compressive strength is necessary to carry the load.

POROUS BEARINGS AND BUSHINGS

Mechanism of Self-Lubrication

Porous bearings are of a metal structure containing a multitude of pores that are connected with each other and also with the surface of the part. To date, bronze has been found to be the most suitable material for use as a bearing under general conditions, but other compositions, especially of the iron-base type, are also widely used. The pore volume incorporated in the bearings varies from about 10 to 40% by volume, but is mostly in the neighborhood of 25%. This pore volume serves as storage for a fluid lubricant with which the part has been impregnated during its manufacture; between 2 and 4% by weight of oil is needed for a pore volume of 25% to be completely satisfied. Although in certain instances provision must be made to furnish lubrication from an outside source, in most applications the lubrication is produced within the bearing itself.

The underlying principle of such "self-lubricating" operation is briefly as follows. When a motor is started, the rotating shaft draws the oil to the bearing surface in a direct as well as an indirect way. The rotating motion of the shaft causes a pumping action, but also creates frictional heat which aids in the flow of the oil through the interconnected pores. At the surface—between shaft and bearing—the oil forms a protective film preventing direct metal-to-metal contact. A steady supply of oil is furnished from the multitude of minute pores to the entire bearing surface, resulting in a continuous and uniform protective film even at low rotating speeds. The thickness of the film is regulated automatically because of the dependency of the oil supply on the temperature, which in turn is governed by the rotating speed. Upon completion of the running cycle of the motor the oil is reabsorbed into the interior of the bearing by capillary effects and cooling of the bearing and housing. However, a thin film of oil is retained by surface tension forces on the surface of the bearing over a wide range of temperatures, thus preventing metal-to-metal contact at all times. This alternate action is repeated every time the motor starts and stops, and, during running, the bearing furnishes adequate lubrication for a long period of time without losses by leakage or dripping.

From this brief description of the mechanism of self-lubrication the significance of close porosity control and proper selection of the lubricant is apparent. A continuous free circulation of oil without loss by drippage of excess is possible only if amount of porosity and pore size are properly matched with the viscosity of the oil. This relationship has been summarized recently by Victor.[1,1a] The pore size can be regulated readily by

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[1] M. T. Victor, *Elec. Mfg., 37,* No. 2, 123, 210 (1946).

[1a] M. T. Victor, *Can. Metals & Met. Ind., 10,* No. 4, 18 (1947).

the type of powder used, the particle ("grain") size generally ranging between 0.0015 and 0.006 in. The percentage porosity is simply controlled in the molding operation by paying special attention to effects of lubrication during compaction and governing the magnitude of pressure and the rate at which it is applied. Thus, for example, a bearing which is to be subjected to heavy loads at high temperatures requires a heavy oil such as type SAE 60, and should be of the high-porosity type with a pore volume of about 35% and a specific gravity of 5.6; in its manufacture, a comparatively coarse powder must be used, with the smallest particles not below 0.004 in. in diameter. For a bearing to be used for high speeds, light loads, and low temperatures, a light oil with a low viscosity (*e.g.*, SAE 20) is required, and a high percentage porosity and large pore size would result in excessive losses of the lubricant; instead, the correct type of bearing for high-speed, light-load applications would have to be produced from rather fine powders (approximately 0.002 in. in smallest particle diameter) and contain a pore volume of not more than 20%. If, on the other hand, the light-duty bearing were mistakenly used with a heavy lubricant (SAE 60), a free and easy circulation of the oil would obviously be impaired by the small size of the pores and the lack of sufficient pore volume, and the bearing would tend to run dry even though an adequate oil supply could be provided.

Victor enumerates a number of factors that will influence the selection of the oil. They include the operating load, speed and temperature, material and finish of the shaft, composition of the bearing, clearance between shaft and bearing, and the type of operation, *i.e.*, whether continuous or intermittent. In low-temperature operations, the viscosity of the oil at the lowest anticipated starting temperature is significant. Another important characteristic to be considered is the load-carrying ability of the oil to be used, the ability of an oil film to resist puncture under pressure being dependent upon such factors as load, speed, temperature, type of metal contacted, surface conditions, etc. The loads that can be carried by an unbroken oil film may range from 3000 psi in plain bearings to 10,000 psi under ideal conditions. If the oil is compounded with lard oil, tallow oil, or soap, the film strength can be increased to 40,000 psi, but such additions are suitable only for oils used in porous bushings, since in bearings the oil circulation would be hampered and the porosity reduced by the formation of solid deposits. The chemical purity of the oil is also an important factor, since it affects wear and corrosion resistance of the bearing; the ash content in the oil has been found of particular significance in this connection.

Porous Bronze Bearings

Copper–tin compositions were originally used alone for porous bearings and bushings, and are still used most commonly, although iron-base bearings of superior strength have been developed recently and are now used in increasing quantities.

MANUFACTURE

Powder mixtures used for the manufacture of porous bronze bearings contain from 5 to 12% tin, and from 0 to 6% graphite, the balance being copper. Other constituents, particularly lead and iron, are added in percentages up to 6% in certain products. Various types of metal powders are used by the industry, such as electrolytic and reduced copper powders of many grades, electrolytic or atomized tin, atomized lead, reduced iron, and several kinds of natural graphite.

TABLE 224

Characteristics of Elemental Powders Used in Manufacture of Porous Graphite-Containing Bronze Bearings

Properties	Copper,[a] electrolytic	Copper,[b] electrolytic	Copper,[c] oxide-reduced	Tin,[d] atomized	Graphite[e]
Apparent density (loading weight), g./cc.	2.51	2.68	2.50	2.90	0.30
Flow rate, g./min. (1/32-in. orifice, 1 min.)	104	107	—	—	—
Screen analysis, %					
+100 mesh	0.3	0	—	—	—
—100 +150 mesh	7.8	3.4	Trace	0	0.1
—150 +200 mesh	22.4	22.8	10.2	0.8	0.8
—200 +250 mesh	2.5	2.2	4.0	1.6	4.0
—250 +325 mesh	28.8	27.0	15.3		
—325 mesh	38.2	44.6	70.5	97.6	95.1
Particle size distribution by microscopic count, %					
0– 5 μ	—	—	0.5	27.1	1.2
5–10 μ	—	—	4.2	30.5	14.8
10–20 μ	—	—	20.7	24.5	19.3
20–30 μ	—	—	18.4	11.6	16.2
30–40 μ	—	—	16.2	2.6	25.6
40–50 μ	—	—	10.5	1.3	18.0
50–75 μ	—	—	18.3	1.4	4.0
75–100 μ	—	—	10.2	1.0	0.8
Above 100 μ	—	—	1.0	0	0.1

[a] Data by Jones,[3] powder specified as "Sample A."
[b] Data by Jones,[3] powder specified as "Sample B."
[c] Data by Hall,[4] powder designated as "M.D. No. 151."
[d] Data by Hall,[4] powder designated as "M.D. No. 101."
[e] Data by Hall,[4] powder designated as "Acheson" type.

As to particle size distribution, the literature indicates variations between wide limits. According to Kieffer and Hotop,[2] powder grades may

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[2] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe*. Springer, Berlin, 1943, p. 332.

range from —50 mesh size down to —325 mesh. Jones[3] gives the properties of two different copper powders which both pass through a 100-mesh screen, and contain —325 mesh fractions of 38.2 and 44.6%, respectively. The complete data are reproduced in Table 224. According to Jones, the tin powder size is of less importance because of the metal's low melting point, but Hall[4] indicates that tin powders of considerable fineness are used extensively by the bearing manufacturers, as shown in Table 224, where the properties of the copper, tin, and graphite components are given and a size distribution is shown according to microscopic count.

The powdered components are blended in tumblers or ball mills. For the sake of easing the molding operation, as well as for promoting a controlled and interconnected porosity, organic lubricants which volatilize during sintering are usually added in amounts of a few per cent by weight.

Since hot pressing has not proved to be suitable for large-scale production, all molding is carried out cold, and generally in quick-acting mechanical briquetting presses (see Volume I, Chapter XI). The pressures used for briquetting vary considerably with the individual manufacturer and also with the type of bearing to be produced. They usually fall within the range of 15 to 35 tsi, but may be as low as 5 tsi or as high as 50 tsi, when an ultimate sizing operation is to be eliminated. Depending on the size and shape of the product, the production rate may vary between six and several hundred pieces per minute.

Sintering is almost exclusively conducted in continuous furnaces (see Volume I, Chapter XVI) in a protective atmosphere, usually consisting of partially combusted hydrocarbons or natural gas (see Volume I, Chapter XVII); but in certain instances protection against oxidation during sintering is achieved by simply packing briquettes together with coke or charcoal inside closed metal boxes. Hydrogen and dissociated ammonia are not generally used because of the higher costs involved. The sintering temperature is, usually, about 800°C. (1470°F.). In many processes sintering is preceded by a presintering step in a low-temperature advance zone of the furnace. The presintering treatment, usually conducted at a temperature between 400 and 500°C. (750 and 930°F.), serves the twofold purpose of expelling the volatile lubricant at a low rate, and at the same time permitting sufficient time for the liquefaction of the tin and its diffusion into the copper; this is accompanied by a complete solidification of the complex structure. Upon further sintering at higher temperatures, the tin-rich phases liquefy again, but are quickly absorbed by the copper-rich matrix as diffusion progresses. By employing a presintering step, the interval during which a liquid phase is present in the struc-

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[3] W. D. Jones, *Principles of Powder Metallurgy*. Arnold, London, 1937, p. 150.

[4] H. E. Hall, *Metals & Alloys, 10,* 297 (1939).

ture during heating of the compact is interrupted, and degassing effects connected therewith can be controlled more closely. In studying microscopically the sintering mechanism of bronze briquettes containing 9.4% Sn, 6% graphite, balance Cu, Hall[4] found the following to take place when the material was heated to 810°C. (1490°F.). The tin is molten after one minute, and the first indication of alloying is apparent; diffusion then progresses rapidly, as seen from colored photomicrographs taken after 3, 7, and 15 minutes of sintering; alloying is substantially complete after 25 to 27 minutes of sintering, as indicated by the predominant appearance of alpha-bronze. This mechanism has been further described in Volume I, Chapter XIV, and schematically illustrated in Figure 229.

Carter and Metcalfe[5] used the x-ray diffraction method for studying the structure of three commercial types of porous graphite-containing bronze bearings made in England, and of experimental bearings made with coarse and fine tin powder under different conditions of sintering, varying compacting pressure, and with and without graphite. The results largely confirm the metallographic examination, *i.e.*, with sintering at about 800°C. (1470°F.) the porosity and phase distribution of the material are influenced sharply by the peritectic reaction, which occurs between the α-solid solution and the liquid phase at 798°C. (1468°F.). It is interesting to note that Carter and Metcalfe recommend that the compacting pressure should not exceed 15 tsi because it affects porosity and compressive strength in opposite ways.

The presence of a transitory liquid phase during sintering brings about volumetric changes of the compacts which generally are not very uniform[6] and, therefore, not easy to control. Sometimes, matters are further complicated by growth phenomena attributed to certain types of graphite. Hence a subsequent sizing operation is common in the manufacture of bearings and bushings. Where products of very fine pore structures are involved, sizing under pressure may result in sealing of the surface pores, and a machining operation is preferable, if necessary, with hard metal or diamond tools. The chief objective of the sizing operation is to produce smooth-surfaced products to precision tolerances. Bearings and bushings that have been sized correctly have a fine burnished finish and are accurate in inside and outside diameters and in height. The sizing procedure is much the same as that used for coining structural parts, except that the briquette does not fit into the die, but is placed on top of it in position, and

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[5] A. Carter and A. G. Metcalfe, *Symposium on Powder Metallurgy*. The Iron and Steel Institute, Special Report No. 38, London, 1947, p. 99.

[6] J. E. Drapeau, Jr., in J. Wulff, *Powder Metallurgy*. Am. Soc. Metals, Cleveland, 1942, p. 332.

forced into the die by the action of the upper punch. A shearing or squeezing action takes place during the operation, which removes or displaces the excess metal (usually about 0.010–0.020 in.) at both the inside and outside diameters. At the same time the required height is coined out. Upon completion, the fully sized product is ejected from the die. Pressures used for the sizing operation are usually considerably smaller than conventionally used for coining for the purpose of densification and may even be below those necessary for the briquetting of the powder. Mechanical presses that are especially adapted for production on a large scale are used exclusively for sizing porous bearings and bushings.

In designing the correct sizing and molding dies and tools, due allowances must be made not only for the dimensional changes that may occur during sintering, but also for the oversize necessary for sizing, which will vary with material and end purpose of the product. Also, such factors as elastic springback and concentricity of the cored hole must be considered. A typical tool and die design for sizing plain cylindrical bearings is shown in Volume I, Figure 135.

The porous products are impregnated with oil either before or after the sizing operation. The operation is usually carried out by heating the parts in the oil at approximately 110°C. (230°F.) for about 10 minutes. Some manufacturers apply a vacuum to facilitate the removal of air prior to the oil impregnation (see also Volume I, Chapter XX).

The production or porous bronze bearings was recently well summarized by Lennox and Brewer[6a]; the methods used in Great Britain for the manufacture of plain bearings and thrust washers were discussed in detail by Tait.[6b]

PROPERTIES

The chief advantage of the porous bronze bearings lies in their self-lubricating properties. They are especially suitable for small loads where close running fits, ease of installation, and a long, trouble-free life without servicing are essential requirements. The porous-type bearings generally have a good damping capacity and run without noise. On the other hand, porous bronze bearings are not suited for high loads coupled with high speeds, and the inherent porosity is the cause for a very low impact fatigue strength.

The strength of the material varies roughly inversely with its porosity, *i.e.*, the lower the porosity the greater the strength and *vice*

[6a] J. W. Lennox and G. Brewer, *Metal Ind. London*, 73, 429 (1948).

[6b] W. H. Tait, *Symposium on Powder Metallurgy*. The Iron and Steel Institute, Special Report No. 38, London, 1947, p. 157.

versa. In compression tests, for example, a material containing 83–85% Cu, 9.5–10.5% Sn, 4–6% Pb, and 1.5% graphite varies from 57,000 psi for high porosity (25–35%) to 70,000 psi for low porosity (10–18%). The corresponding Brinell hardness ranges on the 500-kg. scale from 25–35 up to 45–55. Bearings containing 88% Cu, 10% Sn, and 2% graphite have been found to possess a tensile strength up to 50,000 psi when the porosity did not exceed 10–15%. Since the shock resistance of such material is comparatively high, bearings of this type have been operated successfully at a stress load of 40,000 psi and still possessed a considerable safety factor. They have also withstood such severe operating conditions as loads up to 6000 psi at 30,000 r.p.m. and zero velocity, which are met in trucks that handle heavy loads in low gear, or in bulldozers. The physical properties of one brand of porous bronze bearings, as given by Langhammer,[7] are reproduced in Table 225. For further information the reader is referred to catalogs of the bearing manufacturers[8–14] and also to the ample literature on the subject.[15–22]

TABLE 225
Physical Properties of Self-lubricating Bearing Materials (Langhammer[7])

Physical properties	"Oilite Bronze"[a]	"Super-Oilite"[b]
Ultimate tensile strength, psi	12,500	30,000
Compression to permanent deformation, psi.		
for 0.001-in. set	11,000	30,000
for 0.005-in. set	16,000	47,000
for 0.015-in. set	18,000	58,000
Elongation in 2 in., % (min.)	5	1
Brinell hardness	30	45
Porosity (oil by volume, %)	30	25
Specific gravity	6.0	6.0
Coefficient of thermal expansion, per °C.	18.9×10^{-6}	13.9×10^{-6}
per °F.	10.5×10^{-6}	7.7×10^{-6}
Electrical conductivity, % of Cu	7.68	10.8

[a] Trade mark for a heavy duty oil-cushion bronze bearing produced by Amplex Div., Chrysler Corp.
[b] Trade mark for a heavy duty oil-cushion iron–copper bearing produced by Amplex Div., Chrysler Corp.

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[7] A. J. Langhammer, *Machinery N. Y., 51,* No. 8, 152 (1945).
[8] Chrysler Corp., Amplex Division, Detroit, Mich.
[9] General Motors Corp., Moraine Products Div., Dayton, Ohio.
[10] Bound Brook Oil-Less Bearing Co., Bound Brook, N. J.
[11] Keystone Carbon Co., St. Marys, Pa.
[12] Stackpole Carbon Co., St. Marys, Pa.
[13] Johnson Bronze Co., New Castle, Pa.
[14] The United States Graphite Co., Saginaw, Mich.
[15] S. L. Hoyt, *Metal Progress, 33,* 157 (1938).
[16] D. A. Clark, *Metal Ind. N. Y., 30,* 294 (1932).
[17] H. Chase, *Machinery N. Y., 41,* Nos. 1, 9 (1934).
[18] L. W. Johnson, *J. Inst. Production Engrs., 15,* 645 (1936).
[19] W. R. Lewis, *Intern. Tin Research Development Council, 10,* 13 (1941).
[20] H. C. Watkins, *Metals & Alloys, 15,* 751 (1942).
[21] W. R. Toeplitz, *Trans. Am. Inst. Mining Met. Engrs., 161,* 542 (1945).
[22] M. T. Victor, *Elec. Mfg., 37,* No. 2, 123, 210 (1946).

From an industrial point of view, the porous bronze bearing must possess a number of important properties, notably, low friction, high load-carrying capacity, and, most of all, safety against seizure and wear. This can be assured by an adequate oil film. The proper functioning of a continuous fluid lubrication is therefore of very great importance. Incidentally, most porous bearings have pore structures that act to strain the oil, *i.e.*, the bearing acts as a filter and permits only clean oil to reach the shaft, while all foreign impurities are repelled and accumulated in the oil reservoir.

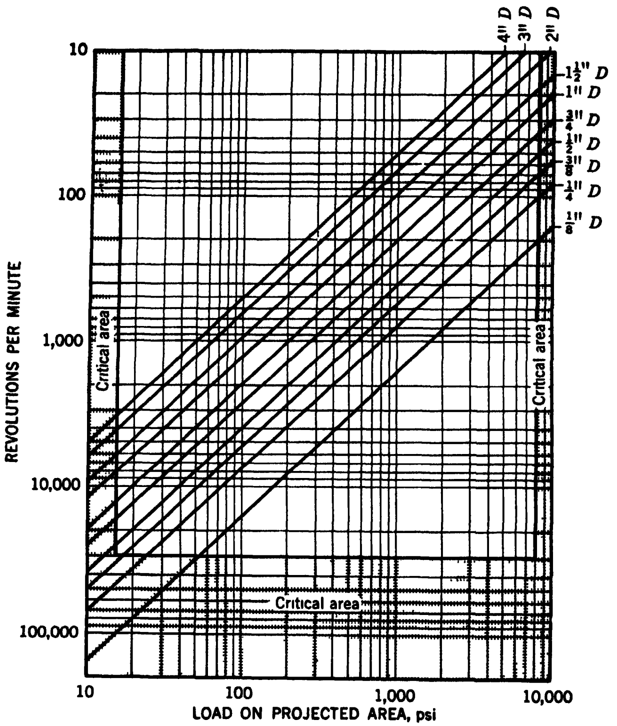

Fig. 553. Load-carrying capacity of porous bronze bearings as expressed by the relation between load on the projected area and shaft revolutions per minute. For bearings, fitting shafts of various diameters (D) from $^1/_8$ to 4 in. are given. Length of bearings is $1^1/_2$ times the diameter. (According to Victor.[23])

As to the high load-carrying capacity of self-lubricating bronze bearings, it may be said that this property has led to their successful use for many heavy-duty applications, including certain universal-joint bushings and king-bolt bushings, where they have successfully assumed much higher loads than normally expected.[22] It may be supposed that upon a sudden overload, part of the oil trapped in the bearing cannot immediately retract into the interconnected pores, and therefore forms a hydraulic cushion which transmits the instantaneous shock directly to the housing without affecting the bearing material. Only if the heavy shock load were continuous would the oil cushion break down and the porous metal be forced to carry the entire load, thereby failing rapidly. The increase in viscosity exhibited by lubricating oils subjected to pressure aids in the load-carrying capacity of the bearings, and enables porous bronze materials to be used safely for pressures up to 8000 psi.[22] Figure 553 gives an indication of the loads possible on porous bronze bearings of various diameters.

Bronzes as metal also show good wear resistance coupled with low friction characteristics. The coefficient of friction (*i.e.*, the ratio of the force necessary to impart or maintain motion divided by the force holding the surfaces together) is drastically reduced through the use of the lubricant in conjunction with a low-friction material, such as copper–tin–graphite bronzes.

Tait[22a] has recently discussed the influence of the microstructure and the modulus of elasticity on the behavior of different bearing materials. A structure consisting of two well-intertwined spongelike continuous phases—the one (copper) strong enough to give good mechanical properties in all directions, and the other (*e.g.*, lead) sufficiently plastic to be squeezed to the surface of the bearing—is produced readily and consistently by carefully controlled powder metallurgy techniques. A low modulus of elasticity, as displayed by porous nonferrous bearings, is of considerable advantage, since it helps to accommodate distortion, such as caused by unequal loading, poor fits, or misalignment of certain parts of the engine, and also permits easier passage of small dirt particles between bearing and journal.

Jones[23] has reported on a graphite-free porous bronze material consisting of 90.5% Cu and 9.5% Sn, and containing very large pores (0.75 mm.), which is claimed to be especially suited for high load applications requiring external oil supply. Without materially reducing the capillarity of the material required for the reabsorption of the oil, the large pore size is a factor in aiding in the distribution of the oil, which would normally be impeded by opposing suction forces. The material contains a major portion of virgin copper particles which are partly enveloped by alpha- and delta-bronze, and the capillary forces may be partly caused by the minute pores present inside the copper particles.

[22a] W. H. Tait, *Symposium on Powder Metallurgy.* The Iron and Steel Institute, Special Report No. 38, London, 1947, p. 157.

[23] W. D. Jones, *Principles of Powder Metallurgy.* Arnold, London, 1937, p. 153.

In a survey of the characteristic properties of the porous bronze bearings, Fronius[23a] has discussed the oil-retaining properties and shown how the results of tests for particle size, density, bearing loads, running speeds, and temperature of the bearings can be correlated.

Unckel[23b] has analyzed the bearing characteristics of porous bronzes and iron on the basis of frictional measurements (see also page 522 and Volume I, Chapter VIII).

Also of considerable importance is the chemical behavior of the porous bronze materials, especially in view of their corrodibility by oxidized or otherwise contaminated oils. A series of interesting experiments on the corrosion resistance of porous sintered bronze compacts have been reported recently by Hallett.[23c] The rates of corrosion of porous bronze compacts and their equivalent solid materials were not appreciably different in nitric acid, hydrochloric acid, and sodium chloride solutions. In sulfuric acid the porous sintered compacts were inferior to their solid counterparts, since pitting was observed more evenly under all test conditions. On the other hand, in caustic soda solutions, the porous bronze specimens were markedly superior (which may be attributed to a more pronounced precipitation of copper from the solutions due to a larger exposed surface, resulting in a more firmly held tin-rich surface film than would be the case with solid bronze with its smoother surface).

APPLICATIONS

Self-lubricating porous bronze bearings have been used to a great extent in small motors of fractional horsepower capacity. Their production on a highly competitive cost basis is possible where large quantities are involved. Applications in which such small motors are used are given by Victor[22] as follows: electric fans and blowers; vacuum sweepers; washing machines; dish washers; clothes dryers; sewing machines; phonographs and record changers; automobile heaters and defrosters; windshield wipers; mechanisms for raising and lowering tops of convertible automobiles; hood and window raisers, antenna reels; food mixers; electric clocks; business machines; refrigerators; heat regulators; air conditioning units; valve grinders of engines and compressors; textile equipment; pulley blocks and winches; and sundry instruments.

The use of porous bearings has been aptly summarized by Tait[24] in connection with a broad review of nonferrous powder metallurgy applications in automobile engineering. A similar review has recently been

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[23a] St. Fronius, *Arch. Metallkunde, 1,* No. 7/8, 352 (1947).

[23b] H. A. Unckel, *Metal Ind. London, 73,* 67 (1948).

[23c] M. M. Hallett, *J. Soc. Chem. Ind., 67,* 57 (1948).

[24] W. H. Tait, *J. Inst. Automobile Engrs., London, 15,* 101 (1946).

presented by Bradley,[24a] while a more general discussion of the properties and design principles connected with porous bearings, bushings, and allied products has been given by Langhammer.[24b]

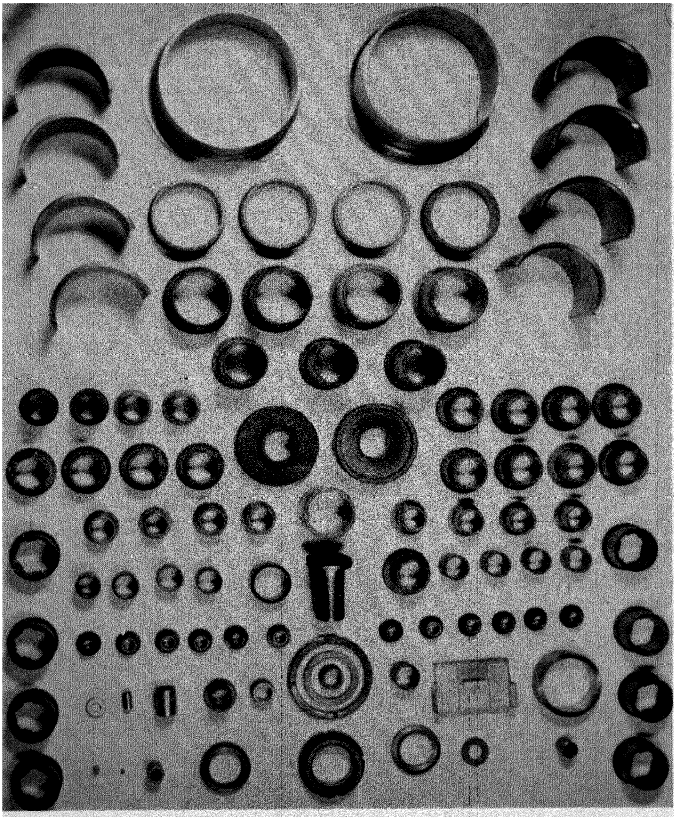

Fig. 554. Assortment of porous bronze bearings and bushings including half-shell and internal-splined types (courtesy of Amplex Division, Chrysler Corp.).

Figure 554 represents a variety of full and half-shell bearings of simple design, while Figure 555 gives an indication of the different sizes that are commercially produced. Figure 556 shows a number of special designs, including a ball bearing race. Most of the motors used for these applications use a shaft size between $^3/_{16}$ and $^5/_{16}$ in. They must operate smoothly and quietly, which requires close-running fits in the order of

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[24a] D. C. Bradley, *Iron Age, 163,* No. 12, 86 (1949).

[24b] A. J. Langhammer, *Proc. Third Annual Spring Meeting of Metal Powder Association,* New York, May 27, 1947, p. 32.

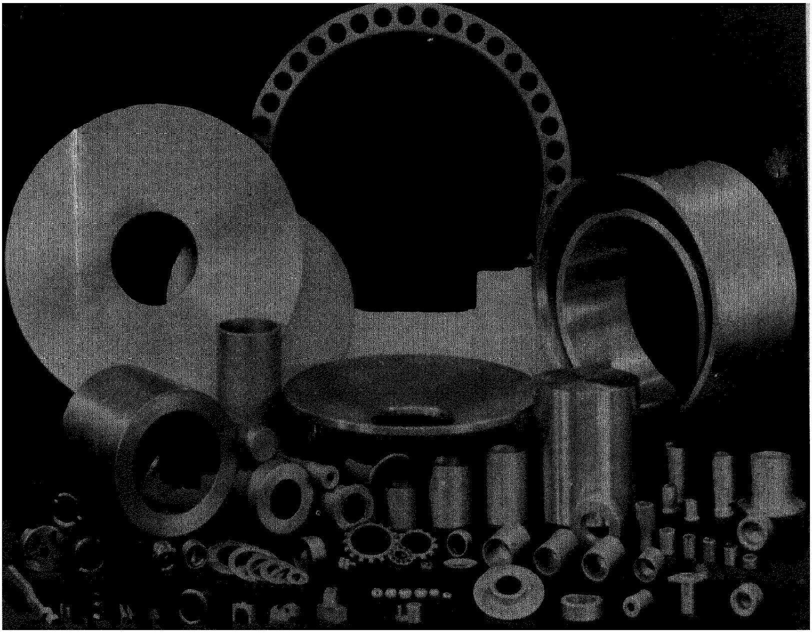

Fig. 555. Display of porous bronze bearings and bushings of various sizes. Also shown in the picture are ball bearing races, porous bronze stock for machining individual bearings, and a number of levers, arms, and similar shapes of more intricate design. The gear assembly at the lower left-hand corner is an oil pump gear set and made of iron. (Courtesy of Amplex Division, Chrysler Corp.)

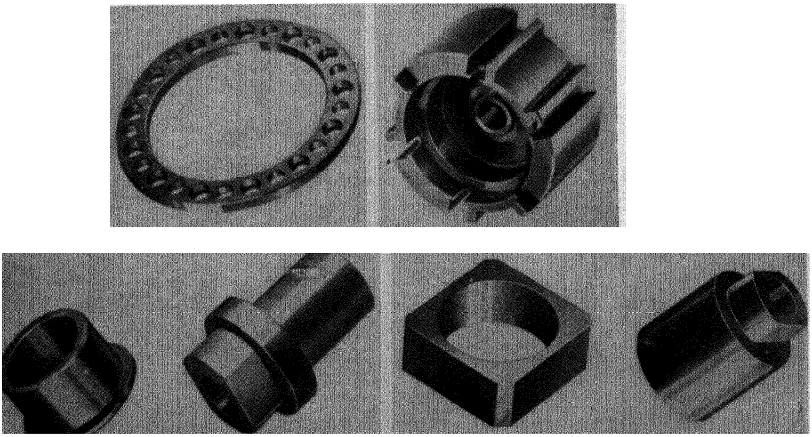

Fig. 556. Various types of porous self-lubricating bearing components

0.0005 in. Where small torques are involved, a self-aligning spherical bearing of the type shown in the sketch of Figure 557 is used. The spherical diameter of the bearing is maintained to a tolerance of 0.002–0.004 in., and

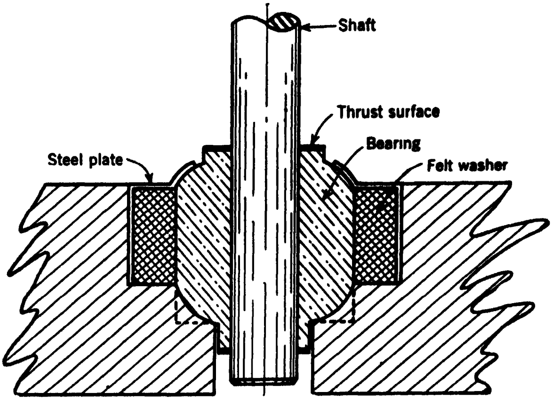

Fig. 557. Schematic presentation of a self-aligning spherical-type porous bronze bearing for applications where small torques are involved (according to Victor[22]).

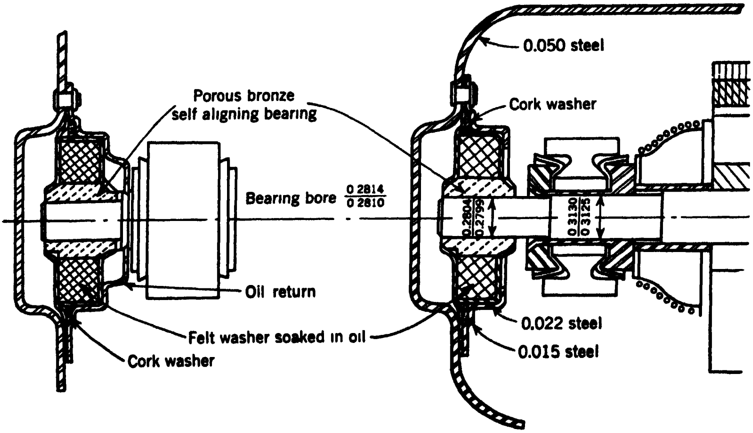

Fig. 558. Schematic presentation of a self-aligning porous bearing installation (according to Toeplitz[21]).

must be concentric with the bore within 0.002–0.003 in. The steel shafts require centerless grinding to a tolerance of 0.002–0.0005 in. Cylindrical bearings and bushings are generally produced to an outside diameter and bore tolerance of ±0.0005 in., while their length is held within ±0.005 in.

Other typical porous bearing installations are shown in Figures 558 and 559.

For most of these applications the bearings are required to operate without servicing for a minimum of 1000 hours under various atmospheric and temperature conditions. These include dry and dusty as well as wet and humid atmospheres and temperatures ranging from —35 to +60°C. (—30 to +140°F.).

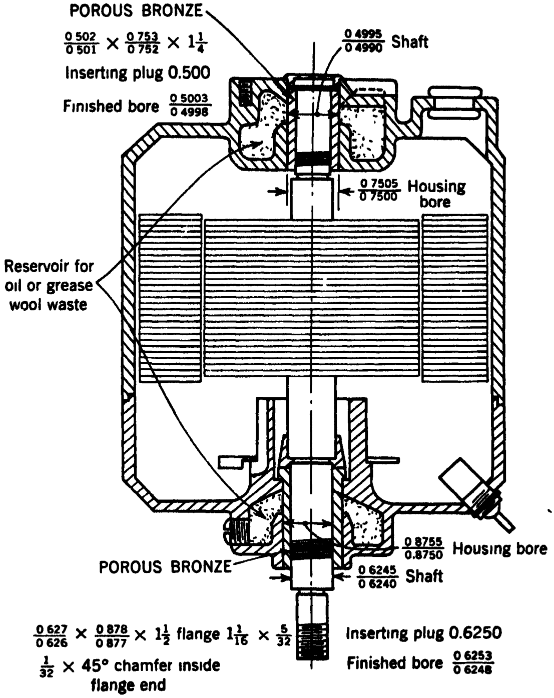

Fig. 559. Schematic presentation of the cross section of a vertical fan with self-lubricating bronze bearings installed (according to Toeplitz[21]).

Other Porous Bearings

COPPER-BASE BEARINGS OTHER THAN BRONZES

While the partial replacement of tin by zinc, lead, and iron has met with a certain measure of success, a complete substitution of tin by such metals as zinc or lead has been advantageous only in rare instances.

TABLE 226. Composition, Processing Conditions, Specific Gravity and

Composition	Molding pressure, tsi	Sintering cycle and atmosphere	Specific gravity		Brinell hardness	
			Before sintering	After sintering	Before sintering	After sintering
(1) 90.5% Cu, 7% Sn, 2.5% graphite	3.5	750°C. (1380°F.) 2.5 hr., vacuum	4.35	4.27	8	6.5
	14.2		5.92	5.78	19	15
	21.3		6.42	6.13	25	21.5
	35.5		6.85	6.60	27	27
	7.1	750°C. (1380°F.) 3.5 hr., N$_2$	5.11	5.11	12.5	9
	14.2		5.94	5.79	17.5	14
	21.3		6.38	6.18	21.5	17.5
	35.5		6.76	6.55	27	25
	7.1	750°C. (1380°F.) 3 hr., CO$_2$	5.10	5.47	13.5	12.5
	14.2		5.97	6.27	25	23
	21.3		6.50	6.67	29.5	27.5
	35.5		7.00	6.95	32.5	29.5
	7.1	650°C. (1200°F.) 3 hr., N$_2$	—	5.01	17.5	16
	21.3		—	6.30	18.5	16.5
	3.5	850°C. (1560°F.) 3 hr., N$_2$	4.48	5.11	16	15
	14.2		5.95	6.40	29.5	20
	21.3		6.52	6.85	27	25
	35.5		7.00	6.70	32.5	29.5
	3.5	750°C. (1380°F.) 1 hr., N$_2$	4.56	4.68	10; 3.5; 9.5	8
	7.1		5.25	5.38	12.5; 7.5; 16	12.5
	14.2		6.09	6.05	23; 15; 23	17.5
	35.5		6.84	6.73	32.5; 27; 27.5	25
(2) 89% Cu, 7% Sn, 4% graphite	3.5	750°C. (1380°F.) 3 hr., N$_2$	4.37	4.32	9	8.5
	7.1		5.12	5.38	12.5	12
	14.2		5.89	6.01	19	17.5
	35.5		6.85	6.68	32.5	30
(3) 93% Cu, 7% Sn	3.5	750°C. (1380°F.) 3 hr., N$_2$	5.35	6.28	26	20
	14.2		6.08	6.84	27	25
	21.3		6.58	7.06	32.5	39.5
	35.5		7.15	7.04	32.5	39.5
	7.1	750°C. (1380°F.) 3 hr., N$_2$	5.21	5.77	18	17.5
	14.2		6.17	6.43	27.5	25
	35.5		7.35	7.03	39.5	38
	7.1	750°C. (1380°F.) 1 hr., N$_2$	5.23	5.59	12; 8.5; 17.5	16
	14.2		6.10	6.30	23.5; 17.5; 21.5	21
	21.3		6.56	6.73	29.5; 27.5; 27	20
	35.5		7.25	7.02	48.5; 43.5; 34.5	32.5
(4) 100% Cu	7.1	750°C. (1380°F.) 3 hr., N$_2$	4.44	4.87	13; 8.5	5
	14.2		6.03	6.65	25; 17.5; 25	21.5
	35.5		6.97	7.38	67.5; 42.5; 32.5	25
(5) 100% Cu (fine grade)	14.2	750°C. (1380°F.) 3 hr., N$_2$	5.47	6.65	21.5; 12.5; 32.5	27
	35.5		6.52	7.24	69; 42.5; 32.5	29.5
(6) 96% Cu, 4% graphite	7.1	750°C. (1380°F.) 3 hr., N$_2$	4.76	4.83	15; 10; 8.5	8
	35.5		6.82	6.77	49.5; 43.5; 27	25
(7) 96% Cu, (fine grade), 4% graphite	35.5	750°C. (1380°F.) 3 hr., N$_2$	6.36	6.82	60.5; 41.5; 29.5	27

Physical Properties of Sintered Porous Copper-Base Alloys (Unckel[25])

	Tensile strength, psi	Compressive strength (longitudinal and transverse), psi						Total compression, %	
		For 0.5% compression		For 10% compression		Ultimate strength			
		L	T	L	T	L	T	L	T
(1)	285	—	—	—	—	—	—	—	—
	2,700	—	—	—	—	—	—	—	—
	4,400	—	—	—	—	—	—	—	—
	5,550	—	—	—	—	—	—	—	—
	1,000	—	—	—	—	—	—	—	—
	3,850	—	—	—	—	—	—	—	—
	3,000	—	—	—	—	—	—	—	—
	4,400	—	—	—	—	—	—	—	—
	—	9,250	3,550	16,780	16,350	40,400	28,000	53.5	55.5
	—	10,000	10,800	20,200	19,500	47,500	37,500	50.5	62
	—	10,650	10,000	24,900	24,200	47,400	37,000	52	50.5
	—	12,100	14,000	27,700	28,900	60,800	46,000	53	50.5
	—	—	—	—	—	—	—	—	—
	—	—	—	—	—	—	—	—	—
	7,100	—		—	—	—	—	—	—
	11,250	—	—	—	—	—	—	—	—
	15,000	—	—	—		—	—	—	—
	8,100	—	—		—	—	—	—	—
	1,565	—		—	—	—	—	—	—
	2,840	—	—	—	—	—	—	—	—
	5,270	—	—	—	—	—	—	—	—
	3,000	—	—	—	—	—	—	—	—
(2)	—	5,130	—	9,400	—	9,640	—	12	—
	—	9,250	—	16,900	—	17,100	—	18	—
	—	11,400	—	21,900	—	31,700	—	37	—
	—	12,800	—	23,900	—	49,000	—	46.5	—
(3)	7,400	—	—	—	—	—	—	—	—
	19,600	—	—	—	—	—	—	—	—
	22,050	—	—	—	—	—	—	—	—
	17,650	—	—	—	—	—	—	—	—
	—	6,400	6,120	23,200	17,900	56,500	59,400	65.5	54.5
	—	8,820	9,950	25,600	29,200	67,500	60,800	67	52
	—	12,100	12,800	32,000	39,800	91,400	70,100	61	42
	8,150	6,400	—	17,100	—	49,700	—	60	—
	8,250	10,700	—	22,100	—	65,000	—	62.5	—
	15,350	12,800	—	31,700	—	71,100	—	58	—
	11,100	21,600	—	37,700	—	74,000	—	58.5	—
(4)	—	2,560	—	10,700	—	12,950	—	48.5	—
	9,820	—	—	—	—	—	—	—	—
	14,800	11,500	—	25,900	—	61,900	—	69	—
(5)	12,400	—	—	—	—	—	—	—	—
	10,500	11,950	—	28,000	—	66,900	—	62.5	—
(6)	—	1,990	—	6,840	—	7,110	—	11.5	—
	4,400	8,700	—	24,000	—	33,600	—	38	—
(7)	—	11,250	—	27,600	—	42,200	—	31.5	—

Table continued

TABLE 226 (*concluded*)

Compositson	Molding pressure, tsi	Sintering cycle and atmosphere	Specific gravity		Brinell hardness	
			Before sintering	After sintering	Before sintering	After sintering
(8) 90% Cu, 6% Fe, 4% graphite	7.1	750°C. (1380°F.) 3 hr., N_2	5.50	4.91	15; 12.5	9.5
	35.5		6.21	6.33	38; 38; 26.5	25
(9) 92% Cu, 8% Pb	14.2	750°C. (1380°F.) 3 hr., N_2	6.15	7.13	21.5; 13; 15	11
(10) 90% Cu, 8% Pb, 2% graphite	14.2	600°C. (1110°F.) 3 hr., N_2	6.16	6.16	23; 17.5; 20	17.5
	14.2	750°C. (1380°F.) 3 hr., N_2	6.25	6.52	27; 17.5; 15	13.5
(11) 88% Cu, 8% Pb, 4% graphite	14.2	750°C. (1380°F.) 3 hr., N_2	5.98	6.17	21.5; 17.5; 15	12
(12) 100% Cu subjected to Zn vapor	35.5	950°C. (1740°F.) 2 hr., N_2	Partly fused		39.5	—
	35.5	925°C. (1700°F.) 2 hr., N_2	7.24	7.33	43.5; 27; 32.5	32
(13) 96% Cu, 4% graphite subjected to Zn vapor	35.5	925°C. (1700°F.) 2 hr., N_2	6.86	6.98	39.5; 27; 32.5	32
(14) 70% Cu, 30% Zn	35.5	900°C. (1650°F.) 3 hr., N_2	7.20	6.00	53.5; 43.5; 20	17.5
(15) 60% Cu, 40% Zn	35.5	900°C. (1650°F.) 3 hr., N_2	6.56	5.14	51; 32.5; 12.5	9.5
(16) 68% Cu, 29% Zn, 3% graphite	35.5	900°C. (1650°F.) 3 hr., N_2	6.32	5.43	43.5; 39.5; 11	10.5
(17) 58% Cu, 39% Zn, 3% graphite	14.2	900°C. (1650°F.) 3 hr., N_2	5.47	5.12	23; 17.5; 10	9
	35.5		6.34	4.58	48.5; 30.5; 8.5	8
(18) 58% Cu (fine grade), 39% Zn, 3% graphite	35.5	900°C. (1650°F.) 3 hr., N_2	6.25	5.01	46.5; 35.5; 8.5	8.5

Brasses generally show lower wear resistance in comparison with bronzes, and are therefore not very suitable for porous bearing materials.

Copper–lead bearing materials, containing from 20 to 40% Pb, balance Cu, are satisfactory for heavy load applications involving speeds up

TABLE 226 (*concluded*)

	Tensile strength psi,	Compressive strength (longitudinal and transverse), psi						Total compression, %	
		For 0.5% compression		For 10% compression		Ultimate strength			
		L	*T*	*L*	*T*	*L*	*T*	*L*	*T*
(8)	—	2,275	—	7,400	—	8,500	—	16.5	—
	—	10,250	—	11,800	—	14,100	—	11.5	—
(9)	—	—	—	—	—	—	—	—	—
(10)	—	8,800	—	15,350	—	16,300	—	22	—
	—	8,550	—	18,650	—	24,200	—	39	—
(11)	—	8,250	—	12,800	—	16,000	—	24.5	—
(12)	—	—	—	—	—	—	—	—	—
	12,500	—	—	—	—	—	—	—	—
(13)	—	—	—	—	—	—	—	—	—
(14)	4,550	5,130	—	18,500	—	18,650	—	10	—
(15)	—	3,000	—	9,250	—	29,200	—	42	—
(16)	4,000	2,700	—	11,400	—	28,200	—	64	—
(17)	—	1,140	—	6,550	—	17,500	—	43.5	—
(18)	1,710	5,120	—	11,100	—	34,500	—	52	—

to 3000 r.p.m. and oil temperatures not exceeding 135°C. (275°F.). Scoring and corrosion effects prevent their use at higher speeds and temperatures. Fatty acids and naphthenic acids, developed in hot lubricating oils as a result of oxidation, tend to attack the lead vigorously. To overcome this difficulty, porous bearing materials of copper or copper–nickel alloys have been impregnated with lead alloys containing 3% each of tin and antimony as outlined in the discussion of dense products (Chapter XXVI).

The physical properties of pressed and sintered porous copper-base alloys have been aptly investigated by Unckel.[25] The effect of molding pressure and sintering temperature on such properties as density, hardness, tensile strength, and compressive strength have been established on a number of copper alloys with zinc, lead, iron, and graphite, and compared with data obtained for pure copper and for bronzes containing 7% tin and various amounts of graphite. The possible substitution of tin by different metals—in particular, zinc—as hardeners, for the soft copper was also studied, but the physical properties of the bronzes could not be matched with any other combination. A summary of the test results is reproduced in Table 226. The interesting method of determining the loss of compacting pressure due to wall friction developed by Unckel has already been discussed in Volume I, Chapter VIII.

IRON-BASE BEARINGS

Porous bearings made from pure iron powders possess certain definite merits,[26] and their practical applications have increased considerably during recent years in this country as well as abroad (the development of iron-base bearings in Germany has recently been surveyed by Eisenkolb[26a]). The main advantages lie in their higher hardness and strength, as compared with bronzes, and in their favorable coefficient of thermal expansion, which is close to that of the steel shaft. The manufacture of porous iron bearings resembles that of bronze bearings, but the briquetting pressures are somewhat higher, and sintering is performed at about 1100°C. (2000°F.). Details concerned with the production, as well as with the properties and applications of iron-base bearings, are given in the recent book on iron and steel powder metallurgy by Kieffer and Hotop.[26b]

Of particular interest are iron–lead alloys containing from 2 to 6% Pb and from 2–4% graphite.[27] As seen from Table 227, iron–lead–graphite bearings can exhibit strength and hardness values corresponding to those measured on solid bronze bearings.[28] The lead is usually added

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[25] H. Unckel, *Z. Metallkunde, 36,* 164 (1944).

[26] O. H. Hummel, *Metallwirtschaft, 22,* 206 (1943).

[26a] F. Eisenkolb, *Arch. Metallkunde, 1,* 345 (1947).

[26b] R. Kieffer and W. Hotop, *Sintereisen und Sinterstahl.* Springer, Vienna, 1948, pp. 340 ff.

[27] H. Odenhausen, *Anzeiger Maschinenwesen, 66,* 3 (1944); *Chem. Zentr., 115, Pt. II,* 154 (1944).

[28] M. Köhler, *Demag Nachr., B14,* 29 (1940).

to the iron–graphite mixture in the form of fine metallic powder, but also as lead oxide, which is then reduced by the furnace atmosphere or by excess graphite during sintering. Close control of the briquetting operation and sintering in sealed retorts prevent substantial lead losses through sweat-out. Sintering is carried out in two steps, the first constituting a presintering operation at about 800°C. (1410°F.); this operation permits partial diffusion of the graphite and gradual escape of carbonaceous gases and volatile lubricants. A final brief sintering at 1100°C. (2010°F.) causes only small size changes and permits retention of the bulk of the carbon in graphitic form.

TABLE 227

Density, Hardness, and Strength of Various Bearing Materials

Material	Density, g./cc.	Brinell hardness	Tensile strength, psi	Compressive strength,[a] psi
Dense bronze .	8 0–8 6	40–60	15,000–25,000	50,000–60,000
Porous bronze . . .	6 0–6 5	20–40	2,800–4,200	30,000–40,000
Porous iron. . .	5 0–6 5	40–50	7,100–21,000	35,000–42,000
Porous iron–lead–graphite	5 5–6 0	40–60	17,000–21,000	42,000

[a] In 10% compression

Iron–copper bearing alloys containing from 2 to 20% Cu and from 0 to 4% graphite have found many uses for special heavy duty applications. Some types withstand pressures in excess of 100,000 psi at zero velocity. The physical properties of a self-lubricating porous iron–copper bearing material are compared with those of a porous bronze bearing in Table 225.[28a]

The physical properties of the most important commercial bearing materials in the United States have been compiled in a summarizing chart by Arata,[29] and are reproduced in Table 228. The survey compares iron–copper and pure iron products with bronzes of varying tin content, and considers the products of five of the leading porous bearing manufacturers.

Figures 560 and 561 show a variety of porous iron-base bearings and structural components together with some self-lubricating bearing parts made from bronze of the kind also shown in Figures 554 and 555.

ALUMINUM-BASE BEARINGS

Among other porous bearing materials studied,[30] those containing aluminum as a major constituent deserve special attention. Aside from

[28a] A. J. Langhammer, *Machinery N. Y.*, *51*, No. 8, 152 (1945).

[29] W. H. Arata, *Product Eng.*, *15*, 561 (1944).

[30] G. Wassermann and R. Weber, *Metallwirtschaft*, *22*, 201 (1943).

TABLE 228

Physical Properties of Bronze, Iron–Copper and Iron from Powdered Metals in Sintered Condition (Arata[29])

Material	Ultimate strength, psi		Loading		Load, psi, for permament set of		Elongation, %	Brinell hardness	Porosity, oil by vol. %	Weight per in.^{3}, lb.	Coeffi. of thermal expansion $\times 10^{-6}$ per °C.(°F.)
	Tensile	Compressive	Static, psi	PV factor[a]	0.001 in.	0.005 in.					
BOUND BROOK OIL-LESS BEARING CO[b]											
Compo Bronze (88.5 Cu, 10 Sn), bearings and parts	12,000	69,000	7,500	50,000	10,500	—	—	25–35	27	0.228	17.6 (9.8)
Powdiron 55-P (95 Fe, 5 Cu), bearings and parts	12,000	140,000	15,000	50,000	16,000	—	—	25–40	32	0.199	13.0 (7.2)
Powdiron 61-1C (90 Fe, 10 Cu), heavy-duty parts.	30,000	140,000	20,000	60,000	17,000	—	—	60–90	25	0.221	13.9 (7.7)
Powdiron 51-1 (100 Fe), special parts.	12,000	130,000	20,000	50,000	22,000	—	—	35–50	25	0.214	12.2 (6.8)
CHRYSLER CORP., AMPLEX DIV.											
Oilite Bronze (90 Cu, 10 Sn)											
Bearings and parts.	12,500	120,000	8,000	75,000	11,000	16,000	5	30	30	0.22	19.4 (10.8)
Machine parts, heavy duty. . .	18,000	200,000	—	—	20,000	25,000	10	30	—	0.25	—
Machine parts, maximum duty	40,000	230,000	—	—	30,000	35,000	20	60	—	0.30	—
Super-Oilite (75 Fe, 25 Cu)											
Bearings and parts.	30,000	198,000	46,000	50,000	30,000	47,000	1	45	25	0.23	13.9 (7.7)
Machine parts, heavy duty. . .	35,000	190,000	—	—	35,000	50,000	2	60	—	0.25	—
Machine parts, maximum duty	45,000	250,000	—	—	40,000	55,000	2	90	—	0.256	—
Iron-Oilite (100 Fe)											
Bearings and parts.	15,000	130,000	20,000	50,000	22,000	40,000	1	40	30	0.22	10.8 (6)
Machine parts, heavy duty. . .	30,000	120,000	—	—	30,000	50,000	2	70	—	0.230	12.2 (6.8)
Machine parts, maximum duty	35,000	150,000	—	—	35,000	55,000	2	90	—	0.24	12.6 (7.0)

KEYSTONE CARBON CO.											
Selflube Bronze (90 Cu, 10 Sn)	14,000	—	—	45,000	11,000[c]	—	—	—	24	0 222	—
Selflube Iron (95 Fe, 5 Cu)	16,000	—	—	50,000	30,000[c]	—	—	—	29	0 195	—
Selflube Iron (90 Fe, 10 Cu)	40,000	—	—	—	50,000[c]	—	—	—	24	0 212	—
MORAINE PRODUCTS DIV., GENERAL MOTORS CORP.											
Durex Iron (98 Fe, 2 Cu)	25,000	—	15,000	50,000	20,000–25,000	—	Nominal	60–90	20–30	0 20–0.22	11 7–12.6 (6.5–7)
Durex Iron (100 Fe)	20,000–35,000	—	—	—	10,000–15,000	—	3–12	35–70	10–25	0 21–0 24	11.7–12.6 (6 5–7)
Durex Bronze (89 Cu, 10 Sn) plus graphite addition	12,000	—	7,500	50,000	11,000	—	—	25–40	20–30	0 22–0 25	18 (10)
Durex Bronze (95 Cu, 5 Sn)	30,000–40,000	—	—	—	12,000–20,000	—	5–10	65–100	—	0 29	—
UNITED STATES GRAPHITE CO.											
Grade 61 (90 Cu, 10 Sn)	21,000	—	7,000	50,000	14,000	18,000	—	—	20–25	0.237	17 5 (9 7)
Grade 81 (90 Cu, 10 Sn), slight graphite addition	14,000	—	6,000	50,000	9,000	13,000	—	—	20–30	0 223	17.5 (9 7)
Grade 86 (85 Fe, 15 Cu), slight graphite addition	20,000	—	15,000	50,000	16,000	24,000	—	—	15–20	0.210	12 8 (7.1)
Grade 139-U (100 Fe)	10,000	—	10,000	50,000	14,000	18,000	—	—	20–25	0.199	12.2 (6 8)
Cast phosphor bronze (83 Cu, 7 Sn, 7 Pb, 3 Zn)	30,000–38,000	—	—	—	—	—	12–20	55–65	—	0.32	18 (10)

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[a] Product of load P per square inch of projected area and shaft velocity V in feet per minute.

[b] Data based on standard ASTM specimens.

[c] In compression-2 per cent.

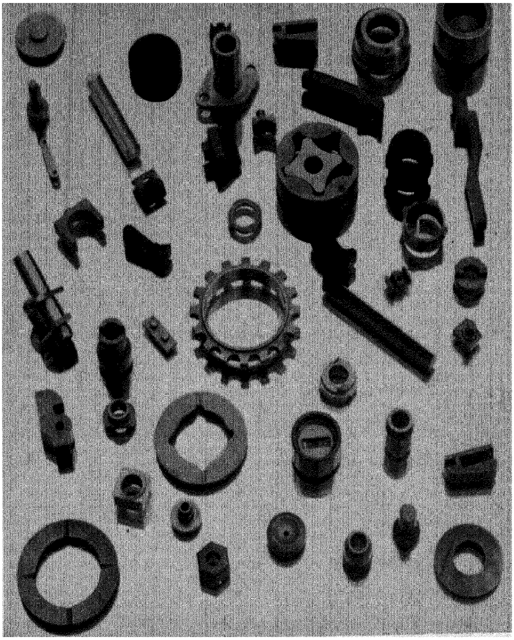

Fig. 560. Assortment of self-lubricating type porous iron-base and bronze parts (courtesy of Amplex Division, Chrysler Corp.).

Fig. 561. Self-lubricating bearing parts made from iron and bronze powders (courtesy of Moraine Products Division, General Motors Corp.).

their excellent corrosion resistance against oxidized oils, and their lightness, they have been found to perform exceptionally well even at fairly low speeds, provided additional external lubrication was used. In fact, some compositions have exhibited good performance at very high limiting loads, thus matching that of self-lubricating bronze bearings.[31] Porous aluminum bearings containing certain intermetallic compounds were found to give smooth operation without scoring, and were suggested in Germany for equipment used in aeronautical machinery.[30] While, in the wrought material, a coarse crystalline structure of the hard compounds tends to cause scoring and nonuniform bearing properties, the powder metallurgy process permits incorporation of the intermetallic compounds (in the form of atomized or pulverized powder) into the soft aluminum base in extremely fine particle size and in uniform distribution. To prevent any possible change or even complete dissolution of the intermetallic compounds by diffusion during sintering, the compounds added to the aluminum are preferably of the type and in a proportion that permit a state of stable equilibrium with the base metal. Compositions found especially suitable and comparing favorably with babbitt metals include 5–9% Al_3Fe, balance Al; 5% Al_5Mn, balance Al; 5% $CuMg_2$, balance Al. A composition containing 20% Al_3Fe, balance Al, however, does not approach the bearing properties of babbitt bearing metals. These bearings may be briquetted at 18–28 tsi and sintered in air at 600°C. (1110°F.) for a period up to 72 hours.

Other known types of aluminum-base bearing alloys are those containing tin or lead. Porous compositions containing 7% Sn, or 15 to 40% Pb, balance Al, are produced from mixtures of the elemental powders or from atomized alloy powders. After sintering at temperatures around 600°C. (1110°F.) for several hours, they are sized and oil impregnated as for bronze bearings. Although preliminary test results have indicated that the composition with tin is slightly superior to the ones containing lead, the over-all performance of these porous bearings—in their present state of development—appears to be not quite as satisfactory as regular babbitt metals, and definitely inferior to porous bronze or iron bearings. Aluminum-base alloys containing thallium as second, soft constituent are also claimed to be suitable for porous bearings.[31a]

POROUS WEAR-RESISTANT PARTS

Applications in which porous parts are subjected to heavy wear or appreciable compressive stresses are closely related to the field of porous bearings and bushings. In fact, some particular parts are distinguished

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[31] H. R. Clauser, *Materials & Methods, 24,* 533 (1946).

[31a] U. S. Pat. 2,418,881.

from simple bearings merely by their more complex design. However, an important consideration in the case of wear-resistant parts which should not be overlooked is that the metal must be sufficiently hard and rigid to withstand the shear and compression stresses—a requirement that does not generally apply to bearing materials. On the other hand—as for bearings—the inherent porosity in the material appears to be advantageous, since the pores at the surface tend to limit the effects of wear to the minute intermediate metal surfaces. Thus porous, wear-resistant materials exhibit more of a "microwear" phenomenon as compared with the "macrowear" characteristics known in solid metals such as steels. An additional advantage of the porosity is that, if it is of the interconnecting type, it can serve as a reservoir for a fluid lubricant, which can be used in conjunction with materials varying greatly in hardness or other physical properties. To date, a growing number of typical products fall into this class of wear-resistant, porous parts. They are mostly made of steel, and include parts for measuring devices, tools, and tool machines. It appears that this field of porous, wear-resistant parts is quite promising, and that further expansion of powder metallurgy products can be expected in this direction.

The previously described oil pump gears[32] (see Chapter IX (Volume I) and Chapter XXV) for automobile engines are a classical example of such a part. A quasi-eutectoid steel skeleton which includes some free graphite inclusions furnishes resistance to wear and plastic deformation of the gear teeth during service, while the oil can freely pass through the intercommunicating pore system, thereby furnishing both lubrication and protection against corrosion. An improved product, as far as dimensional stability and, therefore, smoothness of performance, is concerned, has recently been reported by Ensign,[32a,b] who modified the sizing operation by forcing the sintered gear through a thin extrusion plate of high alloy tool steel.

A product similar in structure (eutectoid or hypereutectoid), though used in a different application, is the porous piston ring developed in England during the war.[33,34,34a] This product has exhibited superior bearing and wear properties (particularly in high-pressure service) as compared

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[32] F. V. Lenel, in J. Wulff, *Powder Metallurgy*. Am. Soc. Metals, Cleveland, 1942, p. 502.

[32a] E. E. Ensign, *Proc. Third Annual Spring Meeting of Metal Powder Association*, New York, May 27, 1947, p. 14; *Automotive Industries, 97*, 30 (1947).

[32b] E. E. Ensign, *Iron Age, 163*, No. 12, 76 (1949).

[33] J. A. Judd, *Automobile Engr., 34*, 379 (1944).

[34] J. A. Judd, *Symposium on Powder Metallurgy*. The Iron and Steel Institute, Special Report No. 38, London, 1947, p. 117.

[34a] J. A. Judd, *Machinery London, 69*, 109 (1946).

with the standard type of piston ring. Apparently, the production of piston rings by pressing and sintering has also proved advantageous from an economic point of view, despite the fact that only comparatively high-priced domestic iron powders (*e.g.*, electrolytic) were available in England during the war. Similar work in Germany, however, proved to be unsatisfactory, according to a report by Leadbeater,[34b] since the piston rings rapidly lost their tension, and also caused excessive wear of the cylinder walls, which, interestingly enough, increased with increasing porosity of the rings.

Another interesting development involves the use of porous dies for molding plastics or pharmaceuticals.[34c] Sintered and hardened steel bushings of carefully controlled porosity are used as die liners, and the die lubricant is steadily metered by passage from an external reservoir through the interconnected pore system to the surface of the die cavity. In order to avoid sealing the surface pores by some of the powder particles during molding, the pore size, as well as the total porosity volume, must be kept comparatively small. Hence, the intercommunication between the pores is less extensive than in most porous bearings, and the flow of the lubricant through the system must be facilitated by external pressure. Jones[35] has reported the successful application of this system in England, during the war, in connection with porous carbide dies, when external lubrication was required for the mass production of penicillin tablets.

The production of hard and wear-resistant porous iron and steel products by means of a special oxidizing treatment has been described by Lenel.[35a,35b] The sintered ferrous parts are subjected to steam at about 580°C. (1075°F.) in a closed container, and protective skins of the magnetic Fe_3O_4, which eventually become impervious to water vapor, form to a certain thickness at the walls of the interconnected pores that are exposed to the steam. After approximately 1 hour, the oxidizing reaction has come to a stop, and a complete network of the oxide has formed throughout the structure. Depending upon the density of the part—which in turn can be controlled by the compacting pressure—the absorption of oxygen can be controlled between 2 and 12%. The steam treatment causes a marked improvement in the hardness and yield point of the sintered part, whereas the tensile strength is reduced by about 15%.

[34b] C. J. Leadbeater, *Symposium on Powder Metallurgy*. The Iron and Steel Institute, Special Report No. 38, London, 1947, p. 191.

[34c] U. S. Pat. 2,444,282.

[35] W. D. Jones, *Communication Second Powder Metallurgy Medal Lecture,* Stevens Inst. of Tech., April 24, 1946; see also *Powder Met. Bull., 1,* No. 3, 48 (1946).

[35a] F. V. Lenel, *Iron Age, 148,* No. 18, 29 (1941); also in J. Wulff, *Powder Metallurgy*. Am. Soc. Metals, Cleveland, 1942, p. 512.

[35b] U. S. Pat. 2,187,589.

The steam-treated iron-base materials have various practical applications, such as for guides for metal cutting saws, for rollers supporting drawers of stoves and refrigerators, and for vanes in Diesel engine fuel pumps. (For additional information, see Volume I, Chapter XX.)

Finally, the mass production in Germany during the war of paraffin-impregnated iron driving bands for bullets of various caliber should be mentioned here.[36,37] These bands, produced from various grades and types of iron powders (atomized, eddy-milled, reduced, etc.) on a truly tremendous scale (reaching a total production of about 100,000 metric tons,[37a] and up to 3500 tons per month during peak production periods[38]), did not only compare favorably with standard copper bands with regard to their own physical properties, but reportedly improved the life of the gun barrels up to 50%.[38,39] Valuable information on details of production and properties has recently been advanced by Ivory,[37] Krebs,[39a] and in the book by Kieffer and Hotop.[37a]

POROUS FILTERS AND SIMILAR PRODUCTS

Filters

The close control of pore size and total pore volume which signifies the self-lubricating bearings and the porous wear-resistant parts can also be advantageously employed in the manufacture of filters, diaphragms, and similar products. Thus, by proper selection and control of the pore sizes it is possible to separate (*1*) solids from liquids, such as impurities in oil, (*2*) liquids from other liquids in nonemulsified mixtures of liquids—such as benzene and water—on the basis of a difference in wetting ability to the metal surface, and (*3*) gases from liquids, such as air from water or oil.[40] Such filters are generally similar to those of the ceramic type. However, the fact that they are made of metal accounts for their considerably superior mechanical strength and their greater resistance to both mechanical and thermal shock.

[36] G. M. Butler, U. S. Dept. of Commerce, Office of Publication Board, P.B. 1834; Combined Intelligence Objectives Sub-committee (London) 21, XXX-8, 13 (1946).

[37] W. Ivory, *Symposium on Powder Metallurgy*. The Iron and Steel Institute, Special Report, No. 38, London, 1947, p. 203.

[37a] R. Kieffer and W. Hotop, *Sintereisen und Sinterstahl*. Springer, Vienna, 1948, pp. 368 ff.

[38] G. J. Comstock, *Communication at Powder Metallurgy Colloquium*. New York University, April 26, 1946.

[39] British Intelligence Objectives Sub-committee, Final Rept. No. 1323 (June, 1947); see also *Met. Powd. Rept., 2,* No. 1, 4 (1947).

[39a] H. L. Krebs, Field Information Agency, Technical (F.I.A.T.), Final Report No. 979 (1947); *Powder Met. Bull.,* 3, No. 2, 42 (1948).

[40] C. Hardy, *Symposium on Powder Metallurgy*. ASTM, Philadelphia, Pa., 1943, p. 1.

MANUFACTURE

The first comprehensive published account of the manufacture o porous filters and their range of uses was recently presented in Englan by Sinclair.[41] A more general review of the production of powdere metal filters and products including the recently developed stainless type has been published by Seymour.[42]

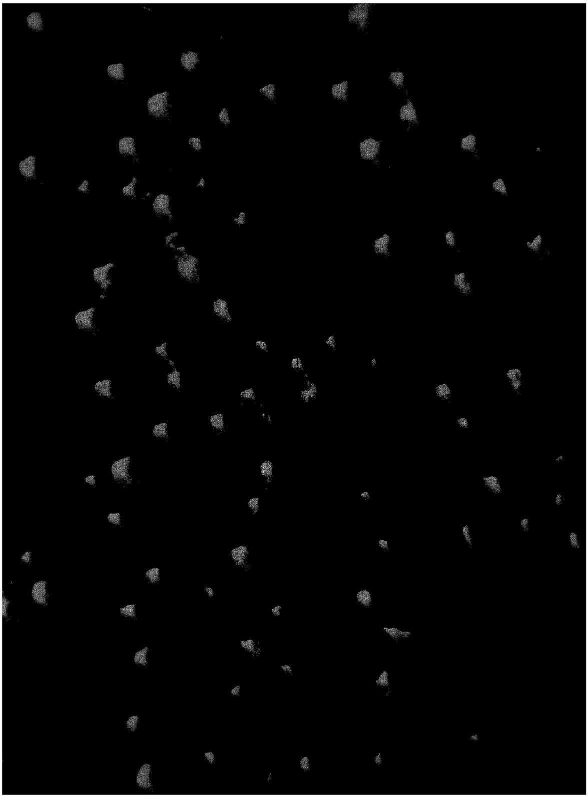

Fig. 562. Surface appearance (×10) of spherical copper powder (courtesy New Jersey Zinc Co.).

The production of metallic filters and related products is rather simpl and resembles that of porous bearings to a certain extent, the main difference being in the type of powder used and in the method of formin

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[41] C. E. Sinclair, *Symposium on Powder Metallurgy*. The Iron and Steel Institute, Special Report No. 38, London, 1947, p. 105.

[42] H. Seymour, *Mining Mag.*, 77, 206 (Oct., 1947).

the product. Filters and diaphragms are made from corrosion-resistant metals, and bronzes, nickel, and stainless steel are particularly suitable; brass, copper, and iron products are also used occasionally for this purpose. Of the bronze compositions, alloys containing from 5 to 12% Sn, balance Cu, are used most generally. Mixtures of elemental metal powders, such as copper and tin—as conventionally used in the manufacture of porous bearings—are not very suitable for filters and similar products, since the high degree of porosity retards diffusion during sintering. Instead, alloy powders, each particle of which contains the correct composition in a homogeneous structure, are usually preferred. Very close control of the particle size distribution is of extreme importance. For some applications, however, tin-coated copper powders are used to advantage, the tin either having been electroplated on the copper particles, or having been coated mechanically with the aid of binders. Powders consisting exclusively of spherical or near-spherical particles, as obtained by the carbonyl process or by special atomizing techniques, greatly facilitate the control of the required porosity characteristics, and lately have replaced to a large extent all other powders in the manufacture of filters and related products. Figure 562 shows the surface appearance of spherical copper powder (for other photographs of spherical powders suitable for metallic filter products see Volume I, Figures 8*B*, 9, 22*A*, and 49).

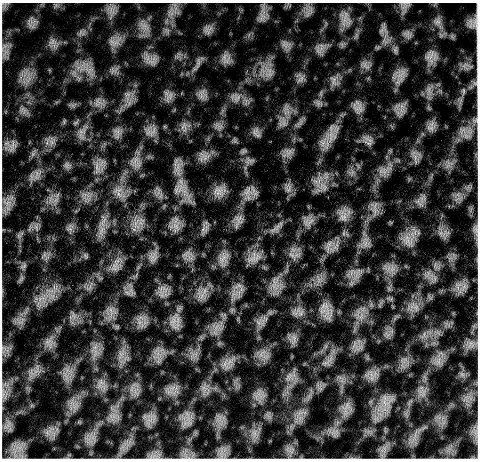

Fig. 563. Degree of perfection of packing (×6) attained with spherical bronze powder (according to Sinclair[41]).

The fact that spherical powders are generally quite resistant to compaction and plastic deformation is of little concern, since the high degree of porosity in most filters calls for loose compaction, as achieved either by light pressures or by loose packing and tamping of the powder in suitable molds. Figure 563 gives an impression of the degree of perfection of packing attained in practice. Thus, for example, loosely packed carbonyl nickel powders—that are settled in a mold by tapping and shaking —are claimed to result after sintering in hydrogen atmosphere for 8 hours at 1000°C. (1830°F.) in porous filters with a porosity of as much as 85%![43]

The loose powder masses are usually sintered at temperatures close to the melting point of the metal or alloy. For example, bronzes are sintered at about 800°C. (1470°F.) for ½ to 1 hour. In the case of the tin-coated copper powders, the tin melts during this operation and diffuses into the particles, leaving additional interstices and voids between the particles. The molds in which the loose powder is sintered are usually made of graphite, but can also be constructed of suitable ceramics or metals (*e.g.*, chromium-plated steels). If made with sufficient accuracy, no additional sizing operation of the products is required.

Conventional cold pressing becomes necessary for products of limited or localized porosity. Here, the spherical powders are less advantageous, and other types (*e.g.*, mechanically disintegrated, electrolytic, etc.) are more suitable.

Conventional molding techniques may prove inadequate for filter bodies of intricate shape or considerable length, and new methods of manufacture are indicated. One of these new techniques has been reported from Germany by Wassermann.[44] Parts of practically any desired length can be produced by filling the metal powder into steel tubes, and drawing the tubes on a drawing bench or squeezing them in a profiling rolling mill until the desired degree of densification of the powder mass is obtained. After sintering, the porous core body has sufficient coherence and strength to withstand extraction from the tubing. In certain instances it may be desirable to retain the steel tubing for the purpose of furnishing a strong backing material for the porous component.

An ingenious method of rendering porous metallic masses corrosion resistant was patented by Marvin and Koehring[45]; the invention relates to the plating of the entire internal surface of those metal sections having interconnected pores. Based on the principle of plating the pore surfaces with a metal lower in the electrochemical series than the base metal, this process has particular value for the production of low-cost metallic filters

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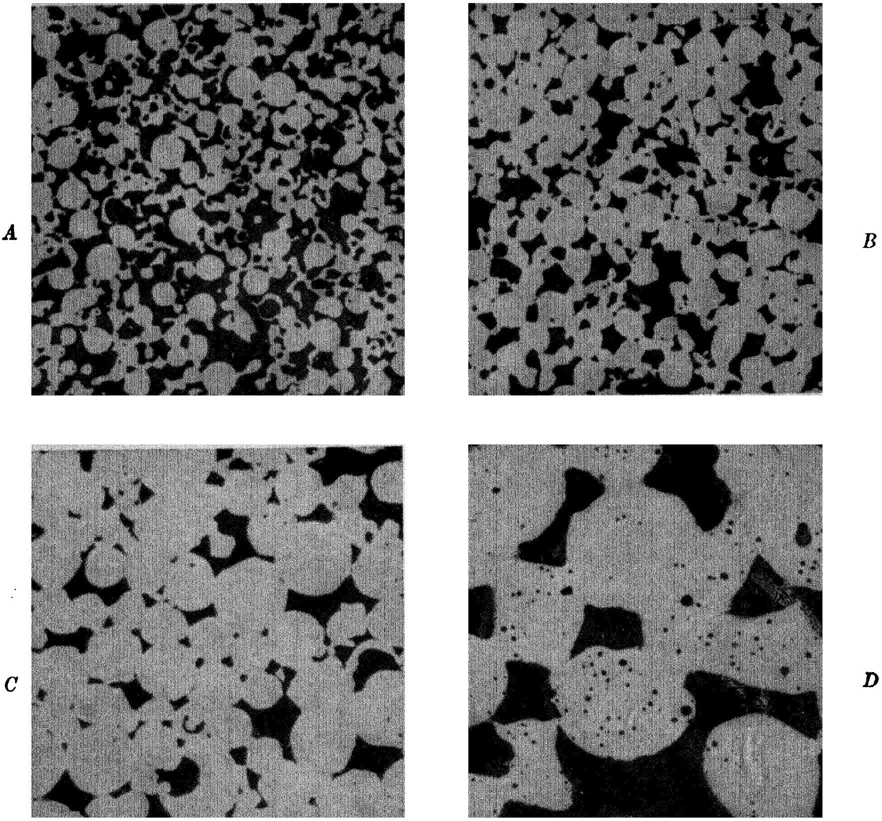
[43] U. S. Pat. 2,198,042.

[44] G. Wassermann, *Metallforschung, 2,* 129 (1947).

[45] U. S. Pat. 2,409,295.



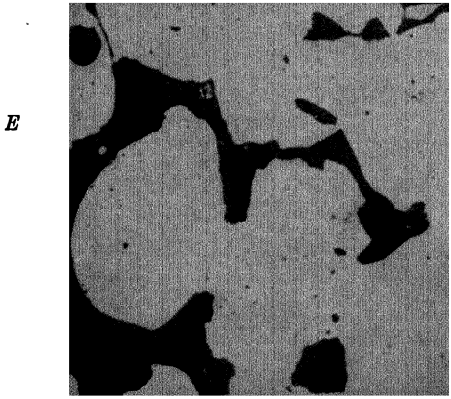


Fig. 564. Change in pore structure (×94) of sectioned bronze filters with increasing grain size of the original powder (according to Sinclair[41]). All sections as polished: *A*, "Porosint," grade A; *B*, "Porosint," grade B; *C*, "Porosint," grade C; *D*, "Porosint," grade D; *E*, "Porosint," grade E.

to be used for chemical applications, and should also be invaluable for certain types of porous bearings that are subjected to the corrosive effects of oxidized lubricating oils. Circulation of the plating salt solution by mechanical pressure supplies sufficiently concentrated solutions to all sections of the interconnected pore system and thus secures satisfactory plating of the entire pore surface. The concentration of the salt in the solution and the time of circulation determine the thickness of the plated surface films. Upon heating, partial or complete diffusion of the plating metal into the base metal can be obtained. Instead of plating with a salt solution, plating can also be accomplished from the gaseous phase. The latter process appears to be particularly desirable for metals having comparatively high vapor pressures, *e.g.*, zinc or cadmium. The vapors of the plating metal are forced through the pore system with the aid of an exhaust pump. Neither process affects the porosity to any appreciable extent, but the surface characteristics of the porous product are changed to those of the plating metal.

PROPERTIES AND APPLICATIONS

Employing metallographic techniques of sectioning filters, Sinclair[45a] shows the effect of varying metal particle size on the distribution of porosity obtained in the sintered product. In Figure 564 a series of photomicrographs shows the change in pore size without substantial change in character of the porosity for increasingly coarse filter grades. The porosity is approximately 37% by volume in all cases. The size of the powder (usually an atomized bronze of near-spherical particle shape and of about 11% Sn content) must be controlled closely by grading in order to assure filtering efficiency as well as economy of the manufacturing process. Depending on degree of porosity, these filters were found to have tensile strengths of 2200 to 4200 psi; they could reach bending angles of 30 to 50°, explaining why the material is comparatively shock resistant and can withstand misalignments in practice.

The chief requirement for porous materials is that the porosity must give the desired filtering performance. In the case of commercial bronze filter products, various grades—distinguished by their different porosities—are available on the market,[46] with a coarse grade being capable of removing particles down to 0.002–0.005 in. in largest diameter, and a fine grade being capable of removing particles down to 0.0005 in. and smaller. The tensile strength of such materials is about 4000–6000 psi, with an

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[45a] C. E. Sinclair, *Symposium on Powder Metallurgy*. The Iron and Steel Institute, Special Report No. 38, London, 1947, p. 105.

[46] T. C. DuMond, *Materials & Methods, 23,* 123 (1946).

elongation varying between 3 and 15%. Compressive strength and deformability in compression are considerably higher. The corrosion resistance of the material compares with that of cast bronze, and the material can be heated in nonoxidizing atmospheres up to 500°C. (930°F.) without serious detriment to the filtering or strength characteristics.

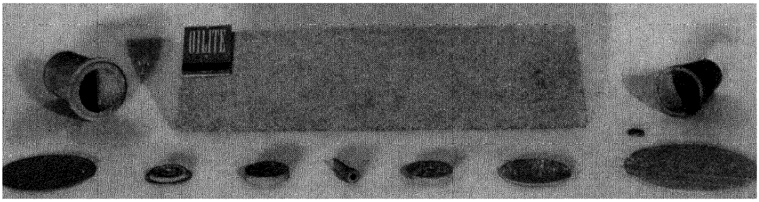

Fig. 565. Display of porous bronze filters of different size and shape (courtesy of Amplex Division, Chrysler Corp.).

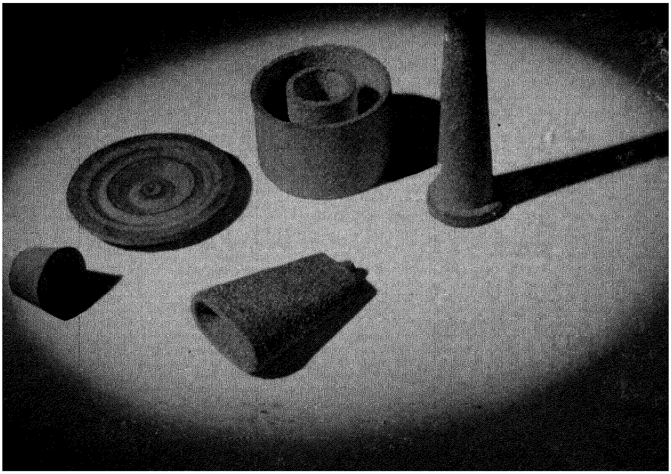

Fig. 566. Porous metal filter structures (courtesy of Moraine Products Division, General Motors Corp.).

Porous filters and diaphragms are used extensively for oils, *e.g.*, paraffin or Diesel fuel, refrigerants, lyes, caustic and other chemical solutions, and emulsions. Other uses include the filtration of water, particularly by the British Services in the field[45a]; sterilization filters and diaphragms producing definite diffusion rates in certain types of control

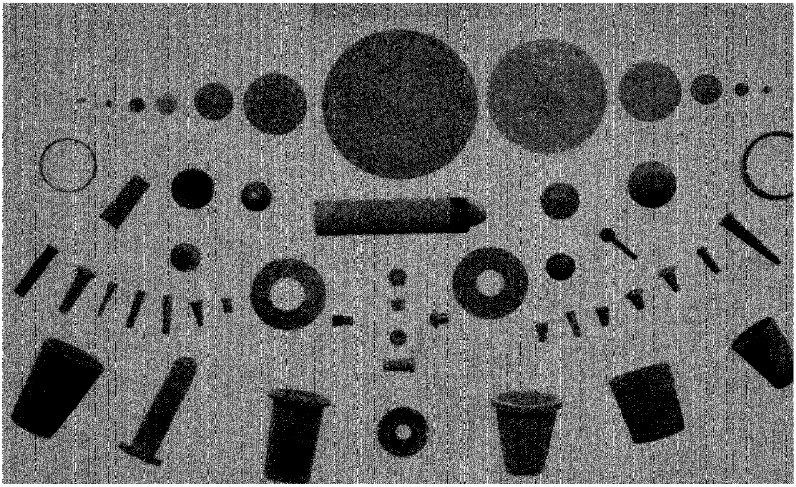

Fig. 567. Assortment of sintered bronze filter cups, disks, washers, and tubes (courtesy of Moraine Products Division, General Motors Corp.).

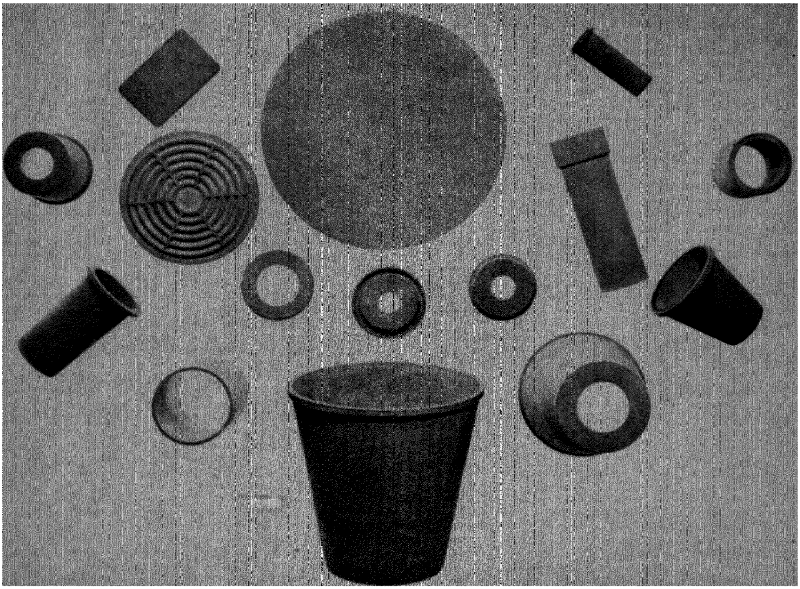

Fig. 568. Variety of sintered porous metal filter shapes (courtesy Moraine Products Division, General Motors Corp.).

instruments; porous nickel filters for concentrated sodium hydroxide solution. Some of the more specific applications include anodes for electrolytic cells and condensers (*e.g.*, porous Ni or Al electrodes),[47,48] electrodes for secondary elements, and electrical contacts and collectors operating in water; porous bronze distributors for the fermentation process in the manufacture of yeast[45a]; porous molds for castings and types for printing, pads for inking wicks, and gaskets of various shapes; sintered porous copper screens as a substitute for wire screens,[49] and porous copper–nickel–tin distributors for the production of cresylic acid.

The great variety of shapes of these filters becomes apparent from Figures 565–568.

Lately, sintered filter bodies have been produced from stainless steel powders (see also Chapter XXV), and the products obtained from these materials possess an excellent combination of desirable properties, especially high strength and ductility coupled with the corrosion resistance of stainless steel. Dale[50] gives an indication of the corrosion resistance of sintered porous stainless steel. When exposing a certain type of material (as used for filters) at a temperature of 21°C. (70°F.) to various corrosive media, the following periods of estimated life result:

68% nitric acid solution	20 years
10% nitric acid solution	30 years
96% sulfuric acid solution	1.3 years
10% sulfuric acid solution	3 weeks
37% hydrochloric acid solution	5 hours
1% hydrochloric acid solution	4 weeks
40% sodium hydroxide solution	10 years
85% phosphoric acid solution	20 years
10% phosphoric acid solution	40 weeks

Available in a wide range of porous sizes, stainless steel filters are used increasingly in laboratory ware, such as filter crucibles, Büchner funnels, gas dispersion tubes.[51] Pall[52] recently reported that filter-type snubbers (checks) made from porous stainless steel of controlled permeability are superior to orifice-type snubbers in preventing pressure gage failures due to pressure shock—the main advantage lying in the complete freedom from plugging of the metal filters.

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[47] German Pat. 708,895.

[48] A. Fleischer, *J. Electrochem. Soc.*, *94*, 289 (1948).

[49] Anonymous, *Wire Ind.*, *13*, 561 (1946).

[50] J. D. Dale, *Proc. Third Annual Spring Meeting of Metal Powder Association*, New York, May 27, 1947, p. 4.

[51] Products of the Micro Metallic Corp., Brooklyn, N. Y.

[52] D. B. Pall, *Instrument Maker*, *15*, No. 5, 26 (1947).

Miscellaneous Products of Controlled Permeability

The development in Great Britain of a system of de-icing aircraft wings with the aid of porous sintered copper–nickel–tin strips through which de-icing liquid is metered constitutes one of the major special applications for powder metallurgy; although especially developed during the war for military planes, the system is said to be standard equipment in practically all new British civil aircraft.[53] The functions of the porous metal distributor are mainly to meter the de-icing fluid by controlling its flow and to direct it and permit its proper spreading along the leading edges of the wing foils. This was best accomplished by partially encasing the porous strips in Monel tubings, so that the de-icing liquid was contained while being pumped and forced through the porous metal to the leading edge, where the air flow swept it back over the top and bottom surfaces of the wing. The flow of the liquid is claimed to be controllable within ±10%. Production of the distributors consists of filling the powder mixture into the assembled Monel tubing section, and sintering in dissociated ammonia whereby bonding of the porous metal to the Monel channel is obtained.

A similar development during the war in Germany has also been reported[54]; the de-icing parts were generally made of tubular copper which had a porosity of about 70% and were impregnated with ammonium chloride.

One of the most significant uses for porous metal products has been developed during the war, when many millions of small cup-shaped porous sintered nickel filters of extremely uniform permeability to gases and mercury were produced for the United States Navy for use in the mercury safety switch of the "V-T" radio proximity fuze.[46,55,56] Figure 569 shows the general appearance of these sintered nickel cups; Figure 570 is a photograph of a section through the fuze indicating the position of the mercury switch that contains the cup.

A development now on the way which promises to become of similar if not greater importance centers around the production of porous sintered metals and alloys having a controlled *permeability* in addition to comparatively high physical properties. These materials are sought for heat-exposed engine components that may be cooled by passing through them a liquid cooling agent which is allowed to evaporate at the

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[53] T.K.S. (Aircraft De-Icing) Ltd., *Symposium on Powder Metallurgy*. The Iron and Steel Institute, Special Report No. 38, London, 1947, p. 110.

[54] C. J. Leadbeater, *Symposium on Powder Metallurgy*. The Iron and Steel Institute, Special Report No. 38, London, 1947, p. 191.

[55] Anonymous, *Steel, 118*, No. 16, 84, 132 (1946).

[56] P. Schwarzkopf, *Powder Metallurgy*. *Macmillan*, New York, 1947, p. 167.

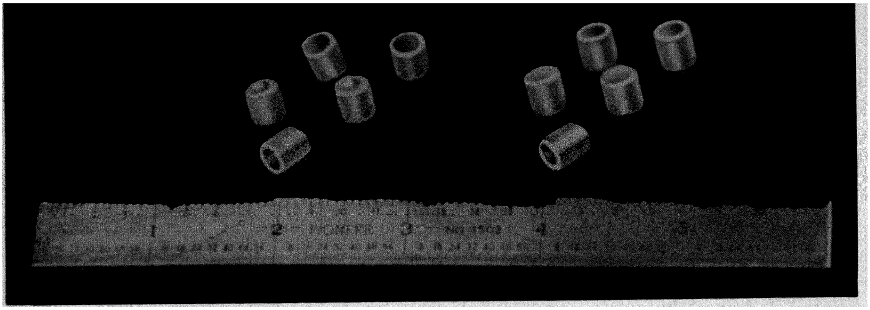

Fig. 569. Sintered porous nickel cups with curved (left) and flat (right) bottom caps, as used in the mercury switch of the proximity fuze (courtesy of American Electro Metal Corp.).

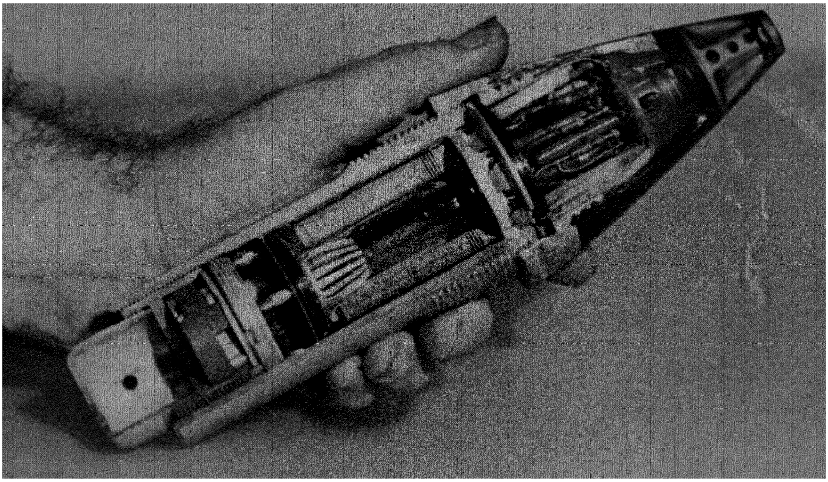

Fig. 570. Photograph of a sectioned proximity fuze indicating (just above the fourth finger of the hand) the location of the mercury switch which contains the sintered nickel cup (courtesy of Applied Physics Laboratory, The Johns Hopkins University.).

exposed surfaces. Duwez and Martens[57] recently reported in a most interesting paper their attempts to develop porous stainless steel and porous nickel–molybdenum–iron (65–30–5) bodies that would be suitable for this "sweat-cooling" ("transpiration-cooling") application. (The heat transfer inside such a transpiration-cooled porous metal body

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[57] P. Duwez and H. E. Martens, *Trans. Am. Inst. Mining Met. Engrs.*, *175*, 848 (1948).

has been analyzed by Weinbaum and Wheeler.[58]) Ammonium bicarbonate was found to be the best pore-creating agent, and the authors were able to correlate the amount of this substance with porosity on the one hand, and the porosity with permeability on the other hand. Optimum tensile strength for certain porosities was obtained when the sintering of stainless steel bodies was performed in helium rather than in hydrogen. While the work by Duwez and Martens has been quite successful for conditions where the flow remains laminar, difficulties were met in the range of turbulent flow, which in practice may be unavoidable. Moreover, better reproducibility and the production of complex shapes as employed in turbines and jet engines may point toward different processing techniques rather than toward the simple static compaction of powder mixtures containing pore-generating substances.

It is interesting to note that the work of Duwez and Martens was apparently anticipated both in this country and abroad. Richardson and Richardson[59] have drawn attention to the fact that the method of using a coolant which moves in a direction opposite to that of the heat flow was patented by one of the authors some time earlier.[60] Meyer-Hartwig[61] reported in 1940 on German development work concerned with suitable materials for the transpiration-cooling of rocket nozzles.

Among the potential applications for porous sintered metals suggested in the voluminous patent literature are such diverse items as heat exchangers, vaporizers, cooling elements for thermal insulators, and porous containers for producing foam, for the aeration of fermentation solutions, and for radioactive substances which emanate gaseous products.

Summary

Powder metallurgy has attained its greatest use, so far, in the production of porous parts, particularly bearings and bushings, which are used in enormous quantities in the automotive, household appliance, and general machine industry. Extensive standardization has aided in establishing an economically sound production process for these parts.

While porous bronze bearings containing about 10% tin and (usually) from 2 to 6% graphite are most widely used, other copper-base compositions and, more important, iron-base compositions have been used increasingly. Especially combinations of iron and copper and iron and lead, with and without additions of small percentages of graphite, have gained in significance due to heavier load-carrying capacity as compared

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[58] S. Weinbaum and H. L. Wheeler, Jr., *J. Applied Phys., 20,* 113 (1949).

[59] E. A. Richardson and G. A. Richardson, *J. Metals, 1,* No. 1 (Sec. 1), 13 (1949).

[60] U. S. Pats. 2,215,532 and 2,311,350.

[61] F. Meyer-Hartwig, U. S. Air Forces, Air Materiel Command, Air Documents Div., Dayton, Ohio, Doc. U 2138 (Sept. 1948).

with the porous bronze materials. Aluminum-base bearings, on the other hand, have found only a few, specific applications, such as in the aeronautical field.

The functioning of the porous bearings is based on free circulation of the lubricant throughout an interconnected pore system. The oil is pumped to the bearing surface by the rotating shaft, and is also circulated by the increased heat of friction, thus furnishing a steady and uninterrupted oil film between journal and bearing. When the rotating motion of the shaft is stopped and the bearing is cooled, the oil retracts into the pore reservoir through capillary action. In order to enable this process to function properly, the porosity must be controlled carefully, both as to pore size and total pore volume, which may vary from about 15 to 35%. Only powder metallurgy methods are capable of giving the desired degree of control of porosity.

Parts made with an intercommunicating pore system are interesting not only for self-lubricating bearings and bushings, but also for products that are subjected to wear and compressive stresses. Thus, porous oil-containing gears and cams are produced for pumps in automobiles, and porous steel or hard metal dies are made for applications that require carefully controlled lubrication during molding of plastics or pharmaceutical goods.

Products of appreciable porosity have been developed for the purpose of filtering solids, liquids, or gases from liquids, or for metering a definite quantity of liquid through the part at a desired rate. Filters and diaphragms—used for a great variety of specific purposes—are usually produced from bronze powders, or, to a lesser extent, from nickel or stainless steel powders. Where high porosities are involved, special powders of spherical particle shape and closely controlled size distribution are most suitable, and no pressure-molding is required. However, only homogeneous alloy powders or coated powders can be sintered efficiently, since diffusion alloying (necessary with mixed elemental powders of the kind used in the bearing manufacture) is greatly retarded by the excessive porosity.

CHAPTER XXVIII

Friction Products

Friction products comprise a comparatively new and unique field quite distinct from other well-known powder metallurgy products. The chief difference is that more metal–nonmetal combinations are used here than in other types of powder metallurgy materials (with the exception of the cemented carbides and diamond compositions). By varying the proportion of the friction-producing nonmetallic ingredients, the composition of the metallic matrix, or the metallic additions to organic-type friction materials, a variety of interesting articles can be produced readily, of which clutch plates, brake bands, brake drums, and packing compositions are outstanding examples. Metallic compositions used as bonding matrices for mixtures of asbestos, graphite, and organic materials include a variety of metals, particularly copper, tin, lead, and zinc. These metals, as well as aluminum and antimony, may be added in minor proportions to asbestos-organic types of friction materials where they serve merely as addition elements and not as matrices or bonds for the products. In the latter case, the metal powders improve wearing characteristics, increase heat conductivity for better cooling, and provide suitable coefficients of friction.[1]

The manufacture of friction materials was pioneered by Wellman, who holds a number of important patents in this field,[2] and is mainly responsible for the present advanced stage of this industry. The steadily increasing importance of wear-resistant and friction-producing materials in the fields of modern transportation and moving machinery—with a trend toward higher speeds and heavier loads—is bound to have a considerable influence on this particular field of powder metallurgy; it is a safe prediction that further important developments may be expected.

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[1] H. E. Hall, in J. Wulff, *Powder Metallurgy*. Am. Soc. Metals, Cleveland, 1942, p. 23.

[2] U. S. Pats. 2,178,527; 2,240,971; 2,258,431; 2,259,094; 2,261,196.

Basic Considerations

ESSENTIAL REQUIREMENTS

The characteristics generally desired in friction materials have been described by Kuzmick.[3] They are:

(*1*) A proper coefficient of friction (*i.e.*, the ratio between the resistance to motion of the part due to friction and the normal pressure between the sliding and fixed surfaces). This is essential for the transmission of the particular torque or braking load involved. A high value is desirable, and by varying the composition of the material a considerable change in the coefficient of friction may be obtained.

(*2*) Stability of the coefficient of friction over the temperature range and climatic conditions encountered in service. The coefficient varies with temperature as well as speed of the moving surface, but can be held within specified limits by selection of the proper ingredients.

(*3*) Resistance to generated heat; this is important for compositions containing low-melting metal ingredients in free form, such as lead. If the operating temperature exceeds the melting point of the lead, the metal will ooze to the surface and form a lubricating film that will cause loss of the frictional properties. Low-melting metals that alloy with the high-melting metals, such as tin or zinc in connection with copper-base materials, are not affected as drastically by the generation of high frictional heat.

(*4*) Good heat conductivity; this is essential for applications involving heavy-duty braking operations where very high temperatures are generated at the braking surface (*e.g.*, in airplane brakes). Conduction of the heat toward the interior tends to minimize warpage of pressure plates or other parts of the assembly.

(*5*) Good mechnical strength; it must be sufficient to withstand centrifugal, shear, or other stresses encountered during service. Because of the comparatively large sizes involved in many types of friction products, the friction-producing material is kept in thin layers, often composed of a number of segments, and is brazed or otherwise joined to supporting steel backings which give the product the required strength.

(*6*) Good wear resistance; the durability of both the friction part and the engaging surface is of importance, and it is particularly in this property that powder metallurgy products have excelled over other materials. Again, variation in composition has a considerable effect on the property.

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[3] J. F. Kuzmick, *Symposium on Powder Metallurgy*. ASTM, Philadelphia, Pa., 1943, p. 44.

(7) Good resistance to "seizing," that is to say, to the transfer and building-up of the friction surface material on the opposite member of the assembly. Seizing causes rapid wear and scoring of either surface, which, in turn, results in erratic action of the clutch or brake. The proper proportioning of the ingredients is an important means of controlling this property.

(8) Smoothness of engagement, that is, functioning of brake or clutch without jerking or noise development. As with the other variables, this property is influenced greatly by the composition of the friction material.

COMPOSITION AND ITS EFFECTS ON PERFORMANCE

In order to meet the various requirements, the composition of the friction products is of deciding significance. Kuzmick[3] and Cox[4] have investigated the components and the effect of variations in composition. Mixtures used for metal powder friction articles usually consist of from 4 to 8 separate ingredients. A change in any one of these will affect the result, thus introducing innumerable combinations and effects. The metal matrix generally consists of a major proportion of copper to which a number of other metals, such as tin, zinc, lead, and iron, are added. In addition to the friction-producing components, such as silica, emery, or asbestos, graphite is also added to furnish the material with a certain degree of lubricating ability. The specific proportions and functions of the ingredients are:

(a) *Copper* is generally used as a base metal in a proportion amounting to about 60–75% by weight. It is desirable because of its high heat conductivity and resistance to frictional heat during service. Furthermore, copper powders are molded readily because of their inherent plasticity, and offer no particular difficulties during sintering.

(b) *Tin,* or sometimes *zinc,* is added in amounts of 5 to 10% by weight as the low-melting copper-soluble metal. The purpose of this addition is to aid in the consolidation of the pressed compact and to strengthen the metallic matrix through alloying during sintering at temperatures above liquefaction of the component.

(c) *Iron,* or a similar higher melting copper-insoluble metal powder, is added also in amounts of 5 to 10% by weight. The purpose of this addition is to increase the coefficient of friction. The harder particles embedded in the soft copper-base matrix also appear to exert a scouring action, which prevents or retards seizing of the friction surface to the opposing member of the assembly.

(d) *Lead* powder, also insoluble in copper, is added in a proportion of

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[4] C. T. Cox, *Trans. Am. Inst. Mining Met. Engrs., 161,* **565** (1945).

5 to 15% by weight and acts as a lubricant during molding. The lead particles dispersed in the matrix form a lubricating film if the temperature of the friction surface exceeds the melting point of the metal. This lubricating film has a self-regulating influence on the temperature, since it reduces the friction and thereby lowers the frictional heat. Within reasonable limits the lead film is also beneficial for the performance of the product, since it tends to make for smooth engagement and to prevent erratic brake and clutch action; this is usually accentuated at higher temperatures, when the metallic matrix tends to score and seize because of greater plasticity.

(*e*) *Graphite* powder has some effects similar to lead. Added in amounts of 5 to 10% by weight, it acts as lubricant during compression and forms a smoothly engaging lining during operation. At the same time, however, it appears to increase the frictional properties by breaking up the metallic matrix and forcing the friction-producing ingredients to appear on the surface and to dislodge themselves in the form of dust.

(*f*) *Silica, emery,* or a similar nonmetallic finely divided friction-producing substance is added in amounts which normally vary from 2 to 7% by weight. A slight variation in the proportion of abrasive powder added has a marked effect on the coefficient of friction.

Cox discusses the effects of minor changes in the proportion of the components of the following composition (given in parts by weight): copper, 76; tin, 6; lead, 10; iron, 8; silica, 5; carbon, 8. This particular mixture results in a product that has a satisfactory coefficient of friction at slow engagement speeds, and the coefficient decreases only moderately with increasing speed. Also, the wear resistance of the material is good, and quiet operation is obtained.

A comparatively small increase in the proportion of graphite from 8 to 9 parts results in a 10% decrease in the coefficient of friction: from 0.50 to 0.45. Operation becomes somewhat more noisy, although the wear remains practically unchanged. A further increase of the graphite content to 10 parts again results in a proportional drop of the coefficient of friction: to 0.39.. Now, however, the wear becomes excessive. But if this increase in graphite content from 8 to 10 parts is accompanied by an increase in silica content from 5 to 6 parts, the coefficient of friction rises above the initial value (to 0.54) and the wear again becomes satisfactory. Corresponding effects are obtained if the proportion of some of the other ingredients are changed. If, for example, the iron content of the original mixture is decreased from 8 to 3 parts, the coefficient of friction decreases from 0.50 to 0.37, and operation becomes noisier. If a further reduction in iron content is made to 1 part, the coefficient of friction decreases still further and the wear becomes rather excessive, but the product unexpectedly becomes quiet again in operation.

These few examples suffice to show that the variations resulting from changes in composition, even though of minor character and affecting only one or two ingredients of the mixture, are quite unpredictable. The problem is further aggravated by the possibility that any or all of the 6 to 8 ingredients may be varied in amount as well as in particle size and shape; in addition, the coefficient of friction is influenced by the speed, pressure, and temperature of operation. Therefore, for specific applications, the most suitable composition must be found empirically on the basis of prolonged and specialized tests under simulated operating conditions, preferably together with actual service tests.

Of considerable interest has been the question whether metallic friction elements of high quality can be developed on an all-iron basis, since this approach obviously would be advantageous from an economic point of view. In 1944, Wellman and Wulff[4a] suggested a wide field of potential use for low-grade sponge iron powders in such ferrous metallic friction products (see also Volume I, page 180). Although the comparatively large proportion of abrasive constituents, such as silica, alumina or other residues of the original gangue associated with the ore, are probably desirable elements in the end products, the chemical instability of the iron-base materials appears to be a serious drawback in the case of most of the conventional types of friction products, and has probably been decisive in retarding this development. Nevertheless, a number of processes[4b] and products, such as brake shoes and blocks (see page 557) and composite friction plates (see Chapter XXX, page 567) were recently reported and further developments in this direction may be expected.

Before leaving the discussion of suitable compositions for metallic friction elements, brief reference is made to a light metal-base friction material developed in Germany during the war for brake linings.[5] Mixtures of equal quantities by weight of aluminum powder of fairly coarse grade ("Grenaille"), diatomaceous earth (kieselguhr), and a phenol resin ("Resinol"), preferably thinned with methanol, which were pressed at very low pressures (approximately 3000 psi) and baked at 140°C. (285°F.) for about 2 hours, compared rather favorably with asbestos brake linings, although the coefficient of friction increased to about 0.42 at a load of 120 psi. Experimental work with mixtures of 25% magnesium powder, 40% kieselguhr, and 35% Resinol gave even

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[4a] S. K. Wellman and J. Wulff, *Powder Metallurgy Merry-Go-Round,* Address given at the First Annual Spring Meeting of the Metal Powder Association, New York, May 5, 1944.

[4b] U. S. Pat. 2,424,557.

[5] *Met. Powder Rept., 1,* No. 5, 74 (1947); British Intelligence Objectives Subcommittee, Doc. F.D. 1076/46.

more promising results, but the tests remained incomplete at the end of the war.

In Table 229 a number of typical compositions are shown for various friction devices.[6]

Manufacture

The manufacture of metal powder friction materials has been described in detail by Cone,[6] Geschelin,[7] and Batchelor.[8] An instructive description of the manufacturing techniques and the products manufactured by The S. K. Wellman Co. has been given by Lowey.[8a] Because of the comparatively large sizes involved, special processing techniques had to be developed; to a certain extent these constitute modifications of the customary powder metallurgy procedures.

The metal powder mixtures used for the friction elements are copper, tin, lead, and iron of 150-mesh size and finer. In addition to powdered natural (*e.g.*, Ceylon) graphite, silica, Alundum, Carborundum, and similar friction-augmenting abrasives are added as equally fine powders. (Addition of 6% molybdenum sulfide as lubricant has also been suggested.[8b]) The preparation of a mixture is shown in Figure 571. The thoroughly blended mixtures are cold-pressed at pressures of 10–15 tsi after having been charged in the die by weight feed. They are molded in hardened steel dies and in heavy hydraulic presses, such as shown in Figure 572. Since the individual parts often exceed 100 square inches in surface area, the presses must have capacities of up to 3000 tons. The resulting briquettes have the form of thin, annular wafers; they are extremely fragile and require careful handling.

TABLE 229

Typical Compositions of Friction Devices (Cone[6])

Friction Devices	Composition, %					
	Cu	Sn	Pb	Fe	Graphite	Silica
Clutch and brake disks....	73	7	14	—	6	—
Friction clutch						
Type 1.............	71	6	11	—	7.5	4.5
Type 2...... . .	62	7	12	8	7	4

Because of the high porosity remaining in the compact (up to about 50%), the abundance of the nonmetallic ingredients in the structure, and the extremely thin cross sections of the wafers as compared to their size, the low strength is not increased appreciably by the sintering operation.

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[6] E. F. Cone, *Metals & Alloys, 14,* 843 (1941).

[7] J. Geschelin, *Automotive and Aviation Inds., 92,* No. 7, 24 (1945).

[8] C. S. Batchelor, *Metals & Alloys, 21,* 991 (1945).

[8a] F. J. Lowey, *Mech. Eng., 70,* 869 (1948).

[8b] Brit. Pat. 628,110.

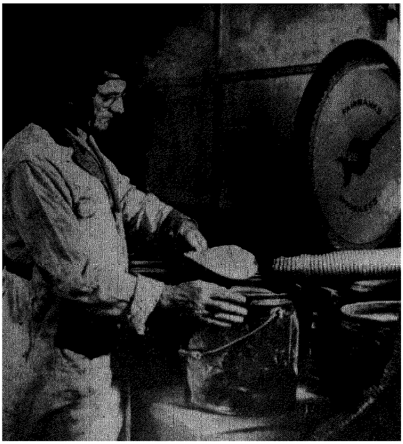


Fig. 571. Weighing and mixing of various powdered ingredients such as copper, lead, tin, silica, and graphite, to make "friction-type" or "bearing-type" mixes for metallic friction elements (courtesy of The S. K. Wellman Co.).

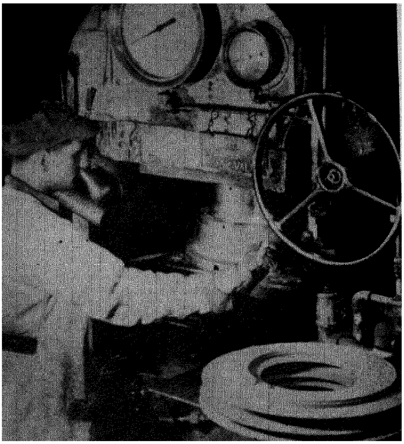


Fig. 572. Pressing of disks from mixtures of powdered metal and friction-producing ingredients in hydraulic press (courtesy of The S. K. Wellman Co.).

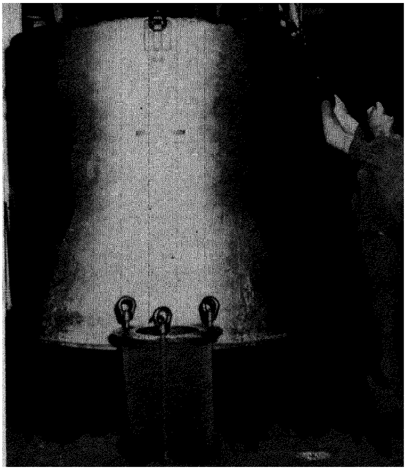


Fig. 573. Preparation of furnace for sintering of metallic friction elements. The bell-type furnace is being lowered over a retort covering a stack of sintered metal clutch facings. The stack in the foreground is ready for a subsequent furnace run. (Courtesy of The Raybestos Division, Raybestos-Manhattan, Inc.)

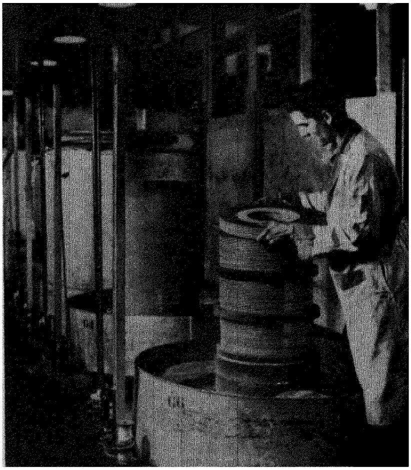


Fig. 574. Discharge of metallic friction elements from sintering furnace. Furnace base showing stack of work just after removal of furnace hood ("can") and heating element. (Courtesy of The S. K. Wellman Co.)

In order to be able to subject the material to the stresses encountered in service, the wafers must be brazed or welded to supporting members of steel. This feature, however, makes it possible to compose several segments into one assembly that is supported by a single steel backing plate.

The brazing or welding of the friction lining to the steel support is usually combined with the sintering operation, which is performed at moderate pressure (pressure-sintering, see also Volume I, Chapter XV) in a reducing atmosphere in especially constructed bell-type furnaces, such as shown in Figures 573 and 574. It is the general practice to stack a number of assemblies of friction wafer plus steel plates (Figs. 573 and 574). Welding of the back sides of the adjacent assemblies in the stack is prevented by applying a protective coating of graphite, mica, or a similar material as a separator. In general, a treatment for one-half to one hour at 725–825°C. (1335–1515°F.) suffices to complete sintering and bonding. The latter is greatly facilitated by first electroplating a thin

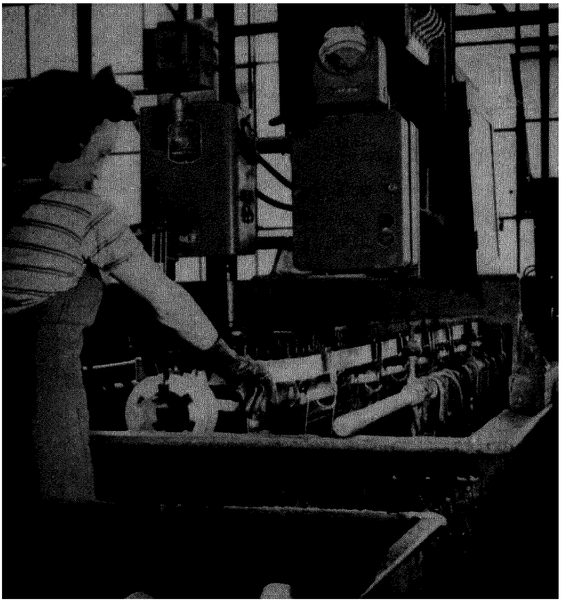


Fig. 575. Electroplating of steel supporting members prior to "bonding" to friction-producing metal powder compacts (courtesy of The S. K. Wellman Co.).

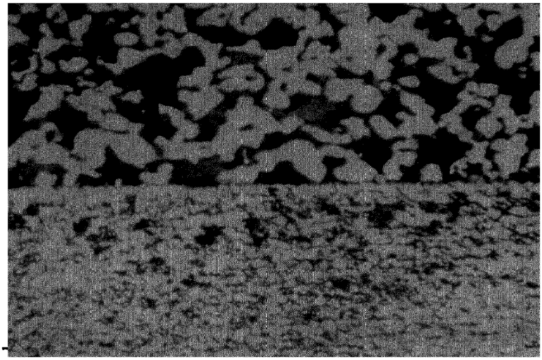


Fig. 576. Microsection (×120) through a metallic friction element showing the perfect bond between the friction-producing layer (top) and the steel backing (bottom) with the aid of an electroplated layer of copper (center). Etched with 2% nitric acid plus alcohol. (Courtesy of The S. K. Wellman Co.)

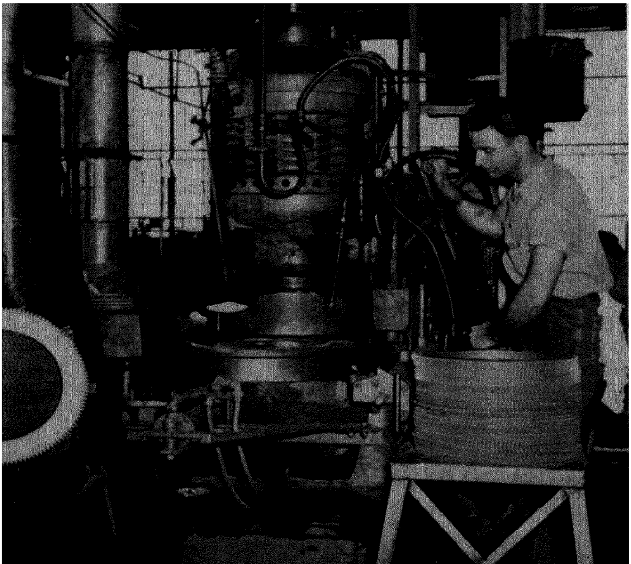


Fig. 577. Blanchard grinding operation on sintered metal gear tooth clutch facings of 91-in.^{2} facing area (courtesy of The Raybestos Division, Raybestos-Manhattan, Inc.).

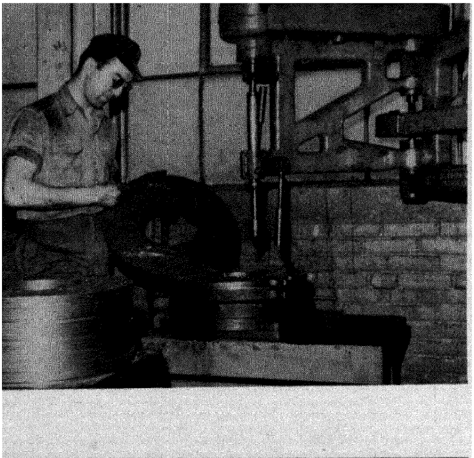


Fig. 578. Drilling and gaging of small holes in sintered metal clutch facings of 204-in.^{2} area (courtesy of The Raybestos Division, Raybestos-Manhattan, Inc.).

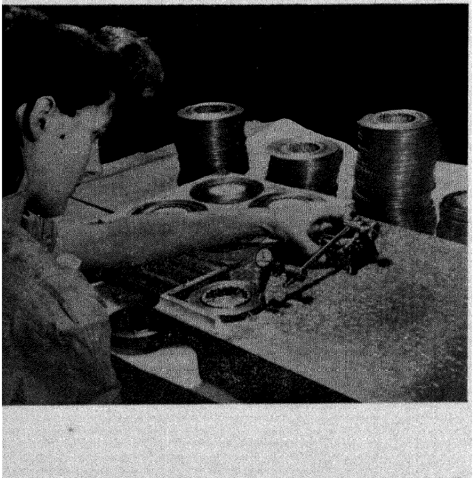


Fig. 579. Final inspection of sandwich-type bimetallic clutch disks used in aircraft supercharger drives (courtesy of The S. K. Wellman Co.).

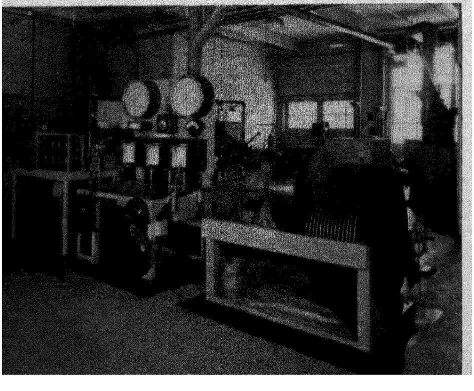


Fig. 580. Quality control of heavy duty sintered metal clutch facings with an inertia dynamometer. The large steel disks in the foreground are sections of the flywheel immediately behind. The inertia of the flywheel is varied to duplicate conditions encountered in heavy duty machines, trucks, or tractors. Horse-power absorption, coefficient of friction, temperature, and durability are measured. (Courtesy of The Raybestos Division, Raybestos-Manhattan, Inc.)

coat (*e.g.*, 0.001 in. thick) of copper or nickel on the contact surface of the steel plate, as illustrated in Figure 575. This plate not only protects the critical surface from harmful oxidation, but also promotes surface diffusion drum, has recently been patented by Wellman.[8c] The method involves of the degree of perfection of the bond that can be attained with the aid of the copper plate.

A somewhat modified process for applying the compacted and sintered powder layer to curved faces, such as a surface of the flange of a brake drum, has recently been patented by Wellman.[8c] The method involves five steps: compaction of the powder into a flat compact; pressure-sintering and bonding to an auxiliary reinforcing member of thin steel sheet; bending of the composite to a shape conforming with the curvature of the flange surface; repeat pressure-sintering of the assembly of the composite of auxiliary sheet, sintered layer, and flange (with the sintered layer in the center); and ultimate removal of the auxiliary reinforcing member by mechanical means.

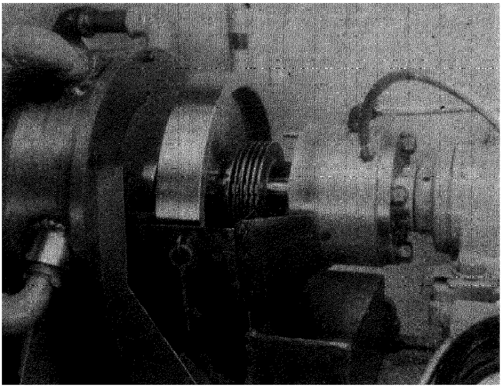


Fig. 581. Close-up view of test machine used in the testing of small sintered metal clutch disks. The flywheel is inertia-loaded via a high-speed air turbine and its rotation is stopped by application of a pack-type clutch containing sintered metal friction elements. Stopping time, coefficient of friction, and durability are determined. (Courtesy of The Raybestos Division, Raybestos-Manhattan, Inc.).

Although all friction assemblies made in this manner require final finishing operations, expensive machining operations can be eliminated by careful control of the dimensional changes (shrinkage) during sintering. Grinding to exact thickness (Fig. 577), drilling of small holes (Fig. 578), and, in the case of brake linings, cold-bending to the required

[8c] U. S. Pat. 2,434,237 and 2,451,264.

radius are finishing operations which cannot be dispensed with; neither can final inspection for dimensional accuracy (Figs. 578 and 579), or final testing for quality control and performance (Figs. 580 and 581).

Applications

Where high resistance to mechanical wear and heat is essential, and where good thermal conductivity and smooth engagement are desired, metal powder friction parts have replaced bonded asbestos friction materials to a large extent. In Figure 582 an assortment of the basically

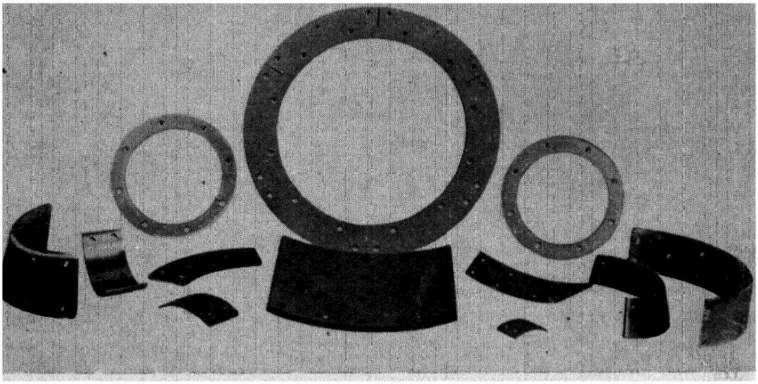
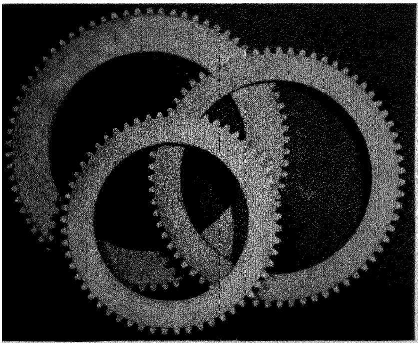


Fig. 582. Display of different metallic friction elements (courtesy of The S. K. Wellman Co.).



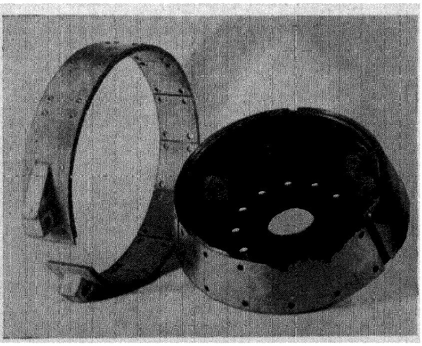


Fig. 583. External gear tooth type metallic clutch disks used in track laying type tractors (courtesy of The S. K. Wellman Co.).

Fig. 584. All-metal cone-type lining and external brake band lining of the type used on heavy earth-moving equipment (courtesy of The S. K. Wellman Co.).

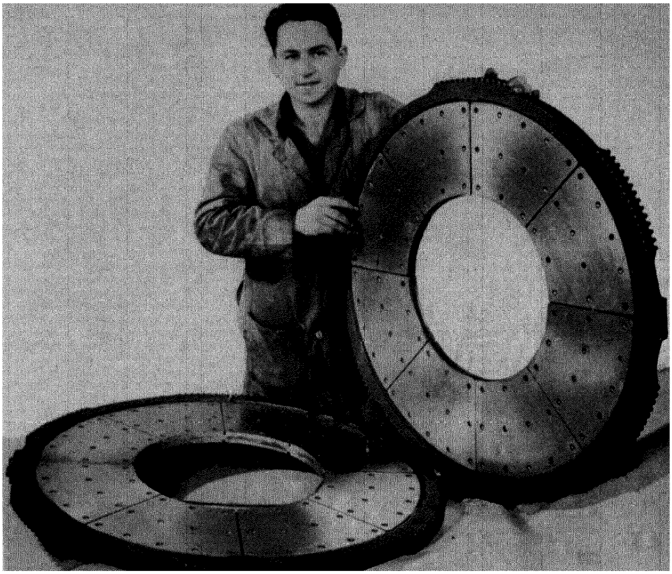


Fig. 585. All-metal clutch facings for use on heavy automotive industrial punch presses (courtesy of The S. K. Wellman Co.).

different kinds of metallic friction elements is illustrated. Brake lining and clutch facings from sintered materials are used for such diverse applications as trucks, tractors, plows, bulldozers, tanks, airplanes, superchargers, punch presses, and turret lathes. Figure 583 shows three different sizes of an external gear tooth type clutch disk used in track laying type tractors; Figure 584 shows an all-metal cone-type lining and external brake band lining of the type used on heavy earth-moving equipment. Two all-metal clutch facings for use on heavy automotive industrial punch presses are shown in Figure 585. A typical internal expanding-type all-metal brake lining is shown in Figure 586; Figure 587 is a photograph of bimetallic brake disks of the type used in multiple-disk type airplane brakes.

Sintered friction elements have been used successfully in brakes up to 930°C. (1700°F.) under 500 psi unit pressures, the absorbed energy amounting to 3,000,000 ft. lb.![4] In some applications, pressures up to 1000 psi have been withstood successfully. It has also been reported that sintered friction materials can be used as flexible external contracting bands, in which instance several individual blocks are employed which are bent and shaped after brazing.[9]

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[9] M. S. Adler, R. B. Aufmuth, and F. J. Lowey, *Product Eng.*, *14*, 218 (1943).

A somewhat obscure picture exists with regard to the application of sintered friction products in the automotive industry. While the sintered material has given excellent performance in automobile clutches for as much as 100,000 miles of service (Figure 588 shows four sizes of automotive-type metallic clutch plates), the decrease in coefficient of friction

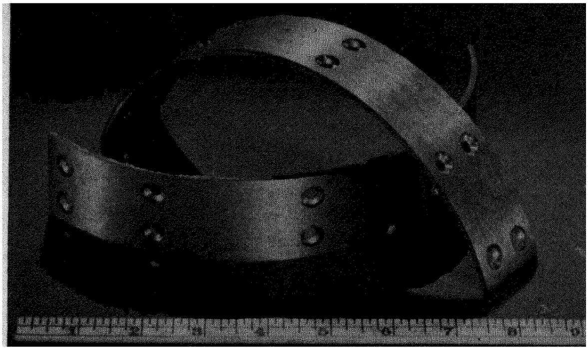

Fig. 586. Internal expanding-type all-metal brake linings (courtesy of The S. K. Wellman Co.).

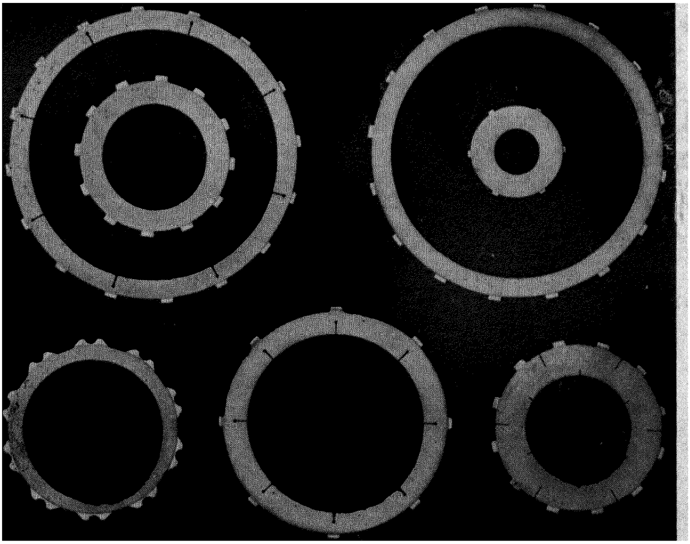

Fig. 587. Bimetallic brake disks of the type used in Goodyear aircraft multiple-disk type airplane brakes (courtesy of The S. K. Wellman Co.).

with increasing speed limits the usefulness of the material for automobile brakes. According to a statement by Kelley,[10] however, brake drums are successfully produced by a large car manufacturer.

Among examples cited by Cox[4] for potential applications that may be satisfactorily met by powder metal friction elements are wooden block brakes for wagon wheels and cast iron brake shoes for railway wheels. As a matter of fact, it has recently come to the author's attention that the latter application is now a reality in one European country.

In other applications, where large production rates prevail, the usefulness of sintered friction products is often limited by their high cost as compared with resin-bonded asbestos friction materials, or else, by a possibly inferior performance. For example, the comparatively high thermal conductivity that is characteristic for sintered metal friction materials is not always favorable, as in the friction material in hydraulically operated airplane brakes which must be a good heat insulator in order to prevent transfer of heat to the rubber seals of the hydraulic devices; otherwise, the material would deteriorate rapidly by the excessive heat that is generated.

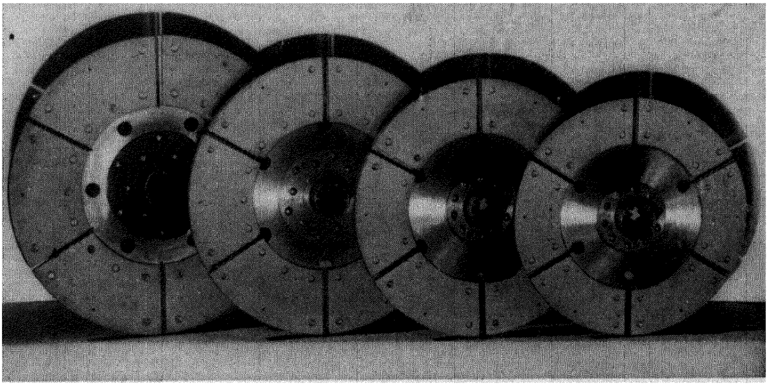

Fig. 588. Automotive-type clutch plates lined with "Velvetouch" powdered metal clutch facings (courtesy of The S. K. Wellman Co.).

Summary

Sintered metals in friction devices constitute a specific powder metallurgy application. Liners and facings for clutches and brakes that require unusual strength and heat resistance are produced more advan-

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[10] F. C. Kelley, *communication*, at Buffalo Chapter Meeting, Am. Soc. Metals, April 1946; *Metals Rev., 19,* No. 6, 6 (1946).

tageously by mixing metal powders and friction-augmenting powdered ingredients than by employing the conventional resin-bonded asbestos-type friction materials. Because of the special size requirements involving large surface areas and very thin cross sections, unique techniques for producing the sintered friction elements have been developed. They require heavy-capacity hydraulic presses and special bell-type furnaces in which the friction elements can be sintered and bonded to supporting steel plates under slight pressure.

The actual performance of the sintered friction materials is influenced considerably by the composition which consists of copper as a major component of the metallic matrix; tin, lead, and iron as minor components of the matrix; graphite as lubricant; and an abrasive as friction-producing ingredient. The coefficient of friction and the wear resistance are particularly affected by comparatively small changes in the proportion of the minor components, but the coefficient of friction is also changed by such variables as speed of the moving surface, unit pressure, and temperature, which all add to the complex relationship of composition, service conditions, and performance.

CHAPTER XXIX

Dental Alloys

Although the use of metal powders for dental purposes represents one of the oldest applications of powder metallurgy,[1] the literature on this subject is surprisingly scant, with only a few references available.[2–6] Since the scope of this particular field is rather interesting, especially from the standpoint of financial turnover, a brief chapter dealing with the subject is believed appropriate.

The amounts of powdered tin, copper, silver, and gold, and their alloys, which are used in conjunction with mercury in dental techniques, are considerable, and Kieffer and Hotop[7] mention that the annual world consumption of silver–tin powders for dental purposes is estimated to be about 80 long tons! The amalgams of these metals are particularly suitable for dental purposes because of their capacity to harden rapidly. Their excellent plasticity makes it possible to press them without great effort, and to fill dental cavities of nearly every shape

Copper Amalgams

Copper amalgams were originally used to some extent because of their durability, easy workability, and moderate cost. Also it was found that in comparison with other amalgams, those containing copper possess a strong antiseptic effect. But copper amalgams have given way almost entirely to those of the precious metals because of their strong tendency to tarnish and to color the adjoining teeth through the formation of copper sulfide.

For the preparation of copper amalgam fillings, freshly precipitated

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[1] E. Raub, *Die Edelmetalle und Ihre Legierungen.* Springer, Berlin, 1940, p. 160.

[2] A. Wetzel, *Füllen der Zähne mit Amalgamen.* Berlin, 1899.

[3] G. V. Black, *The Conserving Dentistry.* Shepard, Chicago, 1913.

[4] L. Speier-Pinkus, *Rezeptarium für Zahnheilkunde und Zahntechnik.* Dentistischer Verlag, Berlin, 1930.

[5] L. Sterner-Rainer, *Edelmetallegierungen und Amalgame in der Zahnheilkunde.* Meusser, Berlin, 1930.

[6] E. W. Skinner, *The Science of Dental Materials.* Saunders, London, 1937, p. 316.

[7] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe.* Springer, Berlin, 1943, p. 374.

or very fine electrodeposited copper powder is mixed and rubbed into twice the amount of mercury, preferably in the presence of concentrated sulfuric acid. The resulting amalgam is then thoroughly washed and dried. It has a silvery color, and is easily deformable. It hardens particularly rapidly if 1 to 2% tin is added. Cooled to room temperature, the copper amalgams are quite solid, but can be made plastic again by the dentist when heating slightly over an open flame immediately before use.

Amalgams of Precious Metals

COMPOSITION AND PREPARATION

Pure silver and gold amalgams are not used in dentistry, and neither are mixtures of pure precious metal amalgams with copper–tin amalgams. Instead, alloy amalgams of the systems Ag–Sn–Hg, Au–Sn–Cu–Hg, etc. are used exclusively. The amalgams are prepared by fusing silver–tin alloys containing from 40 to 75% Ag; certain compositions require the addition of up to 5% Cu and Zn, and up to 0.5% Au, Pt, Cd, or Bi. While tin-rich master alloys are preferred in Germany, alloys of higher silver content approaching the intermetallic compound Ag_3Sn (62.5% Ag, 27.5% Sn) are standardized in the United States.[8] Table 230 compares typical analyses of the two types.

TABLE 230
Typical Analyses of Prealloys for Dental Amalgams (Kieffer and Hotop[7])

Metal	German prealloy, %	U. S. prealloy, %
Silver	48–50	65–68
Tin	45–49	25–28
Copper	0.5–2	4–6
Zinc	0.1–0.5	1–2

The solidified prealloys are mechanically comminuted (*e.g.*, by filing) and are commercialized in the form of fine leafy or needly powders. Aging of these powders or heating to 100°C. (212°F.) for a short time has a retarding, but also stabilizing effect on the amalgamation,[9] and for this reason alloy powders to be used for amalgamation are now aged artificially before shipment to the dentist. The difference in the capacity to dissolve mercury of fresh and aged silver–tin powder mixtures

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[8] F. C. Thompson, *Pubs. Internatl. Tin Research Development Council,* No. 89 (Feb. 1939).

[9] G. Tammann and O. Dahl, *Z. anorg. allgem. Chem., 144,* 16 (1925).

of a composition corresponding to the compound Ag_3Sn is indicated in the diagram of Figure 589.

The exact mechanism of the aging effect on the mercury absorption is not clear. It is presumed that slight oxide films are significant, since they should tend to interfere with the wetting action of the mercury. On the other hand, changes in composition of the prealloy, small work-hardening effects, and transformations of the compound Ag_3Sn, or a combination of several of these effects, may also contribute to this phenomenon.[1]

TABLE 231

Most Favorable Ratios of Prealloy Powder and Mercury for Amalgamation (Wannenmacher[10])

Silver content of prealloy powder, %	Ratio of prealloy powder to mercury
50	5:4.4
60	5:5
67	5:6.1

In contrast to the copper amalgams that are commercially available in final form, the precious metal alloy powders are amalgamated by the dentist. The powder is mixed with approximately the same amount of mercury, and the mixture thoroughly worked in a porcelain mortar, with excess mercury being squeezed out during this operation. The exact amount of mercury required is dependent on the silver content of the prealloy, and rises from about 85–90% for a silver content of 50%, to about 120–122% for a silver content of 68%.[1] Table 231 gives the most

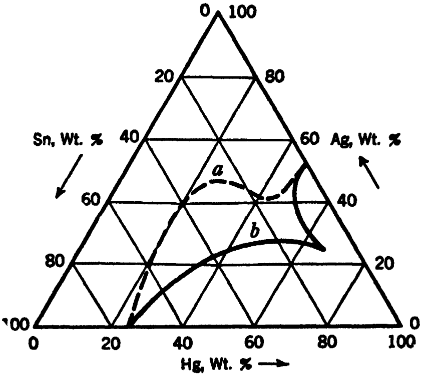

Fig. 589. Mercury content of silver–tin amalgams after mixing for 3 minutes and pressing at 500 psi. for 20 seconds (according to Tammann and Dahl[9]): curve *a* represents a prealloyed powder after aging 1 hour at 100°C. (212°F.); curve *b* represents a freshly prepared prealloyed powder.

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[10] E. Wannenmacher, *Deut. zahnärztl. Wochschr.*, *32*, 367 (1929).

favorable ratios between mercury and the alloy powder for different silver contents of the alloy.[10]

In the technical dental alloys the proportion of mercury that remains in the amalgam after squeezing is inversely proportional to the logarithm of the exerted pressure.[10a] Prolonged mixing and working of the Ag–Sn alloy powder with the mercury causes a higher residue of the latter at a constant pressure.

DIFFUSION AND HARDENING

The metallurgical process of solidification and hardening of silver–tin amalgams is similar to that occurring during sintering of porous copper–tin bronzes or of iron–nickel–aluminum magnets, the apparent difference lying solely in the fact that the amalgams sinter in the presence of a liquid phase at room temperature, or at the temperature prevailing in the human mouth. Upon contact with the alloy powder the liquid mercury dissolves the smallest particles, simultaneously wetting the larger particles. A diffusion process resulting in the formation of tin–mercury solid solution and in an intermetallic phase, roughly corresponding to the compound Ag_3Hg_4, is accompanied by certain volumetric changes, involving first shrinkage and then expansion.[11] The shrinkage may be explained by the diffusion of the liquid mercury into the silver–tin alloy particles, with a corresponding reduction in the over-all volume. The initial shrinkage, however, is stopped by a swelling of the alloy particles that have absorbed the mercury. Eventually, the particles not only contact their neighbors, but cause an over-all growth due to the formation of fine pores and capillaries left behind by the remnants of the liquid mercury. Because of the comparatively low temperature during which the amalgamation proceeds, a complete state of equilibrium cannot be obtained by this diffusion process, and the material consists essentially of the three phases: Ag_3Sn, Ag_3Hg_4, and Sn–Hg solid solution, *i.e.*, with part of the phase Ag_3Sn initially present in the alloy powder still undissolved. Accordingly, the volume changes differ in pattern with changes in the composition of the amalgams, and Gray[12] found that several cycles of expansion and contraction may occur over periods of many days. Evidently, the volume changes are to be associated with certain changes in the relative thicknesses of the several intermediate phase layers surrounding the silver–tin base alloy.

Such factors as interfering oxide films around the alloy particles,

[10a] A. W. Gray, *Trans. Am. Inst. Mining Met. Engrs.*, *60*, 657 (1919).

[11] O. Loebich and L. Nowack, *Deut. zahnärztl. Wochschr.*, *31*, 843 (1928); also *Z. Metallkunde*, *32*, 15 (1940).

[12] A. W. Gray, *J. Inst. Metals*, *29*, 139 (1923).

impurities in the mercury, time of mixing during amalgamation, and differences in temperature have a considerable effect on the diffusion. Furthermore the diffusion process, as well as that of solidification and hardening, is also strongly dependent on time. The minimum hardness necessary for a filling to permit chewing is about 8 Brinell,[18] and is obtained in these dental alloys only after a period of from one-half to one and three-quarter hours. The normal hardness of 30 to 40 Brinell is obtained after approximately 8 hours, and no further increase in hardness is obtained with time.

TABLE 232
Mechanical Properties of Dental Amalgams (Loebich and Nowack[11])

Silver content of the prealloyed powder, %	Compressive strength, psi	Brinell hardness	Flow in 24 hr. under 3500-psi pressure, %
40	16,500–18,000	26–32	20–33
50	20,000–24,000	30–37	15–23
60	26,000–37,000	48–52	2–7
70	29,000–38,500	49–54	1–5

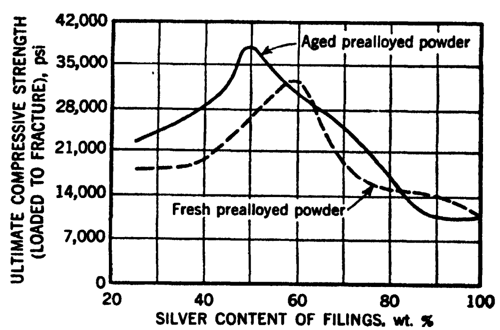

Fig. 590. Effect of silver content on the ultimate compressive strength of silver–tin amalgams (according to Tammann and Dahl[9]).

PROPERTIES

The mechanical properties of the silver–tin amalgams are greatly dependent on the history of the prealloy powder and on the conditions prevailing during amalgamation. The effect of the silver content on the mechanical properties is shown in Table 232.[11] The values for compressive strength and Brinell hardness rise with increasing silver content, while the flow capacity, which is important for the strength of the edges of exposed fillings, decreases considerably. If the silver content of the prealloy powder exceeds 70% the hardness and compressive strength decrease again because of poor cohesion during the amalgamation.

The effect of aging of the prealloyed powder on the compressive

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[18] O. Loebich, *Zahnärztl. Rundschau*, 42, No. 19, 879 (1933).

strength has been studied by Tammann and Dahl,[9] and can be seen from Figure 590, in which the compressive strength is plotted against the silver content of the alloy filings. Aging apparently shifts the maximum values to near 50% Ag content, from about 60% Ag, in the freshly prepared prealloy powder.

Summary

At the present, dental alloys are produced almost exclusively by fusing a master alloy containing silver and tin as major components, and mechanically disintegrating the solidified alloy before mixing with liquid mercury. The precious metal amalgams have replaced copper amalgams, which cause tarnishing of the fillings and discoloring of the teeth.

The composition of the prealloyed powder is of considerable importance, since it determines the correct proportion of mercury to be added. The silver content of the alloy should be between one-half and two-thirds of the total alloying composition, with the tin ranging from one-half to one-quarter. Other metals, such as copper and zinc, are usually added in minor quantities. The amount of mercury added during amalgamation is approximately equal to the proportion of alloy powder, but it rises slightly with increasing silver content in the alloy. The purity of the alloy powder and of the mercury, as well as the method of mixing the two, as employed by the dentist immediately prior to the placing of the filling, have their effect on the formation and hardening of the amalgam, since they affect the alloy formation. The influence of time on the diffusion and hardening processes is also of importance. Since the diffusion process takes place between room temperature and the temperature of the human mouth, the process may be considered to be "cold-sintering" in the presence of a liquid phase.

A phenomenon of particular significance is that prealloyed powders aged at room temperature or heated slightly for a short time tend to absorb the mercury more uniformly, though at a slower rate, with the result that all commercially available prealloyed powders are now in the aged condition.

Dental alloy powders are consumed in surprisingly large quantities, the world consumption amounting to nearly a hundred tons annually, and constituting a financial turnover of considerable measure.

CHAPTER XXX

Miscellaneous Applications for Metal Powders

A survey of the industrial products and applications of powder metallurgy remains incomplete without at least a brief reference to the many minor applications in the field; also, the important uses of metal powders in fields bordering on powder metallurgy are appropriately indicated, since they consume the largest share of the metal powder production in industry. This discussion is based largely on a survey made by Hall.[1]

MOLDED AND SINTERED PRODUCTS

Combinations with Plastics. Various uses have been developed for products that combine plastics and metal powders. If added in minor proportions, the plastic can serve as a binder to facilitate the molding of many metal powders, and can enable the production of more complicated shapes than otherwise possible. This is easily understood if it is realized that the plasticity of most metal powders is rather poor during cold molding. Therefore, the shapes to be molded must be fairly simple, and can only be of a design that permits pressure application along one axis and to the entire cross section of the piece. In the molding of plastics, even lateral flow into narrow projections is possible, and it is reasonable to assume that a combination of the two materials will give intermediate results. Strauss[2] reports success with a bronze alloy to which only 5% vinyl resin is added as the plastic vehicle, and which can be forced readily into lateral, flangelike projections at 65°C. (150°F.). Subsequent heating to 370–410°C. (700–775°F.) causes the resin to decompose completely. Where harder powders are involved, the amount of plastic must be increased accordingly. A typical application, in which about 25% by weight of plastic is added, is that of molded permanent magnet alloy powders of the Alnico type (see Chapter XXIV). During the war, one of the most important uses of lead powders was developed by combining

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[1] H. E. Hall, in J. Wulff, *Powder Metallurgy*. Am. Soc. Metals, Cleveland, 1942, p. 18.

[2] H. L. Strauss, Jr., *Am. Machinist, 89,* No. 20, 113 (1945).

it with a plastic and molding the mixture into projectiles to be used for target practice.

Jewelry, Medals, and Coins. The production of miscellaneous jewelry items has been cited under precious metal products (Chapter XXVI). One of the main advantages of the powder metallurgy technique for this purpose would lie in the lower density of the products, which would mean lower metal cost for a given size piece of jewelry. The porosity can be controlled to such an extent that the surface appearance would be perfectly smooth, and that no corrosive effects would result. The production of medals and coins constitutes one of the oldest applications for powdered metals (see Volume I, Chapter II) and would undoubtedly be of major significance today were it not for the prohibitively high powder costs. On the basis of the extremely fine detail work obtained, the opinion has been expressed that the powder method is superior to the conventional fabricating methods.

Laminated Structures. The production of laminated structures for electrical, magnetic, and ornamental products is possible by the selection of flake powders and specific molding practices. The production of laminated current collector brushes made with directional electrical properties from flake copper and graphite powders has been discussed previously (Chapter XXIII).

Bimetallic and Composite Products. Bimetallic strips (consisting, for example, of iron and nickel) are used in temperature control devices. By means of the relatively simple practice of alternately feeding the different metal powders and pressing them into sandwichlike compacts, materials consisting of two or more layers of different metals can be produced. During sintering, an intricate bonding between the layers is produced by diffusion, usually producing an alloy at the interface. The material is then strong enough to withstand metal-working operations, and thin sheets or strips can be obtained by rolling. An alternate procedure provides for sintering of the multiple-layer powder mass without compaction.

It is also possible to clad steel sheet with metals such as nickel by first pressing and sintering the powder, and then hot working the compact jointly with the steel. Schlecht and Trageser[2a] described a process whereby carbonyl nickel powder containing 0.3–0.5% Mn was pressed lightly into very large ingots (weighing about 2 tons, and having a density of 3.0–3.8 g./cc.); subsequent sintering was performed in hydrogen at 1150°C. (2100°F.) and resulted in blocks of virtually full density (8.85 g./cc.). The extraordinary shrinkage, which was preferably regulated

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[2a] L. Schlecht and G. Trageser, *Metallwirtschaft, 19,* 66 (1940).

to take place in the vertical direction, required molds of carefully controlled dimensions. Forging and sheet rolling together with the steel ingots were carried out at the same temperature as the sintering operation.

A somewhat similar cladding process used in the production of wear-resistant steel sheet has recently come to the author's attention. The process, a post-war development of one of the domestic steel companies, involves the production of composite sandwiches with the steel sheet on the outside, and the abrasive powder layer in between, and parted in the center by a thin alloy steel separating sheet. After hot rolling, the sandwich is parted and the abrasive surface exposed. The abrasive layer consists of one-half by volume of alumina and the other half of reduced iron powder, with the latter amounting up to one-quarter of the total weight of the composite sheet, according to one domestic powder producer.

In this connection, a process for coating copper–titanium alloys on mild steel,[3] known as the "Titanizing" process, appears to be of some significance. Coatings covering a range of compositions have been produced by three different methods: (*1*) by brushing copper-plated steel specimens with a suspension of fine (—300 mesh) titanium hydride in alcohol; (*2*) by using a precast 28% Ti–Cu alloy powder on plated and unplated steel specimens; and (*3*) by applying tamped layers of a powder mixture of titanium hydride and copper onto plated and unplated steel specimens. Cladding was effected by heating in hydrogen under slight pressure at 900–1100°C. (1650–2010°F.), and subsequent diffusion treatments (48 hours at 1060°C., 1940°F., and 96 hours at 1100°C., 2010°F.) resulted in improved adherence to the base metal in all three cases. The first two methods were found to be inferior to the last, since in the first the formation of brittle intermetallic compounds produced a flaky surface, while in the second the fused alloy powder displayed poor spreading characteristics, caused the trapping of large amounts of gas, and resulted in uneven surfaces.

The production of bimetallic steel-backed copper–lead and lead alloy-impregnated copper–nickel bearings has been discussed in Chapter XXVI.

Extruded Products. When the powder metallurgy products are very long in relation to cross section, and the contours do not allow molding along the shortest axis, extrusion practices are indicated. A number of metals can be extruded (*e.g.*, bismuth, aluminum, copper, brass, silver, and even refractory metal composites and cemented carbides). In some cases it is preferable to start with a paste of the powder and an organic vehicle, as in the case of tungsten carbide,[4] while in others, the powder is

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[3] E. J. Chaplin and C. R. Hayward, *Trans. Am. Soc. Metals, 38,* 909 (1947).

[4] Anonymous, *Metals & Alloys, 11,* No. 1, MA-10 (1940).

briquetted and sintered, and extrusion is best performed at elevated temperatures, as in the case of copper.[5,5a] (For further details see Chapters XXII and XXVI, respectively, and also Volume I, Chapter XIII.)

Welding Electrodes. Electrodes for resistance-welding machines are produced in a manner similar to heavy-duty contact metals. Copper-tungsten compositions appear most suitable for this purpose[6] (see Chapter XXIII).

PRODUCTS FOR METALLURGICAL AND CHEMICAL INDUSTRIES

Welding Rods. Metal powders can be added to welding rods in the form of extruded coatings or flux coatings; in England, alone, nearly one ton of Swedish sponge iron is used daily as an addition element in welding rod fluxes.[7] Also, the entire rod can be extruded from metal powders. One successfully developed method[8] provides for a coating of chromium, nickel, manganese, and silicon powders to combine under the welding arc with an ingot iron base wire to produce a weld deposit of stainless steel.

Welding Agents. A new method of welding, brazing, and surfacing employs compositions of finely divided metals together with powdered fluxes by projecting them through the flame cone of a torch onto the work surfaces. Fuel gas, oxygen, and a processing gas (carrying the powder), such as nitrogen, are used simultaneously to provide the necessary temperature control and atmospheric conditions. The "Powder Weld" process makes the use of separate welding rods or fluxes superfluous, and is claimed to be applicable to a great variety of ferrous and nonferrous metals, as well as to metallic oxides, plastic compositions, silicones, etc.[9]

Alloy Cutting Agents. A comparatively recent application for ferrous metal powders, that has by now assumed major scope—a consumption of up to 200,000 pounds per month of reduced iron powder for this purpose has been reported by one domestic powder producer—is as an agent to facilitate cutting of alloys. Powdered iron or iron-rich compositions are introduced into the oxygen stream of a cutting torch to allow the flame to penetrate the refractory oxides in high alloy and stainless steels.[10] Although this powder-cutting process was developed primarily for use

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[5] J. Tyssowski, *Trans. Am. Inst. Mining Met. Engrs.*, *143*, 335 (1941).

[5a] H. H. Stout, *Trans. Am. Inst. Mining Met. Engrs.*, *143*, 326 (1941).

[6] F. R. Hensel, E. I. Larsen, and E. F. Swazy, in J. Wulff, *Powder Metallurgy*. Am. Soc. Metals, Cleveland, 1942, p. 483.

[7] W. D. Jones, *private communication.*

[8] F. G. Daveler, *Materials & Methods*, *23*, 1317 (1946).

[9] Powder Weld Co., Brooklyn, N. Y., Bulletin No. 461.

[10] D. H. Fleming, Jr., *Materials & Methods*, *25*, 73 (1947).

on stainless steel, it is also applicable to the cutting of cast iron, nickel-base alloys (*e.g.*, of the Inconel or Hastelloy type), and high-strength high-temperature materials, as well as to certain nonferrous alloys such as Monel. The process may be applied to these metals when manufacturing the ingot to the finished product, and ingots of various sections and thicknesses up to 26 inches may be cut or scarfed thereby. Cutting speeds are decimated by the fact that the high heat of combustion created by the iron powder in the cutting oxygen stream completely eliminates the time-consuming preheating step.

Brazes and Solders. Copper powder, as well as phosphor-copper, containing approximately 7 to 8% P, or copper–nickel–tin–phosphorus compositions (*e.g.*, 50–35–10–5 Cu–Ni–Sn–P), are used extensively as brazes, and have the advantage over copper wire and sheet in that they can be conveniently applied at and around the joint. It is common practice to use a vehicle with the powder, such as alcohol or a lacquer. Flake powders are used in those cases where the powder must adhere solidly to the surface prior to fusion in the brazing furnace, *e.g.*, where inclined or vertical faces are involved. All types of solders conventionally used are produced in powder form, and are frequently easier to apply than rod or wire. While no fluxes are needed for the brazing of copper powders in a protective atmosphere, lead–tin and silver solders are used in conjunction with flux protection, even if the powders are mixed with a vehicle and applied as a paste. Proper fluxing requires close control of the powder's particle size, and generally the elimination of fine particles.

Metallurgical Addition Agents. Finely divided metals and alloys —whose composition and particle size vary with the purpose—are used to a large extent as metallurgical addition agents. Thus, pure metals, or so-called master alloys, which contain the desired alloying ingredient and the base metal in an exaggerated proportion, can be employed.

Powders of quite fine particle size are used as reducing or precipitating agents in hydro-metallurgical processes, such as zinc for the purification of zinc sulfate solution prior to electrolysis, zinc and aluminum for the precipitation of gold and silver from cyanide solutions, and pulverized iron scrap for the precipitation of copper from waste pickling liquors in copper mining.

Pure metals may be added as coarse, shotted granules, as in the case of aluminum which serves as a deoxidizer in steel melts. During the war, briquettes from incompletely reduced sponge iron and pulverized steel scrap replaced to a certain extent the strategic pig iron charges for blast furnace operations.

Master alloy powders are also added as briquettes. Usually, they give in small percentages a particular alloying ingredient which does not alloy readily with the base metal. Thus, for example, the strongly oxidizing metal, chromium, is added to copper or brasses by mixing the powder with a comparatively large percentage of copper powder, briquetting the mixture, and submerging the briquette quickly into the molten metal bath. A similar procedure can be followed with such metals as aluminum, magnesium, etc., which if added in the elemental form to steels or copper alloys offer the additional difficulty of being extremely light and tending to float at the surface of the molten bath. Master alloys of titanium and copper also belong to this group. The most important type of master alloys, however, are the ferroalloys added to steels in the production of alloy steels. These alloys are available in various particle sizes ranging from 100-mesh powders to coarse granular sizes with pieces several inches across. With the coarser grades constituting the bulk of consumption, the ferroalloys are on the border line, and are generally considered to be outside the realm of powder metallurgy. Powdered ferroalloys are described in some detail in Volume I, Chapter VI.

Specimen Materials for Metallurgical and X-Ray Studies. A small, but important amount of metal powders is constantly used as basic material for metallurgical and x-ray investigations. Several phase diagrams have reportedly been investigated with the aid of sintered powder compacts, *e.g.*, alloys of the systems Fe–Zn[11] and Co–Zn,[12] which cannot readily be prepared by fusion methods because of the great melting point differences and the high vapor pressure of zinc. Trzebiatowski[13] in his classic work on copper and gold powder compacts, for example, used the Debye-Scherrer x-ray powder method for the purpose of detecting work-hardening and grain-growth effects, and Owen and Pickup[14] used the x-ray method to investigate through diffraction patterns the degree of interdiffusion of copper and zinc powders after treatment at various temperatures. The use of x-ray methods on hard metals was broached in Chapter XXII; its use on sintered metals in general is further treated in Chapter XXXIV. Speaking broadly, powders serve as specimen materials for almost any x-ray investigation made today in the metallurgical field.

Surface Coatings. Processes of coating surfaces of metals with the aid of powders of other metals constitute additional important applications of metal powders. The methods involving packing of iron or steel parts in zinc, aluminum, or chromium powders, and heating them to a temperature high enough to allow a marked degree of diffusion to take

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[11] J. Schramm, *Z. Metallkunde*, *28*, 203 (1936).

[12] J. Schramm, *Z. Metallkunde*, *30*, 10 (1938).

[13] W. Trzebiatowski, *Z. physik. Chem.*, *B24*, 75 (1934).

[14] E. A. Owen and L. Pickup, *Proc. Roy. Soc. London*, *A149*, 282 (1935).

place, have been described in some detail in Volume I, Chapter XX. Besides these processes, usually referred to as "powder impregnation" methods, metal powders can also be used as feed materials for metal spray guns of the Schori type. It is claimed that almost any metal available in powder form can be sprayed, and that in some cases the use of powder for this purpose is more economical than that of feed wires. Large quantities of zinc, copper, aluminum, and lead powders are used for this purpose.

A number of metals can also be deposited on metallic surfaces by thermal decomposition of their respective carbonyls. The fact that by varying the conditions in the decomposition chamber either loose powder or coherent layers can be produced with the metals iron, nickel, or cobalt has already been mentioned in Volume I (page 52). More recently, the work by Lander and Germer[14a] has shown that the carbonyl process is also workable for plating molybdenum, tungsten, and chromium on steel, copper, and alloy steels.

Chemical Reagents and Catalysts. A number of powdered metals are most suitable for producing or promoting specific chemical reactions because of their extremely large active surface areas. One of the principal uses is for reducing agents in the chemical industries. Zinc powders, in particular, are used in very large quantities for this work, since they are effective as well as economical. (They are used, for example, for the recovery of gold from cyanide solutions, and also for the recovery of silver from photographic residues.) Other metals used for the same purpose are aluminum, magnesium, iron, and sodium. Powdered magnesium reacts with alkyl iodides in ether to form highly reactive compounds with certain organic substances, which in turn are used in the synthesis of many common organic compounds.

Metal powders are also used quite extensively for the purpose of catalyzing certain chemical reactions.[15] A host of metals can be used as metallic catalysts, including iron, nickel, cobalt, copper, platinum, and lead, and a variety of methods of preparing them have been accepted. While the metals are used in the finely divided form in the majority of cases, some powders are compressed—sometimes in conjunction with other powders that remain inert in the final reaction—and may even be sintered prior to the reaction in order to facilitate handling.

Heat-Generating Agents. Closely connected with their use as reducing and catalyzing reagents is the application of certain highly reactive metal powders for the purpose of heat generation. Aluminum is by far

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[14a] J. J. Lander and L. H. Germer, *Trans. Am. Inst. Mining Met. Engrs., 175,* 648 (1948).

[15] P. H. Emmett, in J. Wulff, *Powder Metallurgy.* Am. Soc. Metals, Cleveland, 1942, p. 155.

the most important metal in this connection. Its use in the form of coarse granules to react with iron oxide in the well-known Thermit process for the welding of heavy steel parts is of great industrial importance. The heat generated by the reaction is sufficient to melt the iron and the oxide slag produced by the reaction. Aluminum is so potent a reducing agent that practically all metal oxides may be reduced to metal in this way, the reaction product being either usable as a weld or as a source of the metal itself. Among the metals reducible by alumino-thermic reaction are silicon and chromium for the production of ferroalloys.

Aluminum—as well as other metal powders—can also be used as a heat-generating source for more moderate temperatures. Iron powder, when allowed to react with potassium permanganate, generates sufficient heat for warming or cooking food. Mixtures of aluminum and copper powders, to which certain reactive chemicals and water are added, give the required temperature in small aluminum pads used for permanent waves in beauty parlors.

Pyrotechnics. During the war almost staggering quantities of aluminum and magnesium powders (ultimately amounting to over one-third of the total domestic metal powder production[16]) have been used for pyrotechnic purposes, including use for incendiary bombs and flares. The underlying process of producing the pyrotechnic effects is very similar to the alumino-thermic reaction in Thermit welding, rapid burning being caused by the mixture of the powdered light metal and some oxidizing agent. Aluminum powder is also used for explosives such as used for blasting in coal mines or for general military purposes (*e.g.*, detonating bombs, explosive heads in torpedoes, etc.). Violent explosive reactions can be obtained when the aluminum is mixed with such oxidizing agents as perchlorates or ammonium nitrate. The use of other metal powders in pyrotechnics has remained limited in extent as compared with aluminum and magnesium.

Radiation Products. Powdered radioactive salts, such as $RaSO_4$, are blended with gold powder, and the product is heated and rolled out to thin sheets and strips for special applications in the electronics field or for the activation of luminous paints (see also Chapter XXVI).

Chemicals and Drugs. Almost any metal powder is available in powdered form in the larger chemical stores, and some metals, such as iron, are also used extensively in the manufacture of drugs.

NONMETALLURGICAL APPLICATIONS

Combinations with Glass and Ceramics. The art of coating glass and ceramics with fine metal powders, particularly gold, platinum, silver,

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[16] J. F. Sachse, *Communication* at meeting of Am. Soc. Metals, N. J. Chapter. Oct. 21, 1946.

belongs to the earliest fields of endeavor in powder metallurgy; decorative work of this kind dates back some 2000 years (see also Volume I, Chapter II). These metals, as well as cobalt, copper, bronzes, tellurium, and selenium, can be applied to ceramic glazes with a liquid carrier and fused into the surface during a high temperature baking treatment.

The incorporation of a minor proportion of powdered metal in pottery and ceramic ware has resulted in materials of improved resistance to mechanical and thermal shock, while, *vice versa,* the addition of refractory oxides and ceramics to metal powders has yielded sintered products of improved resistance to creep and deformation during service at elevated temperatures. An example of the latter—of special interest since its application is in powder metallurgy—is the iron–alumina composite boat construction used by Howe[16a] in sintering Alnico permanent magnets (see also Chap. XXIV, p. 257). Hauser and Held[16b] have reported that iron–clay mixtures (containing 80–85% Fe) can be wet-formed readily into large vessels without using high molding pressures. It appears of importance in the manufacture of these vessels, however, that the water of hydration in the clay (giving oxidizing conditions) is driven off completely before the final sintering temperature is reached.

The possibility of obtaining materials with special electrical properties by combining metal and nonmetal ingredients in powder form into metal ceramics has been explored, both here and abroad. In connection with Hauser's work it was established that iron–clay combinations have only limited applications for electrical purposes. On the other hand, Hausner[17] found that copper and silver powders can yield a material of rather desirable electrical properties if mixed initially with a powdered dielectric substance such as porcelain or zirconia (another dielectric matter recently mentioned in a British patent[18] for the same purpose is polystyrene). In fact, the proper selection of particle size distribution and shape of the copper and the ceramic substances can yield very interesting and novel electrical products, exhibiting a definite degree of conductance —perhaps in a preferred direction—or a controlled temperature coefficient of resistance—possibly approaching zero. If the amount of metal is not predominant, the composite may be baked at temperatures considerably above the melting point of the metal without losses.

Combinations of ceramics and refractory metal oxides with other metals and alloys, especially of the refractory metal type, such as tung-

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[16a] G. H. Howe, in J. Wulff, *Powder Metallurgy.* Am. Soc. Metals, Cleveland, 1942, p. 530.

[16b] M. Hauser and F. Held, *Proc. International Powder Metallurgy Conference,* Graz, July 12–17, 1948, Referate No. 49.

[17] H. H. Hausner, *Ceram. Ind., 47,* 87 (1946).

[18] Brit. Pat. 581,184.

sten–nickel–copper heavy alloys, have been suggested for special high temperature applications, in which any one of the ingredients would perform unsatisfactorily, but a combination would appear to include the desirable properties of each component while depressing the undesirable properties.[19] During the war, such combination materials were developed for turbine blades in Germany;[20] more recently, this drive toward more heat-resistant materials for turbine buckets, jet engine parts, and the like ("Ceramel" or "Cermet" development) has been continued in the United States[20a,20b]—with special emphasis on aluminum oxide-chromium combinations[19,20b]—and further developments may be expected in this direction. (A related development of equal if not greater significance is the production of ceramic coatings on steel[20c] and on molybdenum.[20d])

The whole subject of metallization of glass and ceramic materials with the aid of metal powders and their oxides has become of increasing interest during recent years, especially for the electronics industry, where metal–ceramic seals are of the greatest importance. The application of metal powders for this purpose may be in the form of paints, by evaporation methods, by chemical deposition, or powder flame spraying. One particular technique worth mentioning has been developed primarily for use in vacuum tubes, but also in the manufacture of cathode ray tubes, and involves the coating of the ceramic rods with titanium hydride and copper or silver powders (or paints thereof), followed by a brazing operation in vacuum or extremely pure hydrogen at 1000°C. (1830°F.).[21] Nitrocellulose lacquer was found to be the most suitable vehicle for the 300-mesh titanium hydride powder. An unusually strong bond with the ceramic (*e.g.*, steatite), which in fact is stronger than the ceramic itself, is produced by a silver–titanium alloy formed upon fusion of the silver or silver alloy solder after the bulk of the hydrogen of the titanium hydride has been released. According to Kelley,[21a] even pure titanium hydride, when painted on a ceramic tube and heated in a pure dry hydrogen to 1000–1100°C. (1830–2010°F.), reacts with the ceramic and leaves a firmly adhering coating of titanium on the ceramic to which

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[19] H. H. Hausner, *Proc. Fourth Annual Spring Meeting of Metal Powder Assoc.*, Chicago, April 15, 1948, p. 19. See also Anonymous, *Iron Age, 161,* No. 19, 81 (1948).

[20] Field Information Agency, Technical (F.I.A.T.) Final Report No. 617 (London), Nov. 1946; also *Met. Powder Rept., 1,* 78, No. 51 (1947).

[20a] A. R. Blackburn, *Ohio State Univ., Eng. Expt. Sta. News, 19,* No. 5, 24 (1947).

[20b] A. R. Blackburn, T. S. Shevlin, and H. R. Lowers, *J. Am. Ceram. Soc., 32,* No. 3, 81 (1949).

[20c] Anonymous, *Chemical Age, 59,* 219 (1948).

[20d] D. G. Moore, L. H. Bolz, and W. N. Harrison, National Advisory Committee for Aeronautics, *Tech. Note* No. 1626 (1948).

[21] R. J. Bondley, *Electronics, 20,* No. 7, 97 (1947).

[21a] F. C. Kelley, *Iron Age, 161,* No. 21, 84 (1948).

metal caps can be copper-brazed or silver-brazed, giving vacuum-tight joints. Other metal powders have also been used effectively as coatings for the brazing between ceramics and metals or ceramics of different kind, and ultrafine molybdenum or molybdenum–iron and nickel powders appear to have the advantage of forming low-melting welds with conventional silver-brazing alloys.[21,22] In one instance, a 96–4 mixture of fine molybdenum and carbonyl iron powder is applied in a nitrocellulose–ethyl acetate binder, heat-treated, and cooled. A very thin nickel powder coating is then applied with the aid of the same vehicle and by using a similar treatment. Brazing is performed either onto a 50–50 Fe–Ni alloy or onto a nickel-plated 52.5–42–5.5 Fe–Ni–Cr alloy.[22]

Additions to Cements. Several different metal powders may be added in small quantities to special types of cements. Low-grade iron powders are said to aid in water-proofing and hardening the surface of concrete. The addition of copper powder in amounts not exceeding 10% to magnesium oxychloride cement appears to improve the resistance to softening in water. The cement also becomes harder with increasing time if the copper powder is added. Aluminum powder—added in small percentages to porous concrete mixtures after the water is made slightly alkaline—generates hydrogen, which causes a considerable increase in volume when trapped in the setting concrete. The concrete then contains a myriad of small isolated pores, making it light and particularly suitable for heat- and sound-insulating purposes.

Addition to Lubricants and Oils. Certain metal powders are sometimes added to lubricants which must withstand very heavy loads. Small doses of lead powders are, for example, incorporated in greases, and tin powders in lubricating oils.

A novel development which promises to be of great importance in mechanical engineering is a fluid mixture of light oil and fine iron powder whose consistency can be changed drastically by applying a magnetic field—thereby making the substance ideally suitable as a main element in a greatly simplified and more durable automobile clutch invented by J. Rabinow of the National Bureau of Standards.[22a,22b] In the normal demagnetized condition, the fluid is of low viscosity, and the fine iron particles (preferably of the carbonyl powder type) suspended in the oil are randomly dispersed and float about freely. Upon applying the magnetic field, however, the iron particles become strongly attracted to each other and arrange themselves in chains which run through the fluid and provide

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[22] N. T. Williams, *Rev. Sci. Instruments, 18,* 394 (1947).

[22a] Anonymous, *Natl. Bur. Standards, Tech. News Bull., 32,* No. 5, 54 (1948).

[22b] H. D. Saunderson, *Proc. Fifth Annual Spring Meeting of Metal Powder Association,* Chicago, April 5–6, 1949, p. 93.

a strong binding force. The oil between the particles becomes bound into a dense, homogeneous gel, and the entire mass toughens into a semisolid state. The strength and degree of plasticity of the mass depends on the power of the magnetic field as furnished by a suitable electromagnet.

Addition to Asbestos and Rubber. Various metal powders, such as iron, copper, brass, and lead powders, can be added to asbestos and rubber-base friction materials and packing compositions to improve the heat conductivity, strength, or abrasion resistance of the material. It has even been suggested that iron or aluminum powders be incorporated in rubber for automobile tires to increase traction, wear resistance, and life through better heat conductivity.

Paints and Pigments. The paint and pigment industry is probably the largest and most important consumer of metal powders. However, all powders used for this purpose must be of the flake type, having a high specific surface per unit weight. Good coverage can be obtained only if the flakes are properly oriented, with their flat surfaces parallel to the surface of paint films. This is accomplished by employing highly specialized milling techniques for the production of the pigment powders and by mixing them with the correct type of paint vehicle. Flake aluminum powders are most widely used for all types of decorative and industrial work; flake brass powders of different analyses are used extensively as gold-bronzes for decorative work. Other flake metal powders used for more specific applications include tin, lead, nickel, silver, and gold, and also some special alloys for particular purposes. Recently, flake stainless steel powders have found applications in paints for bottoms of ships and for fan blades exhausting nitric acid fumes.[28]

Summary

Large tonnages of metal powders of all kinds are used for a variety of applications only loosely connected with powder metallurgy, or falling into other than metallurgical industries, but some quantities are also consumed for miscellaneous molded and sintered products. To these belong such products as bi-metal strips, extruded and laminated products, welding rods and electrodes, and medals, coins, and jewelry. Combinations of metal powders with various proportions of plastics, and, to a lesser degree with ceramics, have developed into a major field of application, but must already be placed into the border region of the metal–nonmetal materials.

The use of metal powders in metallurgical industries is very extensive. Great quantities of granular or briquetted metal and alloy powders of various particle sizes are added to molten steel and other metal baths

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[28] Anonymous, *Iron Age*, *160*, No. 8, 61 (1947).

for the purpose of alloying. Powders are also used for brazes and solders, and for surface impregnation and metal-spraying processes. A small but important application for metal powders is their use as specimens for metallurgical and x-ray investigations.

The major applications of metal powders in the chemical industries are as heat-generating sources, including the field of explosive and pyrotechnics, and as catalysts and precipitating or reducing reagents. The uses for drugs and chemicals are only of minor scope.

In the strictly nonmetallurgical industries, metal powders are used to some extent as addition elements to ceramics, cements, lubricants, asbestos, and rubber to introduce certain desired properties in these materials, or to serve decorative purposes. The greatest consumption of metal powders for nonmetallurgical purposes is in the paint and pigment industry, where special flakelike powders, mostly of aluminum or brass, are used in conjunction with a paint vehicle.

Part 2

PHYSICAL POWDER METALLURGY

Practical Evaluation and Theoretical Analyses of the Materials, Products, and Processes

CHAPTER XXXI

Comparison of Physical Properties of Sintered and Fused Industrial Metals and Alloys

The objective of the following chapter is to summarize the physical properties of sintered powder metallurgy products as an aid to the engineer in evaluating and selecting his materials of construction. These properties are not identical with those of metals and alloys produced by conventional methods, and it is important to bear in mind the special production method of the sintered products.

For example, a sintered product that has only 80% of the density of the cast product is not expected to possess the same tensile strength as the cast structure. However, by taking the density ratios into account, we will find that most physical properties of the net material present in the product will be identical in both methods of manufacture; in fact, they may be superior in some ways in the sintered products. On the other hand, the internal notch effects caused by the porosity of the sintered product should be given due consideration (see Chapter XXXIII).

Cold or hot working of the sintered metals and alloys susceptible to such treatment would have essentially the same effect as in the case of the cast counterpart; this treatment would further assure a much higher density of the sintered product—especially by hot working.

The physical and engineering properties pertaining to sintered metals and alloys can advantageously be illustrated by giving their qualitative relationship to variables arising out of the powder metallurgy process of manufacture. Thereupon, quantitative data will be reproduced giving the properties of various industrial metals and alloys produced under different pressing, sintering and heat-treating conditions as compared with those of the fusion products.

QUALITATIVE EVALUATION

The qualitative relationship can best be indicated by trend charts which show how the physical properties of sintered products are

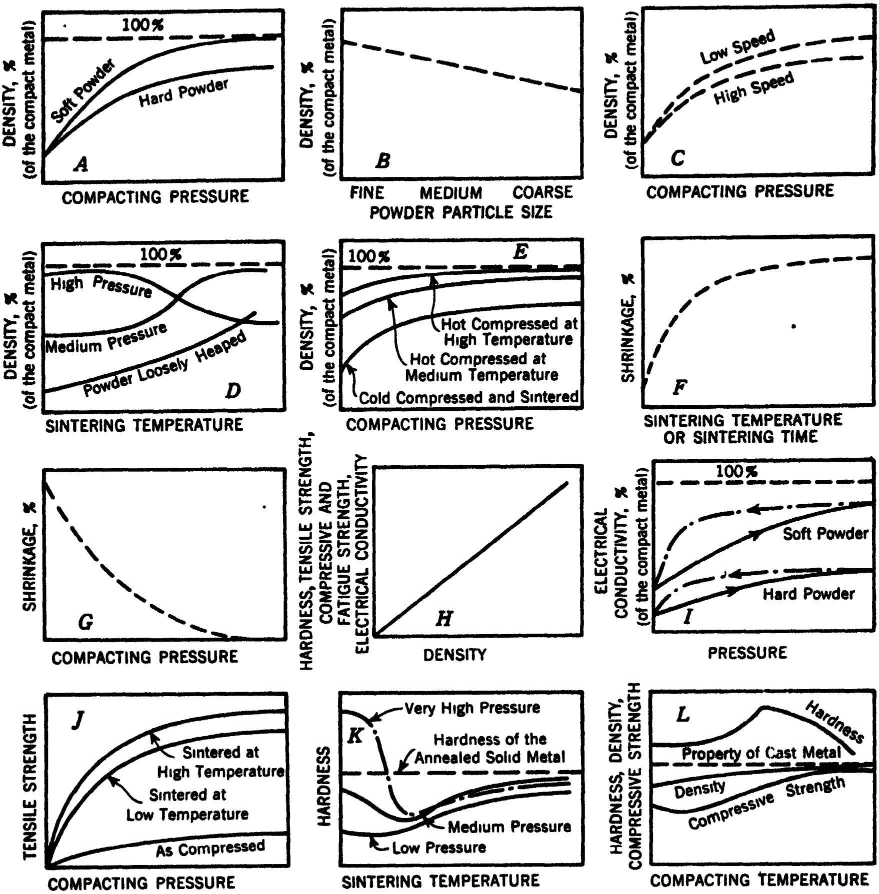

Fig. 591. Diagrammatic presentation of the change in the physical properties of metal powder compacts as effected by a number of variables[3] *A*: Effect of the powder plasticity on the relation between density and compacting pressure. *B*: Relation between density and initial particle size. *C*: Effect of speed of pressing on the relation between density and compacting pressure. *D*: Effect of the order of magnitude of the pressure on the relation between the final density and the sintering temperature. *E*: Effect of the mode of pressing and processing on the relation between density and compacting pressure. *F*: Relation between shrinkage and sintering temperature or time. *G*: Relation between shrinkage and initial compacting pressure. *H*: Relation between density and such physical properties as hardness, tensile strength, compressive strength, fatigue strength, and electrical conductivity. *I*: Effect of the powder plasticity on the relation between electrical conductivity and compacting pressure. *J*: Effect of sintering temperature on the relation between tensile strength and compacting pressure. *K*: Effect of the order of magnitude of the pressure on the relation between hardness and sintering temperature. *L*: Relation between hot-pressing temperature and such physical properties as hardness, compressive strength, and density.

dependent upon a number of variables such as basic materials used, the particle size of the powder, the compacting pressure, sintering temperature, sintering time, sintering atmosphere, subsequent working, and other essential factors.

Such trend charts have been produced by Kieffer and Hotop,[1] for the sintering cycle, and have in part been reproduced in Volume I, Chapter XIV. Hausner[2] has adopted this method to embrace the entire powder metallurgy process by increasing the number of basic trend charts to thirteen. They show that the compacting pressure influences the properties of the sintered product to a large extent and that when metal powder compacts are compressed at high temperatures their physical properties differ considerably from those of compacts compressed at room temperatures and subsequently heat-treated.

The schematic diagrams show that working of the sintered product by repressing, drawing, or hot hammering will increase its density considerably and consequently its hardness, tensile strength, and other physical properties. On the other hand, the ductility of the compact will usually decrease with the degree of working. As with cast products, annealing will have very little effect on the density, but will affect hardness and tensile strength; in general, annealing will enhance ductility to a considerable extent.

In the composite diagram of Figure 591 the principal trend charts are shown indicating the qualitative relationship of the properties of the compact to the various processing steps. The density of the compressed powder compact is generally affected by the nature of the metal, with higher densities resulting from powders of softer metals, and lower densities resulting from powders of harder metals (Fig. 591*A*). Although it is difficult to generalize the effect of the plasticity or brittleness of the powdered metal, alloy, or mixture, the tendency prevails for density to increase with rising compacting pressure more rapidly in the case of soft metals than for hard metals. Close to full densities can only be secured at still feasible high pressures with the softest metals that display a minimum of work hardening. Attainment of complete densities is usually impossible even with highest compacting pressures because of a certain elastic springback expansion of the compact upon pressure release.

The density of the compact decreases as the particle size of the powder increases (Fig. 591*B*). Irrespective of the type of metal, fine powders will result in higher densities, and, assuming that other processing variables remain constant, the density will decrease with coarser powder

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[1] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe*. Springer, Berlin, 1943.

[2] H. H. Hausner, *Am. Machinist, 90,* No. 4, 104 (1946).

grades. *Mixtures of selected sizes of particles following certain laws of packing will result in optimum density.*

The density is affected only little by variations in the speed of pressing (Fig. 591*C*). Compacts pressed at high speed usually show a slightly smaller increase in density with rising compacting pressure as compared with compacts pressed at a slower speed, but the difference can be kept to a minimum if allowances are made for interparticle lubrication and escape of compressed air during the high-speed pressing operation.

The density varies with the sintering temperature in accordance with the state of the powder (Fig. 591*D*). Loosely heaped metal powders will agglomerate into a compact mass with rising sintering temperature, but even the highest feasible temperatures (close to the melting point of the metal) will be insufficient to consolidate the powder mass into a body whose density approaches that of the solid metal. Similarly, powders that are compacted before sintering will increase in density with rising sintering temperature provided that the compacting pressure remains moderate. The optimum compacting pressure for which a maximum density is obtained is a function of the type of metal and the sintering conditions (temperature, time, atmosphere, and rate of heating). If the compacting pressure exceeds the optimal value, the density decreases with increasing sintering temperature.

The density increases significantly with the compacting pressure and the pressing temperature when the metal powder is compacted at elevated temperatures (Fig. 591*E*). The density of hot-pressed compacts is generally greater than the density of the same metal powder compacts cold-pressed at identical pressure and then sintered at or above the temperature employed for hot pressing. If compaction is carried out at high temperatures or at high pressures, or both, the density of the compact reaches that of the solid metal.

The density of a sintered compact is directly related to the volumetric changes that the compact undergoes during sintering. Many metal powder compacts suffer a certain degree of shrinkage, but others grow in size. The type of metal and the sintering conditions have predominant effects on these size changes. Volumetric expansion is generally caused by stress relief after high-pressure compaction, and by the evolution of entrapped and absorbed gases. Shrinkage is fostered by fine powder particle size, increasing sintering temperature, and increasing sintering time (Fig. 591*F*), but it is inversely affected by increasing compacting pressure (Fig. 591*G*). Volumetric changes are kept to a minimum in hot-pressed compacts even if they are afterward subjected to resintering or heat treating.

The physical properties of metal powder compacts are in general directly proportional to the density (Fig. 591*H*). In most cases, an increase in density results in corresponding increases in hardness, tensile strength, compressive strength, fatigue strength, and electrical conductivity, and improvements in other physical properties according to a linear relation. Elongation, reduction of area, impact resistance, bending and torsional properties, as well as ability to withstand cold-working reduction, however, do not generally follow the same linear relation with density but increase to a lesser degree.

The electrical conductivity increases with increasing compacting pressure (Fig. 591*I*) because of the increased number of points of contact between the particles. Soft powders, lending themselves to greater plastic deformation of the particles and increased contact areas, cause a sharper increase in conductivity with rising compacting pressure than hard powders. A reduction or complete release of the compacting pressure results in a retarded decrease of the electrical conductivity of unsintered compacts.

Tensile strength increases with compacting pressure and, in general, becomes higher the closer the sintering temperature approaches the melting temperature (Fig. 591*J*). An exception to this rule is found in materials that suffer marked grain growth or undergo phase changes at high temperatures, or that decrease in density with increasing compacting pressure or sintering temperature for reasons mentioned before. Even compressed powder compacts that are not sintered possess a certain, although very low, tensile strength, that increases very slightly with the compacting pressure.

The hardness of a sintered compact depends on the nature of the metal, the compacting pressure, and the sintering temperature (Fig. 591*K*). If the metal is soft and readily susceptible to work hardening, the hardness will increase drastically with the compacting pressure, thereby usually surpassing the hardness of the annealed solid metal. At rising temperatures during sintering, stress relief will cause an initial sharp decrease in hardness which becomes more pronounced the greater the work-hardening effects during compaction. With progressively increasing sintering temperature, hardness will gradually increase until the value of the annealed solid metal is approached at very high temperatures. Metal powders compressed at very low pressures usually show a steady increase in hardness toward normal values as the sintering temperature rises.

The physical properties of hot-pressed compacts generally improve with increasing compacting pressure due to an increase in density. The maximum density of hot-pressed compacts equals that of the solid metal, and is obtained by the appropriate combination of compacting pressure, temperature, and time. If the metal belongs to the group of soft and plastic materials, maximum density can be obtained by a combination of high compacting pressure with moderate compacting temperature, or, inversely, by a combination of moderate compacting pressure and high compacting temperature. Hard metal powders without soft metal powder additions require a combination of high pressing temperatures and high compacting pressures for attainment of high density. Similar powders with soft binder metal additions (*e.g.*, cemented carbides) require high temperatures (above liquefaction of the binder) and low pressures (to avoid squeeze-out of the latter), and generally carefully gaged times of pressure dwell to counteract the shrinkage forces. An increase in this hot pressing time soon results in saturation values for density, hardness, tensile strength, elongation, etc. The compressive strength increases steadily as the compacting temperature rises, while the hardness increases only initially because of work hardening, and, after attaining a maximum below the recrystallization temperature of the metal, declines to the level of the annealed solid metal (Fig. 591*L*).

Since the trend charts are of qualitative nature, they do not lend themselves *per se* to a predetermination of physical and engineering properties of the compacted metal powders, but they assist in the development of methods of predetermination. However, these methods are not yet too accurate, and, at the present time, production experience seems to be the most reliable method of predetermination.

QUANTITATIVE EVALUATION

The following quantitative evaluation of the physical and engineering properties of powder metallurgy materials and their comparison with corresponding fusion products are based chiefly on the data compiled by Kieffer and Hotop[3] and Schwarzkopf.[4] The discussion includes refractory metals, rare metals, iron and steel, nickel, cobalt, copper, and several examples of hard metals and magnetic alloys produced by sintering.

Pure Metals

REFRACTORY METALS

The refractory metals are characterized by their high melting points, and the application of the sintering process is therefore of prime importance. The metals tungsten and columbium cannot be obtained on a production basis by any of the conventional melting processes. Tantalum,

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[3] R. Kieffer and W. Hotop, *Kolloid Z.*, *104*, 208 (1943).

[4] P. Schwarzkopf, *Product Eng.*, *17*, No. 2, 122 (1946); *17*, No. 4, 268 (1946).

which also belongs to the group of refractory metals, can be fused commercially by the vacuum arc, but the physical properties of the metal obtained are decidedly inferior to the metal obtained by sintering, especially with regard to ductility. Lately, it has also become possible to produce molybdenum by vacuum-arc fusion; special apparatus combining pressing, sintering, melting, and casting enables manufacture of large-sized products.[4a] The properties of the refractory metals are summarized in Table 233, in which is given a general survey of the relevant properties as affected by the history for the metals tungsten, molybdenum, tantalum, and columbium. Additional data can be found in the Tables 86, 89, 92, 96 in Chapter XXI. The following points are worth noting: the high melting point, and the relatively high tensile strength and heat resistance. As indicated before, most properties of the fused metals are not known. Only data for Brinell hardness for tungsten and molybdenum obtained by fusion in the electric arc in hydrogen atmosphere, and data for tensile strength and elongation for the latter, are recorded.

RARE METALS

The rarer metals (titanium, zirconium, thorium, vanadium, and chromium) can be produced by various methods including dissociation by condensation onto tungsten filament at high temperatures,[5] vacuum-arc fusion, or sintering.[6] However, the latter processes generally produce more brittle and therefore less workable materials which may be attributable to impurities from the melting crucibles or from the protective sintering atmosphere. The ductility of titanium and zirconium is affected to a large extent by slight gas contents, such as nitrogen and oxygen, or by carbon, and other impurities. The ductility of chromium is especially depreciated by oxygen and carbon. Thorium, on the other hand, remains ductile with small additions of oxides, since the solubility of thorium in its own oxide is negligibly small. Sintered uranium subsequently fused in crucibles made of thorium oxide or beryllium oxide is very ductile and can even be deep drawn.[6] The properties of these rarer metals are summarized in Table 234.

PRECIOUS METALS

Comparative test results with silver, gold, and platinum, which belong to the group of "precious," or "noble," metals, are given in Table 235.

[4a] R. M. Parke and J. L. Ham, *Trans. Am. Inst. Mining Met. Engrs.*, *171*, 416 (1947).

[5] A. E. Van Arkel, *Reine Metalle*. Springer, Berlin, 1939, pp. 181 ff.

[6] R. Kieffer and W. Hotop, *Kolloid Z.*, *104*, 208 (1943).

TABLE 233

Properties of Refractory Metals: Tungsten, Tantalum, and Columbium (Kieffer and Hotop[3] and Schwarzkopf[4])

Property	Tungsten	Molybdenum	Tantalum	Columbium
Density, g./cc.	Presintered to 1500°C. (2732°F.)..........10.0–13.0	Compacted, unsintered........ 6.1–6.3	—	—
	Sintered as far as 3000°C. (5432°F.)..........16.5–17.5	Sintered at 1800–2000°C. (3272–3632°F.)..........9.2–9.4	16.65	8.58
	Swaged..........18.0–19.0	Swaged..........9.7–10.0	—	—
	Drawn..........19.0–19.3	Drawn..........10.0–10.3	—	—
Melting point[a]	3370°C. (6098°F.)	2620°C. (4748°F.)	2850°C. (5162°F.)	2500°C. (4532°F.)
Lattice type	Cubic-body centered	Cubic-body centered	Cubic-body centered	Cubic-body centered
Lattice parameter	3.158 Å.	3.140 Å.	3.296 Å.	3.294 Å
Brinell hardness	Sintered bar, 18 × 18 mm. (0.7 in. sq.)..........200–250 Swaged to 5 mm. (0.195 in.)..........350–400 Fused with the electric arc in hydrogen atmosphere....260–300	Sintered bar, 18 × 18 mm. (0.7 in. sq.)..........150–160 Forged bar, 8 × 8 mm. (0.32 in. sq.)..........200–230 2-mm. sheet (0.08 in.).......... 240–250 1-mm. sheet (0.04 in.)..........250–255 Fused in the electric arc in hydrogen atmosphere..........160–200	Sintered bar..........40–60 Sheet, unannealed.....150–200 Sheet, annealed........70–120	Sintered, worked, unannealed.....200–250 Same, annealed.... —
Modulus of elasticity, psi	60,000,000	48,000,000	27,000,000	—

Property	Tungsten	Molybdenum	Tantalum	Columbium
Tensile strength, psi[b]	Sintered to 3000°C. (5432°F.)..................18,500 (—) Swaged rod..........50,000–210,000 (—) 1.0-mm. (0.04 in.) drawn wire............250,000 (1–4%) 0.5 mm. (0.02 in.) drawn wire............285,000 (1–4%) 0.2-mm. (0.008 in.) drawn wire..........350,000 (1–4%) 0.1-mm. (0.004 in.) drawn wire............425,000 (1–4%) 0.02-mm. (0.0008 in.) drawn wire.......570,000–590,000 (—) Recrystallized wire...........160,000 (0) Single crystal wire containing thorium as received............Approx. 160,000 (approx. 20%) Above wire, worked..........to 210,000	Vacuum-arc melted,[d] swaged to 1/2 in. dia. ....86,000–96,000 (9–11)% 1.2-mm. (0.47 in.) drawn wire. ..140,000–170,000 (2–5%) 0.4-mm. (0.016 in.) drawn wire....210,000–240,000 (2–5%) 0.05-mm. (0.002 in.) drawn wire.. .250,000–350,000 (2–5%) 1.25-mm. (0.05 in.) annealed wire..........115,000–140,000 (10–20%) 0.4-mm. (0.016 in.) annealed wire..........115,000–170,000 (10–25%) 0.03-mm. (0.0012 in.) annealed wire..........115,000–170,000 (20–30%) Mo single crystal........ Approx. 50,000 (approx. 30%)	Worked .....130,000–170,000 (2–3%) Soft-annealed....50,000–70,000 (10–15%)	Worked......85,000 (2%) Soft-annealed...42,500 (10%)
Elastic limit, psi	0.5–1 mm. (0.02–0.04 in.) annealed wire.........100,000–120,000 Same, unannealed.............250,000	Unannealed and annealed wire 0.1–0.5 mm. (0.004–0.02 in.) diameter.......... 57,000–85,000		
Hot strength of wire, 0.6 mm. (0.024 in.) diameter, psi[c]	— 400°C. (752°F.).........170,000–230,000 (2–3%) 800°C. (1472°F.)........115,000–140,000 (5%) 1200°C. (2192°F.).........57,000–85,000 (6%) 1800°C. (3272°F.).....14,000–43,000 (—)	200°C. (392°F.).......115,000–140,000 (4–5%) 400°C. (752°F.)..........85,000–100,000 (4–5%) 800°C. (1472°F.)...........70,000–85,000 (4–5%) 1200°C. (2192°F.)..........28,000–43,000 (5–6%)		

[a] According to C. D. Hodgman, *Handbook of Chemistry and Physics.* 30th ed., Chemical Rubber Publishing Co., Cleveland, 1947, p. 1798.

[b] Corresponding per cent elongation at 20°C. (68°F.) in parenthesis.

[c] Corresponding per cent elongation in parenthesis; wire tested at various temperatures.

[d] According to R. M. Parke and J. L. Ham, *Trans. Am. Inst. Mining Met. Engrs.*, *171*, 416 (1947).

TABLE 234

Properties of the Rare Metals, Titanium, Zirconium, Thorium, Vanadium, Chromium, and Uranium, Made by Various Manufacturing Processes (Kieffer and Hotop[3])

Metal	Density, g./cc.	Melting Point[a]		Tensile strength, psi	Brinell hardness					
					Cast		Deposited[b]		Sintered	
		°C.	°F.		Soft annealed	Cold worked	Soft annealed	Cold worked	Soft annealed	Cold worked
Titanium	4.45	1800	3272	80,000[c]	—	—	120–160	190–210	210	260
Zirconium	6.49	1900	3452	135,000[d]	—	—	50–60	80–100	—	—
Thorium	11.7	1845	3352	80,000[e]	—	—	—	—	40–45	110–150
Vanadium	6.0	1710	3110	—	—	—	—	260	—	360
Chromium	7.5	1615	2939	—	70–90	144	—	—	150	—
Uranium	18.9	1850	3362	—	200	250	—	—	—	—

[a] According to C. D. Hodgman, *Handbook of Chemistry and Physics.* 30th ed., Chemical Rubber Publishing Co., Cleveland, 1947, p. 1798.

[b] By condensation onto hot W-filament.

[c] Magnesium-reduced, according to B. W. Gonser, *Report of Symposium on Titanium,* Office of Naval Research, Washington, D. C., March 1949, p. 60.

[d] Wire of 0.1 mm. (0.004-in.) diameter.

[e] Annealed.

TABLE 235

Physical Properties of Fused and Sintered Precious Metals (Kieffer and Hotop[3] and Schwarzkopf[4])

Material	Process	Pressure, tsi	Processing temperature		Density		Brinell hardness	Tensile strength, psi	Elongation %
			°C.	°F.	Absol., g./cc.	Per cent of theor.			
Fused silver	Worked and annealed	—	—	—	10.5	—	25	19,500–20,500	48–50
	Cold-worked	—	—	—	10.5	—	85–90	51,000–63,000	2–4
Granulated silver powder, particle size 50–300μ	Compacted, unsintered	14	—	—	8.0	76	—	—	—
	Sintered	14	600	1110	8.0	76	—	—	—
	Sintered	14	800	1470	7.6	73	22	12,000	<5
	Compacted, unsintered	43	—	—	10.0	95	—	—	—
	Sintered	43	600	1110	10.0	95	35	12,000	<2
	Sintered	43	800	1470	9.3	89	41	16,000	<5
	Compacted, unsintered	70	—	—	10.45	99	—	—	—
	Sintered	70	600	1110	10.3	98	34	14,000	<3
	Sintered	70	800	1470	9.0	85.5	36	20,000	<5

Material	Process	Pressure, tsi	Processing temperature		Density		Brinell hardness	Tensile strength, psi	Elongation, %
			°C.	°F.	Absol., g./cc.	Per cent of theor.			
Fine silver powder, reduced from AgCl, particle size 30μ	Pressed sintered	14	800	1470	—	—	—	—	—
	then extruded	—	500	930	10.45	99	33–40	28,000–35,000	20–30
	then 80% cold-rolled	—	—	—	10.50	99.5	85–100	50,000–57,000	1–3
	then annealed after rolling	—	—	—	10.50	99.5	25–30	21,000–24,000	35–45
Fused gold	Worked and annealed	—	—	—	19.37	—	18.5	17,000	40–50
Precipitated gold powder	Compacted, unsintered	43	—	—	15.6	80.5	60	—	—
	Sintered	43	200	390	16.0	83	80	—	—
	Sintered	43	600	1110	16.0	83	20	—	—
	Compacted, unsintered	210	—	—	18.2	94.5	120	—	—
	Sintered	210	200	390	17.1	88.5	120	—	—
	Sintered	210	400	750	16.0	83	40	—	—
	Hot-pressed	105	200	390	—	—	165	(28,000–35,000)	(<5)
	Hot-pressed	105	300	570	19.11	99	138	—	—
	Hot-pressed	105	600	1100	—	—	45	—	—
Fused platinum	Cold-worked	—	—	—	21.45	—	90	53,000	3
	Cold-worked and annealed	—	—	—	21.45	—	50	20,000–23,000	45–50
Precipitated platinum powder	Compacted and sintered	60	1500–1600	2730–2910	17.0–17.7	80–82.5	—	—	—
	then forged	—	—	—	21.25	99	(90)	(<40,000)	(<3)
	then drawn to wire	—	—	—	21.4	99.5	(90)	(<50,000)	(<3)
	Pressed, sintered, rolled, and annealed	60	1500–1600	2730–2910	21.45	100	38–42	(20,000–23,000)	(45–50)

TABLE 236

Physical Properties of Fused and Sintered Pure Iron (Goetzel,[9] Kieffer and Hotop,[3] and Schwarzkopf[4])

Material	Treatment				Properties						
			Processing temperature		Density						
	Process	Pressure, tsi	°C.	°F.	Absol. g./cc.	Per cent of theor.	Brinell hardness	Yield point, psi	Tensile strength, psi	Elongation, %	Reduction of area, %
Fused electrolytic iron	Cast, rolled, and annealed.... ...	—	—	—	7.87	100	45–60	10,000–20,000	35,000–40,000	40–60	70–90
	Compacted and sintered 1 hr.	25	1200	2190	5.8–6.2	74.0–78.6	25.5–36.5	8600–9600	17,900–19,800	6.0–7.0	2.0–7.6
Hydrogen-reduced iron powder, −100 mesh	Compacted and sintered 1 hr.. . ..	50	1200	2190	6.86	87.4	64	21,300	34,600	14.5	18.3
	and repressed at	50	—	—	7.53	95.6	96	52,500	54,700	1.5	11.0
	repressed and resintered 1 hr.	50	1200	2190	7.63	97.0	74	19,400	37,600	25.0	18.4
Coarse electrolytic iron powder, −100 mesh	Compacted and sintered 1 hr.	25	1200	2190	6.94	88 2	40	12,400	20,000	10.5	9.8
	repressed and resintered 1 hr.	50	1200	2190	7.75	98.5	67	15,700	30,500	27.5	32.0
Fine electrolytic iron powder, −325 mesh	Compacted and sintered 1 hr.. . ..	25	1200	2190	6.79	86.3	44	13,700	24,100	10.5	20.7
	repressed and resintered 1 hr. . ..	50	1200	2190	7.65	97.2	67	15,000	30,200	17.5	28.4
Hydrogen-reduced iron powder, −100 mesh	Compacted and sintered 1 hr.. ...	25	1200	2190	—	—	—	—	—	—	—
	then 25% reduced by cold rolling and annealed 1 hr. at............... ..		950	1740	7.15	90.9	60	24,400	37,000	10.5	14.3
	Compacted and sintered 1 hr.. . ..	25	1200	2190	—	—	—	—	—	—	—
	then 75% reduced by cold rolling..........				7.74	98 4	117	52,000	63,700	6.0	18.8
	Compacted and sintered 1 hr..	25	1200	2190	—	—	—	—	—	—	—
	then 75% reduced by cold rolling and annealed 1 hr. at.......		950	1740	7.74	98.4	93	35,800	42,800	27.5	48.6
	Compacted and sintered 1 hr.... ..	25	1200	2190	—	—	—	—	—	—	—
	then 25% reduced by forging at.........		1000	1830	7.65	97.2	107	39,800	52,300	12.0	16.7
	Compacted and sintered 1 hr.	25	1200	2190	—	—	—	—	—	—	—
	then 25% reduced by forging at.		1000	1830	—	—	—	—	—	—	—
	and annealed 1 hr. at........		950	1740	—	—	93	35,400	48,400	21.0	43.2
	Compacted and sintered 1 hr..... .	25	1200	2190	—	—	—	—	—	—	—
	than 75% reduced by forging at..		1000	1830	7.77	98.8	113	44,700	51,600	24.0	45.7
	Compacted and sintered 1 hr.... ..	25	1200	2190	—	—	—	—	—	—	—
	then 75% reduced by forging at		1000	1830	—	—	—	—	—	—	—
	and annealed 1 hr. at		950	1740	—	—	97	30,800	50,400	25.5	54.9

Material	Treatment				Properties						
	Process	Pressure, tsi	Processing temperature		Density		Brinell hardness	Yield point, psi	Tensile strength, psi	Elongation, %	Reduction of area, %
			°C.	°F.	Absol. g./cc.	Per cent of theor.					
German technical iron powder, particle size below 300 μ	Compacted, unsintered	57	—	—	6.0-6.5	76.3-82.7	70-75	—	400-500	—	—
	Compacted and sintered	43-57	1000	1830	6.5-7.0	82.7-89.0	40-50	20,000-24,000	25,000-30,000	8-12	8-12
	Compacted and sintered	43-57	1000	1830	—	—	—	—	—	—	—
	and repressed at	43-57	—	—	7.0-7 3	89.0-93.0	65-70	—	33,000-41,000	0-3	0-3
	Compacted and sintered	43-57	1000	1830	—	—	—	—	—	—	—
	and repressed and resintered	43-57	1000	1830	7 0-7.3	89 0-93.0	55-65	15,000-20,000	33,000-37,000	16-22	16-22
	Hot-pressed	25	810	1490	7.5-7.87	95 0-100	60-100	—	50,000-56,000	15-25	—
	Compacted and sintered	43-57	1000	1830	—	—	—	—	—	—	—
	then hot-forged at		1000	1830	7.87	100	90	30,000	50,000	35	60
Carbonyl iron powder	Compacted and sintered	43-57	1000	1830	—	—	—	—	—	—	—
	then hot-rolled to 0.5-mm. (0.02-in.) sheet at		950	1740	—	—	—	—	—	—	—
	then annealed at		950	1740	7 87	100	56-80	10,000-20,000	25,000-35,000	30-40	70-80
	Compacted and sintered	43-57	1000	1830	—	—	—	—	—	—	—
	then cold rolled to 0.5-mm. (0.02-in.) sheet				7 87	100	170-180	(21,000-25,000)	90,000-93,000	1-2	—

TABLE 237

Physical Properties of Fused and Sintered Nickel and Cobalt (Kieffer and Hotop[3] and Schwarzkopf[4])

Material	Process	Pressure, tsi	Sintering temperature		Density, g./cc.	Brinell hardness	Tensile strength, psi	Elongation, %	Erichsen deep-drawing test	
			°C.	°F.					mm.	in.
Fused nickel	Cast	—	—	—	8.85	70–80	50,000	40	—	—
	Worked and annealed	—	—	—	8.85	68–70	47,000–50,000	40	—	—
	Rolled to 5-mm (0.2-in.) diameter and cold-worked	—	—	—	8.85	160–180	115,000–130,000	2–3	—	—
Carbonyl nickel powder	Compacted, unsintered	6	—	—	4.5	—	—	—	—	—
	Sintered	6	600	1110	4.6	30	2,800	—	—	—
	Sintered	6	1300	2370	7.8	85	36,000	<10	—	—
	Compacted, unsintered	30	—	—	6.1	50	—	—	—	—
	Sintered	30	600	1110	6.4	45	15,000	<5	—	—
	Sintered	30	1300	2370	8.1	100	42,000	<12	—	—
	Compacted, unsintered	70	—	—	7.0	70	—	—	—	—
	Sintered	70	600	1110	7.3	68	23,500	<6	—	—
	Sintered	70	1300	2370	8.3	110	52,000	<15	—	—
	Packed to maximum density without pressing; sintered, rolled to 0.5 to 1.5 mm. (0.02–0.06 in.), annealed	—	1200	2190	8 85	80–90	57,000	50	—	—
	Sheet, 0.5 mm. (0.02 in.)	—	—	—	—	—	—	—	11.7	0.46
	Sheet, 1.0 mm. (0.04 in.)	—	—	—	—	—	—	—	12.7	0.50
	Sheet, 1.5 mm. (0.06 in.)	—	—	—	—	—	—	—	13.3	0.52
Fused cobalt	Cast	—	—	—	8.79–8.86	120–160	115,000	2	—	—
Reduced cobalt powder	Sintered	15	600	1110	4.0	—	—	—	—	—
	Sintered	15	1000	1830	6.5	84	15,500	<3	—	—
	Sintered	15	1300	2370	8.2	90	51,000	<5	—	—
	Sintered	45	600	1110	5.3	—	—	—	—	—
	Sintered	45	1000	1830	7.0	144	21,500	<3	—	—
	Sintered	45	1300	2370	8.2	150	61,000	<7	—	—

Material	Process	Pressure, tsi	Sintering temperature		Density, g./cc.	Brinell hardness	Tensile strength, psi	Elongation, %	Erichsen deep-drawing test	
			°C.	°F.					mm.	in.
Reduced cobalt powder	Sintered	70	600	1110	5.5	—	—	—	—	—
	Sintered	70	1000	1830	7.5	152	24,000	<3	—	—
	Sintered	70	1300	2370	8.0	132	68,000	<8	—	—
	Sintered, cold-rolled to 2 mm. (0.08 in.)	—	—	—	8.76	350–360	130,000–170,000	0	—	—
	then annealed	—	—	—	8.76	160–220	115,000–120,000	1–3	—	—
	Sintered, hot-drawn to 1 mm. (0.04 in.), annealed	—	—	—	8.77	160–220	115,000–130,000	10–12	—	—

TABLE 238

Properties of Cast and Sintered Copper (Kieffer and Hotop,[3] Schwarzkopf,[4] and Goetzel[18])

Material	Process	Pressure, tsi	Temperature		Density, g./cc.	Brinell hardness	Tensile strength, psi	Elongation, %	Electrical conductivity × 10^2, megmhos/cc.
			°C.	°F.					
Cast copper		—	—	—	8.9	40–50	21,000–28,000	15–25	55–57
	Forged, rolled, and annealed	—	—	—	8.93	50	28,000–34,000	38	57–59
	Cold-rolled 80%	—	—	—	8.93	100–110	63,000	10–12	55–57
	Cold-rolled 99%	—	—	—	8.93	110–120	75,000	3	55–57
Copper powder	Sintered	40	600	1110	7.6	45	20,000–23,000	3–4	32–36
	Sintered	200	600	1110	6.9–7.0	40	—	2–3	20–25
	Hot-pressed	60	400	750	8.9	100–110	35,000–42,000	10–20	—
	Hot-pressed	100	400	750	8.9	120–150	43,000–50,000	—	57–59
	Sintered	20	900	1650	7.7–8.2	38–48	12,000–14,000	3–4	35-40
	90% reduced by hot-working, annealed	—	—	—	8.9–9.93	40–50	28,000–35,000	35	59–62
	Sintered, forged	20	900	1650	—	—	—	—	—
	50% reduced by cold-working	—	—	—	8.9–8.93	100–110	50,000–57,000	10–12	55–57

Silver bars with relatively good hot- and cold-working properties can easily be produced from very pure silver powder. Subsequent working will make the sintered product almost identical in its physical properties with its fused counterpart. It is noteworthy that high density of sintered silver products can be obtained at relatively low compacting pressures. Gas pockets cause a reduction of density, especially at higher compacting pressures; therefore, it is advisable to keep the pressure fairly low. Extruded sintered silver, subsequently cold-worked and annealed, gives properties practically identical with those of fused silver if a slightly lower ductility coupled with a correspondingly higher tensile strength is disregarded.

The sintering of gold serves more a scientific than practical purpose. Gold powder has sintering properties very similar to those of silver powder. Trzebiatowski[7] assumes that sintered gold will vary only slightly from fused gold, although it seems that the compacted and sintered gold shows greater hardness, which is even more pronounced in the case of hot-pressed material. This phenomenon is probably caused by the process of precipitating the gold powder from hydrochloroauric acid with alkaline hydrogen peroxide and subsequent reduction, used by Trzebiatowski. The gold powder obtained by this method has a very fine grain, but may contain small quantities of alkalis, which influence the physical properties. Table 235 gives actual test values to which a few estimated values are added in parentheses for the sake of more completeness, since very few values are known from the literature.

Platinum seems to be the only metal in this group which has found some limited interest in the sintered form[8]; this may be attributed to its very high melting point, and also possibly to the fact that sintered platinum seems to be slightly superior to its cast counterpart. Actual test results are given in the last section of Table 235 and a few estimated values are added in parentheses. Because it is necessary to sinter the ingots completely in order to obtain highly ductile platinum (an essential requirement for good drawing properties), sintering at high temperature for a fairly long time is indicated. Subsequently, the sintered metal must be uniformly hot-worked. A platinum sheet produced by this process shows considerably lower hardness than one from fused platinum.

IRON

Table 236 gives the properties of sintered iron obtained from commercial iron powders and carbonyl iron powder in comparison with fused

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[7] W. Trzebiatowski, *Z. phys. Chem.*, *A169*, 91 (1934); *B24*, 75 (1934); *B24*, 87 (1934).

[8] D. McDonald, *Chemistry & Industry*, *9*, 1031 (1931).

electrolytic iron.[8,4,9] The engineering applications of sintered iron products from reduced and electrolytic powders are discussed in detail in Chapters XXIV and XXV. Sintered carbonyl iron has been used to a considerable extent for magnetic applications in which low hysteresis losses are essential,[10] and it can be rolled, forged, and drawn very satisfactorily.[11] Extrusion of sintered iron can be carried out at 800–900°C. (1470–1650°F.) by sintering very pure commercial powder compacted at 70 to 100 tsi.[12]

NICKEL AND COBALT

A comparison of the physical properties of sintered nickel and cobalt with those of the fused metals is made in Table 237.

Tests carried out on sintered nickel specimens produced from carbonyl nickel powder,[13,14] have shown that unworked porous sintered specimens possess strength properties which are almost equivalent to the fused specimens, whereas the ductility is lower. By subsequent hot-working, however, sheets and wires can be obtained from the sintering process which give values identical to those of sheets produced by fusion; in fact, the sintered products may even be superior in ductility and drawing properties.[15]

The metal cobalt is finding wide application in its sintered form in the manufacture of iron–nickel–cobalt and iron–nickel–cobalt–aluminum type, permanent magnets, and sintered hard metals. In order to obtain sintered cobalt bars that can be hot-worked to sheets and wires, very pure powder is required, since the working capacity is affected considerably by traces of silicon, alkalis, and especially carbon, present in the cobalt. Very pure powder can be obtained by reduction from doubly purified cobalt oxalate.[16] The sinter bars can also be cold-worked, but must then be annealed after a 20–40% deformation at 1000–1200°C. (1800–2200°F.) in hydrogen atmosphere.

COPPER

In Table 238 comparative test results are given at different processing stages between fused and sintered copper. The comparison reveals great

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[9] C. G. Goetzel, *Iron Age, 150,* No. 14, 82 (1942).

[10] L. Schlecht, W. Schubardt, and F. Duftschmid, *Z. Elektrochem., 37,* 485 (1931).

[11] O. Hummel, *Metallwirtschaft, 22,* 206 (1943).

[12] R. Kieffer and W. Hotop, *Kolloid Z., 104,* 208 (1943).

[13] G. Grube and H. Schlecht, *Z. Elektrochem., 44,* 367, 413 (1938).

[14] G. Hamprecht and L. Schlecht, *Metallwirtschaft, 12,* 281 (1933).

[15] L. Schlecht and G. Trageser, *Metallwirtschaft, 19,* 66 (1940); *Chem. Fabrik, 12,* 243 (1939).

[16] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe.* Springer, Berlin, 1943, p. 213.

differences in the mechanical properties, especially with regard to ductility, which is inferior in the powder metallurgy product, unless hot-pressed (in which case the properties are almost identical). Annealing the hot-pressed copper specimens at 800–900°C. (1470–1650°F.) will affect the properties in a similar way as in the case of the sintered and the fused products.[17,18]

ALUMINUM

In Table 239, test results obtained with sintered aluminum specimens are compared with the physical properties of cast and wrought pure aluminum. The sintered specimens were tested after a single pressing and heat-treating operation. The effect of an increasing compacting pressure on density is pronounced only for low pressures; at the moderate pressure of 30 tsi, nearly theoretical density values are attained, while higher pressures result in only minor increases in density. The physical properties closely follow the same rule. It is remarkable that, through the application of such simple operations as a compaction at 30 tsi and a sintering treatment at 615°C. (1140°F.) for 1 hour, physical properties are obtainable that are at least equivalent to those found in the cast metal, and that fall midway between the range of properties found in the wrought metal. It is particularly interesting to note the high ductility values found in the sintered metal, indicating that not only refractory metals (after severe working reduction) but also low melting, basically ductile, metals can be produced by powder metallurgy to a high degree of ductility provided that they are practically free of pores.

TABLE 239
Physical Properties of Cast, Wrought, and Sintered Aluminum[a]

Material	Pressure, tsi	Sintering cycle	Density, % of theoretical	Tensile strength, psi	Elongation, %	Reduction of area, %
Cast aluminum	—	—	—	8,000–12,000	20–40	30–60
Wrought aluminum	—	—	—	10,000–15,000	35–45	50–70
Sintered aluminum from −30-mesh powder	10	615°C. (1140°F.), 1 hr., cracked ammonia	88.0	9,900	33	37
	20		95.4	11,810	47	59
	30		98.0	11,850	48	57
	40		98.8	11,790	48	59
	50		99.5	11,900	46	55
Sintered aluminum from −100-mesh powder	10	615°C. (1140°F.), 1 hr., cracked ammonia	85.5	9,700	37	44
	20		94.2	11,810	47	63
	30		97.3	12,000	49	66
	40		98.4	11,970	48	63
	50		99.0	11,900	46	60

[a] Courtesy of P. Schwarzkopf and American Electro Metal Corp., Yonkers, N. Y.

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[17] R. Kieffer and W. Hotop, *Kolloid Z., 104,* 208 (1943).

[18] C. G. Goetzel, *The Influence of Processing Methods on the Structure and Properties of Compressed and Heat-Treated Copper Powders, Dissertation.* Columbia University, New York, 1939.

Alloys

HARD ALLOYS

Tungsten carbide was discovered in the course of a search for a substitute for diamond, especially for use in the production of wire-drawing dies.[19] Although diamond, silicon carbide, and boron carbide have a greater hardness than tungsten and other refractory metal carbides, the latter proved to perform better in many applications on account of greater toughness when alloyed (cemented) with a ductile auxiliary metal (for details see Chapter XXII). In the first part of this chapter we have found that most sintered products are either equal or somewhat inferior to their fused counterparts; in the case of the cemented carbides, however, it can be said that they are far superior if sintered. In fact, sintering has proved to be the most efficient and most economical method of production by far.

Of even greater superiority than the ordinarily sintered cemented carbides are those produced by combining the sintering operation with the application of pressure.

The test results given in Table 240 show that hot pressing produces denser, harder materials than sintering in the usual manner, while the ultimate strength does not change materially.[20]

The same table shows the considerable reduction in quality of physical properties, especially the transverse rupture strength, when producing tungsten carbide–cobalt alloys by casting. This phenomenon is due to the fact that WC decomposes to W_2C, with graphite precipitation resulting, before reaching the melting temperature; during cooling the reverse reaction takes place so slowly that the fused metal consists mainly of brittle W_2C embedded in a carbide-containing cobalt alloy permeated with large graphite veins; the decomposition of the tungsten monocarbide can be reduced considerably by lowering the carbon content, thus preventing the formation of graphite veins. The last two compositions listed in Table 240 represent other carbide alloys with very low additions of auxiliary metal; the hot-pressed alloy has twice the strength of the fused one, although the hardness values are identical.

COMPOSITE CONTACT METALS

A special group of powdered metals have been developed for contact materials. They contain a refractory metal and also a constituent of high electrical conductivity. As the components are not alloyed, the original characteristics are maintained. Powder metallurgy is indeed the only

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[19] H. Moissan, *Der Elektrische Ofen*. Verlag M. Krayn, Berlin, 1900.

[20] German Pats. 420,689; 434,527.

TABLE 240

Properties of Sintered, Hot-Pressed and Cast Tungsten Carbide–Cobalt Alloys (Kieffer and Hotop[17])

Material	Process	C content in WC, %	Co addition, %	Density, g./cc.	Hardness, Rockwell "A"	Transverse rupture strength, psi	Structure
Tungsten carbide	Sintered	—	6	14.8–14 9	90–91	213,000–240,000	Velvety fracture with very fine pores
Tungsten carbide	Hot-pressed	—	6	15–15.1	91–93	213,000–255,000	Fracture similar to above, somewhat coarser, almost free of pores
Tungsten carbide	Cast	6	6	13.5–14.0 (porous)	70–88 (fluctuating)	14,000–28,000	Coarse crystalline, strongly graphitic, containing blow holes, like cast iron
Tungsten carbide	Cast	4.3	6	16.2	91–92	57,000–70,000	Bright-metallic, coarse crystalline
Tungsten carbide	Hot-pressed	6	0.5	15.5–15.6	92–94	70,000–100,000	Velvety fracture with very fine pores
Tungsten carbide	Fused with 0.5% Fe	4	—	17.0–17 2	92–94	43,000–57,000	Bright-metallic, medium crystalline

TABLE 242

Properties of Sintered Magnets Compared with Cast Magnets of Same Composition (Kieffer and Hotop[22])

Alloy constituents of iron-base magnets, %			Manufacturing process	Density g./cc.	Ultimate strength, psi	Residual magnetism, B_r, gauss	Coercive force, H_c, oersteds	External energy, $BH_{max.} \times 10^{-6}$	Demagnetization curve constant ($BH_{max.}/B_rH_c$) × 100, %
Al	Ni	Co							
13–14	27–28	—	Sintering	6.8	140,000–200,000	6480	560	1.3	43[a]
				6.7		6100	515	1.15	38[b]
13–14	27–28	—	Casting	7.0	43,000–70,000	7000	560	1.35	40
				6.9		6500	520	1.25	38
12	21	4	Sintering	6.95	170,000–200,000	7700	400	1.25	44
				6.87		7400	350	1.05	41
12	21	4	Casting	7.05	43,000–70,000	7900	400	1.30	45
				6.95		7600	350	1.10	43

[a] Maximum values.
[b] Average values.

TABLE 241

Physical Properties of Composite Contact Materials (Schwarzkopf[21] and Hausner and Blackburn[21a])

Composition	Density	Conductivity, % I.A.C.S.	Brinell hardness
Mo–Ag 65–35	10	50	120–135
W–Ag 50–50	13.2	59	105–115
W–Ag 85–15	15.2	38	170–190
W–Cu 85–15	16.3	25	190–205

process by which such materials can be produced. Table 241 gives the main physical properties of this type of material.[21,21a] Additional information can be found in Chapter XXIII.

PERMANENT MAGNET ALLOYS

Alloys of iron with about 8–14% aluminum and 18–30% nickel are used for permanent magnets. Additional alloying constituents may be cobalt, titanium, and copper. The practice of casting small-sized magnets has been replaced by the far more satisfactory sintering process. Comparative test results are given in Tables 242 and 243 of cast and sintered magnets, some of which have cobalt additions.[22,23] The test results show that the magnetic properties of the sintered products are slightly inferior. The sintered alloys are, however, far superior to the fused product in so far as ultimate strength is concerned. Values for this property are increased three- to fourfold—owing to the very fine grain structure of

TABLE 243

Magnetic Properties of Cast and Sintered Alloys (Garvin[23])

Alloy	Method of manufacture	Remanence, B_r, in gauss	Coercivity, H_c, in oersteds	Energy product, $BH_{max.} \times 10^{-6}$
Standard Alnico	Cast	7100–7900	580–480	1.4–1.8
	Sintered	6400–7700	550–450	1.4–1.66
High-coercive Alnico	Cast	6300–7200	660–550	1.4–1.8
	Sintered	5800–6400	640–590	1.4–1.66
High-remanence Alnico	Cast	8000–8800	420–320	1.3–1.7
	Sintered	7300–8000	450–350	1.25–1.45
Alcomax II	Cast	12,700	570	4.3
	Sintered	11,200	560	3.3
Hycomax	Cast	8500	790	2.7
	Sintered	7600–8200	820–760	2.4–2.8

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[21] P. Schwarzkopf, *Product Eng.*, *17*, No. 4, 268 (1946).

[21a] H. H. Hausner and P. W. Blackburn, in J. Wulff, *Powder Metallurgy*. Am. Soc. Metals, Cleveland, 1942, p. 470.

[22] R. Kieffer and W. Hotop, *Kolloid Z.*, *104*, 208 (1943).

[23] S. J. Garvin, *Symposium on Powder Metallurgy*. The Iron and Steel Institute, Special Report No. 38, London, 1947, p. 67.

the sintered alloys. Further advantages of sintered magnets lie in their better machinability; they also can be forged to some extent because of the finer structure. The subject is treated fully in Chapter XXIV.

IRON-MOLYBDENUM ALLOYS

Alloys of iron and molybdenum possess interesting physical properties, especially regarding the coefficient of thermal expansion. Alloys with 10% molybdenum and over, and 1% Cu have expansion characteristics that make them suitable for sealing to soft glass.[24] The physical properties of sintered alloys containing 5, 10, 15, and 20% Mo, respectively, are tabulated in Table 244; in the same table they are compared with alloys of the same analysis obtained by fusion. While the sintered alloys, like in the case of permanent magnet materials, displayed a fine grain size, the cast alloys were found to be coarse-grained and exceedingly brittle. Cast alloys containing 10% Mo and above showed increasing amounts of a second constituent that had precipitated at the grain boundaries, whereas in the case of the sintered alloys, a single phase prevailed in the alloys up to 15% Mo content. Also, sintered alloys up to

TABLE 244

Properties of Cast and Sintered Iron–Molybdenum–Copper Alloys (Kurtz[24])

	Alloy number[a]							
Properties	*5a*	*5b*	*10a*	*10b*	*15a*	*15b*	*20a*	*20b*
Density, g./cc.								
Sintered	7.49	—	6.96	—	7.42	—	8.03	—
Cast	—	8.01	—	8.02	—	8.03	—	8 06
Porosity, % *vs.* cast ingot	6.6	—	13.3	—	7.6	—	0.4	—
Shrinkage, %								
Linear	21.6	—	8.8	—	18.5	—	16.8	—
Volumetric	53.2	—	41.3	—	46.6	—	45.2	—
Hardness, Rockwell "B"								
Sintered, annealed	50	—	81	—	84	—	87	—
Cast, annealed	—	57	—	86	—	93	—	94
Thermal expansion[b]	12.62	12.59	11.04	11.64	10.00	10.99	9.15	10.68
Properties of wire[c]								
Tensile strength, psi	62,900	—	74,300	—	79,900	—	—	—
Elongation, %	14	—	14	—	15	—	—	—
Resistance, ohms/mil ft	159	104	256	234	266	—	—	—
Density, g./cc.	8.34	8.41	8.42	8.65	8.77	8.82	8.88	9.26

[a] Alloys marked *a* made by powder metallurgy, *b* by fusion. Numbers correspond to per cent molybdenum.

[b] Coefficient × 10^{-6} for range 20 to 600°C.

[c] Annealed.

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[24] J. Kurtz, in J. Wulff, *Powder Metallurgy*. Am. Soc. Metals, Cleveland, 1942, p. 497.

20% Mo were found to be more easily hot-worked than their cast counterparts.

STEELS AND CAST IRON

Although the number of steel compositions in existence is very large, those produced by the sintering process have so far essentially been of the plain carbon steel variety. The main reason for this appears to be that, for the simply shaped machine parts suitable for mass production by this process, the addition of alloying constituents is generally not economical. Carbon, however, is used extensively as an alloying constituent, and small quantities of silicon and manganese are used as beneficial addition elements.

In Table 245 the properties of forged sintered steels as determined by Koehring[25] are compared with those of regular SAE steels. Carbon-free and low-carbon steels were produced from decarburized steel and reduced iron powders; they were sintered in hydrogen atmosphere at 1050°C. (1920°F.) in closed vessels, which in the case of the steel specimens were filled with carbon. Immediately after sintering, the specimens were repressed (forged) while still hot, in water-cooled dies and again annealed. The hot-forged carbon steels showed a decarburization of about 50%. The specimens produced from the decarburized steel powder showed remarkable physical properties, almost equivalent to the cast and annealed material. On the other hand, the specimens produced from mill scale proved to be unsatisfactory, presumably due to the impurities present.

It seems that high-grade carbon steels (up to 0.9% C) from carbonyl powders can only be obtained by sintering if subsequently subjected to an intensive forging and rolling operation.[26] Steels with higher carbon contents (up to 1.5%) have been produced by addition of lampblack; however, they proved to be heterogeneous on account of irregular carbon distribution. Uniform distribution could be obtained by extremely fine grinding of the carbonyl powder with the lampblack, by adding small quantities of phosphorus and sulfur, or by using less pure, commercial carburizing agents such as graphite and coke powders. Larger additions of manganese result in larger, strongly fluctuating quantities of free carbon and increase the number and size of nonmetallic inclusions.[27]

The sintered steels based on carbonyl iron powder compare closely with fused commercial steels. The lower silicon, phosphorus, and sulfur

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[25] R. P. Koehring, in J. Wulff, *Powder Metallurgy,* Am. Soc. Metals, Cleveland, 1942, p. 304; *Iron Age, 148,* 29 (1941).

[26] E. K. Offermann, *Mitt. Kohle- u. Eisenforsch., 1,* 5, 85 (1936).

[27] F. Duftschmid and F. Houdremont, *Stahl u. Eisen, 51,* 1613 (1931).

TABLE 245
Properties of Hot-Forged Steels (Koehring[25])

Material	Sintering temperature °C.	Sintering temperature °F.	Density, g./cc.	Yield strength, psi	Tensile strength, psi	Elongation in 2 in., %	Reduction in area, %	Hardness, Rockwell "B"
SAE 1010, cold drawn	—	—	—	70,000	80,000	20	48	166
Natural hot-rolled	—	—	—	44,000	70,000	37	63	123
SAE 1030, cold-drawn	—	—	—	72,000	85,000	20	47	179
Natural hot-rolled	—	—	—	46,000	75,000	30	56	137
SAE 1112 steel cuttings with low C and high P content, pulverized mechanically	1050	1922	7.79	38,000	54,000	11	13	59–74
Decarburized steel powder, particle size below 150μ	1050	1922	7.82	37,700	55,000	14	13	61–68
Above steel powder mixed with 0.6% graphite[a]	1050	1922	7.78	51,000	73,000	23	32	64–75
Iron powder, reduced from mill scale, with grain size under 150 μ	1050	1922	7.39	33,000	40,000	3	3	67–82
Above iron powder mixed with 0.6% graphite[b]	1050	1922	7.39	37,000	45,000	4	5	66–74

[a] Carbon content after sintering and forging approximately 0.30% C.

[b] Carbon content after sintering and forging approximately 0.25%, max.

contents may be considered an advantage of the sintered product, with the physical and chemical characteristics apparently being very similar to those of the fusion products. Tensile strength, yield point, hardness, and heat-treating properties are slightly inferior to those of the corresponding fused material unless remelted.[22]

The physical properties of sintered steels of different carbon content produced from electrolytic iron powders and graphite are compared in Table 246 with the corresponding SAE steels.[28] Except for ductility (reduction of area values) the low-carbon sintered steels are approximately equivalent to the regular steels, while the high-carbon sintered steels are generally inferior.

Comparative physical properties of differently heat-treated 0.55% carbon-containing steel specimens formed by conventional and powder metallurgy methods are shown in Table 247, according to Squire.[29] The strength and reduction in area values of the powder products are for all heat treatments considerably lower than those for the wrought specimens, which may be attributed to a lack of manganese in the compacts. Nevertheless, most of the values are considerably higher than any so far reported for ferrous powder compacts. The comparatively high values for impact, elongation, and modulus of elasticity of the heat-treated powder products are particularly noteworthy. The fact that these properties are of the same order of magnitude as those for the wrought steel specimens is an indication ~~of the~~ unusually strong metallic bond that can be achieved in sintered steels. Squire explains this phenomenon by a comparatively low percentage of porosity, ranging between 4 and 5.5%, with the corresponding density figures falling between a minimum of 7.42 and a maximum of 7.54 g./cc. A complete evaluation of the data presented in Table 247 is, unfortunately, not possible, since Squire's report lacks information concerned with the details of the raw materials used, the history of the powder employed (*i.e.*, powder mixtures of iron plus graphite or mechanically comminuted bulk steel), and the processing operations used in forming the compacts. The industrial applicability of these materials is discussed in detail in Chapter XXV.

It may be added that cast iron can be obtained by hot-pressing, with the result that a material with special properties is possible.[30] Gray cast iron with 3.1% C, 1.13% Si, 0.59% Mn, 0.126% S, and 1.15% P has been produced at various pressing temperatures, resulting in properties that

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[28] G. Stern, *Trans. Am. Inst. Mining Met. Engrs.*, *166*, 566 (1946).

[29] A. Squire, *Watertown Arsenal Laboratory Report WAL 671/18* (1944); also U. S. Dept. of Commerce, Office of Technical Services, Report PB 4419, July 20, 1944.

[30] W. D. Jones, *Foundry Trade J.*, *59*, 401 (1938).

TABLE 246

Physical Properties of Standard SAE Steels and Sintered Steels Produced from Electrolytic Iron and Graphite Powder Mixtures (Stern[28] and Schwarzkopf[21])

Material	Process	Sintering temperature		Heat treatment			Tensile strength, psi	Yield strength, psi	Elongation, %	Reduction in area, %	Brinell hardness
		°C.	°F.	°C.	°F.	Type[a]					
SAE 1030	Cold-drawn	—	—	—	—	—	85,000	72,000	20	47	179
	Natural hot-rolled	—	—	—	—	—	75,000	46,000	30	56	137
SAE 1035	Water-quenched from	—	—	843	1550	WQ	—	—	—	—	—
	and drawn at	—	—	320	600	D	117,000	88,000	10	40	241
Sintered, type I; av. C,0.275%; density, 7.54 g./cc.(96.2%[b])	Sintered and furnace-cooled	1095	2000	—	—	FC	56,050	38,350	23.5	25	124
	then oil-quenched	—	—	857	1575	OQ	—	—	—	—	—
	and drawn at	—	—	320	600	D	66,500	51,000	22.5	22.9	134
	As above, drawn at	—	—	704	1300	D	52,450	36,025	34	38.8	120
	As above, water-quenched from	—	—	830	1525	WQ	—	—	—	—	—
	and drawn at	—	—	320	600	D	82,500	65,800	13	20.2	158
SAE 1045	Cold-drawn	—	—	—	—	—	110,000	69,000	19	41	235
	Natural hot-rolled	—	—	—	—	—	99,000	60,000	24	47	200
	Oil-quenched from	—	—	816	1500	OQ	—	—	—	—	—
	and drawn at	—	—	320	600	D	140,000	95,000	11	34	277
	As above, drawn at	—	—	704	1300	D	97,000	66,000	25	55	196
	Water-quenched from	—	—	816	1500	WQ	—	—	—	—	—
	and drawn at	—	—	320	600	D	150,000	114,000	8	32	311
Sintered, type II; av. C, 0.52%; density, 7.47 g./cc. (95.3%[b])	Sintered and furnace-cooled	1095	2000	—	—	FC	66,150	41,000	17	16.5	137
	then oil-quenched from	—	—	830	1525	OQ	—	—	—	—	—
	and drawn	—	—	320	600	D	84,000	57,700	14.5	14.7	146
	As above, drawn at	—	—	704	1300	D	58,800	41,700	25.0	30.0	126
	As above, water-quenched	—	—	830	1525	WQ	—	—	—	—	—
	and drawn	—	—	320	600	D	122,250	102,100	8.0	8.5	203

Material	Process	Sintering temperature °C.	Sintering temperature °F.	Heat treatment °C.	Heat treatment °F.	Heat treatment Type[a]	Tensile strength, psi	Yield strength, psi	Elongation, %	Reduction in area, %	Brinell hardness
SAE 1060	Hot-rolled and annealed	—	—	—	—	—	95,000	59,000	25	52	197
	Oil-quenched from	—	—	816	1500	OQ	144,000	105,000	17	48	293
	and drawn at	—	—	704	1300	D	98,000	72,000	26	61	201
Sintered, type III, av. C, 0.64%; density, 7.43 g./cc. (94.9%[b])	Sintered and furnace-cooled	1095	2000	—	—	FC	69,900	42,975	11.5	10.7	132
	then oil-quenched from	—	—	830	1525	OQ	—	—	—	—	—
	and drawn at	—	—	427	800	D	97,050	72,200	13.0	11.2	161
	As above, drawn at	—	—	704	1300	D	65,725	46,650	16.0	18.6	132
	As above, water-quenched from	—	—	830	1525	WQ	—	—	—	—	—
	and drawn at	—	—	320	600	D	136,000	109,500	8.0	8.5	218
SAE 1080	Hot-rolled and annealed	—	—	—	—	—	103,000	62,000	22	48	217
	then oil-quenched from	—	—	816	1500	OQ	—	—	—	—	—
	and drawn at	—	—	427	800	D	174,000	125,000	13	40	363
	As above, drawn at	—	—	704	1300	D	106,000	81,000	23	56	217
	As above, water-quenched	—	—	800	1475	WQ	—	—	—	—	—
	and drawn at	—	—	427	800	D	183,000	135,000	12	40	388
Sintered, type IV; av. C, 0.87%; density, 7.33 g./cc. (93.3%[b])	Sintered and furnace-cooled	1095	2000	—	—	FC	84,075	63,150	7.0	4.1	158
	then oil-quenched from	—	—	830	525	OQ	—	—	—	—	—
	and drawn at	—	—	427	800	D	109,400	86,500	5.5	5.9	177
	As above, drawn at	—	—	704	300	D	69,550	53,850	9.5	9.1	135
	As above, water-quenched from	—	—	830	525	WQ	—	—	—	—	—
	and drawn at	—	—	320	600	D	152,000	132,000	4.0	3.3	245

[a] WQ = water-quenched; OQ = oil-quenched; D = draw temperature; FC = furnace cool.

[b] Of theoretical.

TABLE 247

Physical Properties of Heat-Treated Wrought and Sintered 0.55-Carbon Steel (Squire[29])

Material and treatment	Hardness		Impact, strength,[a] ft.-lb.	Yield strength, psi	Tensile strength, psi	Elongation, %	Reduction of area, %	Modulus of elasticity, 10^6 psi
	Rockwell	Brinell						
Normalized 1 hr. at 870°C. (1600°F.)								
Wrought	C-6.5	70	52	60,000	110,000	21.3	36.4	28.6
	C-6.5	70	56	54,000	104,800	20.0	36.4	31.4
Powder	B-65	59	22	31,000	73,000	17.5	18.3	27.6
	B-65	59	23	—	—	—	—	—
Water-quenched from 840°C. (1550°F.) tempered 1/2 hr. at 190°C. (375°F.)								
Wrought	C-54	534	9	—	—	—	—	—
	C-54	534	6	—	—	—	—	—
Powder	C-54	534	6	—	—	—	—	—
	C-48	460	6	—	—	—	—	—
Tempered 3 hr. at 260°C. (500°F.)								
Wrought	C-48	460	4	—	230,000	1.3	3.2	27.8
	C-50	484	3	—	255,000	2.5	3.2	27.8
Powder	C-35	322	11	97,000	145,000	5.0	10.1	27.2
	C-27	265	15	110,500	151,600	2.5	10.1	27.2
Tempered 3 hr. at 340°C. (650°F.)								
Wrought	C-41	382	36	201,000	226,000	7.5	21.5	27.8
	C-43	404	36	198,000	224,000	7.5	24.6	29.4
Powder	C-30	283	18	117,500	155,600	5.0	10.1	30.0
	C-16	205	19	95,000	140,000	10.0	18.3	30.0
Tempered 3 hr. at 430°C. (800°F.)								
Wrought	C-38	352	34	164,000	183,600	5.0	21.5	27.8
	C-36	332	33	166,000	179,200	7.5	27.6	29.4
Powder	C-22	240	13	102,000	122,000	7.5	11.7	27.2
	C-18	220	14	106,000	128,400	10.0	19.9	27.2

[a] Values were judged by resistance of 0.227 × 0.227 × 2 in. unnotched specimens and are included only for comparison of the wrought and powder metallurgy steels.

TABLE 248

Physical Properties of Cast, Wrought and Sintered Brass Alloys[a]

Process	Density, g./cc.	Brinell hardness	Yield strength, psi	Tensile strength, psi	Elongation, %	Reduction of area, %	Compressive strength, psi
			90–10 Cu–Zn				
Cast	8.60	—	10,000	33,000	35	—	—
Wrought[d]	8.80	—	11,500	37,500	54	85	—
Alloy powder[c], cold pressed at 50 tsi and sintered at 880 °C. (1615 °F.)	7.99	41	10,300	29,700	34	—	32,700[e]
Alloy powder, cold pressed at 9 tsi, then hot pressed at 4.5 tsi at 900 °C. (1650 °F.)	—	—	17,000	30,500	22	—	—
			70–30 Cu–Zn				
Cast	8 44	55	14,500	37,400	58	—	—
Wrought[d]	8 56	58	11,400	46,100	74	73	—
Alloy powder,[c] cold pressed at 50 tsi and sintered at 850 °C. (1560 °F.)	7.94	39	8,800	34,900	50	—	31,600[e]
Alloy powder, cold pressed at 9 tsi, then hot pressed at 4.5 tsi at 800 °C. (1470 °F.)	—	—	22,000	38,000	16	—	—

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[a] This table contains a composite of data published by the U. S. Dept. of Commerce, Natl. Bureau of Standards, Circular C447 (1943); E. H. Kelton, *Machine Design*, *16*, 129 (1944); and W. D. Jones, *Metal Ind. London*, *56*, 225 (1940).

[b] Rod, 1/2 in. diam., annealed 1 hr. at 480 °C. (900 °F.).

[c] Contains 0.3% phosphorus addition.

[d] Strip, rolled, annealed 2 hrs. at 625 °C. (1155 °F.).

[e] 10% compression.

TABLE 249

Physical Properties of Cast, Wrought and Sintered Bronze Alloys[a]

Process	Density, g./cc.	Brinell hardness	Yield strength, psi	Tensile strength, psi	Elongation, %	Reduction of area, %	Compressive strength, psi
			95–5 Cu–Sn				
Cast	—	59	18,000	40,000	38	34	—
Wrought[b]	—	—	18,700	49,400	73	82	—
Alloy powder, cold pressed at 50 tsi and sintered at 800 °C. (1470 °F.)	8.30	45	—	29,700	12	17	89,000[d]
Alloy powder, cold pressed at 9 tsi, then hot pressed at 4.5 tsi and 800 °C. (1470 °F.)	—	114	24,000	45,000	47	—	—
Alloy powder, cold pressed at 10 tsi, then hot pressed at 50 tsi and 500 °C. (930 °F.)	8.90	108	—	—	—	—	123,000[d]
			90–10 Cu–Sn				
Cast	—	74	20,000	43,200	25	—	—
Wrought[c]	—	—	23,100	63,800	76	73	—
Alloy powder, cold pressed at 50 tsi and sintered at 800 °C. (1470 °F.)	8.50	57	—	34,900	21	27	87,000[d]
Alloy powder, cold pressed at 9 tsi, then hot pressed at 4.5 tsi and 800 °C. (1470 °F.)	—	—	30,000	42,000	71	—	—
Alloy powder, cold pressed at 10 tsi, then hot pressed at 50 tsi and 500 °C. (930 °F.)	8.89	130	—	—	—	—	137,000[d]

[a] This table contains a composite of data published by U. S. Dept. of Commerce, Natl. Bureau of Standards, Circular C447 (1943); W. D. Jones, *Metal Ind. London*, *56*, 225 (1940); and by the author in *Trans. Am. Inst. Mining Met. Engrs.*, *161*, 580 (1945).

[b] Rod, $^3/_4$ in. diam. annealed (to 0.040 mm. grain size).

[c] Rod, $^3/_4$ in. diam., annealed (to 0.090 mm. grain size).

[d] 0.1 in. compression.

show a decided maximum at 980°C. (1800°F.) with tensile strength values in the order of 80,000 psi (for further details see Volume I, Chapter XII).

COPPER ALLOYS

Sintered alloys of copper with zinc or tin as major alloying component have gained steadily in importance as material for structural parts and dense bearings, respectively. Table 248 summarizes the physical properties of two typical binary brass alloys, and Table 249 those of two typical binary bronze alloys. In these tables, values for sintered and hot-pressed material are compared with those for the corresponding cast and wrought alloys.

POROUS POWDER METALLURGY MATERIALS

In the metals and alloys cited so far, porosity was incidental and was generally considered to be disadvantageous to the sintered product; however, in the self-lubricating type of bearings, porosity is decidedly advantageous—in fact, sintering is the only method by which they can be produced with a porous structure so that they can be impregnated with lubricating oil. In Table 250, tensile strength values of various porous bearings are compared with those of dense bronze bearing material, indicating the density in each case.[31] In products of this kind, however, the tensile strength is only of secondary importance as compared with such characteristics as antifriction properties, wear resistance, and permeability. In the case of self-lubricating bearings the porosity factor is coordinated with the rate of oil flow and the viscosity of the impregnant; in porous metallic filters, permeability is the most important property. Further information on this subject is given in Chapter XXVII.

TABLE 250

Strength and Density of Bearing Materials (Schwarzkopf[31])

Bearing material	Tensile strength, psi	Density, g./cc.
Cast bronze (90–10 Cu–Sn)	21,000	8.6
Porous bronze (90–10 Cu–Sn)	2,800–4,200	6.0–6.5
Porous iron	7,100–21,000	5.0–6.5
Porous Fe–Pb graphite (90–5–5 Fe–Pb–C)	17,000–21,000	5.5–6.0

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[31] P. Schwarzkopf, *Product Eng.*, *17*, No. 4, 268 (1946).

Summary

The physical and engineering properties of sintered products are decidedly affected by the variables inherent in the process of manufacture. Qualitative charts give a good indication of the trend of the properties, whereas exact values for the various properties must be studied on the basis of comparison tables, which are particularly valuable in those cases in which the materials can be produced by the sintering as well as the fusion process.

The properties of sintered products are primarily governed by their densities, as is apparent from the trend charts and the property tables. In general, sintered metals match their fused counterparts with regard to strength, but are often considerably inferior in ductility. This rule applies to ferrous products, and especially to heat-treated steels. Only the very soft and plastic metals, or those that have been subjected to drastic metal-working reduction, display ductility and impact resistance values that are comparable with those of the fused metals.

The refractory metals, their carbides, and certain iron-base permanent magnet alloys, however, represent the notable exceptions to this rule. Because of the higher purity and finer grain size, the sintered products are far superior to the materials produced by the fusion process—especially with regard to strength. Hence, the refractory metals and hard metals are almost exclusively produced by the sintering process, and in the case of the permanent magnets only the larger sizes are now produced by casting.

Industrial alloys of iron and copper produced by the sintering process have, in many cases, sufficiently attractive properties to permit their use on a competitive basis with fused and wrought material.

Products with closely controlled pore volume and structure—as required for bearings and filters—constitute characteristic exponents of the powder metallurgy technique, where physical strength is only of secondary importance as compared with properties such as wear resistance, permeability, and antifriction properties.

CHAPTER XXXII

Survey of Sintered Metals and Alloys for Potential Industrial Use

Since the perfection of the methods of manufacturing the refractory metals tungsten, molybdenum, and tantalum via the sintering technique, the interest in this new approach has become so great that laboratories the world over have produced almost all other pure metals and their alloys from the powder state. This development has been called for only in part by the demands of industry for new and better products; it has also been fostered to a great extent by the scientist's and researcher's urge for a clarification of the occurrences during the sintering process, and for a search of new, synthetic metal-base materials with unusual characteristics.

It is the intent of the following presentation to familiarize the reader to some extent with the metals and alloys which, if produced by the powder method, have potential uses in industry or science. In this survey, all those materials that have already matured into industrial products are noted only briefly for the sake of giving a complete picture. The preceding chapters of this volume have been exclusively devoted to a detailed discussion of these materials.

During the last two decades the science of metals has made tremendous headway, and truly revolutionary changes in the modern physical theories of electrons and atomic structure have come to pass. These developments have culminated in the advancement of the basic physics to a point where atomic structure can be changed through nuclear physics; thereby, elements may be transformed into others or into isotopes of different properties. During the same period, equilibrium conditions between a great variety of elements have been definitely determined, which, together with the new physical theories, have been applied directly to the properties of metallic crystals; as a result the fundamental principles underlying alloy structures have been greatly clarified. The atomic constitution and crystal structure of the elements or the electronic background to metallurgy must be considered theoretical prerequisites to any synthetic production of new alloy systems, whether by fusion or by sintering. It is believed to be beyond the framework of this book to discuss these topics in greater detail, but the reader who is seriously

I_A	II_A	III_A	IV_A	V_A	VI_A	VII_A	Transition elements			I_B	II_B	III_B	IV_B	V_B	VI_B	VII_B	VIII_B
1 H 1.008 ⬡																	2 He 4.003
3 Li 6.94 ⊡	4 Be 9.02 ⬡	5 B 10.82 ⬡	6 C 12.01 ⬡											7 N 14.008 ⊡	8 O 16.000 ◊	9 F 19.00	10 Ne 20.183 □
11 Na 22.997 ⊡	12 Mg 24.32 ⬡	13 Al 26.97 □	14 Si 28.06 ◫											15 P 30.98 ⊡	16 S 32.06 ◈	17 Cl 35.457	18 A 39.944 □
19 K 39.096 ⊡	20 Ca 40.08 □	21 Sc 45.10	22 Ti 47.90 ⬡	23 V 50.95 ⊡	24 Cr 52.01 ⊡(α)	25 Mn 54.93 □*	26 Fe 55.85 ⊡(α)	27 Co 58.94 ⬡(β)	28 Ni 58.69 □(β)	29 Cu 63.57 □	30 Zn 65.38 ⬡	31 Ga 69.72 ⊙	32 Ge 72.60 ◫	33 As 74.91 ◊	34 Se 78.96 ⬡	35 Br 79.916	36 Kr 83.7 □
37 Rb 85.48 ⊡	38 Sr 87.63 □	39 Y 88.92 ⬡	40 Zr 91.22 ⬡	41 Cb 92.91 ⊡	42 Mo 95.95 ⊡	43 Ma ⬡	44 Ru 101.7 ⬡	45 Rh 102.91 □	46 Pd 106.7 □	47 Ag 107.88 □	48 Cd 112.41 ⬡	49 In 114.76 □	50 Sn 118.70 ▣	51 Sb 121.76 ◊	52 Te 127.61 ⬡	53 I 126.92 ⊙	54 Xe 131.3 □
55 Cs 132.91 ⊡	56 Ba 137.36 ⊡	57 71 Rare earths see below	72 Hf 178.6 ⬡	73 Ta 180.88 ⊡	74 W 183.92 ⊡	75 Re 186.31 ⬡	76 Os 190.2 ⬡	77 Ir 193.1 □	78 Pt 195.23 □	79 Au 197.2 □	80 Hg 200.61 ◊	81 Tl 204.39 ⬡	82 Pb 207.21 □	83 Bi 209.0 ◊	84 Po ▱	85? 212 (?)	86 Rn 222.0
87? 223 (?)	88 Ra 226.05	89 Ac 227	90 Th 232.12 □	91 Pa 231	92 U 238.07 ◊												

Light metals

Strong electropositive metals

High-melting heavy metals

Low-melting heavy metals

Non-metals

NON-METALS
Inert gases

Rare earths:														
57 La 138.92	58 Ce 140.13	59 Pr 140.92	60 Nd 144.27	61 Il 146 (?)	62 Sm 150.43	63 Eu 152.0	64 Gd 156.9	65 Tb 159.2	66 Dy 162.46	67 Ho 163.5	68 Er 167.2	69 Tm 169.4	70 Yb 173.04	71 Lu 174.99

The numbers in front of the chemical symbols represent the atomic numbers; those following, the atomic weights. The geometric figures indicate the crystal structure at room temperature.

□ = Face-centered cubic ⊡ = Body-centered cubic ⬡ = Hexagon ◊ = Rhombohedral ▣ = Body-centered tetragonal ◫ = Diamond lattice α, β = Modification

□* = Complex cubic ⊙ = One-face centered orthorhombic ◈ = Face centered orthorhombic ▱ = Monoclinic

Fig. 592. Periodic system of the elements (according to Guertler[2]).

interested in the theoretical approach is urged to consult the classical work of Hume-Rothery.[1]

For the purposes of this chapter it appears advantageous to describe the metals and compositions that have been produced by the sintering technique in the order given by the periodic system. The convenience of using the periodic table is further increased by separating the columns into A and B groups as shown in Figure 592, as originally suggested by Guertler.[2]

CLASSIFICATION OF THE METALS IN THE PERIODIC SYSTEM

In the conventional form of the table, the first column representing the valence of 1 includes the elements, H, Li, Na, K, Cu, Rb, Ag, Cs, Au. By separating the elements of the alkali group from the remaining elements (Cu, Ag, and Au), two subgroups I_A and I_B result which contain—with the exception of hydrogen—elements of rather similar properties. With this separation carried out in each of the eight groups the metals fall into three or four "natural" families whose individual members resemble each other more or less closely with regard to melting point, density, strength, chemical behavior, or other important technical properties.

This classification of the metals is of distinct advantage and usefulness in appraising the properties of an "unknown" metal by approximation and comparison with better known members of the family. For example, it may be anticipated that beryllium has properties similar to those of magnesium, and iridium to those of the other five members of the platinum metal group. Although these similarities within each family are distinct, they permit the existence of marked differences between the individual metals caused, to some extent, by differences in crystal lattice structure. Thus, it often becomes possible to improve alloying, chemical behavior, or physical properties by substituting one metal by another one lying near it in the group. Typical examples are the substitution of chromium or titanium for vanadium in steels, molybdenum for tungsten in electronics and x-ray tubes, and cadmium for zinc in corrosion-resistant platings.

In the following classification of the metals in their natural families in the periodic system, seven metals are outstanding in their industrial importance: iron, nickel, copper, aluminum, zinc, tin, and lead. Each of these metals forms a series of technically significant binary alloys. For

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[1] W. Hume-Rothery, *The Structure of Metals and Alloys*. The Institute of Metals, London, Monograph and Report Series No. 1, 1936.

[2] W. Guertler, *Metalltechnischer Kallendar*. Bornträger, Berlin, 1926.

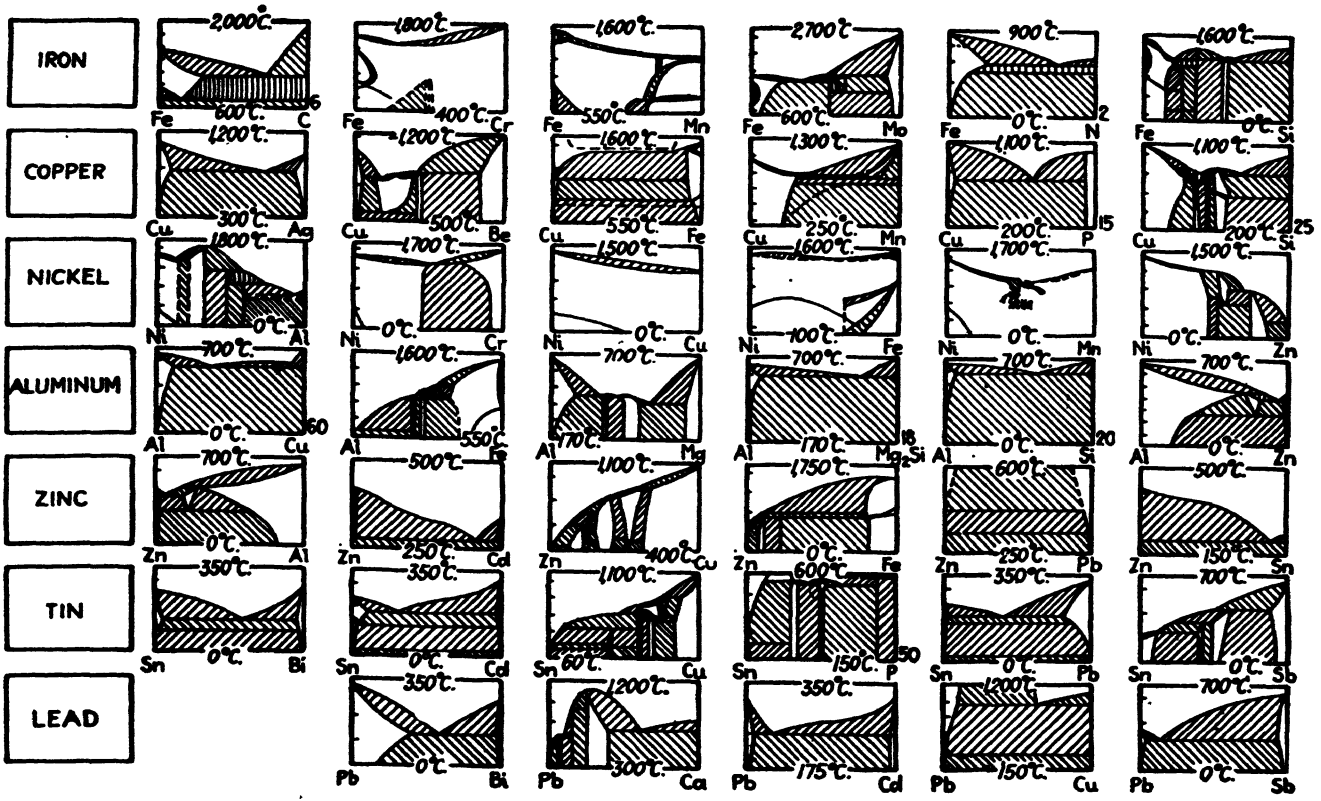

Fig. 593. Constitutional diagrams of some industrially important binary alloys (according to an arrangement by Doan and Mahla[3]).

the reader's convenience, the constitutional diagrams of these alloys are schematically reproduced in Figure 593, according to a representation by Doan.[3]

According to Guertler,[2] the industrially useful metals may be classified into three groups. The first group contains the "high-melting heavy metals" based on one or more of the following elements: iron, nickel, copper, the precious metals, and the refractory metals. With a few exceptions, these metals form alloys with each other and, within the individual families, solid solutions, especially when the system contains more than two components. All of these metals may also be alloyed with metals of other groups such as carbon or silicon to iron, or zinc, tin, lead, or aluminum to copper. The group may best be divided into six subgroups:

(*1*) *Iron alloys,* such as steels, alloy steels, and cast irons, as the most important engineering materials.

(*2*) *Nickel alloys,* such as nickel-iron (Invar), nickel-chromium (Nichrome), and nickel–copper (Monel), similar to the iron alloys in physical properties, but more resistant to corrosion and more expensive.

(*3*) *Copper alloys,* such as brasses, bronzes, and cupro-nickels, similar to the nickel alloys in chemical resistance, but inferior to both the nickel and iron alloys in strength and hardness; intermediate in cost.

(*4*) *Silver alloys,* superior in luster and chemical stability, but more expensive than the nickel alloys.

(*5*) *Noble metal alloys,* with gold or one of the platinum metals as main constituent, of maximum chemical stability, but also most costly.

(*6*) *Refractory metal alloys,* which include such metals as tungsten, molybdenum, and chromium as main constituent; significant in their hot strength or heat resistance; their costs are midway between the nickel and silver alloys.

The second group contains the "low-melting heavy metals" based on the elements zinc, lead, antimony, bismuth, cadmium, and tin. All of them possess a high specific gravity, but melt below 500°C. (930°F.). The alloying capacities of these low-melting metals among themselves and with high-melting metals are considerably reduced, and solubility in the solid state is rare between the different low-melting components. Instead, the alloys usually consist of simple aggregates of two or more kinds of crystals, with properties being those of the average of the component metals. This characteristic has been responsible for their widespread use as bearing metals, solders, and die-casting alloys.

The third group consists of the "light metal" elements based on either aluminum or magnesium. The alloys are outstanding because of their low specific gravity and melting point, which does not exceed 700°C. (1300°F.). In addition to mutual alloying between the two light metals, zinc, tin, copper, and silicon form important alloying components. The

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[3] G. E. Doan and E. M. Mahla, *The Principles of Physical Metallurgy.* McGraw-Hill, New York, 2nd ed., 1941, p. 341.

primary use of the light alloys is for weight-saving applications; a secondary use is for decorative purposes.

HIGH-MELTING HEAVY METALS AND ALLOYS

Iron and Iron Alloys

IRON

The powder metallurgy of iron is described in considerable detail in Chapters XXIV and XXV, with special attention directed at the commercial aspects. The production of iron powders is described fully in Volume I, Chapters III and VI.

IRON ALLOYS

Iron–Carbon. The powder metallurgy of carbon steels and high-carbon–iron alloys with due reference to the industrial implications is also treated in Chapter XXV.

Iron–Nickel. Sintered iron–nickel alloys, especially if produced from carbonyl powders, excel in their magnetic properties and in their closely confined and accurate coefficient of expansion. Alloys containing 35 to 36% Ni have a lower coefficient of expansion if produced by sintering (on account of the greater purity that is obtainable by sintering as compared to melting[4]). As previously shown by the expansion curves in Figure 481 of Chapter XXV, these properties make possible the use of iron–nickel alloys for many electrical temperature control devices. A special interesting application is the manufacture of bimetallic strips by sintering; the molds are filled with layers of powder of different composition, sintered at temperatures of about 1200°C. (2200°F.), and then hot-worked. (See also Chapter XXX, p. 566). Iron–nickel alloys are discussed more fully in Chapters XXIV (p. 285 ff.) and XXV (p. 399 ff.).

Iron–Nickel–Aluminum. Alloys of this type, with and without the addition of cobalt, have found application for the manufacture of permanent magnets, and are described as such in Chapter XXIV. An alloy containing 0.4% Ti, in addition to 12.5% Al and 32% Ni, produced experimentally from a mixture of elemental and prealloyed (50–50 Fe–Al and 50–50 Ni–Al) 200-mesh powders was found to expand about 20% in volume after presintering at 900°C. (1650°F.) for one hour and sintering at 1260°C. (2300°F.) for ten hours in hydrogen atmosphere.[4a] Reheating at 710°C. (1310°F.) for one hour after oil quenching from the

[4] G. Hamprecht and L. Schlecht, *Metallwirtschaft, 12,* 281 (1933).

[4a] British Intelligence Objectives Sub-Committee, Final Report No. 993, Item No. 21 (March 1947); see also *Metal Powder Rept., 1,* No. 8, 119 (1947).

sintering temperature caused no further volumetric changes or distortion of the shape of the specimen. The magnetic properties of the alloy were found to be considerably inferior to those of the corresponding cast alloy, indicating that at least part of the aluminum and titanium had been prevented from alloying by oxide films. By changing the presintering operation into a vacuum treatment at 900°C. (1650°F.) for four hours and otherwise repeating the procedure as before, the expansion was reduced to 2%. The resulting material then exhibited magnetic properties approaching those of the cast alloy.

Iron–Nickel–Aluminum–Cobalt. Alnico-type permanent magnets are described in detail in Chapter XXIV.

Iron–Nickel–Cobalt. Alloys of this type, in particular if about 55–30–15 Fe–Ni–Co in composition, are superior to straight iron–nickel alloys with regard to the coefficient of expansion and have been used in vacuum technique, either as the fused alloy[5,6] or as the sintered product,[7] which proved to be superior owing to the absence of gases, especially by following an accurate manufacturing technique. These alloys, known under the trade names of Kovar and Fernico, are further discussed in Chapter XXV.

Iron–Nickel–Chromium. Sintered alloys of iron with nickel and chromium have been suggested as starting material for electrical resistor wires.[7a] An alloy of a 51–29–20 Fe–Ni–Cr composition to which 0.2% Th is added, is claimed to excel by its unusually long life as a heating element.

Iron–Chromium. These alloys can be produced by sintering compressed iron–chromium powder mixtures at 1250–1350°C. (2280–2460°F.) in an atmosphere of very pure hydrogen. The formation of chromium oxide films which would prevent diffusion of the components can be counteracted by the addition of carbon, *e.g.*, lampblack, and the application of sintering atmospheres at pressures below atmospheric. Chromium may also be introduced by using very pure oxide as raw material,[8] which should be reduced by means of hydrogen in the presence of carbonyl iron powder. Different rates of reduction of such a mixture at varying temperatures and periods are given in Table 251. It is noteworthy that with the specimen containing 20% chromium oxide, approximately 95% reduction took place after eleven hours at 1350°C. (2460°F.). The process can be carried out without difficulties by reducing the oxide in hydrogen

[5] H. Scott, *Trans. Am. Inst. Mining Met. Engrs.*, ***E30***, 506 (1930); *Trans. Am. Soc. Steel Treating*, ***13***, 829 (1928); *J. Franklin Inst.*, ***220***, 733 (1935).

[6] W. Hessenbruch, *Z. Metallkunde*, ***29***, 193 (1937).

[7] R. Kieffer, *Metall u. Erz*, ***37***, 67, 88 (1940).

[7a] German Pat. 744,579; see also *Metal Powder Rept.*, ***2***, No. 7, 109 (1948).

[8] H. H. Meyer, *Mitt. Kaiser-Wilhelm-Inst. Eisenforsch., Düsseldorf*, ***13***, 199 (1931).

atmosphere at subatmospheric pressure in the presence of lampblack.[9] Alternately, the reduction process may be extended by prolonged sintering.[10]

Iron–Chromium–Nickel. Sintered austenitic iron–chromium–nickel alloys, and especially stainless steels of the 18–8 type, can be manufactured by the same method described for the iron–chromium alloys. Nickel may be added in the form of carbonyl powder and chromium as finely pulverized electrolytic powder. Sintering in vacuum or at subatmospheric hydrogen pressures is most advantageous if repeated after intermediary hot-working until a product is obtained that is identical to the fused alloy. A more economical process of sintering stainless steel consists in using powdered raw material obtained from stainless steel scrap,[11] which is annealed to precipitate impurities and carbide along the grain boundaries. After cooling, the precipitates can be removed by

TABLE 251

Reduction of Mixtures of Carbonyl Iron Powder with Chromium Oxide in Relation to Temperature and Time (Meyer[8])

Reduction temperature		Reduction time, hr.	Chromium oxide content in mixture, %	Chromium content in iron, %	Reduction, %	Remarks
°C.	°F.					
1150	2100	2	10	1.92	28.1	
1200–1250	2190–2280	1	30	1.7	8.0	
1250	2280	4	30	6.9	33.7	
1250	2280	4	50	5.9	17.2	Formation of black chromium oxide
1300	2370	5	50	4.0	11.7	
1300	2370	12	25	7.82	45.7	
1300	2370	15	25	8.82	51.5	
1300–1350	2370–2460	6	25	4.8	28.1	Hydrogen from cylinder, purified
1300–1350	2370–2460	6	25	2.0	11.7	Hydrogen from cylinder, as received
1350	2460	1	30	5.3	25.8	
1350	2460	2	20	5.47	40.0	Caked (sintered)
1350	2460	2	20	7.93	58.2	Not caked (sintered)
1350	2460	2.5	30	6.9	33.7	
1350	2460	4	35	13.5	56.4	
1350	2460	11	20	13.03	95.2	
1350	2460	11.5	35	19.1	79.8	
1350	2460	13	25	14.8	86.5	
1350	2460	13	30	7.9	38.5	
1400	2550	0.5	20	2.54	18.5	
1400	2550	1.5	30	7.5	36.7	
1400	2550	2	50	9.8	28.6	Formation of black chromium oxide

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[9] Swedish Pat. 101,410; Brit. Pat. 512,502; Italian Pat. 371,055.

[10] G. Grube and K. Ratsch, *Z. Elektrochem.*, *45*, 838 (1939).

[11] J. Wulff, in J. Wulff, *Powder Metallurgy*, Am. Soc. Metals, Cleveland, 1942, p. 137; see also Anonymous, *Iron Age*, *148*, No. 8, 29, 100 (1941).

etching with sulfuric acid containing copper sulfate. By this method a sintered stainless steel is produced with excellent mechanical properties, which possesses especially high ductility. Although it is not yet practicable to produce chromium–nickel steels that can compete with the fused steels, it seems feasible to produce by sintering those stainless steels that have a very low carbon content, so that the danger of intergranular corrosion is obviated. They would thus be rendered suitable for welding and for processes in which a critical service temperature is encountered for a certain period. It also seems possible that sintering shows certain advantages for mass production of sheet and strip, especially in locations remote from coal deposits. The subject of sintered stainless steels is further treated in Chapter XXV.

Iron–Chromium–Aluminum. Sintered iron–chromium–aluminum alloys were suggested for use as heating elements in 1937.[11a] The chief advantage of using powder metallurgy methods in producing the alloy lies in a better workability due to the finer grain structure. Furthermore, it is possible to add small amounts of alkali metals or rare earth elements in accurately controlled allotments and to retain them throughout the sintering operation without noticeable losses, thereby prolonging the effective life of the heating element.[11b]

Iron–Chromium–Aluminum–Silicon. Iron–chromium–aluminum–silicon alloys of the type known under the trade name "Hoyt Alloy No. 10," containing about 38% Cr, 8% Al, 0.5% Si, balance Fe, are used as resistor elements in electric furnaces. An interesting characteristic of the material, which is responsible at least in part for the good performance and long life of this type of heating element, is its excellent ductility at high temperatures (against extreme brittleness at room temperature). Sintered alloys of this composition can be produced to a quality that permits hot-working to wire or ribbon only if sintering is carried out in high vacuum at about 1200°C. (2200°F.) for at least sixteen hours and if very fine elemental powders (—325 mesh or finer) and extremely pure chromium (*e.g.*, electrolytic powder) are used. Sintering in hydrogen, even if the gas is well dried, tends toward incomplete diffusion of the alloying elements on account of the presence of stable refractory oxide films.

Iron–Manganese. Sintered iron–manganese alloys are produced from mixtures of iron powder with elemental manganese or with ferromanganese powder, but can also be prepared by employing manganese dioxide together with powdered carbon as reducing agent. If sintering is

[11a] U. S. Pat. 2,192,742.

[11b] R Kieffer and W. Hotop, *Sintereisen und Sinterstahl.* Springer, Vienna, 1948, p. 500.

performed in hydrogen atmosphere, the presence of carbon is not necessary because a reduction to metal of the manganese dioxide by hydrogen is facilitated by the presence of the iron which takes the manganese immediately into solid solution.[11c] Use of up to 1.5% manganese additions in the production of steel from carbonyl iron was found[11d] to be helpful in avoiding abnormal structures (see also Volume I, Chapter XIX, and Chapter XXV). It was observed, however, that for high carbon contents (1.5%) the amount of free carbon was rapidly increased by as little as 0.5% Mn, with coarse inclusions and diminished plastic deformability resulting. When experimenting with higher manganese contents, it was found that above 8% the alloys could no longer be forged; this was attributed to the fact that part of the manganese remained unalloyed to either the iron or the carbon. Recently, heat-treatable manganese steels with 2–16% Mn and 0.2–1.6% C were produced from eddy-milled Hametag iron powder and ferromanganese.[11e] Compacts were pressed at 25–50 tsi and sintered in hydrogen for 4 hours at 1150–1200°C. (2100–2200°F.). The porosity varied from 15% for the 2% Mn steels to 12% for the 14–16% Mn steels. Pearlitic, martensitic, and austenitic structures were obtained, depending on composition and heat treatment; only the compositions low in manganese content were susceptible to heat treatment. Further information on the subject can be found in Chapter XXV.

Iron–Manganese–Chromium. The same investigation[11e] also included chromium–manganese steels, and the findings are reported in Chapter XXV. The chromium was added as electrolytic powder, and the alloys were prepared either by a single pressing and sintering operation (up to 5% each of Mn and Cr, 0.5–1.5% C), or by a double pressing and sintering operation (5–20% Mn, 10–20% Cr, 0.5–1.0% C). The physical properties of the high manganese–chromium steels were found to be similar to those of stainless steels, but the chemical properties were much inferior. The alloys have been suggested for use in high wear-resistant machine parts.

Iron–Manganese–Copper. Interesting alloys have also been produced recently by impregnating the aforementioned manganese and chromium–manganese steels with copper and copper alloys containing manganese and nickel.[11e] In the case of medium carbon (0.4%) and manganese (6%) contents, excellent wear resistance was obtained. Despite the high natural and quench hardness, materials of this type are com-

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[11c] R. Kieffer and W. Hotop, *loc. cit.*, p. 539.

[11d] E. K. Offermann, *Mitt. Kohle- u. Eisenforsch.*, *1*, 85 (1936).

[11e] F. Benesovsky and R. Kieffer, *Proc. International Powder Metallurgy Conference*, Graz, July 12–17, 1948, Referate No. 27.

paratively tough, because the hard and brittle martensitic steel skeleton is surrounded by a tough network of the copper alloy.

Iron–Manganese–Molybdenum. Sintered ferrous alloys containing manganese and molybdenum are described in Chapter XXV (p. 385).

Iron–Tungsten. For the sintering process of this alloy very pure carbonyl iron and tungsten powders are recommended.[12] It is important to consider that the speed of diffusion of tungsten in iron is considerably lower than that of molybdenum and tungsten in nickel. However, diffusion can be improved by lengthy ball milling and repeated sintering with alternate mechanical working. The sintered alloys can be hot-worked with a much higher tungsten content than fused alloys. The quenched alloys have a greater corrosion resistance than those cooled slowly. Precipitation-hardening effects in sintered alloys are similar to those of fused alloys.

Iron–Molybdenum. The sintering of iron–molybdenum alloys follows the same principles established for the iron–tungsten alloys. The alloy can be hot-rolled up to 25% molybdenum, provided that the molybdenum powder is at least 99.95% pure.

Iron–Molybdenum–Copper. Alloys containing 5, 10, 15, and 20% Mo, respectively, and 1% Cu were sintered for one hour at about 1200°C. (2200°F.) in hydrogen atmosphere.[13] Again, the sintered alloy had a much finer grain and could be worked more easily than the fused alloy of identical composition. These alloys were recommended for the vacuum technique on account of their favorable coefficient of expansion. Facts pertaining to these alloys are also discussed in Chapters XXI and XXXI.

Iron–Titanium. Sintered iron alloys with titanium as minor alloying element have not yet been developed as a commercial material, probably due to the fact that the very brittle intermetallic compound Fe_3Ti (about 22% Ti) forms readily and makes the product brittle and weak. However, this same characteristic can be utilized in the preparation of pulverized prealloys used in the manufacture of titanium containing permanent magnets.[13a] Another way of adding titanium to these magnets, by incorporating the strongly reducing titanium hydride, has already been discussed in Chapter XXIV (page 254). With rising titanium contents, fabrication of the alloys becomes increasingly difficult due to the

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[12] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe.* Springer, Berlin, 1943, p. 203.

[13] J. Kurtz, in J. Wulff, *Powder Metallurgy,* Am. Soc. Metals, Cleveland, 1942, p. 497; Anonymous, *Iron Age, 148,* No. 18, 29, 100 (1941).

[13a] S. J. Garvin, *Symposium on Powder Metallurgy.* The Iron and Steel Institute, Special Report No. 38, London, 1947, p. 67.

strong affinity of the metal toward all gases save the noble ones. The use of titanium in form of titanium hydride and iron as high-purity carbonyl powder is recommended[13b]; sintering is suitably performed in high vacuum, or under highly desiccated hydrogen that is passed through a ferrotitanium powder pack,[13b] or by heating under alternate vacuum and hydrogen.[13c] Alloys containing titanium as a major component are discussed under titanium alloys (page 704).

Iron–Cobalt. The magnetic properties of binary iron–cobalt alloys with 30, 40, and 50% Co have been recently investigated.[13d] The alloys prepared by diffusion-alloying are susceptible to heat treatment, and the maximum permeability of the 40% Co alloy is more than doubled by an oil quench from above the Curie temperature. Additional information on this subject can be found in Chapter XXIV (page 285).

Iron–Cobalt–Tungsten–Chromium. These alloys can be produced by the same process used for the binary iron-tungsten alloys. In spite of their good magnetic properties,[14] and superior mechanical properties obtainable with the sintered alloys as compared with their cast counterparts, the alloys have not yet found practical application.

Iron–Cobalt–Molybdenum–Chromium. Because of their superior mechanical properties, sintered alloys of this type have been suggested for the manufacture of permanent magnets.[15] Their method of manufacture is similar to the one used for iron–tungsten and iron–cobalt–tungsten–chromium alloys.

Iron–Cobalt–Nickel–Titanium. Iron alloys containing about 28% Co, 16% Ni, and 12% Ti belong to the "Honda" type of permanent magnet materials. They can be produced by sintering,[15a] *e.g.*, of compacted mixtures of the elemental powders in hydrogen atmosphere at or above 1200°C. (2200°F.). The production of a homogeneous structure, however, is possible only by using fine powders (325 mesh or finer) and extended sintering times (24–48 hours). The titanium is added advantageously as titanium hydride, and oxidation of the element, before it is completely diffused, is avoided by careful drying of the hydrogen. An alloy produced experimentally in this manner was found to possess magnetic properties that closely approached those of the cast alloy.

Iron–Copper. Alloys between iron and copper can be produced by

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[13b] R. Kieffer and W. Hotop, *Sintereisen und Sinterstahl.* Springer, Vienna, 1948, p. 525.

[13c] German Pat. 635,644.

[13d] W. Rostoker, *Trans. Am. Inst. Mining Met. Engrs., 180,* 672 (1949).

[14] W. Köster, *Arch. Eisenhüttenw., 6,* 17 (1932/33).

[15] German Pat. 673,877.

[15a] R. Kieffer and W. Hotop, *Sintereisen und Sinterstahl.* p. 476.

the same method described below for iron–silver alloys, and also in any ratio desired.[16,17] It is further possible to produce these materials by soaking a porous sintered iron skeleton in the liquid nonferrous constituent.[18–20] By this method, iron–copper composite structures have resulted which yielded remarkable physical properties. The subject is discussed in greater detail in Chapter XXV.

Iron–Copper–Carbon. The same technique as described for iron–copper alloys can also be employed for alloys in which carbon is combined with the iron in form of pearlitic steel. Alloys of this type have been found to possess excellent physical properties, which could be further improved by heat treating,[19,20] thus making them ideally suitable for structural and engine parts applications.[20a] The alloys are also discussed more fully in Chapter XXV.

Iron–Copper–Chromium–Nickel. Composite structures consisting of a matrix of stainless steel and a network of copper can also be produced by the same method.[20] They have been found equal to ordinary stainless steel in their resistance to atmospheric or salt water corrosion, superior against attack by hydrochloric acid but inferior against attack by nitric acid.[20b]

Iron–Silver. Compositions of iron and silver in any ratio required can be produced by sintering without difficulty. They find practical application in the manufacture of composite contact metals. The conventional sintering method is to mix pure metal powders and then sinter the compact close to the melting point of the lower melting alloy constituent in order to obtain maximum density. Iron–silver alloys made in this way are best sintered in hydrogen atmosphere. They have been found to have a greater resistance to corrosion of hydrochloric and acetic acids than pure iron.[20c–d]

Iron–Zinc. Because of their great differences in melting point and the high vapor pressure of zinc, iron–zinc alloys cannot be prepared readily by fusion; however, no particular difficulties appear during sintering of the mixed powders, and the method was employed to establish

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[16] L. Northcott and C. J. Leadbeater, *Symposium on Powder Metallurgy*. The Iron and Steel Institute, Special Report No. 38, London, 1947, p. 142.

[17] R. Chadwick, E. R. Broadfield, and S. F. Pugh, *loc. cit.*, p. 151.

[18] P. Melchior, discussion of F. Sauerwald, *Z. Metallkunde, 21,* 22 (1920).

[19] F. Peters, *Materials & Methods, 23,* No. 4, 987 (1946).

[20] E. S. Kopecki, *Iron Age, 157,* No. 18, 50 (1946).

[20a] U. S. Pat. 2,456,779.

[20b] Brit. Pat. Applic. 11363/47 (May 1, 1946); see also *Metal Powder Rept., 2,* No. 5, 72 (1948).

[20c] G. J. Comstock, *Metal Progress, 35,* No. 6, 576 (1939).

[20d] C. G. Fink and V. S. de Marchi, *Trans. Electrochem. Soc., 74,* 271 (1938).

the phase diagram of the alloy system.[21,21a] It has also been found possible to sinter a porous iron structure and afterward impregnate the compact with molten zinc.

Iron–Tin. The manufacture by fusion of iron alloys containing tin is as difficult as that of the alloys with zinc. However, by soaking of a sintered porous iron structure in liquid tin under a protective atmosphere followed by a subsequent annealing treatment to obtain diffusion of the alloying elements, it is possible to obtain solid composite alloy structures.[21b] A possible practical application of the alloys would be for bearing materials, where the network of brittle intermetallic compounds formed by diffusion would not be objectionable.

Iron–Lead. The principal method of producing these alloys consists in introducing metal oxides that are reduced by means of hydrogen during sintering. This method has been used successfully for iron alloys containing 1 to 10% Pb, which proved to be highly ductile and suitable for extrusion. An alternate method is to infiltrate the lead into a porous iron sponge. The alloys have found use as porous and dense bearing materials, and are more fully described in Chapter XXV.

Iron–Antimony. Alloys of iron with antimony have been produced from powders for bearing purposes.[21c] Mixtures of the elemental ingredients containing up to 14% Sb could be cold- and hot-worked after pressing and sintering at 1000–1050°C. (1830–1920°F.).

Iron–Mercury. Sintered alloys of iron with mercury have been covered by several patents.[21d–e] They are advantageously produced by the impregnation method, whereby a thin copper film surrounding the iron particles is of help.[22]

Iron–Aluminum. Alloys containing about equal amounts of each metal are used in form of a prealloyed powder in the production of sintered permanent magnets (see also Chapter XXIV). The powder is produced by mechanical disintegration of the fusion-alloyed and solidified master alloy. Iron–aluminum compositions have also been reported in use in the production of heating elements.[22a–b]

[21] J. Schramm, *Z. Metallkunde, 28,* 203 (1936).

[21a] J. Schramm and A. Mohrnheim, *Z. Metallkunde, 39,* 71 (1948).

[21b] R. Kieffer and W. Hotop, *Sintereisen und Sinterstahl.* Springer, Vienna, 1948, p. 258.

[21c] Brit. Pat. Applic. 34528/47 (May 15, 1946); see also *Metal Powder Rept., 2,* No. 7, 105 (1948).

[21d] Brit. Pat. 577,198.

[21e] U. S. Pat. 2,364,713.

[22] R. Kieffer and W. Hotop, *Sintereisen und Sinterstahl.* Springer, Vienna, 1948, p. 523.

[22a] C. J. Leadbeater, *Symposium on Powder Metallurgy.* The Iron and Steel Institute, Special Report No. 38, London, 1947, p. 191.

[22b] P. Schwarzkopf, *Powder Metallurgy Bull., 2,* No. 3, 52 (1947).

Iron–Magnesium. Recent experiments with compacted and sintered iron–magnesium mixtures[22c] have disclosed an optimum ratio of the two elements corresponding to about 50% by weight of magnesium. Such composition was found to possess a Brinell hardness of 56 (against 37 for cast magnesium), a silvery crystalline surface, and the best resistance to attack by a 1% NaCl solution.

Iron–Calcium. Similar experiments with combinations of iron and calcium, with and without the addition of aluminum, met with considerable difficulties, which could only partly be overcome by using a 16–18% Ca-containing prealloy.[22c] However, alloys containing about 33% Ca were found to display an appreciable chemical stability.

Iron–Silicon. Standard iron–silicon alloys for soft magnetic applications are described in Chapter XXIV. The electrical and magnetic properties of alloys containing 1.5 to 6% Si have been studied in connection with the commercial production of certain low-frequency alternating current armatures (page 281).[22d] Alloys with higher silicon contents up to 50% have been produced for the purpose of studying the progress of diffusion.[22e–f]

Iron–Phosphorus. Phosphorus-containing ferrous metal products have been developed[23,24] and either a low-melting iron–phosphorus–carbon eutectic was employed as a cementing agent in the hot-pressing of cast iron powders (see Vol. I, Chap. XII),[23] or the phosphorus was used as alloying element in porous sintered parts, whereby up to 2.5% P could be incorporated without difficulty. Iron powder of commercial grade is mixed with ferrophosphorus, compacted, and sintered immediately below the iron–iron phosphide eutectic (*i.e.*, between 1060 and 1140°C.; 1940 and 2085°F.) in a reducing atmosphere. Carbon-free iron–phosphorus alloys with a phosphorus content up to 1.5% possess marked strength, but this property declines and gives way to increasing brittleness as the phosphorus content increases. (This phenomenon is even more apparent if the alloys contain carbon.) A carbon-free alloy containing 1.5% P possesses a tensile strength of 53,000 psi as compared with 19,600 psi for a straight sintered iron body. (For additional information on the effect of small additions of phosphorus to iron see also Chapter XXV, page 327).

Iron–Sulfur. Alloys of sintered iron, to which small percentages of sulfur are added, are readily produced by mixing iron powder and

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[22c] R. Müller, K. Nitsche, H. Stürzer, and H. Zahabi, *Proc. International Powder Metallurgy Conference*, Graz, July 12–17, 1948, Referate No. 34b.

[22d] R. Steinitz, *Powder Metallurgy Bull.*, *2*, No. 6, 135 (1947).

[22e] F. W. Glaser, *Powder Metallurgy Bull.*, *4*, No. 1, 19 (1949).

[22f] F. W. Glaser, *J. Metals*, *1*, No. 8, 475 (1949).

[23] W. D. Jones, *Foundry Trade J.*, *59*, 401 (1938).

[24] U. S. Pats. 2,226,520; 2,291,734.

pulverized iron sulfide.[25] Additions up to 1% S were found to improve tensile strength and elongation slightly: for a constant density of 6.82–6.84 g./cc., the tensile strength increased from 28,000 psi for 0% S to 31,200 psi for 0.25% S, and then tapered off slightly to 31,000 psi for 0.5% S and 30,000 psi for 1% S; the corresponding elongation values were 6.9% for 0% S, and 8.8%, 7.9%, and 8.1% for 0.25, 0.5, and 1% S, respectively. A similar improvement in the hardness was also found, namely, 57.2 Brinell units for the sulfur-free iron, and 63.8, 60.5, and 62.1 Brinell for the alloys with 0.25, 0.5, and 1% S, respectively. The proposal has been made to use sulfur-containing porous iron for bearings on account of its favorable bearing properties, but it is not known whether this suggestion has been put into practice.[26] Additional information on experiments with sulfur additions to iron[27] can be found in Chapter XXV (page 327).

Iron–Oxygen. The combination of iron with oxygen has been used both for purposes of research[27] (see also Chapter XXV) and for the production of especially high wear-resistant machine parts.[28] The last-mentioned subject has been previously discussed in Volume I, Chapter XX, and in Chapter XXVII. The fact that iron oxides are among the most important sources for the production of pure iron powders has been emphasized throughout the text and requires no further comment here.

Nickel, Cobalt, Manganese, and Their Alloys

NICKEL

Very pure sintered nickel is now being used to some extent in the high vacuum technique for various shapes. Sintered nickel sheets are also employed for cladding steels and for the production of bimetallic sheets, where the comparatively high ductility and weldability have been found of advantage. Porous nickel filters have been used for concentrated solutions and also for the mercury switch in the VT proximity fuze.[29] Further applications of sintered nickel may lie in the production of diaphragms, storage batteries, electrodes, and wicks. A more detailed description of the powder metallurgy of nickel is given in Chapter XXVI; porous nickel products are discussed in Chapter XXVII.

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[25] R. Schwalbe and H. Will in R. Kieffer and W. Hotop, *Sintereisen und Sinterstahl.* Springer, Vienna, 1948, p. 538.

[26] R. Kieffer and W. Hotop, *loc. cit.*, pp. 538–539.

[27] H. Wiemer, *Powder Met. Bull.*, *1*, No. 6, 92 (1946); U. S. Dept. of Commerce, Office of Publ. Board, P.B. 14761.

[28] F. V. Lenel, in J. Wulff, *Powder Metallurgy,* Am. Soc. Metals, Cleveland, 1942, p. 512. See also Anonymous, *Iron Age, 148,* No. 18, 29, 100 (1941).

[29] P. Schwarzkopf, *Product Eng.*, *17,* No. 4, 268 (1946).

NICKEL ALLOYS

Nickel–Iron. Alloys of the system nickel–iron, with nickel as the predominant element and possible small additions of molybdenum, form magnetic materials of high and controllable permeability, such as the "Permalloy" type alloy with 80% Ni. The significance of these alloys in the radio and communications field has been discussed in Chapter XXIV. Sintered alloys containing 50, 65, and 78.5% Ni were developed[29a] and tested for their magnetic properties after sintering and after heat treating (see also Chapter XXIV, page 285).

Nickel–Cobalt. Binary nickel–cobalt alloys have been produced from powders for the purpose of studying diffusion and sintering conditions. Since cobalt was the predominant constituent in these experiments, they will be discussed later under cobalt alloys.

Nickel–Cobalt–Chromium. Alloys containing about 60% Ni, 20% Co, and 20% Cr are produced in England under the trade name "Nimonic-90," and constitute an excellent heat-resistant alloy for turbine blades and similar applications. The strength at service temperatures is further improved by precipitation hardening at higher temperature, made possible through the addition of about 2% Ti; the resistance to scaling is increased through the addition of 1% Al. The alloy can be produced by vacuum sintering of compacts from mixtures of the elemental powders at 1300–1350°C. (2370–2460°F.). The strength at ordinary and elevated temperatures up to red heat is increased with increasing fineness of the powder, and values comparable with the cast metal can be obtained if the powder particles do not exceed 10 microns in size.[30] With indications pointing in the direction of increased creep resistance for sintered products,[31] possibly on account of finer grain size, sintered nickel–cobalt–chromium alloys should become a potentially useful material in the construction of highly stressed members of turbines and jet engines that operate at elevated temperatures under corrosive conditions.

Nickel–Chromium. Alloys containing from 5 to 40% Cr, balance Ni, known under the trade names of "Nichrome," "Nimonic-80," etc., can be satisfactorily sintered in vacuum. The chromium oxide films surrounding the chromium particles, which are very stable, may cause difficulties in sintering in hydrogen. The raw materials most suitable are fine nickel powder, such as carbonyl powder previously treated with hydrogen to free it from oxygen and carbon, and finely pulverized electrolytic chromium. Sintering is best carried out for two to six hours at

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[29a] W. Rostoker, *Trans. Am. Inst. Mining Met. Engrs., 180,* 672 (1949).

[30] T. Raine, *private communication.*

[31] L. B. Pfeil, *Conference on Metallic Creep.* Royal Soc., London, Feb. 1946.

1300–1350°C. (2370–2460°F.) in vacuum or highly purified hydrogen atmosphere, and may have to be repeated after intermediary hot-working operations using alternate vacuum and hydrogen sintering.[32] Nickel–chromium alloys can also be sintered by using very pure chromium oxide, but then sintering of the compact must be carried out in hydrogen atmosphere for a considerably longer period to obtain complete reduction and diffusion.[33] If sintered in vacuum or if subsequently hot-worked, the sintered alloys are practically identical with the fused alloys in their physical properties. If chemically pure chromium powder such as electrolytic powder is used, and if the particle size of both the nickel and chromium is kept below 10 microns, superior sintered products may be obtained which may then find practical application in the field of heat-resistant alloys.

In this connection, reference is made to a German patent[34] which describes in detail the manufacture of electrical resistor heating elements by sintering the compacted powders. A nickel–chromium alloy of the 80–20 type composition to which 0.06% Ca was added (in form of pure metal powder or as a powdered compound such as calcium hydride, calcium oxalate, or calcium acetate) was compared with an iron–nickel–chromium alloy (of the 51–29–20 Fe–Ni–Cr composition) to which 0.2% thorium was added. The powders were compacted at 50 tsi and sintered in highly purified hydrogen or in high vacuum for 6 hours at 1300°C. (2370°F.). At 1000°C. (1830°F.) both types of alloys could be forged, rolled, and drawn into wire. The best procedure found was to forge to 30% reduction, or hot-roll to 40% reduction, followed by an intermediate annealing; after 40–50% hot-working reduction, the materials could be readily worked to wires of 0.015 in. diameter by cold-rolling and -drawing. It is claimed that especially the nickel–chromium wire, when made from powders with the minute additions of calcium (or thorium, barium, and similar elements), has a substantially longer life at elevated temperatures up to 1000°C. (1830°F.) than a wire produced from the conventional cast alloy materials.

Nickel–Chromium–Iron. Sintered alloys of the type known under the trade name of "Inconel," containing 15% Cr, 5% Fe, balance Ni, can also be produced by the same technique applicable to the binary nickel–chromium alloys. Alloys to which about 2% Ti and 1% Al are added for the purpose of precipitation hardening and improved scale resistance, should become increasingly interesting as heat-resistant mate-

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[32] German Pat. 635,644.

[33] G. Grube and K. Ratsch, *Z. Elektrochem.*, *45*, 838 (1939).

[34] German Pat. 744,579; see also *Metal Powder Rept.*, *2*, No. 7, 109 (1948).

rial for steam turbine blades and like applications, especially in view of possible savings in the cost of manufacture.

Nickel–Manganese. Sintered alloys of this type can be produced from nickel powder of highest purity, such as carbon-free carbonyl powder and very fine manganese powder, possibly of the electrolytic type, by sintering for six to eight hours at 1100–1200°C. (2010–2190°F.) in pure hydrogen[35]; alternately, ferromanganese or manganese oxide in the presence of reducing agents may be used. A nickel–manganese alloy containing 4% Mn can be used for spark plug electrodes.[35a]

Nickel–Copper. Alloys of the type known under the trade name of Monel, consisting of about 30% Cu, balance Ni, and possibly containing minor additions of iron and manganese (not exceeding a total of 3%), are not easily reproduced by powder metallurgy methods to the high quality found in the wrought alloy. Sintering temperatures must lie close to the melting point of the alloy, *e.g.*, between 1250° and 1300°C. (2280–2370°F.), and the operation must be carried out either in vacuum or in very dry hydrogen. Very fine powders with particle sizes below 10 microns result in greatest shrinkage and best physical properties, but the ductility of the wrought alloy is approached only if the sintered alloy is subjected to several alternate hot-working reductions and resintering operations.

Nickel–Copper–Beryllium. A sintered alloy containing approximately 36% Cu, 4% Be, balance Ni is precipitation hardenable to approximately 190 Brinell. The alloy is advantageously prepared by compaction at 50 tsi of a mixture of the elemental powders (200 mesh or finer) followed by sintering in purified hydrogen at 1100°C. (2010°F.) for one hour, repressing at 50 tsi, reheating to 1060°C. (1940°F.), and water quenching. A maximum precipitation effect is obtained by aging at 425°C. (800°F.) for one to two hours.

Nickel–Copper–Chromium–Beryllium. The addition of approximately 12% Cr to the ternary Ni–Cu–Be alloy nearly doubles the hardness of the precipitation-treated alloy. An alloy consisting of 37% Cu, 12.5% Cr, and 2.5% Be and produced in identically the same manner as the ternary alloy exhibits a Brinell hardness of 320 after precipitation treatment at 425°C. (800°F.) for one hour.

Nickel–Silver. Nickel and silver do not alloy but form composite materials that are suitable for contact purposes. Since these duplex structures usually contain silver as major constituent, they will be discussed

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[35] G. Hamprecht and L. Schlecht, *Metallwirtschaft, 12,* 281 (1933).

[35a] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe.* Springer, Berlin, 1943, p. 212.

under silver alloys. Reference to these alloys is also made in Chapter XXIII.

Nickel–Tungsten. Alloys containing 75–95% Ni can be sintered in hydrogen at about 1200°C. (2200°F.) and can be hot- and cold-worked very easily.[35a] Alloys containing 60–70% Ni are already too brittle for working. On the other hand, alloys containing 80–95% W can be sintered readily at 1300–1400°C. (2370–2550°F.) if produced from ultrafine tungsten and nickel powders, and are again ductile, a phenomenon that can be explained from the constitution of the alloy system.[36]

Nickel–Molybdenum. Sintered alloys containing 20–25% Mo, balance Ni, have proved to be a satisfactory material for electronic discharge tubes because of their heat resistance and chemical purity.[37]

TABLE 252

Properties of Sintered 58–22–20 Ni–Fe–Mo Alloy Used for High-Vacuum Components (Kieffer and Hotop[39])

Specific gravity at 20°C., g./cc.	8.8
Melting point, °C. (°F.)	1320 (2410)
Tensile strength of fine wire, cold-worked, psi.	up to 150,000
Tensile strength of fine wire, annealed, psi.	110–120,000
Hot tensile strength at 800°C. (1470°F.), psi.	42–56,000
Elongation, cold-worked, %	5
Elongation, annealed, %	25–35
Yield point, cold-worked, psi.	up to 115,000
Yield point, annealed, psi.	45–50,000
Brinell hardness, cold-worked	280
Brinell hardness, annealed	207
Linear coefficient of thermal expansion. cm./cm./°C.	10.7×10^{-6}
Heat conductivity at 20°C., cal./cm./sec./°C.	0.04
Electrical resistivity at 20°C., microhm-cm.	110
Electrical conductivity, megmho/cm.^{3}	0.009

Detailed investigations have been carried out[38] on hardness, electrical conductivity, structure, density, and corrosion resistance of a number of nickel–molybdenum alloys.

Nickel–Molybdenum–Iron. Alloys containing 55–65% Ni, 20–30% Mo, and 22–25% Fe fall into the class generally known under the trade name of Hastelloy A and B, and possess excellent heat-resistance properties. If produced from extremely fine and pure powders by vacuum sintering at 1300–1350°C. (2370–2460°F.), the product is sufficiently pure and gas-free to serve as structural material for electronic discharge tubes.[37] The properties of an alloy containing 58% Ni, 22% Fe, and

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[36] M. Hansen, *Der Aufbau der Zweistofflegierungen.* Springer, Berlin, 1936, p. 960.

[37] W. Espe and M. Knoll, *Werkstoffkunde der Hochvakuumtechnik.* Springer, Berlin, 1936, p. 97.

[38] G. Grube and H. Schlecht, *Z. Elektrochem., 44,* 367, 413 (1938). Also H. Schlecht, *Dissertation,* Univ. of Stuttgart, 1936

20% Mo are given in Table 252.[39] An alloy containing 65% Ni, 30% Mo, and 5% Fe, produced by compacting a mixture of 325-mesh elemental powders at 35 tsi and sintering at 1250°C. (2280°F.) for 24 hours in hydrogen atmosphere with a dew point of —60°C. (—76°F.), displayed a short-time tensile strength of 88,000 psi at room temperature and 60,000 psi at 800°C. (1470°F.); the same alloy composition produced from ultrafine powders (particle size 5–10 microns) and sintered at 1325°C. (2420°F.) for two hours in vacuum of 0.005 mm. pressure exhibited a short-time tensile strength of 105,000 psi at room temperature and 69,000 psi at 800°C. (1470°F.).[40] Compacts have also been processed from alloy powders obtained by the chemical disintegration of the fused alloy, but did not match these properties in tests conducted by the author.

Nickel–Molybdenum–Chromium–Iron. If approximately 15% Cr is substituted for part of the iron in the iron-rich nickel–molybdenum base alloys, and about 5% tungsten added, a material of superior resistance to oxidizing solution type of corrosion is produced. However, these alloys, known under the trade name of Hastelloy C and analyzing about 55% Ni, 18% Mo, 15% Cr, 7% Fe, and 5% W, are more brittle than Cr-free alloys and cannot be forged easily. The quality of sintered alloys is comparable to that of the cast material if very fine virgin metal powders are used (particle size below 10 microns) and if sintering is carried out at 1300–1350°C. (2370–2460°F.) in vacuum[40] (similarly produced compacts from alloy-disintegrated powders were found by the author to be inferior in quality). In the case of the mixture, however, complete diffusion of the chromium is essential to obtain the necessary corrosion resistance; hence, a sintering technique must be used that prevents formation or retention of chromium oxide films. In view of the combined heat and corrosion resistance of the alloy, the sintered alloy is a potential material for high-temperature applications such as in turbines and reciprocal engines.

Nickel–Columbium. Alloys containing 20–30% Cb, balance Ni, can be produced readily by sintering at 1200–1300°C. (2190–2370°F.) in vacuum. A production method interesting from a cost reduction standpoint consists in heating fine Ni powder, *e.g.*, carbonyl nickel, with columbium pentoxide (containing 99.5% Cb_2O_5) in very pure hydrogen atmosphere.[41,42] As yet, no applications have been suggested for these alloys.

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[39] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe.* Springer, Berlin, 1943, p. 194.

[40] T. Raine, *private communication.*

[41] G. Grube and K. Ratsch, *Z. Elektrochem.*, *45,* 838 (1939).

[42] G. Grube, O. Kubaschewski, and K. Zwiauer, *Z. Elektrochem.*, *45,* 88 (1939).

Nickel–Tantalum. Similarly, alloys of nickel and tantalum can be produced by sintering mixtures of fine nickel powder and the oxide of the alloying constituent. The reduction process is facilitated by the addition of lampblack to the mixture and by conducting the sintering operation in hydrogen under pressures below atmospheric.[43] As for the alloys with columbium, the tantalum-containing alloys also lack technical application at the present time.

Nickel–Titanium, –Vanadium, and –Zirconium. Sintered alloys of nickel and titanium, vanadium, or zirconium, respectively, can be produced in a manner similar to that for the nickel–tantalum alloys,[43] but here, too, specific applications have not yet been found for either alloy.

Nickel–Zinc. The production of sintered nickel–zinc alloys can be carried out in the same way as iron–zinc alloys. The sintering method was used successfully in the establishment of the Ni–Zn phase diagram.[44,45] The production of German Silver through the addition of 25% Cu to a 50–50 Ni–Zn alloy is also possible by the same method, but no commercial applications have as yet been reported in the literature.

Nickel–Mercury. Nickel and mercury have no noticeable affinity at room temperature, and amalgamation is possible only if a third element (*e.g.*, copper) is added to the system. This fact has been the basis for the use of sintered porous nickel cups as filters for the electrical-contact-making mercury in the safety switch device on the proximity fuze of the U.S. Navy (see also Chapter XXVII).

Nickel–Aluminum. Nickel–aluminum, in the form of a pulverized prealloy, can be used in the production of sintered permanent magnets. Binary alloys of this system, as well as ternary alloys of the system nickel–iron–aluminum, are also potential materials for electrical heating elements.[46] Present investigations to this effect are concerned with alloys containing from 5 to 10% aluminum.

Nickel–Silicon. Alloys containing about 15% Si, 3% Cu, 2% Al, balance Ni, are known under the trade name of "Hastelloy D" and excel by their resistance against chemical attack at ordinary and moderately elevated temperatures. Difficulties in the production of the alloy from powders stem from the extreme sensitivity of silicon to oxygen. Only vacuum-sintering at 1300°C. (2370°F.) for long periods of time permits complete solution of the alloying ingredients in the nickel. No test results or applications are known for the sintered alloy.

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[43] Swedish Pat. 101,410; Brit. Pat. 512,502; Italian Pat. 371,055.

[44] W. Heike, J. Schramm, and O. Vaupel, *Metallwirtschaft, 11,* 525, 539 (1932); *12,* 115 (1933).

[45] W. Heike, J. Schramm, and O. Vaupel, *Metallwirtschaft, 15,* 655 (1936).

[46] R. Kieffer and W. Hotop, *Sintereisen und Sinterstahl.* Springer, Vienna, 1948, p. 500.

COBALT

The properties of sintered cobalt are much affected by the type of powder.[47] Powder obtained by reduction of cobalt oxide or oxalate, or by pulverization of the fused metal, is used in the production of sintered cobalt. Details of the production of commercial powders are given in Volume I, Chapter VI. In order to obtain a sintered product that can be hot-worked easily, very pure powder is essential. Sintered cobalt offers considerable difficulties in working; these are further aggravated by impurities such as silicon and, in particular, carbon—in contrast to iron and nickel where even significant quantities of oxygen, carbon,

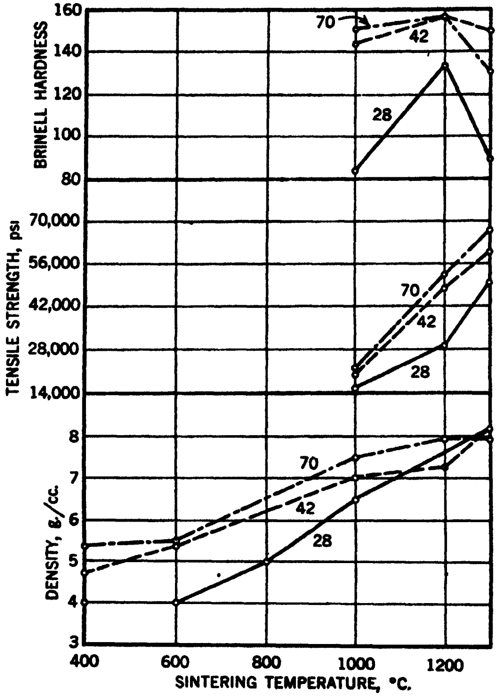

Fig. 594. Effect of the sintering temperature on the density, tensile strength, and Brinell hardness of cobalt bars compacted at different pressures (according to Kieffer and Hotop[48]). All specimens were sintered in hydrogen atmosphere for 2 hours. The numbers on the curves indicate the compacting pressures, in tsi.

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[47] W. P. Sykes, *Trans. Am. Soc. Steel Treating, 21,* No. 5, 385 (1933).

silicon, etc., are not objectionable. These characteristics make sintered cobalt comparable to molybdenum in its workability.

The most ductile cobalt that can be worked to sheet and wire is obtained from very fine powder obtained by hydrogen reduction of twice purified cobalt oxalate at 500–700°C. (930–1290°F.), followed by removal through washing of alkali residues, and hydrogen annealing at 500–700°C. (1110–1300°F.) to remove residual traces of oxygen and carbon. The physical properties of hydrogen-sintered cobalt from such powder have been investigated.[48] In Figure 594 the values are plotted as a function of the sintering temperature between 600° and 1300°C. (1110° and 2370°F.) for a standard sintering time of two hours. The Brinell hardness of hot-rolled and annealed sheet 1 mm. thick is of the order of 260; 1 mm. diameter wire from very pure metal exhibits, after a one-hour annealing at 1000°C. (1830°F.), a tensile strength of 110,000–130,000 psi at 10–12% elongation.[48]

COBALT ALLOYS

Cobalt–Nickel. Sintered cobalt–nickel alloys with cobalt as major constituent were produced for the purpose of investigating shrinkage and grain growth phenomena as affected by cobalt concentration.[49] In this work, artificially produced solid solutions of the metal oxides and mechanical mixtures of the two different oxides were employed as raw material. After briquetting these at about 12 tsi with the aid of a binder, complete reduction was obtained during hydrogen treatment at 500°C. (930°F.) for seven hours. A subsequent sintering treatment was carried out at 650–950°C. (1200–1740°F.) for different periods of time. The results indicated that alloying and shrinkage are facilitated by the "ideal" mixture of the original components as produced by the solid solution of the two oxides. This finding appears of interest not only for the system cobalt–nickel, but also for all alloy systems with low diffusion coefficients that lend themselves to an easy production of solid solutions of the oxides. So far, no commercial applications of particular significance have been found for binary cobalt–nickel alloys. Their use in conjunction with iron (as major constituent) in low-expansivity materials is mentioned under iron alloys, and discussed in detail in Chapter XXV.

Cobalt–Chromium. Sintered binary cobalt–chromium alloys have been produced by methods analogous to those used in the manufacture of nickel–chromium alloys,[50] but as far as is known, they have found as yet no practical applications.

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[48] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe*. Springer, Berlin, p. 214.

[49] S. Cassirer-Bánó and J. A. Hedvall, *Z. Metallkunde, 31,* 12 (1939).

[50] G. Grube and K. Ratsch, *Z. Elektrochem., 45,* 838 (1939).

Cobalt–Chromium–Molybdenum. Cobalt alloys containing approximately 25% Cr, 6% Mo, and up to 0.5% C, generally known under the trade name of Vitallium, are extremely resistant to heat and corrosion. The alloys are too brittle for easy working, but can be precision cast ("Austenal process") into very complicated shapes. Applications for this alloy include buckets and nozzle diaphragm vanes for gas turbines and jet engines, as well as surgical and dental tools, dentures, and braces and supports for bones and tissues. Sintered alloys of this type can be made very ductile on account of higher purity and finer grain size of the finished product.[51] If, for example, very fine elemental powders ranging between 5 and 10 microns in particle size are intimately mixed by prolonged ball milling, compacted at about 35 tsi, and finally sintered in high vacuum at 1300–1325°C. (2370–2420°F.) for at least two hours, a material is produced that can be reduced by cold rolling in 10% reduction steps with intermediate annealings at sintering conditions. The same material is readily hot-workable. Considerable shrinkage occurs during sintering. The sintered product has a density of about 8.3 g./cc.—closely approaching the density of the cast alloy. A recorded tensile strength of 110,000 psi at normal temperature and of 65,000 psi at 800°C. (1470°F.)[51] compares favorably with the corresponding properties of the cast alloy. If present expectations of improved creep resistance in sintered alloys become substantiated by technical evidence, sintered Vitallium may prove to be an ideal material for heat-resistant alloy applications, and the powder process may at the same time offer distinct advantages from the manufacturing point of view. Analogous to the nickel-base Hastelloy-type alloys, Vitallium compacts have also been produced from chemically disintegrated fused material, but in work performed by the author the quality of the products based on the mixed elemental powders could not be matched.

Cobalt–Chromium–Tungsten. Cobalt-base alloys containing 25–35% Cr, 5–17% W, 0.5% C, and Fe and Ni not exceeding 2% each, make up the Stellite-type alloys known under the trade names of H. S. Alloy No. 23 and Stellite-J; essentially they can be produced by the same process as outlined for the cobalt–chromium–molybdenum alloys. However, due to slightly lower melting points of these alloys, the preferred sintering temperature range is between 1210 and 1260°C. (2210–2300°F.). Vacuum-sintering is advisable to eliminate harmful gas films; also, if interferences with rapid diffusion of the elements by stable chromium oxide films are to be avoided. The physical properties of the sintered alloys prepared from ultrafine powders are equivalent to those of the fused alloys, and densities in the order of 8.5–8.6 g./cc. can be

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[51] T. Raine, *private communication.*

obtained. Thus, these alloys constitute another potential engineering material for high-temperature service.

Cobalt–Chromium–Molybdenum–Nickel. Alloys of the standard Vitallium type can be modified by the addition of nickel in amounts up to about 15% (at the expense of cobalt). While the hot strength is not materially altered by this addition, hot workability is improved over that of the nickel-free alloy. In a sintered alloy produced in an identical manner as given before, a nickel content of 5–10% improves the hot workability to such an extent that the alloy can be reduced to thin strip by hot-rolling and intermediate annealing at sintering conditions.[51]

Cobalt–Chromium–Tungsten–Nickel. Cobalt alloys containing about 25% Cr and 10% each of W and Ni, and about 0.5% C possess the best combinations of hot strength, ductility, and creep resistance of the Stellite alloy family. They can be produced to a quality comparing with that of the cast alloy by vacuum-sintering at 1250–1300°C. (2280–2370°F.) as outlined before, and should have a potential use for jet engine blading.

Cobalt–Molybdenum. Sintered cobalt–molybdenum alloys are more ductile than their fused counterparts. The constitution diagram,[52] having been determined by means of fused specimens, shows that in the range between 5 and 25% Mo a considerable change in solubility of molybdenum in cobalt takes place, thus rendering the alloy susceptible to heat treatment. The superior ductility of the vacuum-sintered and hot-worked and annealed product may be attributed to the absence of harmful impurities such as traces of carbon, silicon, manganese, and sulfur. Kieffer and Hotop[53] heat-treated the alloy by quenching from approximately 1250°C. (2280°F.) with subsequent tempering at approximately 550°C. (1020°F.). After this treatment the specimens gave a Rockwell hardness value of about C-60. However, despite this excellent hardness, these alloys have not yet found practical application in industry.

Cobalt–Molybdenum–Boron. The addition of about 2.5% B in the form of a pulverized 86–14 Co–B master alloy to a cobalt–molybdenum alloy containing 15% Mo imparts to the alloy a further slight increase in hardness. When the material was vacuum-sintered at 1250°C. (2280°F.) after compaction at about 15–25 tsi, followed by quenching in oil and tempering at 550°C. (1020°F.) for one hour, a Rockwell C hardness of about 62 was obtained. Sintering at lower temperatures, *e.g.*, 1150°C. (2100°F.), in hydrogen did not produce complete diffusion and

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[52] M. Hansen, *Der Aufbau der Zweistofflegierungen.* Springer, Berlin, 1936, p. 496.

[53] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe.* Springer, Berlin, 1943, p. 216.

precipitation effects, resulting in serious oxidation of the boron phase during the sintering and quenching treatment. The increase in cost caused by the addition of boron hardly appears justified by the results of the hardness tests.

Cobalt–Tungsten. Sintered cobalt–tungsten alloys have been produced and investigated extensively[54]; cobalt powder was obtained from commercial cobalt nitrate which was subjected to air heating at approximately 600°C. (1100°F.) and reduction by hydrogen of the resulting oxide at approximately 700°C. (1300°F.). For the production of tungsten powder, the trioxide was also reduced by hydrogen. The resulting tungsten contained less than 0.2% impurities and the cobalt 0.5%, consisting mainly of Al_2O_3 and SiO_2. Sintered cobalt–tungsten alloys were produced by sintering in hydrogen at 1400–1500°C. (2550–2730°F.) for 25–50 hours.[54] Because of the marked change in solubility limits with temperature in the cobalt-rich side of the phase diagram (a solid solution was found to exist up to 35% W) compositions in this range, like Co-Mo alloys, are capable of undergoing precipitation treatment, *e.g.*, quenching from 1260°C. (2300°F.) and aging at 500–700°C. (930–1290°F.). The hardness values of the sintered and precipitation-hardened alloys are shown as a function of tungsten concentration in Figure 595. The alloys with 20–35% W have been used successfully for jaws in swaging ma-

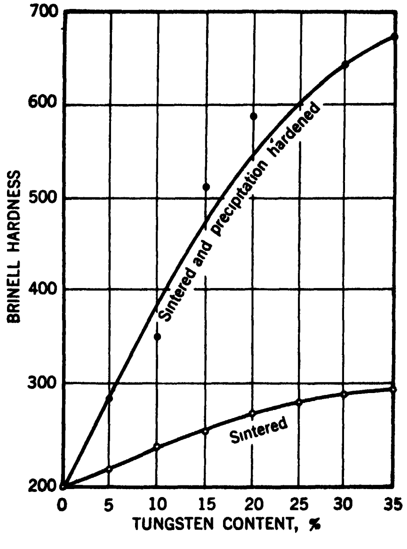

Fig. 595. Effect of increasing tungsten content on the Brinell hardness of binary cobalt-tungsten alloys after sintering and after precipitation hardening (according to Sykes[54]).

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[54] W. P. Sykes, *Trans. Am. Soc. Steel Treating*, ***21***, No. 5, 385 (1933).

chines for working tungsten wire. The jaws are very resistant to wear and tear, especially at elevated temperatures; thus, the indications are that these cobalt–tungsten alloys are superior to tungsten alloy steel for hot-working.[54] An alloy containing 20% W, and normalized to a Rockwell hardness of C-52, appears to be most suited for this purpose; because of its toughness it is superior to an alloy with 33–35% W with a Rockwell hardness of C-63–65. The satisfactory performance of these alloys at the very high temperatures used during the first stages of tungsten swaging (up to 1700°C.; 3100°F.) gives an indication of their excellent heat-resistance and hot-strength properties.

Cobalt–Tungsten–Boron. The addition of 2.5% B (in the form of a pulverized master alloy containing 14% B, balance Co) produces slight increases in the hardness of an alloy containing 20% W, balance Co, if the boron is completely dissolved in the alloy during sintering. Vacuum–sintering at 1400°C. (2550°F.) in a high-frequency furnace, followed by oil quenching and precipitation hardening at 550°C. (1020°F.), produced an alloy with a hardness of about Rockwell C-63, thus being equivalent to the boron-containing cobalt–molybdenum alloy described earlier. Due to the sensitivity of the boron master alloy to oxygen, vacuum-sintering is imperative. Sintering in hydrogen at lower temperatures, *e.g.*, 1200°C. (2200°F.), resulted in incomplete diffusion and an oxidized structure. As in the case of the molyzdenum-bearing alloys the comparatively insignificant improvement in hardness does not seem to warrant the extra cost imposed by the boron addition to the alloy.

Cobalt–Zinc. The constitution diagram of the cobalt–zinc system has been investigated with the aid of sintered alloys, whereby analogous methods were used as in the production of iron–zinc alloys.[55]

Recently, the investigation was extended to include binary cobalt–zinc and ternary cobalt–iron–zinc alloys produced by the impregnation method.[55a] Porous cobalt and prealloyed cobalt–iron bodies could be impregnated fully with molten zinc at 550°C. (1020°F.) when contained in a pressure vessel and subjected to 150 atmospheres (2200 psi). The heterogeneous materials could be homogenized by prolonged annealing, again under pressures above normal. The ultimate composition of these alloys was a function of the zinc absorption which, in turn, was governed by the order and character of the porosity of the original skeleton bodies.

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[55] J. Schramm, *Z. Metallkunde, 30,* 10 (1938).

[55a] J. Schramm and A. Mohrnheim, *Z. Metallkunde, 39,* 71 (1948).

MANGANESE

Sintered manganese metal has not yet found any practical application, since the metal is apparently very brittle—even in its purest state Manganese alloys, on the other hand, are of considerable practical interest, especially in the powder metallurgy of iron and steel.

MANGANESE ALLOYS

Manganese–Iron. Manganese is one of the beneficial addition elements in steels, since it tends to dissolve harmful impurities (*e.g.*, oxyge and sulfur) and to combine with some of the carbon to Mn_3C, whic strengthens the steel appreciably. In addition, manganese lowers th allotropic transformation points, and renders such transformation mor sluggish (*i.e.*, widens the transformation temperature range); this is o particular help in heat-treating case-hardened low-carbon steel. However, it is important that the content of manganese is in the proper proportion to carbon. In sintered steels, manganese plays an equally important role, especially since pores and impurities in the structure ten to produce an uneven and abnormal case during carburizing (see als Volume I, Chapter XIX). Whereas compacts produced from pulverize steel powders or from reduced mill scale contain the necessary amount of manganese, those produced from electrolytic powders or from reduce ores of certain types (*e.g.*, Swedish magnetites) are deficient in manganese. Effective case hardening of the latter type of sintered steel depend on the addition of manganese, which may be effected in various ways.[56] Pure manganese powder can be used only if it is extremely fine and pure and if diffusion is not hampered by oxidation. A more economical and convenient way is to add the metal as powdered ferromanganese (fo analyses see Volume I, Chapter VI), but the resulting diffusion rates are slower, and protection from oxidation remains still significant. Finally, fine manganese oxide can be mixed with iron oxide and jointly reduced, or, preferably, the mixture can be thoroughly oxidized and transformed into a solid solution before reduction. Carbon is the most suitable reducing agent for free manganese oxide; very pure hydrogen under exclusion of carbon is effective as reducing agent only in the case of the solid solution of the oxides, or where manganese dioxide is reduced under conditions permitting simultaneous solution of manganese in iron.[56]

A completely diffused solid solution of a 50–50 Mn–Fe alloy, displaying a degree of toughness considerably in excess of that of pure manganese or standard ferromanganese, can be obtained by sintering

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[56] E. K. Offermann, *Mitt. Kohle- u. Eisenforsch. 1,* No. 5, 85 (1936).

compacted mixtures of electrolytic manganese and iron at 1250°C. (2280°F.) for 4 hours in carefully dried hydrogen or in vacuum. A possible application for this material is in x-ray targets.[56a]

Manganese–Nickel. Alloys of the system manganese–nickel can be produced from mixtures of manganese dioxide and carbonyl nickel containing a major proportion of free carbon, or from mixtures of carbon-free nickel and fine metallic manganese powder.[57] Homogeneous solid solutions have been obtained by sintering for 6–8 hours at 1100–1200°C. (2010–2190°F.) followed by annealing at 800–1000°C. (1470–1830°F.) for 8 hours in hydrogen.[57] The rate of diffusion can be increased by hot-working the alloy. Alloys containing manganese as minor constituent, such as used for spark plug electrodes, have been mentioned under nickel alloys.

Manganese–Vanadium. An alloy containing 50–50 Mn–V can be produced by mixing chemically pure grades of the elemental powders, compacting at 50 tsi, and sintering in dry hydrogen or vacuum at 1300°C. (2370°F.) for at least 4 hours. The alloy is tougher than either of the pure components, and may find possible use as x-ray target material.[56a]

Manganese–Copper–Nickel. Ductile manganese base alloys with copper and nickel have certain unusual physical and electrical properties,[58] such as a zero temperature coefficient of electrical resistance and a very high coefficient of linear expansion in the case of alloys containing about 75% Mn. Alloys containing somewhat less manganese are very resistant to corrosion and have physical properties comparable to nickel silver. Sintered 75–20–5 and 50–40–10 Mn–Cu–Ni can be produced to a quality sufficient to permit gradual hot-working with intermediate annealing at sintering conditions to wire or strip. However, it is essential that very fine (325-mesh or finer) and pure (*e.g.*, electrolytic) powders are used, and that sintering is carried out in well-dried hydrogen or, preferably, in vacuum. The sintering temperature must be below 1000°C. (1830°F.) for the 50–40–10 alloy, and below 1100°C. (2010°F.) for the 75–20–5 alloy, owing to the low melting temperature of the ternary alloys. The sintered alloys have interesting possibilities as resistor materials in electrical and electronic applications.

[56a] C. Hardy, *private communication* (based on Laboratory Report No. 154 of Chas. Hardy, Inc., New York).

[57] G. Hamprecht and L. Schlecht, *Metallwirtschaft, 12,* 281 (1933).

[58] R. S. Dean, *Metal Progress, 36,* No. 4 357 (1939); U. S. Bur. Mines Rept., No. 3477 (1939).

Copper and Copper Alloys

COPPER

Despite rather limited industrial applications, the powder metallurgy of copper has been explored very extensively. The keen academic interest centered around sintered copper may be chiefly attributed to certain convenient characteristics of the metal, *e.g.*, its high ductility, moderate melting point, capacity to form technically useful alloys.

Copper powders are produced in quantity by various methods and of very high purity (see Volume I, Chapter VI), and the reduced and electrolytic types are sufficiently soft to permit compaction at fairly low pressures (*e.g.*, 15–50 tsi) and sintering at moderate temperatures (*e.g.*, 750–1000°C.; 1380–1830°F.) in a reducing atmosphere, such as hydrogen or in vacuum.

Generally superior physical properties can be obtained if the density is brought to near normal values by means of hot-pressing. Figure 596 shows the tensile strength as affected by the sintering temperatures for sintered and hot-pressed specimens.[59-62] As a general rule, the compressive strength is affected in a manner analogous to the tensile strength. Because of their inherent plasticity, most copper powders are susceptible to severe deformation and work hardening—resulting in hardness values considerably in excess of those of ordinary cold-worked copper. This phenomenon has been observed by various investigators, both for cold-

TABLE 253

Relationship of Hardness of Sintered Copper Specimens to Particle Size and Sintering Temperature (Kikuchi[63])

Approximate particle size, μ	Brinell Hardness					
	Pressed at 100 tsi at 20°C. (68°F.)	Sintered at				
		260°C. (500°F.)	530°C. (985°F.)	700°C. (1290°F.)	840°C. (1545°F.)	920°C. (1690°F.)
75	152.4	120.5	78.4	64.0	50.9	43.5
100	141.5	104.5	75.4	64.6	50.7	43.3
150	131.6	98.2	70.5	59.7	50.5	44.0
300	116.9	90.5	65.2	56.4	50.1	45.3

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[59] F. Sauerwald and E. Jaenichen, *Z. Elektrochem.*, *30*, 175 (1924); *31*, 18 (1925).

[60] F. Sauerwald and J. Hunczek, *Z. Metallkunde*, *21*, 22 (1929).

[61] F. Sauerwald and St. Kubik, *Z. Elektrochem.*, *38*, 33 (1932).

[62] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe.* Springer, Berlin, 1943, p. 159.

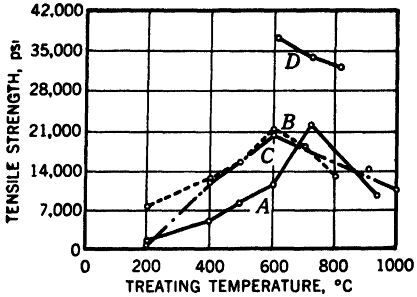

Fig. 596. Effect of the treating temperature on the tensile strength of cold-pressed and sintered, and hot-pressed copper compacts. Curve *A*, compacts cold-pressed at 10 tsi, and subsequently sintered at the indicated temperature (according to Sauerwald and Jaenichen[59]); curve *B*, compacts cold-pressed at 35 tsi, and subsequently sintered at the indicated temperature (according to Sauerwald and Kubik[61]); curve *C*, compacts cold-pressed at 70 tsi, and subsequently sintered at the indicated temperature (according to Kieffer and Hotop[62]); curve *D*, compacts hot-pressed at 25 tsi, at the indicated temperature (according to Sauerwald and Hunczek[60]).

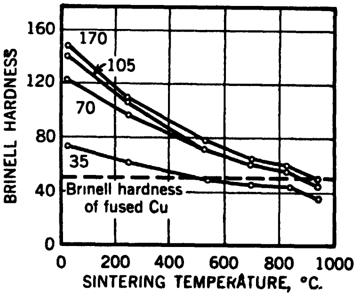

Fig. 597. Effect of the sintering temperature on the hardness of copper compacts pressed from coarse powder at 35, 70, 105, and 170 tsi, (according to Kikuchi[63]).

pressed compacts[63,64] and for hot-pressed compacts,[65,66] with the hardness increasing with powder fineness. Table 253 and Figure 597 show the hardness of cold-pressed and sintered copper as affected by particle size and sintering (*i.e.*, annealing) temperature.[63] The hardness of hot-

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[63] R. Kikuchi, *Science Repts. Tôhoku Imp. Univ.*, First Ser., *26*, 125 (1937).

[64] C. G. Goetzel, *The Influence of Processing Methods on the Structure and Properties of Compressed and Heat Treated Copper Powders.* Dissertation, Columbia University, 1939.

[65] W. Trzebiatowski, *Z. physik. Chem.*, *A169*, 91 (1934); *B24*, 75, 87 (1934).

[66] C. G. Goetzel, *Wire and Wire Products, 16*, 217, 274 (1941).

pressed copper is discussed together with other properties in detail in Volume I, Chapter XII; the reader is particularly referred to the diagrams of Figures 160, 161, and 163. In spite of the excellent compactibility and sintering capacity of copper, the ductility of the final products is not nearly equal to that of fused and soft-annealed copper, unless hot-pressed[64] or severely worked.[66] In this respect, sintered copper is similar

		Sintering atmosphere, hydrogen		Sintering atmosphere, vacuum	
Initial powder	Compacting and repressing pressure tsi	Compressed and sintered state	Compressed, sintered, repressed, annealed state	Compressed and sintered state	Compressed, sintered, repressed, annealed state
A	5 10 15 25 45				
B	5 10 15 25 45				
C	5 10 15 25 45				
LC	5 10 15 25 45				
R	5 10 15 25 45				

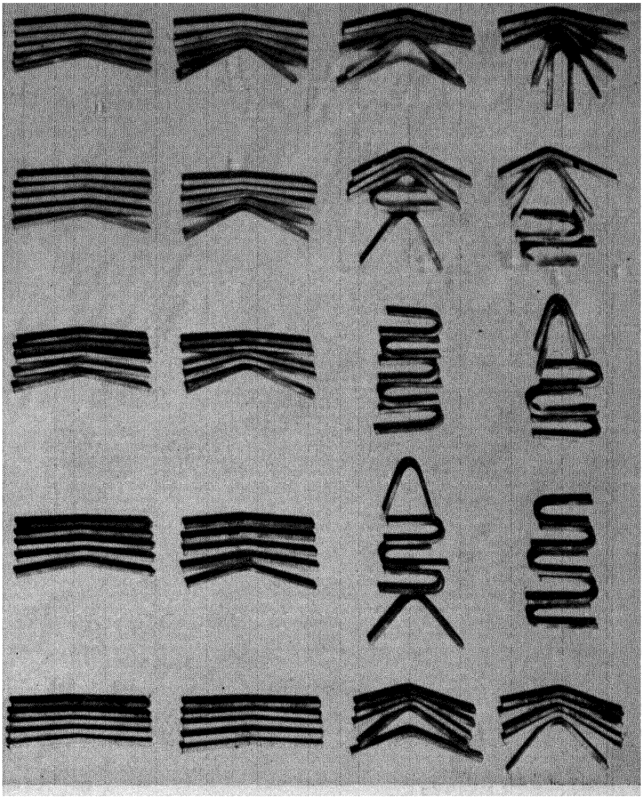

Fig. 598. Bend test specimens of sintered copper after testing. (All specimens were bent to the angle where incipient break occurred, or to 180° without break, respectively.)

to the somewhat stronger metals, iron and nickel, and not to the more plastic metals, silver and aluminum, which, in the densely sintered state, can exhibit a ductility equivalent to that of the fused counterpart. However, with increasing compacting pressure and sintering temperature, the ducility of sintered copper improves within limits, especially if sintering is carried out in vacuum. Figure 598 is a photograph of a series of test specimens whose ductility was established by a bend test.[64] The kind of initial powder, pressure of compaction, number of pressing and sintering operations, and type of sintering atmosphere were introduced as variables, and give a clear indication of the beneficial effect of a vacuum treatment as far as ductility is concerned.

Thus, the fact that sintered copper can be produced to a high degree of ductility and purity by vacuum sintering and to unusually high hardness by high compacting pressures, possibly at slightly elevated temperatures, should open for it a new territory of industrial applications in the electronic field, where small precision parts of intricate design from pure and gas-free components are required for electronic tubes and the like. Other uses of sintered copper are described in Chapters XXIII and XXVI.

COPPER ALLOYS

Copper–Zinc. Of the great number of sintered copper alloys that have been produced on a laboratory scale, brasses and bronzes are the only alloys shown to be suitable for parts on a large scale in industry. For many years sintered brasses have been considered a desirable substitute for the customary bronzes in nonferrous precision parts for reasons of reduced cost, but only very recently has the sintering technique of brass been perfected to an extent that makes mass production of brass powder products competitive with the die casting and stamping processes.[66a] There have been 2 major contributory developments: the commercial supply of alloy powders of high compactibility and the control of dezincification during sintering through the use of moisture-free controlled atmospheres and special sintering practices, such as sintering in closed retorts. The latter permits blending of the zinc vapor with the furnace atmosphere at pressures slightly above atmospheric, whereby a gas–metal equilibrium condition is approached. The addition of small percentages of phosphorus to the brass powders increases the ductility of the sintered product without materially affecting the other physical properties[67,68]; at the same time, it lowers the optimum sintering temperature while broadening the temperature range at which sintering is effec-

[66a] D. C. Bradley, *Prod. Eng.*, *19*, 10, 107 (1948).

[67] E. H. Kelton, *Machine Design*, *16*, 129 (1944).

[68] Anonymous, *Iron Age*, *155*, No. 4, 60 (1945).

tive. In a 70–30 brass, for example, the addition of a 0.3% P reduces the optimum sintering temperature from 900°C. (1650°F.) to 850°C. (1560°F.) and broadens the sintering temperature range from 40°C. (70°F.) to 55°C. (100°F.).[69]

The physical properties of sintered brasses are given in greater detail in Chapter XXVI, those of hot-pressed brass compacts in Volume I, Chapter XII; the industrial applications of sintered brass parts are also described more fully in Chapter XXVI.

Copper–Tin. Until the present, sintered bronzes have been used principally in bearing applications, but also, because of their comparative ease of manufacture, in nonferrous precision parts that must possess certain chemical or physical properties. Sintered alloys of approximately 90–10 Cu–Sn composition have found widespread industrial uses in the form of bearings and structural parts. Minor additions of such elements as carbon or lead are used to improve the bearing properties of the alloy and lead additions are also advantageous where machining operations are required. The properties and applications of dense bronzes are discussed in Chapter XXVI, those of porous bronzes in Chapter XXVII.

Copper–Tin–Zinc. Ternary bronzes containing zinc in small proportion (*e.g.*, up to 5%) can be employed at an economic advantage over binary bronzes for structural parts, but the final properties of the alloy depend largely on the success of controlling dezincification. If the zinc is completely retained and alloyed during sintering, the machinability is improved. Whereas the addition of zinc in the form of atomized brass powder tends to reduce zinc losses during sintering, diffusion and homogenization, as well as compactibility, are improved when pure zinc powder of very fine grade (*e.g.*, 325 mesh) is admixed. In the latter case, dezincification can be controlled by sintering in closed containers in which the zinc vapor can blend with the moisture-free atmosphere at pressures slightly above atmospheric.

Copper–Tin–Lead. Structural bronze parts that require extensive finishing operations are rendered freely machinable by the addition of about 2% Pb. However, it is essential that the lead is distributed evenly throughout the bronze structure, which necessitates the addition of very fine and pure lead powder, or, preferably, a prealloyed copper–lead powder. One kind, produced by the liquid disintegration method (see page 477, also Volume I, Chapter III), appears particularly adaptable for this purpose, as its particles contain minute lead spheres evenly dispersed within the copper matrix.

Copper–Tin–Zinc–Lead. The development of more complex

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[69] H. Chase, *Materials & Methods, 24,* No. 6, 1439 (1946).

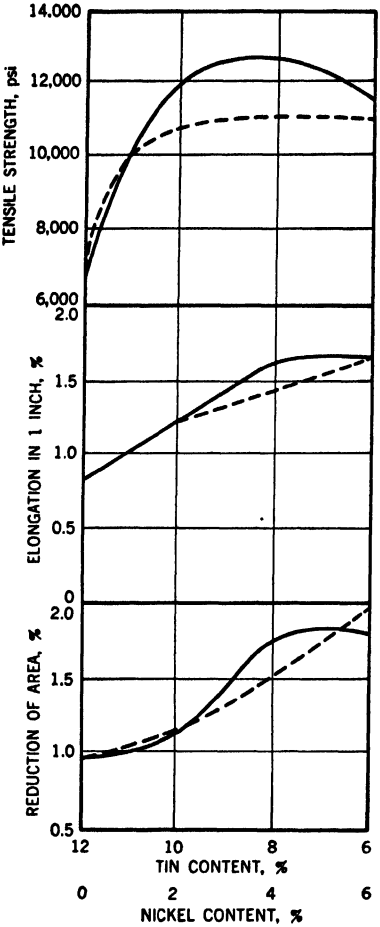

Fig. 599. Tensile properties of sintered copper–tin–nickel compacts as a function of the tin–nickel ratio. All compacts were pressed at 20 tsi, and sintered in hydrogen at 825°C. (1515°F.) for 12 hours. The average density of the compacts was 75% of solid. (Solid line, carbonyl nickel powder; broken line, electrolytic nickel powder.)

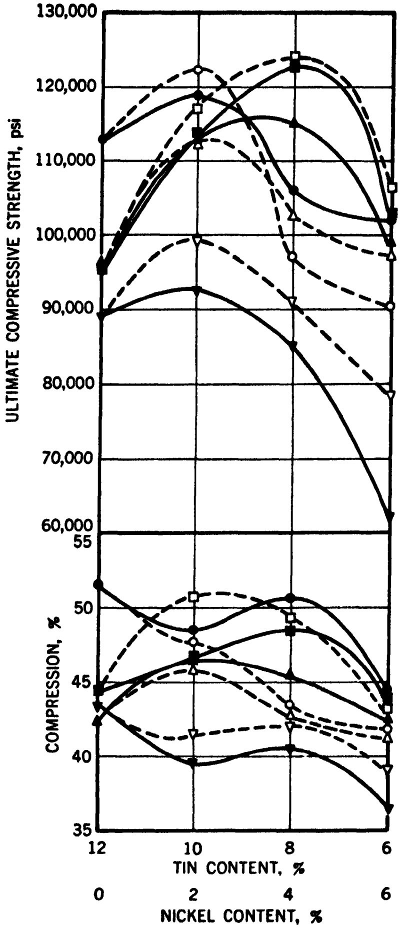

Fig. 600. Compressive properties of sintered copper–tin–nickel compacts as a function of the tin–nickel ratio. All compacts were pressed at 20 tsi, and sintered in hydrogen. The average density of the compacts was 75% of solid. (The symbols are identified in the caption for Figure 601.)

bronzes by powder metallurgy methods is promising, from both an economic and a technical point of view. Thus, for example, can part of the tin be replaced by the less expensive metals, zinc and lead, without materially sacrificing the physical or bearing properties. Again, however, precautions must be taken against dezincification during sintering. An alloy containing 4% each of Sn, Zn, and Pb can be used as seal metal for bearings and washers in refrigeration and pump machinery. Diffusion and homogenization during sintering are aided by the use of fine grades (*e.g.*, —325 mesh) of the elemental powders (except for the lead which is best added through liquid-disintegrated Cu–Pb powder). The lead and zinc components impose a temperature limit of about 750°C. (1380°F.) for the sintering cycle, with excessive zinc and lead losses resulting from treatments at higher temperatures. Sintering times can be reduced from about 14 to 4 hours by using the fine elemental powders and by a thorough mixing procedure.

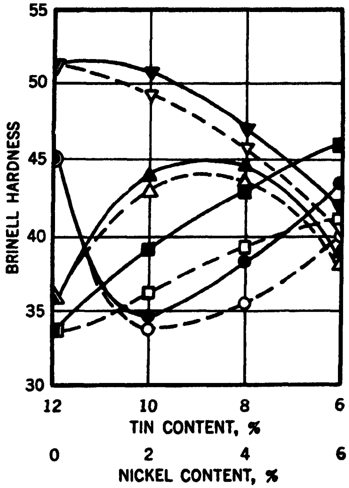

Fig. 601. Brinell hardness of sintered copper–tin–nickel compacts as a function of the tin–nickel ratio. All compacts were pressed at 20 tsi, and sintered in hydrogen. The average density of the compacts was 75% of solid. (▼) Carbonyl nickel powder, sintered for 30 minutes at 700°C. (1290°F.); (▽) electrolytic nickel powder, sintered for 30 minutes at 700°C. (1290°F.); (▲) carbonyl nickel powder, sintered for 30 minutes at 825°C. (1515°F.); (△) electrolytic nickel powder, sintered for 30 minutes at 825°C. (1515°F.); (●) carbonyl nickel powder, sintered for 30 minutes at 950°C. (1740°F.); (○) electrolytic nickel powder, sintered for 30 minutes at 950°C. (1740°F.); (■) carbonyl nickel powder, sintered for 12 hours at 825°C. (1515°F.); (□) electrolytic nickel powder, sintered for 12 hours at 825°C. (1515°F.).

Copper–Tin–Nickel. The partial substitution of tin by nickel in dense and porous bronzes increases their strength substantially and simultaneously improves their corrosion resistance slightly. The diagrams

TABLE 254

Density, Hardness, and Compressive Properties of Sintered and Hot-Pressed 95–5 Cu–Mn Compacts[a]

Type of powder	Process	Processing			Density, g./cc.	Brinell hardness (average)	Compressive strength		Total compression, %	Increase in area, %
		Pressure, tsi	Temperature °C. (°F.)	Time, min.			Max. stress, psi	In 0.1 in. compr., psi		
Powder mixture[b]	Sintered	5	700 (1290)	60	4 95	11.0	18,850	10,800	36.75	19.5
		10			5 86	14.5	47,900	31,900	42.9	53.5
		15			6 32	22.5	65,000	50,000	43.9	64.8
		25			7.29	34.25	90,000	57,000	44.8	74.7
		50			7 88	47.75	133,000	63,600	52.0	109.6
		5	800 (1470)	60	5.14	11.75	57,800	45,500	55.1	74.0
		10			5.93	17.5	77,900	55,500	50 1	74.8
		15			6.35	21.0	116,400	60,600	55.6	94.6
		25			7.22	34.25	171,900	71,100	55.9	127.9
		50			7 69	40.25	223,800	83,000	62.4	160.9
	Hot-pressed	5	400 (750)	10[d] + 1[e]	6 53	40.0	18,650	—	2.63	2.80
		10			6 99	50 25	27,400	—	3.54	5.59
		15			7 43	60.5	35,950	—	5.95	8.08
		25			8 02	82.25	56,000	—	18 55	28 24
		50			8.57	111.0	85,200	—	26 6	41.6
		5	600 (1110)	10 + 1	7.51	56 25	96,000	56,000	48 8	94.5
		10			8.00	69.75	127,800	63,300	54.1	124.2
		15			8 48	61.25	170,000	70,000	62.5	185.9
		25			8 68	67.25	219,500	79,000	65.5	210.0
		50			8.68	62 25	234,000	83,900	68.3	220.2

Alloy powder[c]	Sintered	5	700 (1290)	60	—	—	—	—	—	—
		10			5 59	—	18,720	—	12.02	—
		15			6 23	—	18,070	—	15.82	—
		25			7 09	32 0	37,050	—	20.88	29.38
		50			7 75	43.75	54,800	—	22.65	33.63
		5	800 (1470)	60	4 56	—	9,300	—	10.51	—
		10			5 50	12 0	20,200	—	24 4	—
		15			6 16	16 75	47,300	36,300	37 8	54.0
		25			6 97	33.75	74,500	54,000	42 5	81.7
		50			7 66	46.0	114,800	64,000	47 0	88.9
	Hot-pressed	5	400 (750)	10 + 1	5 92	33.0	15,210	—	4.48	8.08
		10			6 18	37.0	17,700	—	5.11	10.23
		15			6 62	46.25	23,900	—	7 25	11.50
		25			7 20	61 5	35,700	—	12.0	18.33
		50			7.99	98.75	62,500	—	11.36	15.20
		5	600 (1110)	10 + 1	6.42	37 5	24,025	—	14.38	15.84
		10			6.58	41 75	26,650	—	14 46	20.17
		15			7 03	53.5	37,350	—	15.81	23.59
		25			7 70	77.0	50,700	—	15.87	29.81
		50			8 50	117 5	90,500	—	27.85	48.1

[a] Author's investigation, unpublished data.

[b] Electrolytic copper and manganese powders of 100-mesh grades with 35% of −325-mesh fraction.

[c] Powder mixture diffusion-alloyed by heating at 700°C. (1290°F.) for 4 hours in hydrogen; pulverized and annealed at 550°C. (1020°F.) for 1 hour in hydrogen.

[d] Time of drawing at temperature.

[e] Time of pressure dwelling at temperature.

TABLE 255
Density, Hardness, and Compressive Properties of Sintered and Hot-Pressed 85-15 Cu-Mn Compacts[a]

Type of powder	Process	Processing			Density, g./cc.	Brinell hardness (average)	Compressive strength		Total compression, %	Increase in area, %
		Pressure, tsi	Temperature °C. (°F.)	Time, min.			Max. stress, psi	In 0.1 in. compr., psi		
Powder mixture[b]	Sintered	5	700 (1290)	60	5.05	10.25	12,590	—	23.3	27.44
		10			5.82	17.0	31,900	26,100	32.0	40.0
		15			6.23	20.0	44,000	33,300	33.65	49.9
		25			6.85	29.0	64,400	43,600	34.25	55.8
		50			7.48	38.5	89,500	49,500	43.4	83.5
		5	800 (1470)	60	5.09	12.75	51,600	36,600	49.1	67.2
		10			5.73	16.7	78,100	54,800	50.9	82.5
		15			6.11	20.4	99,400	59,900	51.7	94.2
		25			6.60	29.25	136,700	63,600	54.4	108.6
		50			7.10	36.75	159,000	70,900	56.9	122.9
	Hot-pressed	5	400 (750)	$10^d + 1^e$	6.59	44.75	22,200	—	3.77	6.23
		10			6.91	53.75	29,810	—	6.51	9.05
		15			7.33	77.5	40,500	—	10.03	10.88
		25			7.80	84.0	54,800	—	10.49	17.05
		50			8.28	111.75	72,400	—	16.23	23.61
		5	600 (1110)	10 + 1	7.58	62.0	82,100	54,800	39.7	68.0
		10			7.92	69.75	94,800	64,400	42.4	78.8
		15			8.11	75.5	103,200	73,200	45.4	92.2
		25			8.36	78.5	120,100	75,000	53.5	144.7
		50			8.45	75.75	148,300	78,300	60.6	188.8

Alloy powder[c]	Sintered	5	700 (1290)	60	—	—	—	—	—	—
		10			5 28	—	7,420	—	11.61	—
		15			5 70	—	11,910	—	9.93	—
		25			6 39	28 75	23,300	—	12.23	26.06
		50			7 17	45 5	50,100	—	20 02	37.39
		5	800 (1470)	60	4 36	—	4,460	—	22.94	—
		10			5 09	11 8	10,340	—	20.76	—
		15			5 50	15 3	22,850	—	24.65	—
		25			6 14	—	45,200	35,800	32.5	46.0
		50			6 85	41 5	84,400	54,400	40.1	62.0
	Hot-pressed	5	400 (750)	10 + 1	5 55	23 0	11,500	—	3 75	5.27
		10			5 79	36 0	16,450	—	3.95	5.91
		15			6 14	45 75	23,890	—	4.50	7.14
		25			6.64	62 25	31,050	—	4.97	8.39
		50			7 35	93.75	61,800	—	6.29	15.15
		5	600 (1110)	10 + 1	6 06	38 5	22,010	—	7.25	10.87
		10			6 46	48 25	30,050	—	8.08	13 67
		15			6 93	64 0	41,800	—	8 77	15.83
		25			7 43	87 0	56,000	—	9.23	18.95
		50			8 09	133 0	88,500	—	14.64	22.38

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[a] Author's investigation, unpublished data.

[b] Electrolytic copper and manganese powders of 100-mesh grades with 35% of −325-mesh fraction.

[c] Powder mixture diffusion-alloyed by heating at 700°C. (1290°F.) for 4 hours in hydrogen; pulverized and annealed at 550°C. (1020°F.) for 1 hour in hydrogen.

[d] Time of drawing at temperature.

[e] Time of pressure dwelling at temperature.

TABLE 256

Density, Hardness, and Compressive Properties of Sintered and Hot-Pressed 75–25 Cu–Mn Compacts[a]

Type of powder	Process	Processing			Density, g./cc.	Brinell hardness (average)	Compressive strength		Total compression, %	Increase in area, %
		Pressure, tsi	Temperature °C. (°F.)	Time, min.			Max. stress, psi	In 0.1 in. compr., psi		
Powder mixture[b]	Sintered	5	700 (1290)	60	4.84	10.5	5,240	—	10.0	13.32
		10			5.69	15.5	19,500	—	20.66	25.38
		15			6.06	19.5	27,200	—	23.23	36.36
		25			6.59	26.5	40,500	—	27.0	47.6
		50			7.07	35.5	52,200	—	28.9	49.5
		5	800 (1470)	60	4.85	15.25	34,450	21,150	41.2	49.0
		10			5.52	15.75	61,000	47,000	41.3	53.6
		15			5.83	20.75	76,400	54,400	43.0	67.5
		25			6.25	24.5	98,200	58,800	46.8	78.9
		50			6.69	33.75	113,900	63,300	46.9	81.8
	Hot-pressed	5	400 (750)	$10^d + 1^e$	6.33	42.75	18,400	—	1.65	2.80
		10			6.61	49.75	24,150	—	3.11	4.35
		15			6.90	58.25	29,900	—	5.34	5.90
		25			7.33	76.0	41,900	—	5.81	7.14
		50			7.87	100.75	60,700	—	6.00	8.39
		5	600 (1110)	10 + 1	7.05	57.75	50,200	—	22.18	33.66
		10			7.35	67.5	57,000	—	23.33	37.0
		15			7.69	79.0	65,000	—	24.34	38.8
		25			7.89	79.5	71,600	51,100	33.3	66.0
		50			8.16	80.25	72,700	55,500	37.9	77.3

Alloy powder[c]	Sintered	5	700 (1290)	60	—	—	—	—	—	—
		10			—	—	7,250	—	9.15	—
		15			5.53	—	10,000	—	12.12	—
		25			6.06	21.25	20,210	—	15.70	—
		50			6.76	39.0	42,300	—	17.17	—
		5	800 (1470)	60	—	—	—	—	—	—
		10			—	—	8,090	—	19.37	—
		15			5.30	—	114,100	—	21.18	22.50
		25			5.83	17.25	24,950	—	29.59	50.0
		50			6.33	31.75	56,100	—	37.75	79.9
	Hot-pressed	5	400 (750)	10 + 1	5.07	—	8,390	—	4.22	4.44
		10			5.37	—	11,490	—	6.66	6.96
		15			5.67	40.0	17,090	—	9.79	9.97
		25			6.02	50.0	25,750	—	9.94	10.23
		50			6.62	82.25	46,200	—	10.10	15.55
		5	600 (1110)	10 + 1	5.66	36.5	17,490	—	3.94	9.00
		10			6.16	50 0	25,550	—	4.46	9.63
		15			6.33	62 25	31,190	—	5.55	10.88
		25			6.80	80.0	44,200	—	7.29	15.15
		50			7.60	137.5	84,000	—	12.82	21.75

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[a] Author's investigation, unpublished data.

[b] Electrolytic copper and manganese powders of 100-mesh grades with 35% of −325-mesh fraction.

[c] Powder mixture diffusion-alloyed by heating at 700°C. (1290°F.) for 4 hours in hydrogen; pulverized and annealed at 550°C. (1020°F.) for 1 hour in hydrogen.

[d] Time of drawing at temperature.

[e] Time of pressure dwelling at temperature.

of Figures 599 and 600 show the tensile and compressive properties, and that of Figure 601 the Brinell hardness, as they vary for different sintering conditions with increasing nickel and decreasing tin content for alloys containing 88% Cu. The alloys were produced from mixtures of the elemental powders of commercial grades, *i.e.*, 100-mesh electrolytic copper, 200-mesh atomized tin, and either 150-mesh electrolytic or 325-mesh carbonyl nickel. The density of the material was kept within 75 and 80% of theoretical by compaction at 20 tsi. The best physical properties are displayed by the bronze alloy containing 8% Sn and 4% Ni. On the basis of equal porosity the tensile strength is twice that of the binary bronze, and the compressive strength approximately one-third higher. A sintering period of one-half hour at 825°C. (1515°F.) is sufficient to diffuse the carbonyl nickel into the bronze structure. A Brinell hardness of 40–45 and an oil absorption capacity of 0.045–0.055 g./cm.^{2} compare with values obtainable in regular porous bronze bearings. Thus, the material appears to have potentialities for heavy duty bearing applications, especially when corrosive conditions prevail in the oil or atmosphere.

Copper–Nickel. Sintered alloys of the binary system copper–nickel have been described in detail in Chapter XXVI. The sintering process of a 70–30 Cu–Ni composition has been made the basis for extensive theoretical study of diffusion and homogenization.[70,71] In spite of their excellent physical and anticorrosion properties, which can be influenced by the sintering cycle over a considerable range, no important commercial applications have yet been reported for these alloys.

Copper–Nickel–Zinc. Alloys containing 15–30% Ni, 0–25% Zn, and 50–65% Cu, generally referred to as German Silver and Nickel Silver alloys, can be produced readily by the powder metallurgy technique. However, as is the case with other zinc-containing alloys, dezincification during sintering must be prevented. Despite the widespread use of these alloys in the cast or wrought form for cutlery and bijouterie applications, sintered products have only lately come into limited use (see also Chapter XXVI).

Copper–Nickel–Tin. Sintered cupro-nickel alloys containing about 25% Ni and 5% Sn are of particular interest on account of their excellent stability in salt water and their susceptibility to precipitation hardening.[71a] Although manufacture and control of the ternary alloy are more complicated than those of simpler Cu alloys, it appears to have definite possibilities as a structural material in applications requiring

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[70] F. N. Rhines and R. A. Colton, in J. Wulff, *Powder Metallurgy*. Am. Soc. Metals, Cleveland, 1942, p. 67.

[71] F. N. Rhines and R. A. Meussner, in *Symposium on Powder Metallurgy*, A.S.T.M., Philadelphia, Pa., 1943, p. 25.

[71a] W. N. Pratt, *Powder Metallurgy Bull.*, *1*, No. 3, 43 (1946).

moderate strength combined with good corrosion resistance. The alloy has been described more fully in Chapter XXVI.

Copper–Nickel–Beryllium. Ternary copper-base alloys with nickel and beryllium as minor constituents have been discussed in Chapter XXVI. Results concerning the precipitation hardening of the material are given in Volume I, Chapter XIX. Alloys of this type have been considered for heavy duty bearings.[72]

Copper–Nickel–Phosphorus. Sintered copper alloys containing small percentages of nickel and a fraction of one per cent of phosphorus have also been discussed in Chapter XXVI, with their heat treatment reported in Volume I, Chapter XIX. The alloy has been suggested as a bearing material.[72]

Copper–Nickel–Silicon–Phosphorus. Like the silicon-free composition, the quaternary alloy appears suitable for heavy duty bearings.[72a] A precipitation-hardened material, containing 2.4% Ni, 0.8% Si, and 0.3% P, balance Cu, possesses a Rockwell hardness of B-75, a tensile strength of 61,500 psi with an elongation of 2.5%, an elastic limit up to 38,000 psi, and a fatigue strength up to 17,500 psi. The alloy is further described in Chapter XXVI; its heat treatment is discussed in Volume I, Chapter XIX.

Copper–Nickel–Cobalt. Alloys containing about 45–50% Cu, 25–30% Co, and 25% Ni possess very good magnetic properties and in the heat-treated condition approach the quality of a medium-type Alnico permanent magnet. These alloys, known under the trade name of Cunico, compare favorably with Alnico with regard to their deformability and machinability, and have found application in wires, strips, and springs. The material can be produced readily by the sintering technique[73] as discussed in greater detail in Chapter XXIV.

Copper–Nickel–Iron. A magnetic alloy of quality similar to the foregoing is obtained if the cobalt is replaced by iron. The material, known under the trade name of Cunife, analyzes about 20% each of nickel and iron, balance copper. Its production by powder metallurgy is, to the best of the author's knowledge, still in the laboratory stage.

Copper–Manganese. Binary copper–manganese alloys of different manganese contents have been produced on an experimental basis by the author to study their properties as affected by certain processing varia-

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[72] F. R. Hensel, E. I. Larsen, and E. F. Swazy, *Trans. Am. Inst. Mining Met. Engrs.*, *166*, 533 (1946).

[72a] F. R. Hensel, E. I. Larsen, and E. F. Swazy, *Trans. Am. Inst. Mining Met. Engrs.*, *166*, 548 (1946).

[73] R. Steinitz, *Powder Metallurgy Bull.*, *1*, No. 3, 45 (1946).

TABLE 257

Density, Hardness, and Compressive Properties of Sintered and Hot-Pressed 95–5 Cu–Al Compacts[a]

Type of powder	Process	Processing			Density, g./cc.	Brinell hardness (average)	Compressive strength		Total compression, %	Increase in area, %
		Pressure, tsi	Temperature °C. (°F.)	Time, min.			Max. stress, psi	In 0.1 in. compr., psi		
Powder mixture[b]	Sintered	5	800 (1470)	60	4.41	10.75	24,760	14,700	40.5	41.4
		10			5.05	13.5	56,700	36,000	44.5	45.2
		15			5.57	18.25	100,400	57,500	46.5	66.6
		25			6.14	24.25	103,300	59,500	50.5	69.1
		50			6.54	34.25	107,700	59,900	49.9	79.9
		5	1000 (1830)	60	4.35	7.75	24,600	14,400	41.75	49.7
		10			4.99	12.25	61,200	46,400	46.9	53.7
		15			5.57	16.25	136,200	60,600	55.3	76.8
		25			5.90	19.25	148,100	63,000	57.0	83.0
		50			6.28	20.75	161,600	65,400	59.2	118.2
	Hot-pressed	5	400 (750)	10[d] + 1[e]	5.85	22.25	18,620	—	10.06	10.21
		10			6.07	35.0	26,400	—	16.12	16.14
		15			6.50	43.25	34,450	—	17.43	25.15
		25			6.95	52.25	43,450	—	18.10	28.22
		50			7.79	93.75	58,500	—	18.81	29.66
		5	600 (1110)	10 + 1	7.20	63.0	118,300	60,800	50.2	98.4
		10			7.55	70.0	125,900	62,500	53.0	107.9
		15			7.73	76.75	145,100	66,600	55.5	123.5
		25			7.93	89.5	194,100	84,600	63.0	183.1
		50			7.98	89.75	196,100	86,000	67.4	195.2

Alloy powder[c]	Sintered	5	800 (1470)	60	4.04	—	—	—	—	—
		10			4.54	—	3,960	—	11.80	—
		15			5.00	—	6,990	—	12.82	—
		25			5.51	—	12,380	—	13.45	—
		50			5.93	—	22,220	—	15.63	—
		5	1000 (1830)	60	4.14	—	—	—	—	—
		10			4.37	—	4,440	—	15.87	—
		15			4.97	—	8,310	—	17.98	—
		25			5.00	—	14,300	—	26.39	—
		50			5.31	57.0	22,580	16,600	32.24	36.60
	Hot-pressed	5	400 (750)	10 + 1	5.83	39.25	11,900	—	4.62	4.35
		10			6.12	45.75	17,700	—	5.71	6.21
		15			6.69	58.25	23,250	—	7.58	7.75
		25			7.01	77.25	33,550	—	11.05	11.50
		50			7.79	118.5	72,600	—	18.45	18.87
		5	600 (1110)	10 + 1	6.69	57.75	33,900	—	15.10	19.26
		10			6.76	58.25	44,000	—	16.63	22.65
		15			7.37	82.0	73,800	—	20.72	29.5
		25			7.85	102.25	84,900	—	21.80	30.75
		50			8.08	115.75	88,800	—	22.22	32.5

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[a] Author's investigation, unpublished data.

[b] Electrolytic copper and atomized aluminum powders of 100-mesh grades with 35% of −325-mesh fraction.

[c] Powder mixture diffusion-alloyed by heating at 700°C. (1290°F.) for 4 hours in hydrogen; pulverized and annealed at 550°C. (1020°F.) for 1 hour in hydrogen.

[d] Time of drawing at temperature.

[e] Time of pressure dwelling at temperature.

TABLE 258

Density, Hardness, and Compressive Properties of Sintered and Hot-Pressed 90-10 Cu-Al Compacts[a]

Type of powder	Process	Processing			Density, g./cc.	Brinell hardness (average)	Compressive strength		Total compression, %	Increase in area, %
		Pressure, tsi	Temperature °C. (°F.)	Time, min.			Max. stress, psi	In 0.1 in. compr., psi		
Powder mixture[b]	Sintered	5	800 (1470)	60	4.23	17.5	38,240	24,240	31.39	29.75
		10			4.79	32.25	59,000	39,900	30.91	29.20
		15			5.32	44.25	76,600	—	28.21	32.23
		25			5.83	63.75	84,800	—	21.49	21.93
		50			5.97	73.5	90,100	—	22.78	23.25
		5	1000 (1830)	60	4.14	14.0	61,400	36,400	45.2	47.0
		10			4.77	29.7	98,600	58,600	46.5	61.5
		15			5.50	40.25	133,100	73,700	50.1	64.2
		25			5.92	53.0	126,600	72,600	46.6	62.4
		50			6.06	59.25	120,100	70,900	44.7	60.6
	Hot-pressed	5	400 (750)	10[d] + 1[e]	5.74	37.75	34,790	—	20.96	25.25
		10			6.08	43.25	36,630	22,220	38.0	44.4
		15			6.42	52.75	39,300	25,300	30.95	37.0
		25			6.82	71.75	48,250	—	29.0	33.5
		50			7.17	89.0	59,900	—	27.05	29.81
		5	600 (1110)	10 + 1	6.66	70.5	80,500	53,000	35.2	56.0
		10			6.82	75.75	83,500	55,900	40.6	70.1
		15			7.02	85.75	117,800	57,900	52.2	105.9
		25			7.17	95.75	187,300	77,300	61.6	181.1
		50			7.23	98.25	189,700	77,700	62.0	187.0

Alloy powder[c]	Sintered	5	800 (1470)	60	—	—	—	—	—	—
		10			—	—	—	—	—	—
		15			4.45	—	3,275	—	6.95	—
		25			4.71	—	6,950	—	8.58	—
		50			5.43	—	16,570	—	8.40	—
		5	1000 (1830)	60	—	—	—	—	—	—
		10			—	—	—	—	—	—
		15			4.33	—	3,525	—	8.61	—
		25			4.69	—	7,610	—	10.82	—
		50			4.89	20.0	20,500	—	13.70	—
	Hot-pressed	5	400 (750)	10 + 1	4.74	26.25	9,320	—	3.09	2.79
		10			5.00	38.75	12,480	—	3.35	4.35
		15			5.39	50.25	17,910	—	4.87	6.21
		25			5.79	71.0	30,730	—	5.59	8.08
		50			6.40	104.5	62,700	—	6.31	8.08
		5	600 (1110)	10 + 1	5.46	52.25	24,820	—	5.39	7.77
		10			5.86	66.75	37,400	—	5.75	9.33
		15			6.09	78.25	41,800	—	7.75	12.75
		25			6.59	109.75	58,300	—	7.75	15.83
		50			7.05	195.25	88,500	—	5.66	9.23

[a] Author's investigation, unpublished data.

[b] Electrolytic copper and atomized aluminum powders of 100-mesh grades with 35% of −325-mesh fraction.

[c] Powder mixture diffusion-alloyed by heating at 700°C. (1290°F.) for 4 hours in hydrogen; pulverized and annealed at 550°C. (1020°F.) for 1 hour in hydrogen.

[d] Time of drawing at temperature.

[e] Time of pressure dwelling at temperature.

TABLE 259

Density, Hardness, and Compressive Properties of Sintered and Hot-Pressed 85–15 Cu–Al Compacts[a]

Type of powder	Process	Processing			Density, g./cc.	Brinell hardness (average)	Compressive strength		Total compression, %	Increase in area, %
		Pressure, tsi	Temperature °C. (°F.)	Time, min.			Max. stress, psi	In 0.1 in. compr., psi		
Powder mixture[b]	Sintered	5	800 (1470)	60	3.90	21.75	10,800	—	4.74	9.24
		10			4.53	51.75	23,700	—	7.06	10.95
		15			4.88	72.75	40,300	—	11.05	12.32
		25			5.29	127.5	49,500	—	14.04	—
		50			5.33	136.0	54,100	—	10.05	—
		5	1000 (1830)	60	3.83	18.5	12,460	—	5.38	10.69
		10			4.43	45.5	23,800	—	12.95	16.91
		15			4.95	71.75	46,600	—	14.02	26.75
		25			5.29	133.75	53,500	—	5.12	—
		50			5.37	140.0	60,000	—	3.13	—
	Hot-pressed	5	400 (750)	10[d] + 1[e]	5.19	22.25	17,100	—	6.62	7.77
		10			5.53	39.0	24,500	—	9.40	13.04
		15			5.91	50.25	32,800	—	14.20	20.40
		25			6.26	64.75	42,050	—	14.30	22.38
		50			6.57	82.25	51,000	—	14.88	23.33
		5	600 (1110)	10 + 1	6.14	70.0	75,500	50,300	35.8	60.2
		10			6.39	89.0	77,500	53,500	33.39	54.0
		15			6.59	104.75	81,700	55,500	30.30	44.4
		25			6.63	114.0	84,800	—	23.63	33.95
		50			6.66	114.75	85,000	—	14.70	23.75

Alloy powder[c]	Sintered	5	800 (1470)	60	—	—	—	—	—	—
		10			—	—	—	—	—	—
		15			—	—	—	—	—	—
		25			4.69	—	4,270	—	3.13	—
		50			5.00	—	5,890	—	5.59	—
		5	1000 (1830)	60	—	—	—	—	—	—
		10			—	—	—	—	—	—
		15			—	—	—	—	—	—
		25			4.43	—	5,810	—	8.04	—
		50			4.98	—	8,310	—	7.64	—
	Hot-pressed	5	400 (750)	10 + 1	4.19	—	—	—	—	—
		10			4.39	—	—	—	—	—
		15			4.68	46.75	9,000	—	8.18	—
		25			5.00	70.0	14,750	—	10.82	—
		50			5.55	119.75	47,000	—	17.65	—
		5	600 (1110)	10 + 1	4.62	62.0	6,200	—	3.29	—
		10			4.96	86.75	33,700	—	11.56	—
		15			5.64	107.5	47,700	—	10.29	—
		25			6.28	194.75	66,600	—	10.91	—
		50			6.36	262.0	89,500	—	10.33	—

[a] Author's investigation, unpublished data.

[b] Electrolytic copper and atomized aluminum powders of 100-mesh grades with 35% of −325-mesh fraction.

[c] Powder mixture diffusion-alloyed by heating at 700°C. (1290°F.) for 4 hours in hydrogen; pulverized and annealed at 550°C. (1020°F.) for 1 hour in hydrogen.

[d] Time of drawing at temperature.

[e] Time of pressure dwelling at temperature.

bles. Compacts were produced from mixtures of the elemental powders and from powders prepared by diffusion alloying at 700°C. (1290°F.) for 4 hours; these powders were either cold pressed and sintered at 700 or 800°C. (1290 or 1470°F.) for 1 hour; or they were hot pressed at 400 or 600°C. (750 or 1110°F.). Otherwise, the procedure used was identical with the one previously described (Volume I, Chapters XII and XIII, and this volume, Chapter XXVI). The physical properties of the various alloys so produced are given in Tables 254–256. They are generally far inferior to their fused counterparts, with near solid densities being reached only by hot-pressing at 600°C. (1110°F.) at high pressures. The more favorable results obtained with prealloyed powder in the case of brasses and bronzes (see Vol. I, Chapter XII) were not observed in the copper–manganese alloys. Apparently, the strong oxidizing tendencies of the manganese inhibits alloying to a large extent in the case of both powders. Owing to the poor physical properties and the inherent manufacturing difficulties, no industrial applications have yet been developed for these binary copper–manganese alloys.

Copper–Manganese–Aluminum. An alloy that is more interesting from an academic standpoint than from a practical one is known as Heusler's Magnetic Alloy, containing 25% Mn, 10% Al, balance Cu. Although none of the three components is magnetic in itself, their ternary solid solution is magnetic. The cast alloy is very brittle, but sintering can produce a more malleable product because of a finer grain structure. Extremely pure powders (*e.g.*, electrolytic copper, manganese, and low-oxygen aluminum) are required to prevent oxidation of the alloying components, and sintering is best carried out in vacuum or in highly purified hydrogen. Prolonged diffusion times, preferably interrupted by intermediate cold-working through repressing at high pressures, and sintering temperatures between 650° and 750°C. (1200° and 1380°F.) are necessary to produce a homogeneous alloy. Optimum magnetic properties are obtainable by solution treating for 15 hours at 575°C. (1070°F.) followed by water quenching and precipitation treating at 300°C. (570°F.) for 4 hours. The sintered alloy has a Brinell hardness of about 95 after quenching and 145 after the precipitation treatment.[73a]

Copper–Manganese–Phosphorus. The addition of a fraction of one per cent of phosphorus to sintered copper–manganese alloys results in precipitation-hardening materials.[72] The test results for one particular composition are reported in Volume I, Chapter XIX.

Copper–Aluminum. Binary aluminum bronzes of various aluminum contents have been produced experimentally by the author who

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[73a] C. Hardy, *private communication* (based on Laboratory Report No. 29 of Chas. Hardy, Inc., New York).

in this work employed similar processing variables as in the case of the previously mentioned copper–manganese alloys. The physical properties of the sintered and hot-pressed compacts are given in Tables 257–259. Like the copper–manganese alloys, the sintered copper–aluminum alloys are inferior in their physical properties as compared with their fused counterparts, but hot-pressing at 500°C. (930°F.) at high pressure results in nearly dense compacts of appreciable hardness. No particular advantage can be seen in employing prealloyed powders produced by a diffusion–heat treatment of mixtures of the elemental powders. If hot-pressing is carried out at 600°C. (1110°F.), *i.e.*, above the melting point of aluminum, and if oxidation of aluminum is prevented by the addition of 1–2% of lampblack or titanium hydride to the powder mixture, complete consolidation can be achieved at the moderate pressure of 15 tsi. A subsequent solution treatment at 800–850°C. (1470–1560°F.) pro-

TABLE 260
Hardness of Sintered and Coined Copper–Aluminum–Iron Alloys[a]

Treatment	Brinell hardness	
	Alloy A 83–10–7 Cu–Al–Fe	Alloy B 84–11.5–4.5 Cu–Al–Fe
Compacted at 45 tsi and sintered in hydrogen at 600 °C. (1100 °F.) for 2 hr	98	—
Sintered in hydrogen at 650 °C. (1200 °F.) for 4 hr	—	100
Compacted at 65 tsi and sintered in hydrogen at 650 °C. (1200 °F.) for 20 hr	—	110
Coined at 45 tsi	—	120
Coined at 65 tsi	—	128
Sintered alloy water quenched from 750 °C. (1380 °F.) after reheating in charcoal pack at 760 °C. (1400 °F.) for 2 hr	75	90
Coined alloy water quenched from 750 °C. (1380 °F.) after reheating in charcoal pack at 760 °C. (1400 °F.) for 2 hr	—	145
Sintered alloy precipitation treated at 300 °C. (570 °F.) for 2 hr	87	—
Sintered alloy precipitation treated at 240 °C. (465 °F.) for 2 hr	—	125
4 hr	—	124
8 hr	—	120
Coined alloy precipitation treated at 240 °C. (465 °F.) for 2 hr	—	166
4 hr	—	175
8 hr	—	171

[a] Courtesy Charles Hardy, Inc., New York, N. Y. Data abstracted from Laboratory Report No. 16

duces a homogeneous structure and physical and chemical properties comparable with those of the fused alloy. A 95–5 Cu–Al alloy compact prepared in this manner exhibited a density of 8.23 g./cc., a Brinell hardness of 88, and a compressive strength of 97,000 psi for 0.1-in. compression; a similarly produced compact from a 90–10 Cu–Al powder mixture exhibited a density of 7.70 g./cc., a Brinell hardness of 97, and a compressive strength of 107,000 psi for 0.1-in. compression. Thus, it appears that hot-pressing in the presence of a liquid aluminum phase, analogous to the cases of copper–zinc and copper–tin, produces a material of excellent physical properties that could find potential use in dense structural parts, such as gears or bearings for maritime applications.

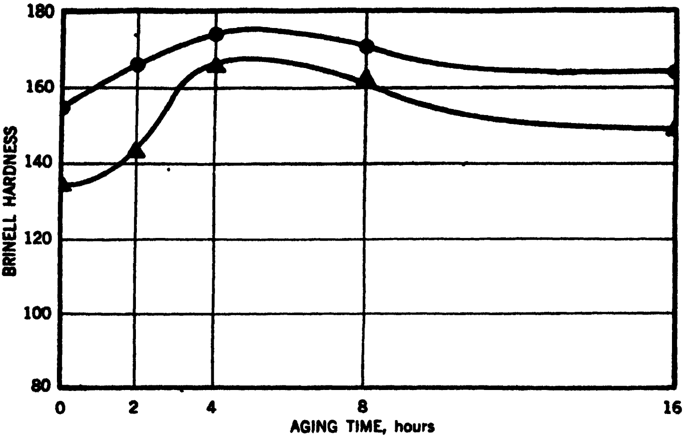

Fig. 602. Effect of aging time on the Brinell hardness of sintered 84–11.5–4.5 copper–aluminum–iron alloy. Compacts were produced from a mixture of the elemental powders by pressing at 45 tsi, and sintering in hydrogen for 20 hours at 650°C., 1200°F. One series (●) was repressed at 45 tsi and resintered at 760°C., 1400°F. for 2 hours; the other series (▲) was directly resintered at 760°C., 1400°F. for 2 hours. All compacts were precipitation treated at 240°C. (465°F.) for the time indicated after water quenching from the resintering temperature.

Alloys containing 5, 10, and 20% have recently[73b] been produced in a state of partial equilibrium by controlling diffusion during sintering. The properties were found to be largely dependent upon the degree of diffusion obtained, and to a lesser extent upon the purity of the ingredients. The alloys were appraised for their possible use as bearing materials.

Copper–Aluminum–Iron. Alloys of the system copper–alu-

[73b] E. Nachtigall, *Proc. International Powder Metallurgy Conference*, Graz, July 12–17, 1948, Referate No. 30.

minum–iron, with 10–12% Al and 4–7% Fe, can be precipitation treated without materially impairing their chemical resistivity to salt water or sulfuric acid. In Table 260, hardness values are given for two slightly different sintered alloys after sintering and aging. An increase in hardness from about 100 to 175 Brinell units gives an indication of the effectiveness of the precipitation treatment. This is apparent from Figure 602, which shows precipitation-hardening curves for an alloy containing 11.5% Al and 4.5% Fe. Compacts of this composition were compressed

TABLE 261

Hardness of Sintered and Coined Copper–Aluminum–Nickel–Iron Alloy (79–10–8–3 Cu–Al–Ni–Fe)[a]

Treatment	Brinell hardness
Compacted at 25 tsi and sintered in hydrogen at 650 °C. (1200 °F.) for 18 hr.	50
Coined at 25 tsi	60
Compacted at 50 tsi and sintered in hydrogen at 650 °C. (1200 °F.) for 18 hr.	72
Coined at 50 tsi	88
Sintered alloy water quenched from 750 °C. (1380 °F.) after reheating in charcoal pack at 760 °C. (1400 °F.) for 2 hr.; initially compacted at 25 tsi	50
50 tsi	60
Coined alloy water quenched from 750 °C. (1380 °F.) after reheating in charcoal pack at 760 °C. (1400 °F.) for 2 hr.; compacted and coined	
at 25 tsi	72
at 50 tsi	88
Sintered alloy initially compacted at 25 tsi, quenched, and precipitation treated at 240 °C. (465 °F.) for 2 hr.	53
4 hr.	57
7 hr.	55
10 hr.	46
20 hr.	42
Sintered alloy initially compacted at 50 tsi, quenched, and precipitation treated at 240 °C. (465 °F.) for 2 hr.	80
4 hr.	82
7 hr.	77
10 hr.	62
20 hr.	58
Coined alloy compacted and coined at 25 tsi, quenched, and precipitation treated at 240 °C. (465 °F.) for 2 hr.	62
4 hr.	64
7 hr.	61
10 hr.	51
20 hr.	46
Coined alloy compacted and coined at 50 tsi, quenched, and precipitation treated at 240 °C. (465 °F.) for 2 hr.	102
4 hr.	112
7 hr.	100
10 hr.	75
20 hr.	70

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[a] Courtesy Charles Hardy, Inc., New York, N. Y. Data abstracted from Laboratory Report No. 50.

TABLE 262

Density, Hardness, and Compressive Properties of Sintered and Hot-Pressed 98–2 Cu–Si Compacts[a]

Type of powder	Process	Processing			Density, g./cc.	Brinell hardness (average)	Compressive strength		Total compression, %	Increase in area, %
		Pressure, tsi	Temperature °C. (°F.)	Time, min.			Max. stress, psi	In 0.1 in. compr., psi		
Powder mixture[b]	Sintered	5	700	60	4.69	11.0	18,780	10,750	40.9	50.5
		10	(1290)		5.49	14.0	39,700	27,750	41.8	56.7
		15			5.85	16.5	56,100	36,900	42.5	59.5
		25			6.40	23.0	66,900	47,000	43.4	74.7
		50			7.05	34.25	93,500	56,500	47.3	92.5
		5	900	60	5.03	11.5	64,600	44,400	55.5	63.0
		10	(1650)		5.83	14.25	93,500	53,000	56.1	80.5
		15			6.10	16.5	105,700	55,900	57.4	95.3
		25			6.97	23.0	147,900	67,000	60.3	130.4
		50			7.17	31.75	149,000	66,900	59.9	131.1
	Hot-pressed	5	400	10[d] + 1[e]	6.32	41.75	20,480	—	5.17	6.21
		10	(750)		6.66	50.0	27,000	—	5.45	8.08
		15			7.14	65.5	35,500	—	6.61	12.12
		25			7.70	77.75	57,000	—	13.79	18.81
		50			8.38	112.0	82,900	—	25.00	37.05
		5	600	10 + 1	7.43	57.0	97,200	57,700	43.4	70.8
		10	(1110)		7.89	75.0	114,000	64,000	47.2	91.3
		15			8.33	84.75	115,900	65,300	49.8	97.7
		25			8.58	86.0	119,400	66,600	50.2	100.7
		50			8.63	90.75	123,000	66,900	49.7	103.7

Alloy powder[c]	Sintered	5	700 (1290)	60	4.63	—	8,240	—	23.17	—
		10			5.52	9.75	22,440	16,800	34.11	43.8
		15			5.98	13.25	42,500	32,500	40.3	51.7
		25			6.70	17.5	73,000	47,000	47.0	74.0
		50			7.21	22.5	97,450	55,000	50.5	91.9
		5	900 (1650)	60	4.36	—	8,950	6,960	41.6	50.5
		10			5.52	8.25	54,900	24,800	52.0	76.3
		15			5.90	11.5	82,100	42,000	56.4	97.9
		25			6.36	14.75	114,400	54,600	58.4	108.8
		50			7.05	19.0	154,300	64,000	66.1	136.0
	Hot-pressed	5	400 (750)	10 + 1	6.50	36.0	17,100	—	9.94	9.14
		10			6.96	45.75	24,550	—	13.56	13.67
		15			7.44	60.75	33,300	—	16.60	18.96
		25			8.02	83.25	48,250	—	17.35	19.23
		50			8.38	111.0	77,700	—	17.75	20.50
		5	600 (1110)	10 + 1	7.48	50.25	53,500	33,300	33.23	47.7
		10			8.08	68.0	68,800	53,000	37.39	59.7
		15			8.38	81.25	87,900	57,900	40.0	77.0
		25			8.65	95.5	107,500	66,000	43.3	80.1
		50			8.65	95.75	114,000	63,900	40.4	77.5

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[a] Author's investigation, unpublished data.

[b] Electrolytic copper and metallic silicon powders of 100-mesh grades with 35% of −325-mesh fraction.

[c] Powder mixture diffusion-alloyed by heating at 700°C. (1290°F.) for 4 hours in hydrogen; pulverized and annealed at 550°C. (1020°F.) for 1 hour in hydrogen.

[d] Time of drawing at temperature.

[e] Time of pressure dwelling at temperature.

TABLE 263

Density, Hardness, and Compressive Properties of Sintered and Hot-Pressed 96–4 Cu–Si Compacts[a]

Type of powder	Process	Processing			Density, g./cc.	Brinell hardness (average)	Compressive strength		Total compression, %	Increase in area, %
		Pressure, tsi	Temperature °C. (°F.)	Time, min.			Max. stress, psi	In 0.1 in. compr., psi		
Powder mixture[b]	Sintered	5	700	60	4.63	9.75	12,900	8,800	34.85	2.65
		10	(1290)		5.29	13.75	38,100	26,050	36.85	34.25
		15			5.50	17.0	52,700	36,000	36.95	41.6
		25			6.27	25.5	58,900	38,800	37.25	47.5
		50			6.63	31.25	68,900	46,600	39.5	54.5
		5	900	60	4.91	11.25	43,500	23,900	48.9	73.4
		10	(1650)		5.44	14.25	91,400	41,400	55.2	96.4
		15			5.64	16.5	108,800	56,000	56.5	111.2
		25			6.50	32.25	171,800	75,500	57.4	112.3
		50			6.85	38.5	159,900	69,900	55.7	109.9
	Hot-pressed	5	400	10[d] + 1[e]	6.00	41.75	17,700	—	4.08	5.82
		10	(750)		6.30	48.25	25,900	—	8.91	12.42
		15			6.72	59.25	38,800	—	11.03	16.42
		25			7.19	79.0	52,000	—	15.58	28.85
		50			7.70	102.25	81,900	—	25.58	51.25
		5	600	10 + 1	7.25	63.0	126,500	56,500	63.8	99.8
		10	(1110)		7.70	81.0	125,300	69,000	59.9	106.1
		15			7.95	92.25	131,400	65,300	59.6	117.1
		25			8.13	98.75	146,200	65,000	59.0	132.8
		50			8.23	98.75	135,000	64,200	57.3	115.1

Alloy powder[c]	Sintered	5	700 (1290)	60	—	—	—	—	—	—
		10			—	—	—	—	—	—
		15			5.17	—	5,660	—	16.1	—
		25			5.67	—	9,590	—	17.5	—
		50			6.52	15.5	26,400	—	23.8	—
		5	900 (1650)	60	—	—	—	—	—	—
		10			5.02	—	3,500	—	16.84	—
		15			5.40	—	8,800	—	24.45	—
		25			5.78	9.5	14,730	—	27.35	17.17
		50			6.55	14.75	47,700	—	38.24	47.6
	Hot-pressed	5	400 (750)	10 + 1	5.83	32.25	13,650	—	5.18	6.21
		10			6.16	40.25	19,550	—	5.76	7.15
		15			6.54	49.25	26,390	—	8.08	8.08
		25			6.93	63.5	38,000	—	12.35	12.72
		50			7.45	83.25	62,600	—	15.15	24.24
		5	600 (1110)	10 + 1	6.70	47.0	32,050	—	9.35	—
		10			7.04	55.75	47,000	—	13.33	12.53
		15			7.41	63.75	65,500	—	21.48	21.75
		25			7.89	92.5	115,700	65,700	31.46	61.5
		50			8.18	122.0	122,410	72,600	52.7	122.2

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[a] Author's investigation, unpublished data.

[b] Electrolytic copper and metallic silicon powders of 100-mesh grades with 35% of −325-mesh fraction.

[c] Powder mixture diffusion-alloyed by heating at 700°C. (1290°F.) for 4 hours in hydrogen; pulverized and annealed at 550°C. (1020°F.) for 1 hour in hydrogen.

[d] Time of drawing at temperature.

[e] Time of pressure dwelling at temperature.

at 65 tsi from a mixture of the elemental powders, and first sintered for a considerable time (20 hours) at a temperature immediately below the melting point of the aluminum (650°C.; 1200°F.); a final sintering treatment was carried out at 750°C. (1380°F.) for 2 hours, the specimens then being water quenched and precipitation treated at 240°C. (465°F.) for 4 hours. The effect of intermediate coining at 45 tsi was investigated on an alternate set of specimens.

Copper–Aluminum–Nickel–Iron. The precipitation-hardening characteristics of the copper–aluminum–iron alloys are not destroyed, though reduced, by the addition of nickel, whereas the malleability appears to be slightly improved. In Table 261, the hardness is shown for a sintered alloy containing 10% Al, 8% Ni, and 3% Fe after various stages of production. The maximum Brinell hardness of 112 is considerably below the hardness values obtained with the nickel-free alloy.

Copper–Silicon. Binary copper–silicon alloy compacts containing 2 and 4% Si were prepared by the author in a manner similar to that previously described for copper–manganese alloys. The physical propperties of the sintered and hot-pressed compacts are given in Table 262 and 263. They are inferior to those of the wrought or cast alloy, with the exception of the density, which reached equivalent figures in hot-pressed compacts that were pressed at 600°C. (1110°F.) at 25 and 50 tsi. The strong tendency of the powdered silicon to combine with oxygen at elevated temperature deprives the material of the alloying benefits that the element imparts to the fused alloy. Instead, stable silica inclusions are produced in abundance during sintering; naturally, the structure is consequently weakened. Prealloying by diffusion treatment of the mixed powdered ingredients does not prevent this effect. The addition of a pulverized, silicon-rich fused master alloy would offset the oxidation effect, but at the same time the compactibility of the mixture would be impaired to an extent that would make production molding very difficult. Probably because of these manufacturing difficulties and the generally unsatisfactory properties obtained so far with these alloys, no industrial applications have become known.

Copper–Beryllium. Sintered copper alloys containing about 2% Be can only be produced with difficulty. Analogous to the copper–silicon alloys, the strong oxidizing tendency of powdered beryllium prevents effective diffusion during sintering. If a pulverized beryllium-rich fused master alloy is added instead of the pure metal powder, the danger of oxidation is lessened, but the compactibility is consequently reduced. Sintering in high vacuum at 850°C. (1560°F.) for a minimum of 6 hours produces homogeneity of the structure in the case of mixed elemental components, but the addition of 1% lampblack is advantageous as an additional precaution against oxidation. After reheating in hydrogen to 800°C. (1470°F.), water quenching and precipitation-treating at 300°C. (570°F.) for 4 hours, a compact of 92% density was found to have a Brinell hardness of 270 as compared with 96 after quenching.[78c] Because of the inherent difficulties in producing this type of alloy by powder metallurgy methods, no industrial applications have so far been developed.

Copper–Cobalt–Beryllium. Sintered copper-base alloys containing small percentages of cobalt and beryllium are precipitation-hardenable, and have been suggested for heavy duty bearings and contacts.[72] Test results obtained with one particular composition have been reported in Volume I, Chapter XIX.

Copper–Cobalt–Phosphorus. Test results[72] with a copper–cobalt alloy in which the beryllium was replaced by phosphorus as third component have also been given in Volume I, Chapter XIX.

Copper–Chromium–Phosphorus. The precipitation hardening of a ternary copper-base alloy containing a small percentage of chromium and a fraction of one per cent phosphorus[72] has also been reported in Volume I, Chapter XIX.

Copper–Lead. Since the metals copper and lead are practically insoluble in the solid state and produce a large miscibility gap from about 38 to 93% Pb in the liquid state, only copper-rich alloys can be produced by centrifugal casting, while special casting and chilling techniques are necessary for alloys with more than 30% Pb. But compositions containing from 30 to 50% Pb exhibit good bearing properties, especially for heavy duty applications. Therefore, this type of alloy offers an excellent opportunity for the powder metallurgy approach. Various methods have been developed to assure maximum dispersion and minimum loss of lead during sintering, which operation must necessarily be carried out at temperatures above the melting point of the metal.

One method widely used today in the manufacture of copper–lead bearings is based on a powder obtained by the liquid disintegration of a copper–lead emulsion kept in constant turbulence (see Volume I, Chapter III); since the lead inclusions in each particle are only of microscopic size, they are not capable of coagulating to any great extent during sintering, with the result that lead losses by sweat-out are kept to a minimum.

Another method is based on the production of copper-coated lead powder, either by electrolysis or by chemical replacement (see Volume

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[78c] C. Hardy, *private communication* (based on Laboratory Report No. 88 of Chas. Hardy, Inc., New York).

I, Chapters III and VI, and also Figure 12A). Although the individual lead globules are considerably coarser (there is only one lead globule inside each coated particle, whereas there are many lead inclusions of minute size in each fusion-disintegrated particle), lead losses remain negligible up to a sintering temperature of 700°C. (1290°F.). The microstructure of a 60–40 Cu–Pb alloy from coated powder after sintering for 12 hours at 700°C. (1290°F.) has been previously shown in Figure 541, Chapter XXVI. Recrystallization and a coalescence of the copper coatings into larger grains during sintering open the path for the liquid lead to escape from the copper envelopes and to form liquid films around the newly formed copper grains. Upon solidification, a nearly continuous network of lead is formed, which is believed to be essential for the performance of the bearing.

TABLE 264

Density and Hardness of Sintered and Coined Copper–Lead–Tin–Nickel Alloys (71-25-3-1 Cu-Pb-Sn-Ni)[a]

Alloy	Treatment					Properties	
	Compacting pressure, tsi	Sintering temperature		Time, hr.	Coining pressure, tsi	Density, g./cc.	Brinell hardness
		°C.	°F.				
A[b]	25	550	1020	1	—	7.77	24.5
	25				25	8.50	35.0
	50				—	8.20	47.0
	50				50	8.88	54.5
B[c]	25	700	1290	1	—	7.57	15.0
	25				25	8.53	39.0
	50				—	7.55	19.0
	50				50	9.10	70.0

[a] Courtesy Charles Hardy, Inc., New York, N. Y. Data abstracted from Laboratory Report No. 78.

[b] Alloy prepared from mixture of elemental powders: electrolytic copper, atomized lead, atomized tin, carbonyl nickel, all −325 mesh.

[c] Alloy prepared from mixture of copper-coated lead powder (60–40 Cu–Pb), electrolytic copper, atomized tin, carbonyl nickel, all −325 mesh.

Copper–Lead–Tin. Ternary and more complex alloys of the copper–lead type can be produced by identical methods, as used in the manufacture of the binary alloys. An alloy that contains about 20% Pb, 5% Sn, balance Cu is suitable for seal rings and bushings in hydraulic and refrigeration machinery. It can be produced readily with ternary fusion-disintegrated alloy powder or with heavily copper-coated lead powder to which the tin powder is added. In the latter case diffusion is obtained during sintering at 600°C. (1110°F.) for 1 hour. An alloy compacted at 50 tsi has a final density of about 8.0 g./cc. and a Brinell hardness of about 70.

Copper–Lead–Tin–Nickel. No appreciable difference in hardness or density is obtained if part of the tin in the ternary alloy is replaced by nickel. Table 264 gives these properties for an alloy containing 25% Pb, 3% Sn, and 1% Ni and prepared from a mixture of 60–40 copper-coated lead powder, 325-mesh copper and tin powders, and carbonyl nickel.

Copper–Silver. Alloys of copper and silver can be produced by powder metallurgy, but sintering is advantageously carried out in vacuum because of the tendency of finely divided silver to absorb considerable quantities of hydrogen and other gases. The sintering temperature must be below 780°C. (1435°F.)—the eutectic temperature of the binary system. Small percentages of silver (up to 3%), silver–cadmium, silver–zinc, and silver–antimony produce slight increases in hardness of sintered copper.[74] Table 265 shows the hardness of these alloys—and of some containing small percentages of cadmium and zinc—in various stages of processing. Sintered copper–silver alloys have been suggested as contact metals, but it is not known to the author whether they have found commercial application.

Copper–Carbon. Composite structures of copper and graphite for electrical products are discussed in Chapter XXIII.

Silver and Silver Alloys

SILVER

Silver can be sintered without difficulty from very pure silver powder, and the product has excellent forming properties. The powdered raw material is obtained by various methods, including atomizing of high purity silver, precipitation from silver chloride in HCl solution with zinc, electrolysis, or fine granulation. The hardness of sintered silver obtained from fine silver powder is but slightly superior to that obtained from coarser powder. In contrast to other metals, it was found that the density decreases with increasing sintering temperature; this phenomenon may be attributed to occluded or absorbed gases or to the relief of excessive stresses lodged in highly compressed compacts. In analogy to other metals, it is possible to obtain mechanical properties of sintered silver almost identical to those of the cast product by subjecting the former to subsequent hot- or cold-working.

Sintered silver has a potential field of application in the bearing metal, contact metal, and jewelry industries. Additional data on manufacture and properties are given in Chapters XXVI and XXXI.

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[74] C Hardy, *Metal Progress, 36,* No. 1, 57 (1939).

TABLE 265

Hardness and Size Changes in Sintered and Coined Copper Alloys Containing Minor Additions of Silver, Cadmium, Zinc, and Antimony (Hardy[74])

Addition[a] to copper[b]	Size before sintering, mm.		After first sinter			After first repress			After second sinter			After second repress			After reheat 1 hr. at 235°C. Brinell hardness
			Size, mm.		Brinell hardness	Size, mm.		Brinell hardness	Size, mm.		Brinell hardness	Size, mm.		Brinell hardness	
	Diam.	Height	Diam.	Height		Diam.	Height		Diam.	Height		Diam.	Height		
None	30.7	17.6	30.3	17.3	46	30.7	15.8	74	30.7	15.7	48	30.7	15.3	67	67
1.0% Ag	30.7	17.6	30.3	17.3	44	30.7	15.8	78	30.7	15.7	48	30.7	15.4	67	70
2.5% Ag	30.7	17.6	30.3	17.4	44	30.7	15.9	78	30.7	15.8	50	30.7	15.4	70	71
1.0% Cd	30.7	17.6	30.5	17.3	45	30.7	15.9	75	30.7	15.8	50	30.7	15.4	65	69
2.5% Cd	30.7	17.6	30.8	17.4	39	30.7	16.0	74	30.7	16.0	50	30.7	15.5	70	69
1.5% Zn	30.7	17.6	30.4	17.0	47	30.7	15.9	74	30.7	15.8	56	30.7	15.5	70	71
3.0% Zn	30.7	17.6	30.4	17.5	43	30.7	15.9	77	30.7	15.9	56	30.7	15.6	71	71
1.5% Ag_2Cd_3	30.7	17.5	30.9	18.1	40	30.7	16.3	74	30.9	16.6	49	30.7	15.9	74	77
3.0% Ag_2Cd_3	30.7	17.5	31.1	17.9	34	30.7	16.0	77	31.5	16.6	43	30.7	15.7	74	77
1.5% Ag_2Zn_5	30.7	17.6	30.5	17.5	47	30.7	16.0	80	30.7	16.0	55	30.7	15.7	74	80
3.0% Ag_2Zn_5	30.7	17.8	30.5	17.8	44	30.7	16.0	80	30.7	16.0	51	30.7	15.7	72	80
1.5% Ag_2Sb	30.7	17.7	30.7	17.9	45	30.7	16.2	80	30.8	16.4	50	30.7	15.9	71	78
3.0% Ag_2Sb	30.7	17.7	30.8	18.1	39	30.7	16.3	80	31.2	16.7	50	30.7	16.2	72	80
1.5% Zn_5Sb_2	30.7	17.8	30.5	17.5	46	30.7	16.0	83	30.7	16.0	60	30.7	15.8	73	80
3.0% Zn_5Sb_2	30.7	17.8	30.6	17.5	49	30.7	16.1	86	30.7	16.1	60	30.7	15.7	76	80

[a] All ingredients added in form of elemental powders, −325 mesh.

[b] From −325-mesh electrolytic copper powder.

SILVER ALLOYS

Silver–Iron. Mechanical mixtures of the metals silver and iron, which are mutually insoluble in the solid state and, over a wide range, insoluble in the liquid state, have been produced[75] by sintering below the melting point of silver, but no practical applications have yet been found for these materials. Mechanical mixtures of the system silver–iron have been investigated more recently,[75a] as already mentioned in Chapter XXVI (page 485).

Silver–Nickel. Analogous to iron and silver, nickel and silver are practically insoluble in each other in the solid and liquid states. Composite structures have been produced[75a] by sintering below the melting point of silver. For silver-rich compositions, the method of infiltrating molten silver into a nickel skeleton is feasible. The industrial applications of silver–nickel compositions, with and without the addition of tungsten, molybdenum, and cadmium for contact metals, are described in Chapter XXIII.

Silver–Copper. The metals silver and copper form a eutectic at 780°C. (1435°F.) and are not entirely soluble in the solid state. Sintered alloys have been tested for the purpose of obtaining scientific data, and especially for the purpose of finding the reactions of materials to be sintered in the presence of a liquid phase.[75–79] If sintered below the eutectic temperature, diffusion rates are very slow[75a] (see also Chapter XXVI, page 485), and a porous product is obtained in all cases. On the other hand, by increasing the sintering temperature above the eutectic temperature, density values are obtained which are practically identical with those of the fused alloy, an effect caused by the predominance of processes connected with the liquid phase present over the particular solubility of the components in the solid state. For the eutectic composition (72% Ag), sintering above 780°C. (1435°F.) results in liquefaction of the whole specimen, *i.e.*, at a temperature far below the melting points of either of the elements. The hardness of the material sintered below the liquid range lies between the hardness values of the elements in accordance with the volumetric proportion of either in the duplex structure. This, however, does not apply to the material sintered at higher temperatures, where, owing to the alloying effect, an increased

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[75] G. Comstock, *Metal Progress, 35,* No. 6, 576 (1939).

[75a] E. Raub and W. Plate, *Proc. International Powder Metallurgy Conference,* Graz, July 12–17, 1948, Referate No. 4.

[76] G. H. S. Price, C. J. Smithells, and S. V. Williams, *J. Inst. Metals, 62,* 239 (1938).

[77] W. D. Jones, *Metal Treatment, 5,* 13 (1939).

[78] F. V. Lenel, *Trans. Am. Inst. Mining Met. Engrs., 175,* 878 (1948).

[79] G. Masing, *Z. anorg. Chem., 51,* 330 (1906); *62,* 265 (1909).

hardness can be obtained. This effect is a marked exception to the general tendency of hardness to decrease with increasing sintering temperature.

Further data on silver–copper alloys are given under copper alloys, and also in Chapter XXVI.

Silver–Copper–Nickel. Sintered alloys of this system may be suitable for jewelry, cutlery, or coins; they are discussed in Chapter XXVI.

Silver–Tungsten. Composite contact compositions of the silver–tungsten type are described in detail in Chapter XXIII. While for contacts, compositions of high silver concentration play a less important role than those in which the tungsten constitutes the predominant phase, they are believed to be a potential heavy duty bearing material, especially if the silver is alloyed with minor addition elements such as cadmium, lead, or indium.

Silver–Molybdenum. Analogous to silver–tungsten, silver–molybdenum compositions serve also as contact materials, and, as such, are described in Chapter XXIII.

Silver–Lead. Alloys of this binary system have also been investigated to obtain scientific data on the constitution and solubility conditions.[75a] The system has a eutectic composition with 2.5% Ag, melting at 304°C. (575°F.). The conditions regarding changes in solubility are similar to those with silver–copper and tungsten–copper–nickel alloys. Therefore, silver–lead alloys show a correspondingly high density if sintered in the liquid range.[76] A convenient way of producing these alloys is by infiltrating molten lead into a sintered porous silver compact. Alloys of this system may find industrial applications as bearing materials.

Silver–Cadmium. Sintered alloys of silver with cadmium,[75a] with and without additions of copper may find applications as contact materials, and have as such been mentioned in Chapter XXIII.

Silver–Zinc and Silver–Antimony. Silver alloys with zinc or antimony—with and without additions of copper—have also been produced by sintering,[74,75a] but no particular uses for this material have yet been found.

Silver–Tin. Alloys of the system silver–tin are essential materials for dental amalgams. The silver–tin master alloys are first fused and then pulverized and mixed with mercury before insertion into the dental cavity. The metallurgy of dental alloys is described in more detail in Chapter XXIX.

Silver–Carbon. Contact metal compositions containing mechanical mixtures of silver and graphite in various proportions have been described in Chapter XXIII. Composite materials of this general type may also be used in the future as bearing materials,

Precious Metals and Their Alloys

GOLD

Sintered gold specimens have been investigated for purely theoretical considerations.[80] Comparisons between sintered gold produced from hydrochloroauric acid and gold produced by fusion are given in Chapter XXXI, Table 235. The material sintered with lower compacting pressure shows a steady increase in density with increasing sintering temperature; however, the opposite tendency can be observed—in fact, more pronounced—when compacts are formed at extremely high compacting pressure (cf. Vol. I, p. 512, Fig. 193). This phenomenon may be attributed to alkaline impurities used in the production of the gold powder and to gas pockets. (High sintering temperatures may cause sudden gas eruptions, thus reducing the density.) With hot-pressing, a density of 19.11 g./cc. can be obtained, which is only 0.5% below the theoretical value. Corresponding values are obtained for hardness, showing the essential influence of compacting pressure on the results. Tests relating to the electrical resistivity of hot-pressed gold show a tendency similar to that of copper specimens[80] (see also Volume I, p. 541).

Sintered gold has found few applications to date. Besides being used occasionally for coins and medallions, the only recent application of significance is as carrier metal for radioactive materials. This development has been described in greater detail in Chapter XXVI, and is further treated in this chapter on page 743.

GOLD ALLOYS

Alloys of gold with silver, copper, and nickel can be produced by sintering,[75a] *e.g.*, for prolonged times below 950°C. (1740°F.); in the case of gold–silver compositions, the treatment can be carried out in air, while alloys containing copper or nickel require a protective sintering atmosphere. Sintered ternary alloys containing about 60% Au and 20% each of Ag and Cu, corresponding to 14 carat gold, have been used for coins and medallions; because of the greater hardness of the alloy, these articles displayed superior wear resistance over their counterparts from pure gold.

PLATINUM

The powder metallurgy of platinum[80a] constitutes the basis for the modern industrial development of sintered refractory metals (for details of this historical work see Volume I, Chapter II).

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[80] W. Trzebiatowski, *Z. physik. Chem.*, *A169*, 91 (1934); *B24*, 75 (1934); *B24*, 87 (1934).

[80a] W. H. Wollaston, *Phil. Trans. Roy. Soc.*, *119*, 1 (1829).

Although the melting of platinum on a large scale no longer presents any difficulties, the sintering process is still used occasionally for the production of very pure platinum.[81] The manufacture of very pure platinum by sintering is still carried out by precipitating very pure platinum powder by organic reducing agents. The dry powder is then compacted in a steel die at a pressure of about 5 tsi. As in the case of tungsten, the compacted bar is sintered by resistance heating through the direct passage of current (or by other methods) to a temperature near its melting point; its grain size can likewise be controlled by the addition of 0.1–1.0% ThO_2 to the powder.[82] In order to improve ductility, it is advisable to forge the sintered product. The various stages of the manufacturing process can be followed by considering the increase in density as the process progresses; actual density values are as follows:[83]

Stage	Density, g./cc.
Wet platinum mud	4.3
Wet-compacted pieces	10.0
Highly sintered pieces	17.0–17.7
Forgings	21.25
Drawn platinum bar	21.4

Sintered platinum is somewhat superior to the fused product (see also Table 235, Chapter XXXI) with regard to its metallurgical and physical performance,[84] which may be attributed to the fact that absorption of gases and impurities from the furnace lining is avoided in the sintering process. This subject is also discussed in Chapter XXVI.

Recent experimental data[84a] indicate a markedly superior creep resistance in wire produced from sintered ingots, as compared with conventionally produced wire—for which fact an inherent porosity having the effect of hindering recrystallization is believed responsible at least in part. This may be considered of significance in view of possible analogies to be found in other refractory metals and heat-resistant alloys.

PLATINUM ALLOYS

The production of platinum alloys by the sintering technique is chiefly of historic interest. Alloys containing from 26–72% Pt, 16–64%

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[81] R. H. Atkinson and A. R. Raper, *J. Inst. Metals, 59,* 179 (1936).

[82] Brit. Pat. 578,956.

[83] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe.* Springer, Berlin, 1943, p. 219.

[84] D. McDonald, *Chemistry & Industry, 9,* 1031 (1931).

[84a] A. B. Middleton, L. B. Pfeil, and E. C. Rhodes, *J. Inst. Metals, 75,* 595 (1949).

Au, 3–15% Ag, and up to 4% Cu were produced by the Incas in Ecuador.[85] Lately, sintering studies have been reported for platinum-iridium alloys containing from 10 to 50% Ir.[86] Complete homogenization of the alloys was obtained by vacuum sintering at 1300–1500°C. (2370–2730°F.). The constitution of the binary systems of platinum with iron, cobalt, and nickel (and order–disorder transformations as caused by superstructures) has been investigated with the aid of alloy powders made from the platinocyanates by heating in hydrogen at 500–600°C. (930–1110°F.).[87]

Platinum–tungsten alloys were recently investigated[88] over the range of 25–100% W. It was found that the solidus temperature of the alloys appears to be influenced considerably by the purity of the tungsten component. The melting point of the platinum solid solution is increased to 2460°C. (4460°F.) at 65% W, at which composition a peritectic reaction between the liquid phase and a tungsten solid solution apparently occurs. The alloys rich in tungsten are hard, brittle, and nonworkable. A significant hardness maximum (of 880 Vickers *vs.* 160 for pure sintered tungsten) was observed at the limit of solid solubility of 5% Pt in tungsten. However, addition of platinum to tungsten does not improve the oxidation resistance at 1205°C. (2200°F.) materially until the composition of the alloys is well within the platinum solid solution (*i.e.*, 50% Pt minimum). On the other hand, small additions of tungsten to platinum have apparently no effect on the stability of the latter at 1425°C. (2600°F.) in still air.

IRIDIUM

The experimental production of pure iridium metal by the sintering technique has been reported,[89] but nothing is known about the quality of the material.

OSMIUM

Sintered osmium has only historic interest today. As stated in Volume I, Chapter II, filament wires were made in 1900 by mixing osmium powder with organic binders and extruding the plastic mixture in diamond dies. The threads thus obtained were then heated just below the melting

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[85] P. Bergsøe, *Ingeniørvidenskab. Skrifter, A,* No. 44 (1937).

[86] O. E. Zvyagintsev, A. G. Bakhshtadt, and M. A. Vladimirova, *Metallurgia, 34,* No. 202, 195 (1946); see also *Metal Powder Rept., 1,* No. 2, 24 (1946).

[87] L. Weil, *Compt. rend., 224,* No. 12, 923 (1947); see also *Metal Powder Rept., 2,* No. 1, 12 (1947); *Powder Metallurgy Bull., 3,* No. 6, 130 (1948).

[88] R. I. Jaffee and H. P. Nielsen, *Trans. Am. Inst. Mining Met. Engrs., 180,* 603 (1949).

[89] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe.* Springer, Berlin, 1943, p. 218.

point of the metal in vacuum or a reducing atmosphere. The organic substance evaporated leaving a porous, brittle filament wire.[89] Later, however, this method was superseded by the more efficient and economical manufacture of tungsten filaments.

PALLADIUM, RHODIUM, AND RUTHENIUM

To the best of the author's knowledge, no experimental results are available for these metals except the historic report by Wollaston, who in 1805, obtained very fine rhodium powder by reducing sodium rhodium chloride with hydrogen.[90]

Refractory Metals and Their Alloys

TUNGSTEN

The powder metallurgy of tungsten is described extensively in Chapter XXI.

TUNGSTEN ALLOYS

The alloys of tungsten with other refractory metals, such as molybdenum, tantalum, columbium, and thorium, and with iron, nickel, and nickel and copper are also discussed in Chapter XXI; the hard metal structures based on tungsten carbide are described fully in Chapter XXII, and the composite structures which tungsten forms with such metals as copper and silver are discussed within the framework of electrical contact materials in Chapter XXIII.

Tungsten–Rhenium. Alloys of rhenium and tungsten with various rhenium concentrations have been prepared by compacting mixtures of the elemental powders and sintering in a bell-type furnace in reducing atmosphere at temperatures near the melting point of rhenium (about 3200°C.; 5400°F.).[91] Melting of the sintered alloys in the electric arc enabled the establishment of the tungsten–rhenium phase diagram as shown in Figure 603, but no practical applications have been reported so far for these alloys.

Tungsten–Chromium. Alloys of the system tungsten–chromium are very hard and brittle, but can be produced readily by compacting mixtures of the elemental powders and sintering in hydrogen at 1625°C. (2960°F.).[92] The constitution of the system is not yet clarified, with

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[90] A. W. Deller, in J. Wulff, *Powder Metallurgy*. Am. Soc. Metals, Cleveland, 1942, p. 551.

[91] K. Becker and K. Moers, *Metallwirtschaft*, *9*, 1063 (1930).

[92] C. J. Smithells, *Tungsten*. 2nd ed., Chapman & Hall, London, 1936.

evidence of a limited solubility at the tungsten side of the system.[98,98a] Alloys in which tungsten is the predominant phase have been used as wire-drawing die material, and compositions in which both metals are represented about equally have been suggested for high-temperature service, requiring high heat and corrosion resistance. For additional information the reader is referred to the section on chromium alloys (page 691).

Tungsten–Silver. Of the composite-type tungsten-base alloys, tungsten–silver compositions have been found to be excellent for certain heavy duty bearing materials, especially for applications that involve extra heavy loads, or where the bearing must form a seal against high pressures.

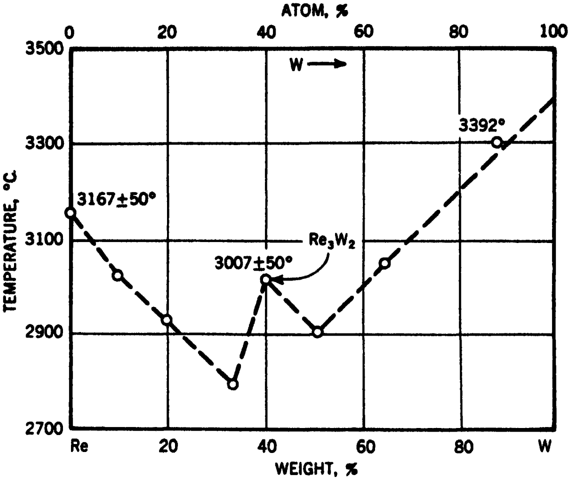

Fig. 603. Fusion temperature diagram for the system tungsten–rhenium (according to Becker and Moers[91]).

Tungsten–Lead. Composite structures of tungsten and lead are believed to be applicable for the same purpose. One source[94] has reported that a material containing 70% W and 30% Pb is superior to most of the presently employed heavy duty bearing alloys, chiefly because of its favorable coefficient of friction, which is lower than that encountered in conventional copper–lead alloys. A material of the above composition has a density of 15.4 g./cc. and a Brinell hardness of about 108 at room

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[98] O. Kubaschewski and A. Schneider, *Z. Elektrochem.*, *48*, 671 (1942).

[98a] W. Trzebiatowski, H. Ploszek, and J. Lobzowski, *Anal. Chem.*, *19*, 93 (1947).

[94] C. Hardy, *private communication*, based on information obtained from P. R. Mallory & Co., Indianapolis, Ind.

temperature. The decrease in hardness with rising temperatures is indicated in Table 266.

The production of such alloys has been attempted by compacting and sintering mixtures of the powdered ingredients, since infiltration of molten lead into porous W compacts is made difficult by the poor wetting characteristics of the lead.[95] Sintering below the melting point of lead, however, does not yield a coherent and strong material for tungsten-rich compositions. Infiltration of the molten lead into the pore volume is only possible in a vacuum treatment at 400–500°C. (750–930°F.). A high-density material results if certain precautions are taken, such as thorough deoxidation of the lead, high-temperature sintering of the porous tungsten body, and caustic etching of the tungsten immediately prior to contacting with the molten lead. In fact, it was found that the method can even be used for the production of large-size plates by employing lead as a metallic binder for loosely heaped coarse-crystalline tungsten powders. Alloys of approximately 50–50 W–Pb content (by weight) with densities of about 15 g./cc. and produced at about half the cost of pure tungsten powder should find increasing interest as shielding metal against intense and penetrating radiation.

TABLE 266

Hardness–Temperature Characteristics of 70–30 W–Pb Bearing Alloy (Hardy[94])

Temperature		Brinell hardness	Temperature		Brinell hardness
°C.	°F.		°C.	°F.	
27	80	108	177	350	59
65	150	84	204	400	48
93	200	91	232	450	50
121	250	91	260	500	43
149	300	75			

MOLYBDENUM

The powder metallurgy of molybdenum has been described in Chapter XXI. The potential applications of molybdenum include such varied products as:[96]

(*1*) Heating elements for ultra high-temperature electric furnaces without element protection.

(*2*) Blades, nozzles, and firing chambers for ultra high-temperature gas turbines and rockets.

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[95] G. H. S. Price, S. V. Williams, and C. J. O. Garrard, *J. Gen. Elec. Co., London, 11,* No. 4, 1 (1941).

[96] J. Gelok, *Materials & Methods, 26,* No. 3, 86 (1947).

(*3*) Dies for die-casting brass or other alloys melting at relatively high temperatures.

(*4*) Hot and cold metal working tools of good stability and long life.

(*5*) Liners for tanks, vessels, and pipes for which corrosion properties are a factor.

(*6*) Seamless tubing and valves for the petroleum and chemical industries

(*7*) Crucibles for melting materials of very high melting points.

(*8*) High-temperature resisting barriers.

(*9*) Construction material for use at elevated temperatures.

(*10*) Dies for hot pressing, drawing, and extrusion.

During the last war, a process was developed whereby molybdenum could be produced by melting.[97] The pressed and sintered molybdenum bars are fused under controlled atmospheric conditions with an electric arc, and the molten metal is collected and solidified in a water-cooled copper mold. A special apparatus combining pressing, sintering, melting, and casting of molybdenum in vacuum makes possible the production of products of very large size.

MOLYBDENUM ALLOYS

Molybdenum-base alloys with tungsten, nickel, iron, and iron and copper have been discussed in Chapter XXI, and composite structures of molybdenum with silver have been discussed in Chapter XXIII in connection with electrical contacts.

Molybdenum–Thorium. Alloys of molybdenum and thorium can be produced either from mixtures of the metal powders or from mixtures of molybdenum, thoria, and carbon. The oxide can be completely reduced if sufficient carbon (*i.e.*, three times the theoretical amount) is added to the mixture and sintering is conducted in hydrogen. An alloy containing about 5% Th can be worked in the same way as pure molybdenum metal; wires of this composition are used as thermionic emission cathodes.[98]

Molybdenum–Chromium. Alloys of the system molybdenum–chromium, just as of the system tungsten–chromium, are very hard and brittle. They can be produced by mixing the powdered metallic ingredients and sintering the compacted mixtures in hydrogen at about 1600°C. (2910°F.). The system was found to be a continous series of solid solutions.[93a,99] No practical applications have yet been found for these alloys, but it is believed possible that compositions containing about equal weight proportions of the elements may be suitable for high-temperature

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[97] R. M. Parke and J. L. Ham, *Trans. Am. Inst. Mining Met. Engrs.*, *171*, 416 (1947).

[98] P. Schwarzkopf, *Powder Metallurgy*. Macmillan, New York, 1947, p. 186.

[99] W. Trzebiatowski and H. Ploszek, *Naturwissenschaften*, *26*, 462 (1938).

applications requiring resistance to heat and corrosion. Further reference to alloys of this system is made under chromium alloys (page 690).

Molybdenum–Copper. Molybdenum-base composite structures with copper as low-melting binder have been produced by the same process used for the manufacture of tungsten–copper and molybdenum–silver alloys. Whereas molybdenum–copper compositions are definitely advantageous from the economic point of view, their performance as contact materials is apparently somewhat inferior to that of either the molybdenum–silver or the tungsten–copper materials. Therefore, molybdenum–copper compositions are used only in special cases as contact metals.

Molybdenum–Copper–Cobalt. Sintered alloys containing approximately 40% Mo, and 30% each of Cu and Co have been suggested as matrix for diamond tools, but no other applications are known for alloys of this type.[100]

TANTALUM, COLUMBIUM, AND THEIR ALLOYS

The powder metallurgy of tantalum, columbium, and their alloys is described in Chapter XXI; the hard metal compositions based on tantalum carbide are discussed in Chapter XXII.

VANADIUM AND VANADIUM ALLOYS

Vanadium. Sintered vanadium was first used about forty years ago together with tantalum and columbium for electric lamp filaments.[101] The process used involved mixing of vanadium pentoxide powder with paraffin to aid compaction, partial reduction to vanadium trioxide by burying the oxide compacts in a mass of powdered carbon and heating for several hours at 1700°C. (3090°F.), and final dissociation of the trioxide during vacuum sintering. The resulting vanadium metal, however, was rather porous and not sufficiently ductile for easy working into wire. On the other hand, granular vanadium of high ductility can be obtained by reducing the vanadium pentoxide with metallic calcium.[102] These granules can be cold-rolled, but are too coarse for briquetting and sintering purposes. Finer particle sizes are obtainable only by pulverization of the granules (*e.g.*, in eddy mills) or by suitable modification of the calcium reduction process whereby the vanadium pentoxide is directly converted into a fine powder[103] (a purity of 99.7% has been claimed to

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[100] German Pat. 583,630.

[101] W. von Bolton, *Z. Elektrochem.*, *11*, 45 (1905).

[102] J. W. Marden and M. N. Rich, *Ind. Eng. Chem., Ind. Ed.*, *19*, 786 (1927).

[103] W. Kroll, *Z. Metallkunde*, *28*, 30 (1936).

be possible by this method.[103a]). Compacts made from this powder are hot-rollable after sintering for only a half hour at 1400°C. (2550°F.) in vacuum. The rolling operation, however, must be carried out at 1200°C. (2190°F.) while the metal is covered with a protective film of borax. The sheet exhibits a Brinell hardness of 360. Other methods of producing sintered vanadium include fusion electrolysis[104] and decomposition of vanadium iodide in contact with hot tungsten filaments (further details of this method are described under titanium, page 692).[105] The last method yields extremely pure powders, and the resulting metal is very ductile and has a Brinell hardness of only 260.

Vanadium Alloys. While fused ferrovanadium plays an important role in steel making, there appears to be no information available on vanadium alloys produced by the sintering technique.

CHROMIUM

In its purest form, the metal, chromium, also possesses some ductility. The following principal methods of producing chromium have been reported:

(*1*) Electrodeposition in solid form followed by annealing in high vacuum.[106]

(*2*) Distillation of electrodeposited chromium in high vacuum followed by remelting under argon in beryllium oxide crucibles.[106]

(*3*) Deposition from the vapor phase by dissociation of chromium iodide in contact with hot tungsten wire.[105]

(*4*) Presintering of compacts from very pure chromium powder in vacuum followed by high-temperature sintering in argon.[104]

The first three methods lead to a more or less ductile product that can be hot-forged or hot-rolled without difficulties into billets or sheet with a Brinell hardness of 120–180.[103] For the large-scale production of pure chromium, however, these methods appear less suitable than the last one. There are many ways of producing powder of sufficient purity:

(*1*) Reduction of $CrCl_3$ by sodium under pressure in a steel retort.[107]

(*2*) Reduction of $CrCl_3$ by magnesium in the presence of KCl.[108]

[103a] Discussion of J. D. Fast, *Proc. International Powder Metallurgy Conference*, Graz, July 12–17, 1948, Referate No. 20.

[104] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe*. Springer, Berlin, 1943, pp. 179–180.

[105] A. E. van Arkel, *Metallwirtschaft*, *13*, 405, 511 (1934).

[106] W. Kroll, *Z. anorg. allgem. Chem.*, *226*, 23 (1935).

[107] M. A. Hunter and A. Jones, *Trans. Electrochem. Soc.*, *44*, 23 (1923).

(*3*) Reduction of $CrCl_3$ by calcium in the presence of alkalis or their chlorides.[108]

(*4*) Reduction of Cr_2O_3 by calcium in the presence of $CaCl_2$ and $BaCl_2$.[106]

(*5*) Reduction of Cr_2O_3 by carbon and hydrogen at subatmospheric pressure. [109,110]

(*6*) Reduction of Cr_2O_3 by calcium hydride.[111]

(*7*) Mechanical comminution of electrodeposited chromium and subsequent annealing of the powder in vacuum[104] (*e.g.*, at 1250°C. (2280°F.) for 1 hour at 0.01 mm. Hg pressure[112]).

The production of ductile chromium has been described in detail.[106] A powder was used as raw material that had been obtained by precipitation of Cr_2O_3 from a chloride or sulfate solution, and reduction of the oxide with $CaCl_2$ and $BaCl_2$. A second reduction with calcium under argon resulted in extremely pure powder of good compactibility. The compact was first presintered at 1300°C. (2370°F.) for several hours in high vacuum and then sintered at 1600–1700°C. (2910–3090°F.) under argon of 100 mm. Hg pressure to avoid sublimation under high vacuum. The sintered metal could be readily hot-rolled at 1200°C. (2190°F.) under a protective cover of $BaCl_2$. Annealed sheets of 1-mm. thickness produced in this manner exhibited a Brinell hardness of 150. At room temperature the sintered chromium sheet is more brittle than tungsten or molybdenum sheet of corresponding thickness, but at temperatures above 200°C. (390°F.) the chromium sheet can be bent without cracking. The resistance of chromium to nonoxidizing acids, such as HCl and H_2SO_4, is less than that of tungsten or molybdenum, whereas, against oxidizing acids (*e.g.*, HNO_3), chromium is more stable on account of its passivity against oxygen.

Ductile chromium has found no important application to date. Its high vapor pressure near the melting point excludes its use as a high vacuum material, and its instability against most common acids outrules its use in the chemical industry.

CHROMIUM ALLOYS

Sintered and worked binary alloys of chromium containing 3 to 9% of iron, nickel, cobalt, molybdenum, tungsten, vanadium, tantalum, titanium, zirconium, aluminum, and silicon have been produced[113] in order to study

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[108] German Pat. 441,639; U. S. Pat. 1,760,367.

[109] Brit. Pat. 512,502.

[110] T. P. Colclough, U. S. Dept. of Commerce, PB No. 350.

[111] P. P. Alexander, *Metals & Alloys*, *5*, No. 1, 37 (1934).

[112] H. T. Greenaway, Council for Scientific and Industrial Research, Division of Aeronautics, Structures and Materials, Note 163 (Dec. 1947).

[113] W. Kroll, *Z. Metallkunde*, *28*, 317 (1936).

their effect on the ductility and rollability of the metal. The powder mixtures were pressed at about 20 tsi and presintered in high vacuum below 1200°C. (2190°F.). High-temperature sintering was carried out at 1500–1700°C. (2730–3090°F.) under slight argon pressure as in the technique used for pure Cr. The compacts were then hot-rolled with intermediate anneals to 1-mm. sheets under a protective borax cover at 1200°C. (2190°F.). The rollability, hardness, and a description of the metallographic and x-ray structure of the different alloys are given in Table 267. In most cases, the identification of the different phases was not possible because of the homogenization treatment to which the sheets were subjected in their final annealing. The alloys containing titanium, aluminum, and silicon formed solid solutions during the first high-temperature sintering operation, and it may be assumed that prolonged annealing will also result in solid solutions in most of the other compositions. It appears

TABLE 267

Properties and Structure of Sintered Chromium Alloys (Kroll[113])

Alloy constituent		Rollability as compared with Cr	Hardness	Microstructure	X-ray diffraction pattern
Element	%				
Sintered chromium	None	—	—	Rough matrix, chromium grains not incorporated	—
Rolled chromium	None	—	—	Rough matrix	—
Rolled chromium	None	Hot short	—	Oxide inclusions	—
Ta	9.1	Inferior	120	Yellow compound, pure grain boundaries	Shift in lines
V	9.1	As Cr	218	Grain boundary constituent	Shift in lines
Mo	9.1	As Cr	260	. . . .	Shift in lines
W	9.1	As Cr	450	Yellow crystals	New interference
Co	9.1	As Cr	218	Some intergranular substance, fine inclusions	Shift in lines
Ni	9.1	Hot short	430	Pure grain boundaries, fine inclusions	Shift in lines
Zr	9.2	As Cr	218	Yellow compound	Shift in lines
Si	4.7	As Cr	300	Pure grain boundaries; solid solution, very porous	Shift in lines
Ni	4.7	Inferior	315	Pure grain boundaries	Shift in lines
Fe	4.7	Superior	315	Homogeneous	Shift in lines
Al	3.0	Inferior	315	Pure grain boundaries; chromium grains not in solution, porous	Shift in lines
Ti	4.7	Inferior	218	Homogeneous; pure grain boundaries, porous	Shift in lines

remarkable that even considerable quantities of chromium oxide inclusions did not cause hot shortness and that alloys with iron improved the workability, while those with nickel depreciated the same property. Inclusions of foreign oxides and carbides impaired the hot-rollability of the alloys appreciably.

More recently, an extensive investigation of binary and ternary chromium alloys was undertaken for the purpose of studying the behavior of these alloys in air at temperatures above 1000°C. (1830°F.).[113a] Alloys of the systems Cr–W, Cr–Mo, Cr–Ta, Cr–Cb, Cr–Ta–Cb, Cr–Cb–W, Cr–Ta–W, Cr–Cb–Ni, and Cr–Ta–Ni were produced by melting mixed and pressed metal powders (sintered alloys were found unsuitable for the oxidation-resistance experiments). Of the entire complex, the ternary alloys with tantalum and nickel showed greatest promise[113b] (see also below). The oxidation of alloys high in chromium content does not differ appreciably from that of pure chromium. But, below 70% chromium, binary alloys of chromium with tungsten and molybdenum, or ternary alloys of chromium with columbium and tungsten, or with tantalum and tungsten, display a much higher rate of oxidation because of the appreciable volatility at temperatures above 1000°C. (1830°F.) of the compounds MoO_3 or WO_3 formed. The systems Cr–Ta and Cr–Cb were found to consist of two phases (Cr_3Ta_2 and Cr_3Cb_2, respectively) and a wide range of homogeneity; the oxidation resistance (at 1200°C.; 2190°F.) was found highest at the compositions corresponding to these compounds, which were found to oxidize only to one-half to one-third the extent of pure chromium under the same conditions. Ternary alloys of chromium with tantalum and columbium displayed very irregular behavior during the oxidation tests because of the formation of fissures at the grain boundaries and lifting of the oxide layers.

Chromium–Molybdenum. Metallographic and x-ray investigations on the sintered alloys have indicated a continuous series of solid solutions[114]; the previously known phase diagram[115] differing probably because less pure chromium (obtained by aluminothermic reduction) was employed. Latest melting point determination tests, however, indicate the possible presence of a eutectic, melting at 1700°C. (3090°F.), in the vicinity of 15 atom per cent (24.6 weight per cent) of molybdenum.[116] Chromium-base alloys containing 60% Cr, 15–25% Mo, and 25–15% Fe have been developed recently for ultimate use as turbine and jet engine

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[113a] O. Kubaschewski and A. Schneider, *J. Inst. Metals, 75,* 403 (1949).

[113b] O. Kubaschewski and H. Speidel, *ibid.,* p. 417.

[114] W. Trzebiatowski and H. Ploszek, *Naturwissenschaften, 26,* 462 (1938).

[115] E. Siedschlag, *Z. anorg. allgem. Chem., 131,* 191 (1923); see also M. Hansen, *Der Aufbau der Zweistofflegierungen.* Springer, Berlin, 1936, p. 533.

[116] W. Trzebiatowski, H. Ploszek, and J. Lobzowski, *Anal. Chem., 19,* 93 (1947); see also *Powder Metal Bull., 2,* No. 4, 90 (1947).

buckets, which are subjected to very high temperatures.[117] The inherent brittleness of the fusion products has so far been the chief obstacle in the path of further rapid development of this type of alloy but it is noteworthy that the alloy has exhibited the highest recorded stress-rupture strength at 870°C. (1600°F.).[118] With the advantages of greater purity of the raw material and finer grain size of the end product, the sintering technique may possibly furnish a material of greater ductility without sacrifice of hot strength, creep resistance, and other significant physical properties.

Chromium–Tungsten. The binary alloy system of chromium–tungsten was also found (on the basis of x-ray studies) to consist of a continuous series of solid solutions.[116,119-121] Most of these studies were performed on compacted mixtures of chromium and tungsten in various ratios (*e.g.*, steps of 10%) from 0–100% Cr. The compacted bars were then sintered in a sinter-bell or an electric furnace, depending on the various cycles necessary to effect diffusion (*e.g.*, 1550°C. (2820°F.) for 1 hour[121] or 1700°C. (3100°F.) for 1–7 hours[116]). It is believed that sintered alloys containing from 20 to 30% W will possess at least equal, if not superior, heat resistance and hot strength as the corresponding alloys of chromium and molybdenum, and it has also been reported[122] that even 13% Cr is sufficient to render tungsten oxidation-resistant up to about 1100°C. (2000°F.). The higher density of these alloys, however, may be considered to be disadvantageous for such applications as rotor bladings.

Chromium–Tantalum–Nickel. A preliminary investigation of the constitution of the systems Cr–Ta, Ni–Ta, and Cr–Ta–Ni with the aid of thermal, microscopic, and x-ray methods on specimens produced by melting mixed and compacted powders was recently reported.[122a] In the system Cr–Ta, an intermediate phase (Cr_3Ta_2), having a broad homogeneous field (from about 62% Ta toward the tantalum-rich compositions), was found. The solid solubility of tantalum in chromium was ob-

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[117] R. M. Parke and F. B. Bens, in *Symposium on Materials for Gas Turbines*, A.S.T.M., Philadelphia, Pa., 1946, p. 80.

[118] J. W. Freeman, E. E. Reynolds, and A. E. White, National Advisory Committee for Aeronautics, Technical Note No. 1314, Washington, D. C., May 1947.

[119] F. Weibke and U. v. Quadt, *Z. Elektrochem.*, *46*, 635 (1940).

[120] O. Kubaschewski and A. Schneider, *Z. Elektrochem.*, *48*, 671 (1942).

[121] H. T. Greenaway, Council for Scientific and Ind. Res. Div. of Aeronautics, Structures and Materials, Note 162 (Dec. 1947).

[122] S. Isida, H. Asada, and S. Higasimura, *Rept. Aeronaut. Research Tokyo Inst. Imp. Univ.*, *13*, 195 (1938) (Abstract in English); *Iron Steel Inst. Japan*, *25*, 106 (1939).

[122a] O. Kubaschewski and H. Speidel, *J. Inst. Metals*, *75*, 417 (1949).

served to be several per cent. In the system Ni–Ta, two phases corresponding to compositions approximating the compounds Ni_3Ta and Ni_2Ta_3 were found. In the ternary system Cr–Ta–Ni, the two binary phases Cr_3Ta_2 and Ni_3Ta are believed to form a continuous series of solid solutions; the three eutectics of the border systems lead to a ternary eutectic at 37% Cr, 46% Ni, and 17% Ta which has a melting point of 1165°C. (2130°F.). Of particular interest is the behavior of the ternary alloys under oxidation at very high temperatures (up to 1250°C.; 2280°F.). Alloys with relatively high oxidation resistance were found in the range of 10–25% Cr, 10–40% Ta, and 50–80% Ni; alloys of this type displayed a Brinell hardness of 150–350 at room temperature and a solidus temperature ranging between 1250 and 1380°C. (2280 and 2515°F.). The oxidation resistance at 1250°C. (2280°F.) of an alloy containing 25% Ta and 62.5% Ni was found to be about ten times higher than that of pure chromium. Alloys in the concentration range of 5–40% Cr, 45–56% Ta, and 25–50% Ni possess a higher solidus temperature; their oxidation resistance, while lower than in the aforementioned range, is still twice as good as that of pure chromium at 1200°C. (2190°F.).

TITANIUM

Compact titanium metal of relatively high purity and appreciable ductility—permitting direct reduction by cold-rolling—has been originally produced by thermal decomposition of titanium iodide onto tungsten wire maintained at incandescence.[123,123a-b] The process involves reacting the crude metal in an evacuated glass bulb with iodine at a slightly elevated temperature, and decomposing the resultant iodide on the hot filament. While the filament thus grows in diameter with the metal deposited (until the electrical, mechanical, or thermal limits of the apparatus are reached) iodine is regenerated and available for carrying on the cycle. Lately, this process has been much improved[123c-d] by replacing the tungsten filament by a titanium wire, and the glass bulbs by metal containers. Thereby the operation has become simpler and practical for solid rods up to $^5/_8$-in. diameter. At the same time, contamination by the filament is eliminated, and the product is of highest purity, as indicated by an excellent combination of properties.

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[123] A. E. van Arkel, *Reine Metalle*. Springer, Berlin, 1939, pp. 181–220.

[123a] A. E. van Arkel and J. H. de Boer, *Z. anorg. allgem. Chem., 148,* 345 (1925).

[123b] J. H. de Boer and J. D. Fast, *Z. anorg. allgem. Chem., 153,* 1 (1926); *187,* 177 (1930).

[123c] B. W. Gonser, *J. Metals, 1,* No. 1, Section 1, 6 (1949).

[123d] I. E. Campbell, R. I. Jaffee, J. M. Blocher, J. Gurland, and B. W. Gonser, *J. Electrochem. Soc., 93,* 271 (1948).

Relatively ductile titanium can also be produced from very pure powders by sintering in high vacuum, and can be readily hot-rolled to sheet. However, in contrast to the extremely pure and ductile metal produced by the iodide decomposition process, the sintered metal generally tends to fail in cold working, possibly due to minor impurities in the initial powder.

Pure titanium powders are best produced by reduction of the oxide with metallic calcium, preferably followed by a second reduction with calcium hydride,[124 126] or by reduction of the tetrachloride in a pressure vessel with alkali metals or magnesium. The latter process[127] was found most practical for large-scale operation, and has been used in a recent study of the production and properties of ductile titanium with a view toward industrial utilization of the metal.[128,129] The reduction of $TiCl_4$ with magnesium was carried out at about 800°C. (1470°F.) in an unlined iron pot under a protective static helium atmosphere. The reduction efficiency of the magnesium was 69%, and the yield accounted for 92% of theoretical for 15-pound batches that could be conveniently produced in a vessel 12 in. in diameter and 14 in. high. The cooled reaction mixture had to be crushed, leached with cold HCl solution, ground wet, again leached, and finally dried. In order to prevent a pyrophoric reaction during drying or handling, and to keep the oxygen content (introduced by surface reoxidation) at a minimum, the powder was used in a comparatively coarse grade, with the impurities as follows:

Magnesium	0.50%, max.
Iron	0.10%, max.
Silicon	0.10%, max.
Titanium dioxide	0.30%, max.
Hydrogen	25 ml per g. of titanium

Both the hydrogen and magnesium are driven off during sintering, and the oxide is completely reduced. The iron alloys with the titanium, while the silicon remains free, but apparently does not impair the ductility of the metal.

Titanium metal was produced by compacting the powder at 50 tsi and sintering in a vacuum of 0.0001 mm. for 16 hours at different temperatures.[128,129] In Table 268 the effect of rising sintering temperature

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[124] Brit. Intelligence Objectives Sub-committee, Final Rept. No. 1179, Item No. 21 (May 1947); see also *Metal Powder Rept. 1*, No. 10, 155 (June 1947).

[125] W. Kroll, *Z. anorg. allgem. Chem., 234*, 42 (1937).

[126] W. Kroll, *Z. Metallkunde, 29*, 189 (1937).

[127] W. Kroll, *Trans. Electrochem. Soc., 78*, 35 (1940).

[128] R S. Dean, J. R. Long, F. S. Wartman, and E. L. Anderson, *Trans. Am. Inst. Mining Met. Engrs., 166*, 369 (1946).

[129] R. S. Dean, J. R. Long, F. S. Wartman, and E. T. Hayes, *Trans. Am. Inst. Mining Met. Engrs., 166*, 382 (1946).

(up to 1080°C., 1975°F.) is shown on hydrogen evolution, weight loss, porosity, and hardness of the cooled metal. A sintering temperature of 850–1000°C. (1560–1830°F.) yielded compacts that could be cold-worked, with temperatures between 950 and 1000°C. (1740 and 1830°F.) giving most ductile products. Higher temperatures caused absorption of oxygen in sufficient quantity to impair the ductility of the metal. If annealing during intermediate stages of the working reduction was performed in high vacuum, up to 50% cold-rolling reduction was found

TABLE 268

Effect of Sintering Temperature on Hydrogen Evolution, Weight Loss, Porosity, and Hardness of Vacuum-Sintered Titanium[a] (Dean, Long, Wartman, and Anderson[128])

Sintering temperature		Hydrogen evolved, cc./g.	Loss in weight, mg./g.	Pore volume, %	Hardness, Rockwell "A"
°C.	°F.				
550	1020	24.5	—	17.0	30
600	1110	26.3	—	17.9	31
650	1200	25.9	0.38	15.8	29
700	1290	25.8	0.44	15.5	31
750	1380	25.5	0.65	14.5	34
800	1470	25.5	1.17	15.2	34
850	1560	25.5	1.50	13.3	37
900	1650	25.4	4.05	10.0	42
950	1740	25.3	4.83	8.0	45
1000	1830	25.0	4.95	7.5	47
1040	1905	25.4	4.59	7.5	49
1080	1975	26.0	4.42	5.4	51

[a] Compacts pressed at 50 tsi from Mg-reduced powder (−30 mesh, 20% max. −200 mesh); sintered for 16 hr. in vacuum of 0.0001 mm. Hg.

TABLE 269

Properties of Sintered Metallic Titanium (Dean, Long, Wartman, and Anderson[128])

Physical constants		Mechanical properties	Treatment	
			Cold-worked	Annealed
Melting point, °C.	1725	Tensile strength, psi	126,000	82,000
°F.	3140	Yield strength, psi	100,000	62,000
Electrical resistivity, ohm/cc. × 10^{-6}	56	Proportional limit, psi	72,000	55,000
Density, g./cc.	4.5	Young's modulus of elasticity, psi × 10^6	15.4	16.8
Crystal structure		Elongation in 2 in., %	4	28
up to 880 ± 20°C. (1615 ± 35°F.), hexagonal close packed, lattice parameter a	2.95 Å.	Hardness, Rockwell "A"	65	55
c	4.73 Å.			
above 880 ± 20°C. (1615 ± 35°F.), body centered cubic, lattice parameter a	3.32 Å.			

possible without visible surface defects or cracking at the edge, and 0.6 to 0.8 mm. strips could be flexed readily.

A somewhat different but rather intriguing method of producing titanium from powder on a commercial scale involves consolidation by a sheath-working process requiring no particular vacuum manipulations.[129a] This process provides for the incorporation of the powder inside an iron pipe which afterwards is closed on both ends by welding. The pipe is then worked down in easy steps either by cold rolling followed by hot forging, or by hot rolling. The resulting titanium sheet is readily separated from the iron sheath. The primary advantages of the sheath rolling as opposed to the conventional pressing and vacuum-sintering technique are: (*1*) elimination of the necessity to compact the powder at high pressures; (*2*) elimination of the need for vacuum sintering; (*3*) possibility of preparing almost unlimited volume of metal in a single piece; and (*4*) high density and surface smoothness in addition to excellent physical properties, especially ductility and susceptibility to additional cold working. Also of interest appears to be the possibility that a number of pressed, but unsintered, compacts can be made into one piece by this method, and that alloys can be prepared as well, by simply mixing the alloying elements with the titanium powder.

The properties of sintered and worked metal are given in Tables 269 and 270, those of the subsequently annealed sheet material in Table 271.[128,129] The corrosion resistance of the metal is very similar to that of the 18–8 type stainless steels; it is attacked by concentrated HCl and H_2SO_4, but is consumed more slowly by dilute H_2SO_4; concentrated or dilute HNO_3 has no appreciable effect. Titanium is resistant to tarnish and salt spray, and, in its final wrought form, is resistant to burning—up to temperatures of at least 800°C. (1470°F.).

The thermal and electrical properties of ductile, sintered titanium were recently investigated by Greiner and Ellis.[129b]

In a comprehensive symposium,[130] the available data on recent research were correlated as follows. The commercially pure metal has a relatively high tensile and yield strength in combination with good elongation in the annealed state. Even a moderate amount of cold work raises the strength values considerably further. This can be seen from Figure 604, which shows the tensile properties as a function of the degree of cold working. An indication of the heat resistance over a moderate

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[129a] J. R. Long and E. T. Hayes, U. S. Dept. of Interior, Bureau of Mines, Rept. Investigation No. 4464 (1949).

[129b] E. S. Greiner and W. C. Ellis, *Trans. Am. Inst. Mining Met. Engrs.*, *180*, 657 (1949).

[130] Symposium on Titanium, sponsored by Office of Naval Research, Washington, D. C., December 16, 1948 (Rept. March 1949). See also E. S. Kopecki, *Iron Age*, *162*, No. 26, 101 (1948); Anonymous, *ibid.*, No. 27, 41 (1948); T. C. Dumond, *Materials & Methods*, *29*, No. 2, 45 (1949).

TABLE 270

Mechanical Properties of Cold- and Hot-Worked ${}^{1}/_{16}$-In. Titanium Sheet[a] (Dean, Long, Wartman, and Hayes[129])

State	Reduction in thickness	Tensile strength, psi	Yield strength (0.2% offset), psi	Proportional limit, psi	Elongation in 2 in., %	Hardness Rockwell "G"
Cold-rolled	0[b]	78,700	62,800	56,600	25.2	76
	10	99,500	90,500	65,300	11.5	81
	20	110,500	101,100	76,900	8.2	86
	30	116,900	107,600	81,100	7.7	88
	40	122,200	113,300	84,400	7.5	91
	50	123,000	113,500	83,300	7.8	91
	60	111,500	—	86,600	1.5	92
Hot-rolled at 500 °C. (930 °F.)	0[c]	74,600	58,600	51,000	22.7	75
	30	90,400	82,900	64,700	15.0	82
	50	96,900	88,600	69,200	15.1	87
	60	100,800	92,300	71,900	12.5	87
	70	100,300	90,500	66,700	10.0	88
	80	101,700	92,500	68,000	14.8	88

[a] Obtained by pressing −35-mesh Mg-reduced powder at 50 tsi into plates 3 × $1^{1}/_{2} \times {}^{3}/_{8}$ in., sintering for 16 hr. at 1000 °C. (1830 °F.) in vacuum (0.0004 mm. Hg), cold-forging to 25% reduction, and annealing for 6 hr. at 1000 °C. (1830 °F.) in vacuum.

[b] Zero cold-worked condition represented by 40% cold reduction followed by annealing for 2 hr. at 800 °C. (1470 °F.).

[c] Zero hot-worked condition represented by 60% hot reduction followed by annealing for 2 hr. at 800 °C. (1470 °F.).

TABLE 271

Effect of Annealing Temperature on Properties of Cold- and Hot-Worked ${}^{1}/_{16}$-In. Titanium Sheet[a] (Dean, Long, Wartman, and Hayes[129])

Type of working	Annealing temperature °C.	Annealing temperature °F.	Tensile strength, psi	Yield strength (0.2% offset), psi	Proportional limit, psi	Elongation in 2 in., %	Hardness, Rockwell "G"	Grain size, mm
Cold-rolled to 40% reduction	400	750	99,200	92,100	76,500	15.3	87	—
	500	930	90,700	81,300	71,100	18.5	87	—
	600	1110	82,100	69,400	63,400	22.9	79	—
	700	1290	79,000	64,700	59,500	25.2	78	0.025
	800	1470	79,100	64,000	58,800	24.7	76	0.035
	900	1650	78,500	65,000	58,000	23.8	77	0.045
	1000	1830	80,500	64,500	44,800	22.5	67	0.045
	1100	2010	81,500	65,400	41,100	21.5	68	0.090
Hot-rolled at 500 °C. (930 °F.) to 60% reduction	500	930	92,000	84,100	69,000	17.6	81	—
	600	1110	78,700	63,200	56,300	18.9	75	0.010
	700	1290	73,900	59,800	53,400	25.2	74	0.025
	800	1470	73,500	59,600	55,100	26.2	74	0.035
	900	1650	73,300	59,700	53,400	25.4	76	0.035
	1000	1830	80,300	64,800	43,200	22.4	65	0.120
	1100	2010	79,500	66,700	45,900	20.2	67	0.120
	1200	2190	83,000	67,800	44,600	21.1	70	0.150

[a] Obtained by pressing −35-mesh Mg-reduced powder at 50 tsi into plates 3 × $1^{1}/_{2} \times {}^{3}/_{8}$ in., sintering for 16 hr. at 1000 °C. (1830 °F.) in vacuum (0.0004 mm. Hg), cold forging to 25% reduction, and annealing for 6 hr. at 1000 °C. (1830 °F.) in vacuum.

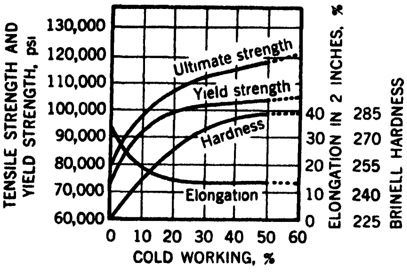

Fig. 604. Work-hardening characteristics of commercially pure titanium (according to C. I. Bradford[130])

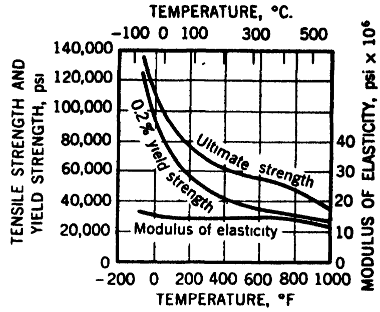

Fig. 605. Influence of temperature on the short-time tensile properties of commercially pure titanium forged bar stock (according to Bradford[130]).

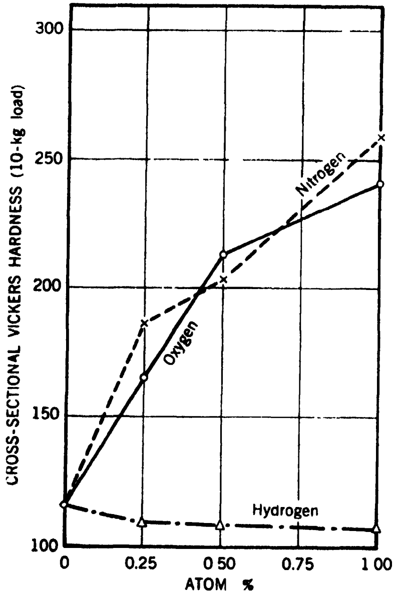

Fig. 606. Average cross-sectional hardness values for alloys of iodide titanium with oxygen, nitrogen, and hydrogen (according to H. C. Cross[130]).

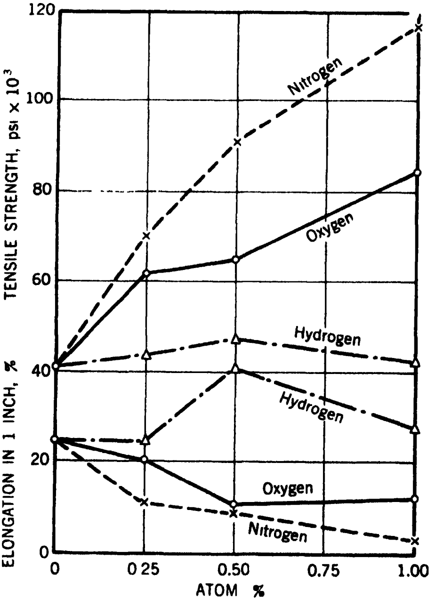

Fig. 607 Tensile strengths and elongations of alloys of iodide titanium with oxygen, nitrogen, and hydrogen (according to Cross[130]).

temperature range can be seen from Figure 605, where the short-time tensile properties are plotted against rising temperature up to 540° C. (1000°F.). The strong tendency of titanium to absorb gases, which results in the formation of hard and brittle phases, is borne out in a change in the physical properties. Figure 606 shows the effect of increasing amounts of oxygen, nitrogen, and hydrogen on the hardness, and Figure 607 the same on tensile strength and elongation. The gases were diffusion alloyed with ductile titanium obtained by decomposition of the iodide. The titanium is hardened and embrittled to about the same extent by oxygen and nitrogen, but not so by hydrogen, where no apparent change in these properties was found up to 1 atom % (0.021 weight %) of absorbed gas.

Because of this adverse tendency to absorb gases, sintered titanium metal has so far found no important uses at elevated temperatures; however, it is potentially useful in high-vacuum applications.

Although the production of pure, ductile titanium by fusion is considered a prerequisite for a sound economic development of the metal into a light-weight, high-strength construction material, the method is still in its infancy, as was clearly shown during a discussion of some of the major production problems at the aforementioned symposium.[130] The raw metal produced by powder metallurgy methods can be fused under vacuum in a graphite crucible with the aid of an electric arc, but this operation causes an absorption of about 0.8% C by the metal,[130a] resulting in embrittlement of the cast metal. The refining of the fusion product and the development of improved processing techniques for ductile titanium constitute some of the most interesting and challenging tasks in present-day metallurgical engineering.

Several comprehensive literature surveys of titanium and its alloys have recently been published.[131,131a]

TITANIUM ALLOYS

A series of sintered alloys of titanium, with additions consisting of 2 to 9% of tungsten, molybdenum, tantalum, zirconium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, aluminum, beryllium, and silicon have been produced[126] in order to determine the effect of impurities on ductility. The pure titanium powder was mixed with the addition element, pressed at about 15 tsi into cylinders about $^3/_4$-in. diameter and $^1/_4$ in. high, presintered in high vacuum, and high-temperature sintered in argon atmosphere at 50 mm. Hg pressure. The cylinders

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[130a] J. D. Fast, *Proc. International Powder Metallurgy Conference,* Graz, July 12–17, 1948, Referate No. 20.

[131] R. S. Dean and B. Silkes, *U. S. Dept. of Interior, Bureau of Mines, Information Circ. 7381* (Nov. 1946).

[131a] C. S. Dumont, *Bibliography on Titanium, Its Production, Properties and Uses.* Battelle Memorial Institute, Columbus, Ohio, 1947.

were then covered with a protective salt coating and hot-rolled into small strips of 1-mm. thickness. The test results are given in Table 272. As embrittling elements, oxygen, carbon, silicon, and absorbed gases are most harmful. On the other hand, the metals forming solid solutions, tungsten, molybdenum, and tantalum, as well as the metals of the iron group which do not completely dissolve in the titanium, appear not to be detrimental to the hot-rollability. The Brinell hardness of all alloys investigated is considerably above that of pure titanium, which is only 122–188 in the most ductile metal produced by dissociation at hot tungsten wire, 210 in the sintered metal, and 260 after cold-working.[125,126]

TABLE 272

Rollability, Hardness, and Structure of Sintered Titanium Alloys (Kroll[126])

Alloy constituent				
Element	%	Rollability	Brinell hardness	Microstructure
Mo. .	4.77	Good	363	Solid solution
W.. .	4.77	Good	363	Solid solution
Ni....	4.77	Excellent	410	Ti crystals in brown matrix
Fe....	4.77	Excellent	363	Ti crystals in gray matrix
Co....	4.77	Excellent	477	Ti crystals in dark gray matrix
Be. ..	1.96	Hot-short	229	Compound, Ti matrix and grain boundary constituent
Si.. .	1.96	Good	477	Ti matrix, bluish compound
Mn...	4.77	Good	410	Ti crystals, grain boundary constituent
Cr.. .	4.77	Good	451	Ti crystals, grain boundary constituent
Cu. .	4.77	Moderate, fibrous	410	Compound, grain boundary constituent, deeply etched
Al....	1.86	Moderate, fibrous	477	Yellow compound, little grain boundary constituent, Ti matrix
Zr.. .	4.77	Moderate, fibrous	363	Compound, grain boundary constituent, Ti matrix
V.....	4.77	Good	477	Ti matrix, grain boundary constituent
Ta....	9.09	Excellent	363	Solid solution

The previously mentioned, recently developed sheath-working technique[129a] was also successfully employed in preparing titanium alloys from powder mixtures; promising results were obtained with alloys containing iron, nickel, cobalt, chromium, silicon, and copper.

Also recently, sintered titanium alloys were investigated,[130] that contained up to 20% of molybdenum, tungsten, tantalum, columbium, or chromium; up to 5% of vanadium, manganese, or aluminum; and up to 1% of beryllium, indium, silicon, boron, or carbon. Figure 608 shows the effect of the alloying ingredients of the first group on the tensile strength and elongation of hot-rolled material; Table 273 lists the physical properties of a number of alloys of the other groups in the hot-rolled, cold-rolled, and annealed condition. Molybdenum, tungsten, tantalum, and columbium progressively increase the tensile strength and lower the elongation, up to the 20% limit of the alloying additions, whereas chromium shows the same effect only up to 10%—probably due to the formation of excessive amount of brittle intermetallic compound in

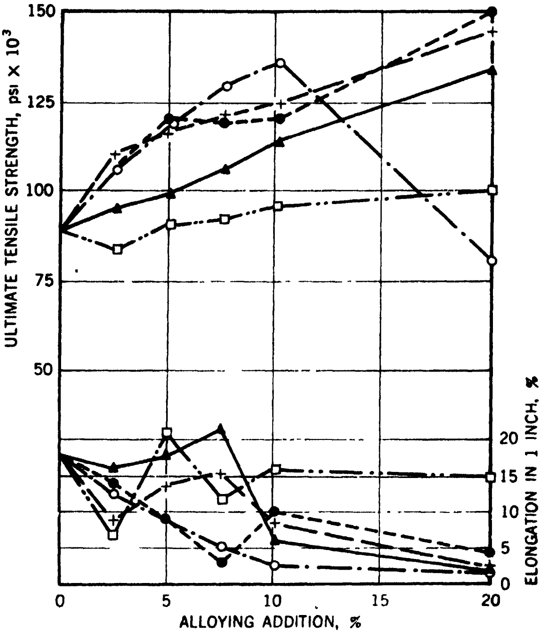

Fig. 608. Effect of chromium, molybdenum, tungsten, columbium, and tantalum on the tensile strength and ductility of titanium. Alloys were hot rolled at 900°C. (1650°F.) and furnace cooled (according to Cross[130]).
(○) Chromium; (+) molybdenum; (●) tungsten; (▲) columbium; (□) tantalum.

compositions higher in chromium content. Ternary alloys of chromium, molybdenum, or tungsten, with titanium have slightly higher tensile properties than those of the binary alloys with equivalent alloy content. Of the other titanium alloys investigated, those with aluminum and manganese contents up to 5%, and with beryllium, silicon, and boron up to 1% appear to be the most promising from a practical point of view.

Table 274 lists another compilation of data on the properties of the binary sintered and worked titanium alloys stemming from the same in-

TABLE 273

Physical Properties of Various Sintered, Worked and Annealed Titanium Alloys (Larsen, Swazy, Busch, and Freyer[130,131b])

Alloy, % (Balance, Ti)	Working, %	Rockwell hardness, A		Ultimate tensile strength, psi		Elongation, %	
		Worked	Annealed	Worked	Annealed	Worked	Annealed
0 37 Be	70 (C.R.)	64	59	115,000	93,000	3.2 (in 1 in.)	25 (in 1 in.)
	71 (C.R.)	66	61	'24,000	86,000	3 (in 1 in.)	12 5 (in 1 in)
1 07 Be	77 (H.R.)	61		96,000		4.5 (in 2 in.)	
	77 (H.R)[a]	69		151,000		3 (in 1 in.)	
	77 (H.R.)[b]	57		82,500		3 (in 1 in.)	
	77 (H.R.)[c]	61		101,500		6.25 (in 1 in.)	
	77 (H.R.)[d]	53		68,500		6.25 (in 1 in.)	
0 33 Al	77 (H.R.)	65	62	106,500	91,400	6.25 (in 2 in.)	12.5 (in 2 in.)
2 64 Al	77 (H.R.)	66	62	118,000	109,000	6 25 (in 2 in.)	7.8 (in 2 in.
0.33 Al	77 (H.R.)[e]	65	- -	159,000	—	3 (in 2 in.)	—
2 64 Al	77 (H.R.)[f]	67	—	155,000	—	3 (in 2 in.)	—
0.98 In	73 (C.R.)	67	60 5	132,500	100,000	None	7.8 (in 2 in.)
	76 (C.R.)	63	63	110,000	106,800	4 7 (in 1 in.)	12.5 (in 2 in.
1 28 C	77 (H.R.)[f]	63	—	137,000	114,500	4.6 (in 2 in.)	8 3 (in 2 in.)
1 18 C	77 (H.R.)[g]	—	- -	104,600	96,700	12.5 (in 2 in.)	19 (in 2 in.)
1 06 Si	80 (C.R.)	71	64	160,800	113,700	1.5 (in 2 in.)	4 3 (in 2 in.)
4 06 V	82 (C.R.)	68	—	153,000	—	None	—
10 21 Mo	77 (H.R.)	66	62	—	110,000	—	None
	77 (H.R.)	68	66	—	135,000	—	3.9 (in 2 in.)
3 53 Mn	70 7 (C.R.)	70	68	—	147,000	—	3 (in 1 in.)
5 62 Mn	77 (H.R.)	69	- -	164,000	—	4 5 (in 2 in.)	—
4 30 Mn	77 (H.R.)[h]	69	66	—	138,000	—	9 4 (in 2 in.)
6 02 Mn	77 (H.R.)[h]	69	68	—	101,000	—	None
7 22 Mn	77 (H.R.)[h]	69	69	—	164,500	—	None
13 00 Mn	77 (H.R.)[h]	72	64	—	141,000	—	6 (in 2 in.)

[a] 1000 °C. (1832 °F.); water quench; properties as heat treated.
[b] 1000 °C. (1832 °F.); slow cool; properties as heat treated.
[c] 850 °C. (1562 °F.); water quench; properties as heat treated.
[d] 850 °C. (1562 °F.); slow cool; properties as heat treated.
[e] Cold swaged 65%.
[f] Cold swaged 19%.
[g] Hot swaged 88%.
[h] Followed by anneal.

vestigation.[131b] In view of the great importance which the author attributes to this work within the framework of the rapid development of titanium metallurgy toward commercial realization, the most significant

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[131b] E. I. Larsen, E. F. Swazy, L. S. Bush, and R. H. Freyer, *Metal Progress*, *55*, No. 3, 359 (1949).

TABLE 274. Mechanical Properties and Electrical Resistivity of Titanium and Some Binary Sintered and Rolled Titanium Alloys (Larsen, Swazy, Busch, and Freyer[131b])

Composition, %		Condition^{a}	Rockwell		Tensile strength, psi	Elongation, %	Electrical resistivity, microhm-cm.
Intended	Analyzed		A	C			
UNALLOYED TITANIUM							
100 Ti	—	H.R. 77%	62½	24	100,000	7.8 (2 in.)	60
100 Ti	—	H.R. 77%, Ann.^{b}	62	23	90,700	9.5 (2 in.)	60
100 Ti	—	H.R. 77%, C.S. 52%	61	21	147,000	0	62
TITANIUM–BERYLLIUM ALLOYS							
0.5 Be	—	H.R. 77%	65	29	115,200	7.8 (2 in.)	64
0.5 Be	—	C.R. 73%	67	33	141,000	3 (1 in.)	—
0.5 Be	—	C.R. 90%	66	31	142,300	2.4 (2 in.)	—
0.5 Be	—	H.R. 77%, Ann.^{c}	61½	22	107,700	7.8 (2 in.)	67
0.5 Be	—	C.R. 73%, Ann.^{c}	61½	22	100,000	9.5 (2 in.)	65
0.5 Be	—	C.R. 90%, Ann.^{c}	56	—	86,000	6.2 (2 in.)	67
1 Be	0.37 Be	C.R. 70%	64	27	115,000	3.2 (1 in.)	—
1 Be	0.37 Be	C.R. 71%	67	33	124,700	3 (1 in.)	—
1 Be	0.37 Be	C.R. 70%, Ann.^{c}	59	—	93,000	25 (1 in.)	—
1 Be	0.37 Be	C.R. 71%, Ann.^{c}	61	21	103,000	12.5 (1 in.)	66
1 Be	1.07 Be	H.R. 77%	61	21	96,000	4.5 (2 in.)	62
1 Be	1.07 Be	W.Q.^{c}	69	37	151,000	3 (1 in.)	75
1 Be	1.07 Be	S.C.^{c}	57	—	82,500	3 (1 in.)	67
1 Be	1.07 Be	W.Q.^{b}	61	21	101,500	6.2 (1 in.)	68
1 Be	1.07 Be	S.C.^{b}	53	—	68,500	6.2 (1 in.)	61
TITANIUM–BORON ALLOYS							
0.1 B	—	C.R. 76½%	66	31	130,000	3 (2 in.)	—
0.1 B	—	C.R. 76½%, Ann.^{c}	60	19	99,700	9.4 (2 in.)	58
0.5 B	—	C.R. 72%	67	33	139,000	3 (2 in.)	—
0.5 B	—	C.R. 72%, Ann.^{c}	63	25	114,400	6.5 (2 in.)	58
TITANIUM–ALUMINUM ALLOYS							
1 Al	0.33 Al	H.R. 77%	65	29	106,500	6.2 (2 in.)	78
1 Al	0.33 Al	H.R. 77%, Ann.^{b}	63	25	91,400	12.5 (2 in.)	—
1 Al	0.33 Al	H.R. 77%, C.S. 65%	65	29	159,000	3 (2 in.)	77
3 Al	2.64 Al	H.R. 77%	66	31	118,000	6.2 (2 in.)	130
3 Al	2.64 Al	H.R. 77%, Ann.^{b}	66	31	109,000	7.8 (2 in.)	—
3 Al	2.64 Al	H.R. 77%, C.S. 65%	67	33	155,000	3 (1 in.)	125
TITANIUM–INDIUM ALLOYS							
3 In	0.98 In	H.R. 76%	63	25	110,000	4.7 (1 in.)	85
3 In	0.98 In	H.R. 76%, Ann.^{c}	63	25	106,800	12.5 (2 in.)	—
3 In	0.98 In	C.R. 73%	67	33	132,500	0	99
3 In	0.98 In	C.R. 73%, Ann.^{c}	60½	20	100,000	7.8 (2 in.)	—

TABLE 274 (*concluded*)

Composition, %		Condition[a]	Rockwell		Tensile strength, psi	Elongation, %	Electrical resistivity, microhm-cm.
Intended	Analyzed		A	C			
TITANIUM–CARBON ALLOYS (PREPARED BY MELTING)							
—	1.28 C	H.R. 77%, C.S. 19%	63	25	137,000	4.6 (2 in.)	61
—	1.28 C	H.R., C.S., Ann.[d]	—	—	114,500	8.3 (2 in.)	—
—	1.18 C	H.S. 88%	—	—	104,600	12.5	—
—	1.18 C	H.S. 88%, Ann.[d]	—	—	96,700	19	—
TITANIUM–SILICON ALLOYS							
0.5 Si	—	C.R. 80%	67	33	126,000	1.5 (2 in.)	74
0.5 Si	—	C.R. 80%, Ann.[c]	62	23	115,300	9.4 (2 in.)	61
1 Si	1.06 Si	C.R. 80%	71	41	160,800	1.5 (2 in.)	102
1 Si	1.06 Si	C.R. 80%, Ann.[c]	64	27	113,700	4.3 (2 in.)	88
TITANIUM–ZIRCONIUM ALLOYS							
10 Zr	—	H.R. 77%	68	35	131,000	3 (2 in.)	76
20 Zr	—	H.R. 77%	69	37	104,000	3 (2 in.)	80
30 Zr	—	H.R. 77%	69	37	74,500	1.5 (2 in.)	94
40 Zr	—	H.R. 77%	73	45	49,000	0	115
TITANIUM–VANADIUM ALLOYS							
0.5 V	—	C.R. 77%	66	31	130,500	3 (2 in.)	—
0.5 V	—	C.R. 77%, Ann.[c]	61	21	98,700	12.5 (2 in.)	73
5 V	4.06 V	C.R. 82%	68	35	153,000	0	87
TITANIUM–MOLYBDENUM ALLOYS							
10 Mo	10.21 Mo	H.R. 77%	66	31	—	—	—
10 Mo	10.21 Mo	H.R. 77%, Ann.[b]	62	23	110,000	0	80
20 Mo	12.52 Mo	H.R. 77%	68	35	—	—	—
20 Mo	12.52 Mo	H.R. 77%, Ann.[b]	66	31	135,000	3.9	98
TITANIUM–MANGANESE ALLOYS							
—	3.53 Mn	C.R. 70.7%	70	39	—	—	—
—	3.53 Mn	C.R. 70.7%, Ann.[c]	68	35	147,000	3 (1 in.)	88
—	4.30 Mn	H.R. 77%	69	37	—	—	—
—	4.30 Mn	H.R. 77%, Ann.[c]	66	31	138,000	9.4 (2 in.)	93
—	5.62 Mn	H.R. 77%	69	37	164,000	4.5 (2 in.)	116
—	6.02 Mn	H.R. 77%	69	37	—	—	—
—	6.02 Mn	H.R. 77%, Ann.[c]	68	35	101,000	0	105
—	7.22 Mn	H.R. 77%	69	37	—	—	—
—	7.22 Mn	H.R. 77%, Ann.[c]	69	37	164,500	0	118
—	13.00 Mn	H.R. 77%	72	43	—	—	—
—	13.00 Mn	H.R. 77%, Ann.[c]	64	27	141,000	6 (2 in.)	—

[a] H.R. = hot rolled, C.R. = cold rolled, Ann. = annealed, W.Q. = water quenched, S.C. = slowly cooled, C.S = cold swaged, H.S. = hot swaged. [b] Temperature 850 °C. (1560 °F.). [c] Temperature 1000 °C. (1830 °F.). [d] Temperature 700 °C. (1290 °F.).

occurrences during processing of the different alloys are discussed to some detail in the following.

Titanium–Iron. A 90–10 Ti–Fe alloy sintered in vacuum for 1 hour at 1200°C. (2190°F.) displayed normal shrinkage. An indication of comparatively poor ductility may be seen in the fact that the material could withstand only 14.5% cold-rolling reduction, and, after vacuum annealing for 1 hour at 1000°C. (1830°F.), only an additional 5%.

Titanium–Nickel. An alloy containing 10% Ni displayed even greater brittleness, since it could only be reduced 6% by cold rolling after identical sintering treatment—the shrinkage amounting to about 2%.

Titanium–Cobalt. Sintering in vacuum at 1200°C. (2190°F.) of a 90–10 Ti–Co alloy resulted in fusion; sintering at 1125°C. (2055°F.) resulted in the formation of blisters on the specimens. Further lowering of the sintering temperature to 1050°C. (1920°F.) produced satisfactory material the shrinkage being about 3%). Again, a comparatively low ductility was indicated by the fact that the alloy could only be reduced 15% by cold rolling, and not more than an additional 1% after vacuum annealing for 1 hour at 1000°C. (1830°F.).

Titanium–Manganese. Alloys containing about 3.5–15% Mn could be sintered and worked with ease, but alloys containing larger amounts of manganese (up to 40%) displayed serious defects (expansion and warpage) during sintering. Loss in manganese was found considerable, amounting to as much as 50%. Segregation of the elemental powders during mixing was also noticed, and persisted in some instances throughout processing to sheet. Wet mixing improved this condition, but did not entirely eliminate it. An oxygen content of up to 1% was found to be of help in mixing. Microstructures and physical properties were found to depend much upon the uniformity of the manganese distribution, as well as on the thermal history (cooling rates after hot rolling and after annealing).

Titanium–Tungsten. A 90–10 Ti–W alloy could be readily sintered in vacuum at 1200°C. (2190°F.) for 1 hour, but shrank about 8% during this operation. It could be reduced 21% by cold rolling, and, after vacuum annealing for 1 hour at 1000°C. (1830°F.), could be further reduced 10%. The annealing treatment lowered the hardness from Rockwell A-67 to A-62.5; the resistivity was 87 microhm-cm.

Titanium–Molybdenum. Only alloys up to 20% Mo could be vacuum sintered satisfactorily at 1200°C. (2190°F.) for 1 hour—the shrinkage varying from 2 to 4%; alloys containing 30 to 40% Mo displayed defects (bending and cracking) or expansion during sintering under the same conditions. A 90–10 alloy specimen could be cold rolled

68%; other specimens of the 90–10 and 80–20 compositions could be hot rolled 77% at 800°C. (1470°F.).

Titanium–Vanadium. Sintering at 1200°C. (2190°F.) for 1 hour in vacuum resulted in satisfactory specimens in the case of alloys containing 0.5, 5, and 15% V. The latter was found too brittle for any noticeable cold-rolling reduction, but the first two alloys could be cold rolled to reductions of 25 to 58%.

Titanium–Chromium. A 90–10 Ti–Cr alloy showed signs of partial fusion upon sintering at 1200°C. (2190°F.), but could be sintered satisfactorily with a shrinkage of 3% at 1125°C. (2055°F.). The sintered alloy could be reduced 26% by cold rolling, and, after vacuum annealing at 1000°C. (1830°F.) for 1 hour, an additional 9%. But no appreciable change in hardness could be detected after the annealing treatment, the hardness being Rockwell A-62.5; the resistivity was measured as 93 microhm-cm.

Titanium–Zirconium. Alloys with 10, 20, 30, and 40% Zr could be readily vacuum sintered at 1200°C. (2190°F.) for 1 hour, and reduced by hot rolling 77% at 800°C. (1470°F.) in steel tubes (sheath rolling). Zones of undiffused zirconium could not be entirely eliminated during the metal-working operation.

Titanium–Indium. In the production of these alloys, fine powders (—100 mesh) were found necessary to prevent segregation. In alloys prepared from mixtures containing up to 5% In, volatilization losses of about two-thirds during sintering were observed. Regardless of the type of heat treatment applied, the microstructure gave evidence of a single phase after sintering, working, and annealing.

Titanium–Aluminum. Alloys containing 1 and 3% Al could be readily sintered in vacuum at 1200°C. (2190°F.), and thereafter hot rolled at 800°C. (1470°F.) to reductions of 77%. A composition with 10% Al disclosed abundance of a second, aluminum-rich phase, and was therefore abandoned. The alloys containing the smaller amounts, however, did not only display an ability to be easily hot- and cold-worked, but also proved to be considerably more resistant to oxidation than pure titanium.

Titanium–Beryllium. Successful production of specimens of this type of alloys required the use of fine beryllium powder (—150 mesh) and intimate mixing with the titanium powder, in order to prevent segregation and localized fusion during sintering. Only the 0.5% Be alloy could be sintered satisfactorily at 1200°C. (2190°F.); higher beryllium contents required lower sintering temperatures and longer times. An alloy containing 3% Be was found to melt at 975°C. (1785°F.), one with 10% Be at 950°C. (1740°F.). Sintered alloys with up to 1% Be could be cold rolled as much as 50% before annealing became necessary.

Titanium–Silicon. Compositions with 3 and 10% Si fused during vacuum sintering at 1225 and 1100°C. (2235 and 2010°F.), respectively, but bars with 0.5 and 1% Si could be sintered satisfactorily at 1200°C. (2190°F.). The 0.5% alloy could be readily cold rolled to a reduction of 55%, after both sintering and vacuum annealing. The 1% alloy could be cold rolled to a total reduction of about 80% by alternate reductions of 26 and 34% and vacuum annealing for 1 hour at 1000°C. (1830°F.), followed by a final reduction of 38%.

Titanium–Boron. Alloys with 0.1, 0.5, and 5% B could be satisfactorily sintered at 1200°C. (2190°F.), in spite of the fact that the boron powder contained about 4% magnesium as primary impurity. The alloys of low carbon content could be reduced by cold rolling as much as 45% before vacuum annealing became necessary; thereafter, an additional cold-rolling reduction of 49–58% was found possible. The 5% boron alloy, however, could not be cold worked appreciably. It is noteworthy that the electrical resistivity of 58 microhm-cm. for both the cold-rolled and vacuum-annealed material was the lowest value observed for any of the titanium alloys of this investigation.

Titanium–Carbon. The titanium–carbon alloys of this investigation were obtained by melting the metal in a graphite crucible. The carbon content of the ingot varied between 0.5 and 1.5%; an alloy containing 1.28% C could be hot rolled 77% and, after annealing, cold swaged an additional 19%. No experiments with titanium–carbon powder mixtures that were sintered were apparently carried out, which is somewhat surprising in view of the importance of the powdered carbide of titanium in industry.

Among the alloys and compounds of titanium, titanium carbide plays a most important part as a constituent in the cemented multicarbides used for high-speed cutting of steels (see Chapter XXII). Cemented titanium carbide, free of tungsten carbide, appears to have great promise as a heat-resistant structural material. In spite of the handicap of excessive brittleness of sintered titanium carbide, it has apparently been possible, by selection of the proper technique and the most suitable binder material, to produce a material which possesses a surprising combination of physical properties.[132] A density of 5.5 g./cc., in conjunction with a Rockwell "A" hardness of 91.0 to 92.0 and a transverse rupture strength of 175,000 to 210,000 psi, was found in a composition of approximately 80% by weight of TiC (density 4.9 g./cc.) and 20% of cobalt

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[132] Anonymous, *Materials & Methods, 26,* No. 6, 85 (1947).

binder (density 8.9 g./cc.). The material has its potential use in turbine buckets because of its excellent high-temperature properties, as indicated by a tensile strength of 15,000 to 21,000 psi at 1000–1100°C. (1800–2000°F.) and a perfect resistance to combustion gases up to a gas temperature of 1150°C. (2100°F.), corresponding to a temperature of the material of about 900°C. (1650°F.). Other potential uses include Diesel engine valve seats, furnace parts, and roll guides for hot-rolling mills. The material is further described in Chapter XXII. It is believed possible to enhance the heat resistance further, if the cobalt binder is replaced by other metals[132a] or some of the corrosion-proof alloys. Also, other carbides such as TaC or CbC, present in the material in small quantities, result in very hard and strong solid solutions and yield products of still superior oxidation resistance at high temperatures.[132b]

Powdered titanium hydride serves as master alloy ingredient and deoxidizer in certain metallurgical processes, such as in titanium–copper master alloys for nonferrous alloys and in titanium–nickel master alloys for permanent magnets.[133]

ZIRCONIUM AND ZIRCONIUM ALLOYS

Zirconium. Zirconium metal has also been used to a limited extent as powder and sheet in the vacuum technique as a getter material.[134] The production of zirconium metal is similar to that of titanium, the powder being obtained either by reduction with an alkali (*e.g.*, magnesium or calcium) of the oxide, or the tetrachloride (which is prepared from zircon sand via the carbide), or through thermal decomposition of zirconium iodide on a hot tungsten filament.[135] The ductile metal is produced by presintering in vacuum, high-temperature sintering in argon at subatmospheric pressure, and hot-rolling under protective salt cover. The resulting product is more ductile than titanium and also considerably softer, with Brinell hardness values of between 80 and 100.[136]

One specific procedure has recently been described in a report on experiments with the preparation of the ductile metal.[137] Pure zirconium oxide was prepared by igniting and burning zirconium oxychloride octahydrate ($ZrOCl_2.8H_2O$) at 1100–1200°C. (2010–2190°F.), the latter having been produced from either zirconium chloride, zirconium oxy-

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[132a] A. R. Bobrowsky, *Trans. Am. Soc. Mech. Engrs.*, *71*, 621 (1949).

[132b] J. C. Redmond and E. N. Smith, *Trans. Am. Inst. Mining Met. Engrs.*, *185*, 987 (1949).

[133] H. W. Zabel, *Chem. Inds.*, *60*, No. 1, 37 (1947).

[134] J. D. Fast, *Philips tech. Rundschau*, *3*, 353 (1938); *5*, 221 (1940).

[135] G. Meister, *Metal Progress*, *53*, No. 4. 515 (1948).

[136] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe*. Springer, Berlin, 1943, p. 175.

[137] W. C. Lilliendahl and H. C. Rentschler, *Trans. Electrochem. Soc.*, *91*, 237 (1947).

chloride, or zirconium nitrate. A reduction with either pure calcium or calcium in the presence of calcium chloride resulted in very pure zirconium metal. For instance a powder with 0.1% Ca could be produced when performing the reduction process with 100% excess Ca and 1 mole $CaCl_2$ per mole ZrO_2; the use of specially dehydrated $CaCl_2$ resulted in a powder containing only 0.04% Ca. The most suitable procedure for the reduction process was found to consist of heating the mixture of powdered ingredients in an iron or molybdenum container under a silica cover in argon under slight negative pressure (0.75 atm. abs.) at 1100°C. (2010°F.) for 30 minutes. The reaction product yielded 86% Zr metal powder of a medium grade (about $^2/_3$ plus 200 and $^1/_3$ minus 200 mesh). Upon processing the two fractions individually it was found that the coarser grade gave a less brittle product. Compacts pressed at 40–50 tsi and sintered in vacuum for 10–12 hours at 1000°C. (1830°F.), or 4–5 hours at 1200°C. (2190°F.), respectively, displayed a density of 6.5 g./cc. as compared with 6.8 g./cc. for the material as cast. The sintered material was found to be more ductile, softer, and easier to machine than vacuum-fused metal prepared by melting pressed powder compacts on layers of thoria in beryllia crucibles.

Another procedure reported recently[138] involves the production of ductile, high purity zirconium by vacuum fusion of the raw metal in graphite crucibles (during this operation only 0.15% C is absorbed). The raw zirconium metal is produced by instantaneous reduction of large quantities of zirconium chloride with magnesium under a liberal cover of helium gas.

During the war, zirconium has been used in Germany as a getter coating on radio valve parts from iron, nickel, carbon.[139,139a] The coatings were produced by electrodeposition from a paste or solution containing the metal hydride in a colloidal state, or by spraying. After deposition, the parts from iron and nickel were sintered in a vacuum furnace at 800–1000°C. (1470–1830°F.) and those from carbon at 1500–1600°C. (2730–2910°F.).

The development of zirconium into an industrially significant material is anticipated in view of the outstanding chemical resistance of the metal against both acid and alkaline attack.

Zirconium Alloys. Sintered zirconium alloys with nickel and iron, or nickel and cobalt, respectively, have been produced experimentally

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[138] J. D. Fast, *Proc. International Powder Metallurgy Conference,* Graz, July 12–17, 1948, Referate No. 20.

[139] Brit. Intelligence Objectives Sub-committee, Final Rept. No. 276, Item No. 7 (May 1946). See also *Metal Powder Rept., 1,* No. 1, 11 (1946).

[139a] W. Espe, *Powder Metallurgy Bull., 3,* No. 5, 100 (1948).

for permanent magnet applications, and are described in Chapter XXIV. Zirconium–lead alloys are claimed to be useful in the manufacture of flints for lighters.[133] They constitute the only sintered zirconium alloys for which information is available. Zirconium carbide has not gained any significance for hard metals, since it is highly soluble in the auxiliary metal.[139b] Powdered zirconium hydride[140] is used as an intermediate in the manufacture of a zirconium–magnesium master alloy.[133]

HAFNIUM, RHENIUM, AND THEIR ALLOYS

Hafnium. As far as is known, hafnium metal has not yet been produced by the sintering technique; the metal, however, has been produced in ductile form by dissociation in the presence of hot tungsten wire.[141,142]

Rhenium. Pure rhenium metal powder can be obtained without difficulties by the reduction at high temperature of ReO_2 by means of hydrogen.[143,144] Sintering is the only process suitable for the production of ductile rhenium because of the high melting point of the metal, 3170±60°C. (5750±110°F.); this process must be carried out by resistance heating by the passage of electric current through the compact. Rhenium specimens sintered in this manner at temperatures close to the melting point have a fair ductility and can be hot-worked.[143,144]

Rhenium Alloys. Sintered tungsten–rhenium alloys have been produced, but mainly for the determination of the constitution diagram[145] (see also under tungsten alloys, page 682).

URANIUM, THORIUM, AND THEIR ALLOYS

Whereas on the basis of available information[146,147] the present processes used for the separation of fissionable radioactive elements from thorium and uranium for the purpose of production of nuclear fuels and

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[139b] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe*. 2nd. ed., Springer, Berlin, 1948, p. 175.

[140] U. S. Pat. 2,411,524.

[141] A. E. van Arkel, *Reine Metalle*. Springer, Berlin, 1939, pp. 181–220.

[142] J. H. de Boer and J. D. Fast, *Z. anorg. allgem. Chem., 187,* 193 (1930).

[143] I. Noddack and W. Noddack, *Das Rhenium*. Voss, Leipzig, 1933.

[144] I. Noddack and W. Noddack, *Z. anorg. allgem. Chem., 215,* 129 (1933).

[145] K. Becker and K. Moers, *Metallwirtschaft, 9,* 1063 (1930). See also M. Hansen, *Der Aufbau der Zweistofflegierungen*. Springer, Berlin, 1936, p. 1028.

[146] H. D. Smyth, "A General Account of the Development of Methods of Using Atomic Energy for Military Purposes Under the Auspices of the United States Government, 1940–1945," U. S. Dept. of War, Rept. Aug. 10, 1945 (Superintendent of Documents, Washington, D. C.).

[147] United Nations Rept. on Scientific and Technical Aspects of the Problem of Control of Atomic Energy, Committee 3, U. N. Atomic Energy Commission, Lake Success, N. Y., Sept. 28, 1946.

power by-pass powder metallurgy for practical reasons, powdered thorium and uranium metals are potential sources of atomic energy that are of tremendous significance and could conceivably change the entire complexion of the art. At present, two principal processes are known by which concentrated nuclear fuel can be produced from uranium: (*1*) by the separation of the isotope U-235 through gaseous diffusion, thermal diffusion, or electromagnetic separation methods and (*2*) by the burning of the U-235 content of natural uranium to produce plutonium.[147] While the first process involves the purification and conversion of uranium into special uranium compounds such as gaseous uranium hexafluoride, the second involves a most careful chemical purification of the uranium as received from the refinery in preparation for the partial conversion to plutonium in a "primary reactor" which sets up a chain reaction with the aid of a "moderator" material such as graphite or beryllium. The correct functioning of this process depends on the proper interspersing of the uranium and moderator material, and requires the uranium in the form of slugs or very coarse granules, which are more efficiently produced by fusion than from powder.[146,147]

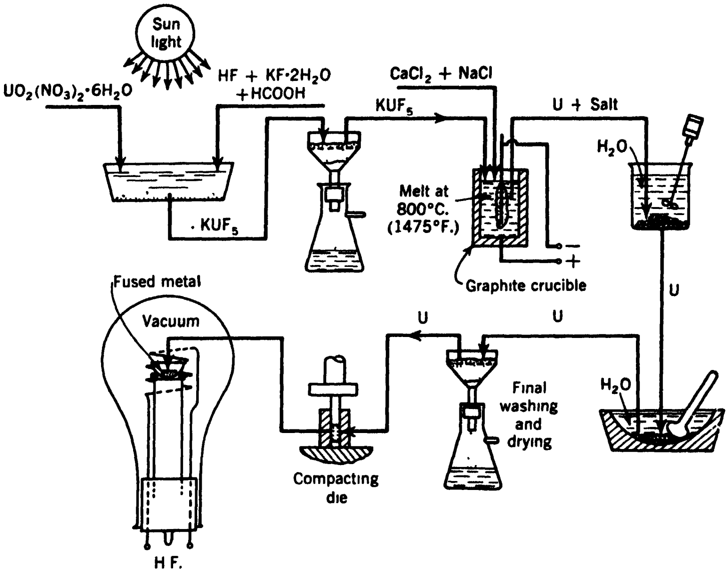

Fig. 609. Diagram of Driggs and Lilliendahl's original electrolytic process for producing uranium powder and its subsequent steps to make fused nuggets of 99.9% purity.

Uranium. Uranium powder has been produced by reduction of U_3O_8 by means of calcium in the presence of $CaCl_2$,[148] by decomposition of U_3O_8 by means of calcium hydride,[149] or by electrolysis of KUF_3 in a fused mixture of NaCl and $CaCl_2$ in graphite mortars.[150] The apparatus for the fusion electrolysis of uranium has been shown schematically in Figure 15, Volume I, Chapter III; Figure 609 is a flow diagram for producing the powder and vacuum-fused metal. At one time during the war the electrolytic method was used on a much larger scale, with the daily output reaching 500 pounds. The potassium–uranium fluoride was prepared by photochemical reduction of a purified uranyl nitrate solution. A total of 65 tons was prepared during a critical period in the atomic bomb project,[151] before the process was superseded by a more efficient process (developed by Spedding and his associates at Iowa State College and Rodden at the National Bureau of Standards). Because of its extreme fineness (generally —150 mesh and finer), the powder produced by reduction with calcium hydride displayed pyrophoric characteristics, which prohibited its use on a larger scale.[152] After washing away all traces of lime residue and subsequent drying, the hydride-reduced powder equaled the electrolytic type in purity. Sintered uranium produced by the above methods has low ductility and may be remelted in beryllium or thorium oxide crucibles. Remelting in beryllium oxide crucibles produced a metal with more than twice the hardness (480 Brinell) of the product from thorium oxide crucibles (200 Brinell); in both cases, however, a ductile material was obtained which could be formed easily to thin sheets and to wires 0.0004 in. in diameter.[153]

Uranium Alloys. No information on sintered uranium alloys is available to date, but wartime experiments with sintered uranium carbide have been reported from Germany.[154] The carbide could be successfully cast, but even at a density of 15.5 g./cc. the hardness was far below that of tungsten carbide, making the material unsuitable for the intended use as projectile cores. Sintering experiments with uranium carbide powder, obtained by mixing U_3O_8 with lampblack and effecting carburization by heating the mixture in a graphite crucible in a hydrogen atmosphere,

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[148] W. Kroll, *Z. Metallkunde*, *28*, 30 (1936).

[149] P. P. Alexander, *Metals & Alloys*, *9*, No. 10, 270 (1938).

[150] F. H. Driggs and W. Lilliendahl, *Ind. Eng. Chem., Ind. Ed.*, *22*, 516, 1302 (1930); *23*, 634 (1931).

[151] G. Meister, *Metal Progress*, *53*, No. 4, 515 (1948).

[152] F. G. Foote, Communication, at Meeting of American Society for Metals, New York Chapter, May 10, 1948.

[153] R. Kieffer and W. Hotop, *Pulvermetallurgie und Sinterwerkstoffe*. Springer, Berlin, 1943, p. 183.

[154] Brit. Intelligence Objectives Sub-committee, Final Rept. No. 1076, Item No. 21 April 1947); see also *Metal Powder Rept.*, *1*, No. 10, 150 (1947).

failed to produce a satisfactory product, as either unreduced oxides interfered with uniform shrinkage and sintering, or excessive carburization resulted in low density material.

A similar procedure has recently been used in producing the three carbides UC, UC_2, and U_2C_3.[154a] The monocarbide, for example, is obtained by compacting a mixture of 7.5 parts (by weight) of UO_2 and 1 part graphite powder at 26 tsi to a bar, and heating the bar in a graphite crucible for 20 minutes at 2275–2320°C. (4130–4210°F.). X-ray studies[154b] have disclosed that UC is face-centered cubic (a = 4.951Å.) and has the NaCl-type crystal structure; UC_2 is body-centered tetragonal (a = 3.517Å., b = 5.987Å.) and has the CaC_2-type structure. Carbon is soluble in the dicarbide at high temperatures, and the evidence points toward the existence of U_2C_3 above 2000°C. (3630°F.). The structures of uranium nitride (UN) and uranium oxide (UO) were found to be face-centered cubic.

Thorium. Thorium finds potential application in high-vacuum techniques on account of its opacity to x-rays[155] and its good getter properties.[155a] Th powder can be produced by fusion electrolysis from $KThF_5$ in a NaCl–KCl bath at 750–775°C. (1380–1425°F.),[150,155b] or by reduction of the oxide with Ca metal in a molten $CaCl_2$–$BaCl_2$ bath in vacuum.[148,155c,d] The pure powder is pressed and sintered in high vacuum into a metal that compares in ductility with tantalum. A detailed report on the processing of thorium metal in Germany during the war has recently been published.[156,156a] The pure metal, obtained by reduction (of ThO_2 with Ca and $CaCl_2$ at 1100°C. (2010°F.) under vacuum) and leaching in HCl, was pressed after washing and drying at about 20 tsi and then sintered under vacuum in a high-frequency or electric resistance furnace at 1320–1360°C. (2410–2480°F.) for 3 hours. The bars were then alternately cold rolled and annealed in vacuum at sintering temperatures for one hour—up to nine times, depending upon the degree of total reduction required. Rods and wires were produced by swaging, with intermediate anneals as mentioned. The chief impurities in the metal were oxygen (as thoria), calcium, sodium, and iron.

[154a] U. S. Pat. 2,448,479; see also *Powder Metallurgy Bull.*, *3*, No. 6 (1948).

[154b] R. E. Rundle, N. C. Baenziger, A. S. Wilson, and R. A. McDonald, *J. Am. Chem. Soc.*, *70*, 99 (1948).

[155] *Thoriummetall.* Bulletin of Auergesellschaft, A. G. Berlin, Abt. Chemie.

[155a] W. Espe, *Powder Metallurgy Bull.*, *3*, No. 5, 100 (1948).

[155b] U. S. Pat. 2,446,062.

[155c] Brit. Pat. 606,930; French Pat. 920,631.

[155d] Brit. Pat. 623,160.

[156] Brit. Intelligence Objectives Sub-committee, Final Rept. No. 276, Item No. 7 (May 1946); see also *Metal Powder Rept. 1*, No. 1, 119 (1946).

[156a] W. Espe, *Powder Metallurgy Bull.*, *4*, No. 1, 17 (1949).

Due to the insolubility of thoria in the pure metal (in contrast to the metals titanium and zirconium), no appreciable reduction of the ductility and cold workability is caused by the presence of oxygen, and only "mechanical" inclusions result. Cold-rolled and annealed sheets from electrolytic powder are extremely ductile and soft, exhibiting a Brinell hardness of only 39–54.[157] However, a thorium sheet produced from the reduced type of powder exhibits a Brinell hardness of 150 after a 90% cold-rolling reduction.[148]

Thorium Alloys. Alloys of thorium with other refractory metals, such as tungsten and molybdenum, have been discussed in Chapter XXI under tungsten alloys and earlier in this chapter under molybdenum alloys.

LOW-MELTING HEAVY METALS AND ALLOYS

Zinc and Zinc Alloys

ZINC

In spite of the large quantities of powder (dust) that are produced in the metallurgy of zinc, the metal has not become significant in powder metallurgy. Early attempts to utilize zinc dust for the molding of products have met with little success, presumably due to the high oxide content of the powder. Zinc powder compacts sintered at 360°C. (680°F.) displayed little coherence because of the presence of interfering oxide films.[158] In zinc compacts formed at 70 tsi and sintered at various temperatures, the particle size, within the range of 75 to 300 microns, has little influence on hardness.[159] However, hardness decreases with increasing temperature from about 92–94 Brinell units after compaction to 45–53 Brinell after sintering at 400°C. (750°F.). It was also found[159] that a specimen heated to 450°C. (840°F.), *i.e.*, above the melting point of the metal, did not liquefy sufficiently to lose its contours; at the peak temperature, the surface tension forces of the liquid particles caused spheroidizing, but the oxide films prevented fusion. Experiments made by the author with a very pure, electrolytic zinc powder produced a Brinell hardness of 52 and a tensile strength of 12,000 psi for a compact pressed at 50 tsi and sintered in dissociated ammonia for 4 hours at 400°C. (750°F.); the density after this treatment was 6.0 g./cc. (90% of theoretical), but the elongation was nil.

Very recently, a report has come from Germany concerning some work done with zinc and zinc alloys obtained by extruding rods of $^1/_2$-in.

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[157] A. E. van Arkel, *Reine Metalle.* Springer, Berlin, 1939, pp. 181–220.

[158] F. Sauerwald, *Z. anorg. allgem. Chem.*, *122*, 277 (1922).

[159] R. Kikuchi, *Science Repts. Tôhoku Imp. Univ.*, First Ser., *26*, 125 (1937).

diameter from powder pressings at 300 and 350°C. (570 and 660°F.) and 6 tsi.[160] Processing of zinc powder in this manner yielded products of 100% density with mechanical properties corresponding to those of cast materials, but the original objective—to produce porous zinc products suitable for bearing purposes—could not be realized. A slight variation in physical properties in the direction of extrusion was also observed, and the tensile strength varied from 25,900 to 24,900 to 25,400 psi for the beginning, center, and end of the rod with corresponding elongations of 6, 3, and 5%. Although additions of graphite up to 6% were found possible, the tensile properties decreased markedly even for an addition of 2%, to 19,900, 20,900, and 21,600 psi, respectively, with a uniform elongation of 2.5%. The effect of the graphite additions on the bearing properties were not yet established,[160] but experiments with mixtures of zinc powder with copper and aluminum powders were unsuccessful, since satisfactory alloying could not be achieved by the processing technique used.

ZINC ALLOYS

A number of zinc-base alloys of compositions used for die-casting purposes have been produced successfully by powder metallurgy methods; but the generally low ultimate physical properties, together with the necessary high pressures, long sintering periods, and high raw material requirements, outrule the powder approach on a competitive basis.

Zinc–Copper. Binary zinc-base alloys with copper as minor constituent were produced[159] with the result that the hardness of the alloys (as for pure zinc) decreases distinctly with increasing sintering temperature, and that increasing copper content—up to 25%—produces a similar change in the property after sintering. The Brinell hardness of a series of compositions of the zinc–copper system are given in Table 275.

TABLE 275

Relationship of Hardness of Sintered Zinc–Copper Alloys to Sintering Temperature (Kikuchi[159])

Composition		Brinell hardness		
Zn, %	Cu, %	Pressed at 70 tsi at 20°C. (68°F.)	Sintered at 260°C. (500°F.)	Sintered at 400°C. (750°F.)
100	0	94.0	73.9	47.1
90	10	98.2	53.7	37.9
75	25	103.9	65.8	27.9
50	50	116.9	78.0	80.4
25	75	128.6	97.2	85.9
10	90	136.9	110.7	84.6
0	100	139.6	116.9	98.2

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[160] W. Wolf, *Arch. Metallkunde, 1,* No. 7/8, 361 (1947).

Zinc–Aluminum. A binary zinc-base alloy of the die-casting type containing 4% Al could be produced readily by the author by sintering mixtures of the elemental powders, provided that the powders were of fine grade (325 mesh) and of the highest possible purity (electrolytic zinc, atomized aluminum with 0.1% O_2, max.). A compact produced by compression at 70 tsi, and sintering in dry hydrogen for 16 hours at 360°C. (680°F.), *i.e.*, 20°C. (36°F.) below the melting point of the alloy, exhibited a Brinell hardness of 72, well within the hardness range of the die-cast alloy (60–90 Brinell). The specimen was sufficiently plastic to permit coining to high accuracy, and the Brinell hardness could be increased to 80 by repressing at 50 tsi, and to 85 by repressing at 70 tsi. The density of the sintered product was found to be 6.0 g./cc. (90% of the cast alloy), that of the coined material 6.3–6.4 g./cc. (94–96%); the tensile strength, however, was considerably below that of the cast alloy (*e.g.*, 23,000 psi after sintering, and 33,000 psi after coining at 70 tsi), and the elongation nil in both cases.

Zinc–Aluminum–Copper. A ternary zinc alloy containing 4% Al and 3% Cu, and produced, as in the previous binary zinc–aluminum alloy, from very fine (325 mesh) and pure powders (electrolytic zinc and copper, atomized aluminum with 0.1% O_2, max.) possessed properties that were slightly superior to those of the binary alloy. After pressing at 70 tsi and sintering for 16 hours at 360°C. (680°F.) the Brinell hardness reached 81, again well within the range of the cast alloy (75–100), and the tensile strength reached 27,000 psi; by coining at 70 tsi, the Brinell hardness increased to 103, the tensile strength to 37,000 psi. The density of the ternary alloy was similar to that of the binary alloy, and the elongation was again nil for both the sintered and coined materials.

Other Zinc Alloys. Sintered binary alloys of zinc with cadmium and magnesium have been investigated[161] in a theoretical study of the reactivity of the metals in the solid state, but no significant results have been reported. The constitution of the systems zinc–iron, zinc–cobalt, and zinc–nickel have been studied with the aid of the sintering process,[162,162a,b] and the hardness has been investigated[159] of compositions of the systems zinc–carbon and zinc–silicon, whose components are soluble neither in the solid nor in the liquid states.

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[161] G. Masing, *Z. anorg. Chem.*, *62*, 265 (1909).

[162] J. Schramm, *Z. Metallkunde*, *28*, 203 (1936); *30*, 10 (1938).

[162a] J. Schramm and A. Mohrnheim, *Z. Metallkunde*, *39*, 71 (1948).

[162b] W. Heike, J. Schramm, and O. Vaupel, *Metallwirtschaft*, *11*, 525, 539 (1932); *12*, 115 (1933); *15*, 655 (1936).

Cadmium and Cadmium Alloys

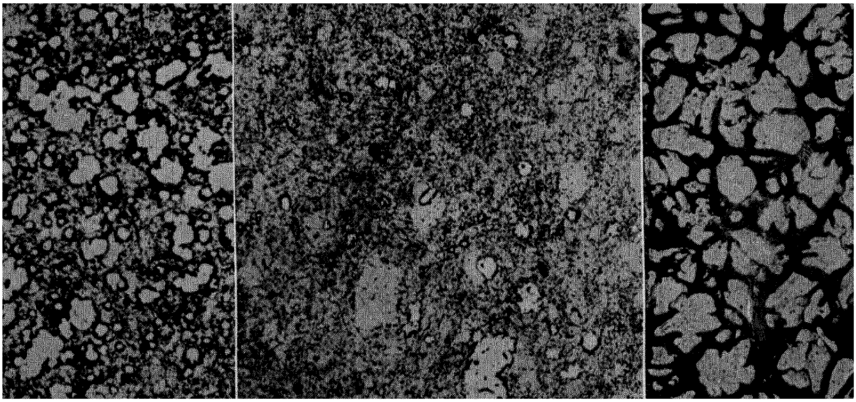
CADMIUM

To the best of the author's knowledge, sintered cadmium metal in its pure form is not yet used for any industrial purpose.

CADMIUM ALLOYS

Cadmium alloyed with copper has found some application in the electrical contact field; the same industry also employs composite materials containing cadmium oxide (see Chapter XXIII).

Cadmium-base bearing alloys with about 1.3% Ni, or with about 0.7% Ag and 0.5% Cu, have been produced by the author by sintering at 300°C. (570°F.) under various atmospheric conditions. Best malleability and uniformity in hardness were obtained by sintering in nitrogen or carbonaceous atmosphere produced from a charcoal pack; sintering in hydrogen produced excessive swelling, which in some cases amounted to as much as 100% increase in the relative volume. The Brinell hardness of the Cd–Ni alloy was 21 or 22 after compaction at 45 tsi and sintering in nitrogen for 3 or 16 hours, respectively; after coining at 45 tsi, the



A *B* *C*

Fig. 610. Microstructure (×100) of cadmium-base bearing alloys. Compacts were prepared from mixtures of the elemental powders by pressing at 30 tsi and sintering for 48 hours at 275°C. (525°F.) in charcoal gas. Etched with standard chromic acid. *A*, Sintered alloy containing 1.3% nickel, balance cadmium; *B*, sintered alloy containing 0.5% copper, 0.7% silver, balance cadmium; *C*, cast alloy containing 0.5% copper, 0.7% silver, balance cadmium.

hardness reached a value of 30.5. Slightly higher hardness values were measured for the cadmium–silver–copper alloy, namely, 26 or 27 Brinell units after compaction and sintering for 3 or 16 hours, respectively, and 34.5 Brinell units after coining at 45 tsi. The alloys can be bonded to steel by pressure sintering onto cadmium-plated corrugated steel strip. Because of lack of uniformity in structure, for which the compulsory low-sintering temperature is responsible, the bearing properties of the sintered alloys are assumed to be inferior to those of the cast counterparts. The heterogeneous character of the sintered structure becomes apparent from Figure 610*A* and *B*, in which the photomicrographs of the sintered binary and ternary alloys are shown and compared with the cast silver-containing bearing metal (Fig. 610*C*).

Tin and Tin Alloys

TIN

Sintered tin has received only academic interest so far; but the compaction of tin has recently been investigated[162c] in connection with pressing rate and density distribution studies. Compressed tin powder compacts are frequently used as masters or control plugs in powder metallurgy die construction. Tin powder is so plastic that it can be compacted to nearly full density at 5 tsi. The low pressure does not cause noticeable elastic expansion of a steel die, so that true replicas of the die cavity may be produced. The advantage of the pressed powder compact over the casting lies in the complete elimination of shrinkage effects. If the densely compressed tin compact is stored at room temperature for a prolonged period of time, it undergoes a slow sintering process. This is evidenced by a gradual decrease in hardness from about 20 Brinell units after compaction at 10 tsi to approximately 10 Brinell units after storage of 48 hours and about 7 Brinell units after storage of one month. Further "aging" results in no change in hardness. Compressed pure (*e.g.*, electrolytic) tin powders are sufficiently malleable immediately after compaction to permit reduction by rolling or extrusion of up to 90% without cracking, but they appear to embrittle appreciably after storage of several hours so that working reduction is no longer possible. Sintering at elevated temperatures of up to 200°C. (390°F.) appears to speed up the embrittlement process, since plain heating in air or hydrogen atmosphere up to sintering temperature and immediate cooling are sufficient to completely destroy the workability. The chief cause for this peculiar behavior of the metal is undoubtedly its affinity to oxygen, while the existence of a brittle phase

[162c] R. Kamm, M. A. Steinberg, and J. Wulff, *Trans. Am. Inst. Mining Met. Engrs., 180,* 694 (1949).

(γ-tin) above 160°C. (320°F.) should have no bearing on the state of the compact at room temperature after cooling and transformation into the regular tetragonal form (β-tin). Even extremely pure tin powder (*e.g.,* electrolytic—containing 99.9% Sn) will form thin oxide films around its particles during handling and compaction, and sintering even in purified hydrogen will not reduce these films, because tin oxides are very stable below the melting point of the metal. However, it has been found possible to sinter tin compacts in the absence of oxygen by submerging them in oils under vacuum, or in reducing acids (*e.g.,* formic acid). The resulting products could be worked with approximately the same ease as the compressed powder compacts.

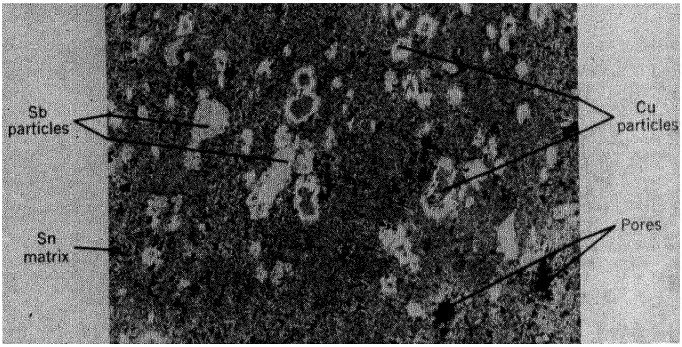


Fig. 611. Incompletely diffused microstructure (×250) of a sintered tin-base bearing alloy after sintering for 24 hours in hydrogen atmosphere at 200°C. (390°F.). Alloy contains 3½% copper, 7½% antimony, balance tin. Etched with 2% nital.

TIN ALLOYS

Alloys of tin with copper, with the latter as major constituent, are extensively used in bearings and friction material, and have been discussed in detail under copper alloys in this chapter, and also in Chapters XXVI–XXVIII. As an addition element to mercury, tin plays an important part in the dental amalgams (see Chapter XXIX).

Sintered tin-base alloys have been suggested as possible substitutes for Babbitt-type bearings. Figure 611 shows the microstructure of a tin alloy containing 7.5% Sb and 3.5% Cu after sintering for 25 hours at 200°C. (390°F.). The treatment was not effective enough for a complete homogenization of the structure, but both the copper and antimony particles were found to be surrounded by diffusion zones of a thickness corresponding to the particle size. As compared with a Brinell hardness of 23 for the cast alloy, the sintered alloy had a hardness of 31 after compaction at 45 tsi and sintering for 2 hours, of 30 after resintering for 23 hours, and of 35 after repressing at 45 tsi. However, it may be presumed that sintering of an atomized tin–antimony–copper alloy powder of low oxygen content would result in a homogeneous structure and in hardness values and bearing properties that closely resemble those of the cast Babbitt alloy.

Lead and Lead Alloys

LEAD

Sintered pure lead has not gained importance as far as is known, but the high specific gravity of the metal, coupled with its comparatively low cost, makes compressed powdered lead a potential material for radiation shield specialties. During the war, very large quantities of powdered lead were used in combination with plastics for machine gun bullets used in target practice (see also Chapter XXX). In combination with other metals in the form of alloys and composite structures, however, lead powders play an important role in industry today.

LEAD ALLOYS

Lead is used as an alloying ingredient in dense and porous copper-base and iron-base bearings (see also Chapters XXV–XXVII). Except for the binary copper–lead heavy duty bearing alloys, the lead content usually does not exceed 6% by weight. Lead is also used as an ingredient in friction materials (see Chapter XXVIII), and in ferrous machine parts that require a certain specific gravity. Lead is added as a powder in bearing and friction products; it is infiltrated in the molten state into sintered ferrous high-density parts. In spite of the apparent lack of affiinity of the metals, composite structures of lead and tungsten were used in World War I for projectile cores because of their high specific gravity.[163,164] The use of tungsten–lead alloys as shielding material for x-rays[165] has also been suggested repeatedly and should now gain renewed interest as a potential radiation shield material in atomic energy work.

Sintered binary lead-base alloys with up to 1% of cobalt or indium have been suggested for bearing materials of improved corrosion resist-

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[163] A. Polster, *Techn. Rundschau, 38,* 278 (1915).

[164] H. Alterthum, *Wolfram.* Vieweg, Braunschweig, 1925.

[165] German Pats. 643,567; 681,403.

ance.[166] Pressures of 25 tsi produce a completely dense compact (11 g./cc.) if .325-mesh powders with a maximum oxygen content of 0.1% are employed. After sintering for 2 hours at 300°C. (570°F.) in dry hydrogen, the compacts are cold-rollable to strip, sheet, or foil. Diffusion rates between the lead and cobalt or indium, however, are reduced appreciably if excessive oxide films surround the lead particles, since the necessarily low temperatures employed for the sintering operation are inadequate for reduction of the comparatively tenacious oxides. While repeated working and sintering tend to crack the films, thereby aiding the diffusion, the use of atomized or electrolytic alloy powders with low oxygen content appears preferable.

Antimony, Bismuth, and Their Alloys

ANTIMONY

No information is available on the sintering of pure antimony.

BISMUTH

Sintered bismuth has been produced that possesses a higher ductility than the cast metal. In extruding cast bismuth into wire used for low-temperature thermostats, embrittlement becomes pronounced which is the result of grain boundary impurities or minute alloying ingredients that precipitate in the boundaries. This difficulty was overcome by the author through hydrogen-sintering very pure bismuth powder compacts, resulting in wires, which, when extruded at room temperature through a 0.035-in. die, retained their ductility after storage over several months. The powder had to be purified carefully—preferably by annealing at 150°C. (300°F.) for 4 hours in hydrogen of a dew point of —60°C. (—76°F.), followed by degassing in vacuum at the same temperature for 2 hours. After compression at 40 tsi to 1-in. diameter, 1-in. high compacts of nearly complete density, sintering had to be performed again in hydrogen of a dew point of —60°C. (—76°F.). The operation required treatment for at least 48 hours under very carefully controlled temperature conditions, which permitted a fluctuation of only about ±5°C. (10°F.) from the mean sintering temperature of 260°C. (500°F.), *i.e.*, 11°C. (20°F.) below the melting point of bismuth. No improvement in ductility of the extruded wire was obtained by repressing or resintering the compact, or by sintering in high vacuum, or by annealing the wire after extrusion either in hydrogen or in vacuum.

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[166] C. Hardy, *private communications,* based on Laboratory Repts. Nos. 11, 98, and 173 of Chas. Hardy, Inc., N. Y.

BISMUTH ALLOYS

Bismuth has been suggested as an alloying ingredient of major proportion for composite contact metals for special electrical control applications, in bearings where bismuth imparts high antifriction properties at slightly elevated temperatures, and also as rectifying disks after chemical treatment to form stable oxides, sulfides, selenides, or tellurides of bismuth.[167] Of particular interest is the fact that the electrical resistance of bismuth increases in a magnetic field with the strength of the latter, while it varies inversely with a change in temperature. These properties are utilized in composite alloys of bismuth with metals such as copper, silver, aluminum, tungsten, and molybdenum. Whereas these composite structures can be readily produced by pressing the mixed powders and sintering at a temperature considerably above the melting point of bismuth, the impregnation method is preferred, since the production of strong and dense structures are assured by the fact that bismuth expands upon solidification.[167] To produce composites containing from 40–60% Bi, the impregnation of the higher melting skeleton bodies is carried out advantageously at 625°C. (1160°F.) in a hydrogen atmosphere.

Germanium, Gallium, Indium, Thallium, and Their Alloys

To the author's knowledge the pure metals, germanium, gallium indium, and thallium, have not been produced by the sintering technique and neither have alloys of the first two metals. However, indium has been used as minor alloying addition to lead (see page 719). Thallium alloys of the systems bismuth–thallium and lead–thallium have been produced from mixtures of the elemental powders,[168] and it was found that, even at room temperature, formation of solid solutions and intermediate phases took place to a noticeable extent. A polyphase structure could be developed in a compact from a mixture of 63% Bi and 37% Tl (filings) after heating in air for 5$^1/_2$ hours at 120°C. (248°F.), and microscopic observation disclosed the growth of an intermediate bandlike phase at the interface between the original bismuth and thallium particles. The diffusion rate was thereby increased 1000- to 2000-fold, and a sufficiently extended sintering time produced a structure which corresponded completely with that of the fused alloy. Aluminum–thallium alloys have recently been suggested as a porous bearing material.[169] Such bearings are made by incorporating thallium or its alloys into aluminum powders to the extent of 0.5 to 45% Tl. The thallium may be added by impreg-

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[167] Brit. Pat. 590,412.

[168] G. Masing, *Z. anorg. Chem., 51,* 330 (1906); *62,* 265 (1909).

[169] U. S. Pat. 2,418,881.

nating the compacted aluminum-base metal, or it may be added in powdered form to the aluminum powder before molding. An example of the base composition is a mixture of 70% by volume of an aluminum-base alloy powder containing 7% Sn, balance Al; the remaining 30% by volume consists of a 50–50 Pb–Tl alloy. Compaction is best performed at 30 tsi, sintering at 400°C. (750°F.). After repressing at 50 tsi the bearings display good thermal conductivity, low coefficient of friction, low specific gravity, and a marked resistance to corrosion.

Mercury and Amalgams

Mercury has played an important part in the early history of tungsten powder metallurgy. In the amalgam process, tungsten filaments were obtained by mixing tungsten powder with cadmium and bismuth amalgams (42% Cd, 5% Bi, 53% Hg) and pressing the plastic mixture through nozzles, followed by sintering, whereby the amalgams were distilled off.

In the manufacture of dental amalgams the essential elements are mercury, silver, and tin. The powder metallurgy of dental amalgams is discussed in Chapter XXIX.

LIGHT METALS AND ALLOYS

Aluminum and Aluminum Alloys

ALUMINUM

The subject of sintered pure aluminum has been discussed at length in Chapter XXVI.

ALUMINUM ALLOYS

Whereas pure sintered aluminum has found no industrial application to date, sintered aluminum alloys have been used to a limited extent in the production of lightweight parts and bearings; they have the advantage of lightness, high heat conductivity and resistance to oil oxidation. These materials have potential applications in highly stressed structural parts, porous bearings for washing machines and household appliances, and dense heavy duty bearings for airplane engines, airplanes, rockets, lightweight surface vehicles of all kinds. They may also find use as friction elements in clutches for automobiles and other high-speed engines, where a reduction in weight will cause a reduction in the kinetic energy of the disk—increasing the life of the clutch considerably. One of the principal handicaps, however, is the cost involved, since the presently available raw materials (*e.g.*, granular aluminum powder and atomized oxygen-free alloy powders) and the closely controlled manufacturing conditions, especially as they pertain to the molding operation, are still rather costly. With the advancement of the art, however, it is believed quite possible that both the raw material costs and the costs connected with the molding, powder mixing, and sintering operations will be reduced drastically, thereby enabling the powder metallurgy of light alloys to become one of the main branches of the field.

Sintered aluminum alloys of high density suitable for structural parts have been described in Chapter XXVI; porous aluminum-base alloys adaptable for self-lubricating bearings have been discussed in Chapter XXVII. At present, however, the most important use of aluminum in powder metallurgy is as a minor alloying component in the Alnico-type permanent magnet, in which the element, in order to prevent excessive oxidation, is added as a powdered master alloy with iron or nickel (see Chapter XXIV).

Aluminum–Copper. Binary aluminum–copper alloys with 4 to 5% Cu are most promising for use in lightweight structural parts. The alloy is readily obtained by sintering compacted mixtures of the elemental powders in air for a comparatively short time (4 hours); the resulting physical properties are excellent. Compacts compressed at 40 tsi and sintered at 550°C. (1020°F.) were found to have a tensile strength of 38,000 psi, a yield strength of 16,000 psi, and an elongation of 17% (see also Table 219, Chapter XXVI). Difficulties of compaction and ejection encountered in pure aluminum powders are lessened considerably by the addition of the copper, since the copper particles tend to dislodge adhesions of aluminum particles to the die walls. The use of atomized alloy powder eliminates the molding and ejection difficulties entirely, but the resulting products are generally of inferior quality because of a greater rigidity of the particles and therefore an increased porosity of the compact formed at conventional pressures (30–50 tsi).

Recent German research[169a] on binary compositions containing 10 and 20% Cu established that, in alloys in a state of partial equilibrium as obtained by a controlled sintering process, the properties are much dependent not only upon the degree of diffusion achieved but also upon the presence of impurities (similar observations on copper-rich alloys are described in the section on copper–aluminum alloys). Even in the non-equilibrium state, certain alloys can be sufficiently plastic to undergo extrusion.

[169a] E. Nachtigall, *Proc. International Powder Metallurgy Conference*, Graz, July 12–17, 1948, Referate No. 30.

Aluminum–Copper–Silicon. Additions of silicon to the aluminum–copper alloys are not usually too effective because of the strong oxidizing tendency of the silicon, which interferes with diffusion. Sintering temperatures are too low, and ordinary reducing atmospheres (hydrogen, ammonia) not potent enough to reduce the silica films once they are formed. However, a certain precipitation-hardening effect can be obtained if very pure powders are used and if the silicon is added in the form of a pulverized master alloy (*e.g.*, 85–15 Al–Si). The author found that sintering for a prolonged period of time (*e.g.*, 16 hours) at 530°C. (985°F.) in hydrogen of a dew point of —60°C. (—76°F.) results in a substantially diffused alloy, which, after water quenching and precipitation hardening at 120°C. (250°F.), exhibits a hardness in the order of 110 Brinell units, a tensile strength of 27,000 psi, and an elongation of 3%. Aging curves for this alloy are shown in Figure 612.

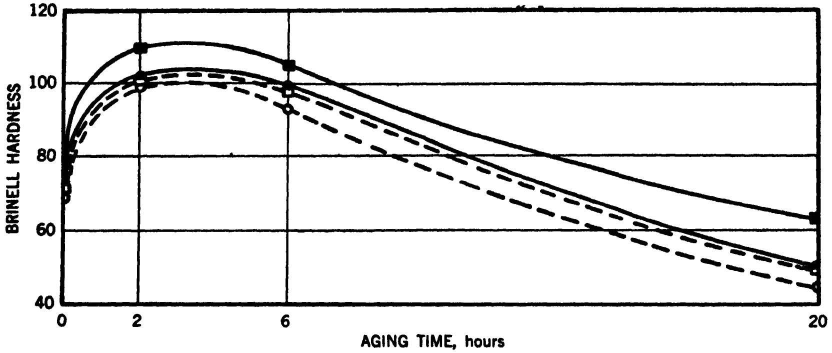

Fig. 612. Effect of aging time on the Brinell hardness of sintered 94–4.5–1.5 aluminum–copper–silicon alloy. Compacts were produced from a mixture of the elemental powders at the pressures indicated, followed by sintering in hydrogen for 16 hours at 500°C. (930°F.) and furnace cooling. One series was repressed at the pressures indicated, and then reheated to 530°C. (985°F.) and water quenched; the other series was directly reheated to 530°C. (985°F.) and water quenched. All specimens were precipitation treated at 120°C. (250°F.) for the time indicated. (○) Compacts pressed at 35 tsi; (●) pressed and repressed at 35 tsi; (□) pressed at 70 tsi; (■) pressed and repressed at 70 tsi.

More complex alloys, containing about 7% Cu, 5% Si, and Fe, Zn, and Mg in minor proportions not exceeding a total of 5%, which were produced in the same way as the ternary alloy, showed no marked improvement in physical properties. The maximum hardness obtainable by precipitation treatment was 105 Brinell units, and the corresponding tensile strength was 29,000 psi. Table 276 reproduces some of the hardness values obtained with this type of alloy.

Aluminum–Copper–Magnesium. Sintered alloys containing copper and magnesium as major alloying constituents, and manganese or iron as minor addition elements, have found special interest in powder metallurgy. Known generally as Duralumin, these alloys are superior in their susceptibility to precipitation hardening and produce physical properties that compare with those of a mild steel. An alloy of the Duralumin type, containing 4% Cu and 0.5% each of Mg and Mn, produced by compacting mixtures of the elemental powders at 50 tsi, and sintering in dry nitrogen at 580°C. (1075°F.) for 30 minutes, has been reported[170] to

TABLE 276

Hardness of Sintered and Coined Aluminum–Copper–Silicon Base Alloys[a]

	Brinell hardness	
Treatment	Alloy A[b]	Alloy B[c]
Compacted and coined at 25 or 50 tsi; sintered in hydrogen at 450°C. (840°F.) for 4 hr.; reheated in charcoal pack at 450°C. (840°F.) for 1 hr. and water quenched		
Sintered alloy, compacted at 25 tsi	53	38
50 tsi	72	60
Coined alloy, compacted and coined at 25 tsi	63	56
50 tsi	77	70
Precipitation treated at 150°C. (300°F.)		
Sintered alloy, compacted at 25 tsi		
precipitation treated for 2 hr.	60	41
4 hr.	62	43
7 hr.	64	46
10 hr.	66	46
20 hr.	57	39
Sintered alloy, compacted at 50 tsi		
precipitation treated for 2 hr.	84	63
4 hr.	85	64
7 hr.	98	66
10 hr.	96	65
20 hr.	75	53
Coined alloy, compacted and coined at 25 tsi, precipitation treated for		
2 hr.	72	61
4 hr.	78	63
7 hr.	78	63
10 hr.	87	65
20 hr.	70	53
Coined alloy, compacted and coined at 50 tsi, precipitation treated for		
2 hr.	86	71
4 hr.	88	80
7 hr.	105	76
10 hr.	102	74
20 hr.	86	58

[a] Courtesy Charles Hardy, Inc., New York, N. Y. Data abstracted from Laboratory Report No. 49.

[b] 82.5–7–5.5–3–1.5–0.5 Al–Cu–Si–Mg–Fe–Zn.

[c] 85–7.2–5.5–1.5–0.5–0.3 Al–Cu–Si–Fe–Zn–Mg.

exhibit a tensile strength of 33,000 psi after solution treatment, and 50,000 psi after aging at room temperature for 4 days, with an elongation of 10% remaining unchanged by the precipitation treatment. The effect of precipitation hardening at 120°C. (250°F.) for Duralumin compacts pressed and coined at different pressures and sintered at 500°C. (*i.e.*, below the eutectic temperature) for 16 hours followed by water quenching, is shown in Figure 613.

Compacts produced from fusion-alloyed Duralumin powder appear to lack the excellent physical properties produced with the powder mixtures, possibly because of increased resistance to deformation of the alloy powder which results in greater porosity and brittleness. A compact pressed at 50 tsi from atomized Duralumin powder and sintered for 30 minutes at 580°C. (1075°F.) exhibited only a tensile strength of 30,000 psi with an elongation of 3% after water quenching; aging for 4 days at room temperature increased the tensile strength to only 33,000 psi and reduced the elongation to zero. Even lower tensile results (3000 psi) were reported for a Duralumin alloy powder compact sintered at 500°C. (930°F.).[170]

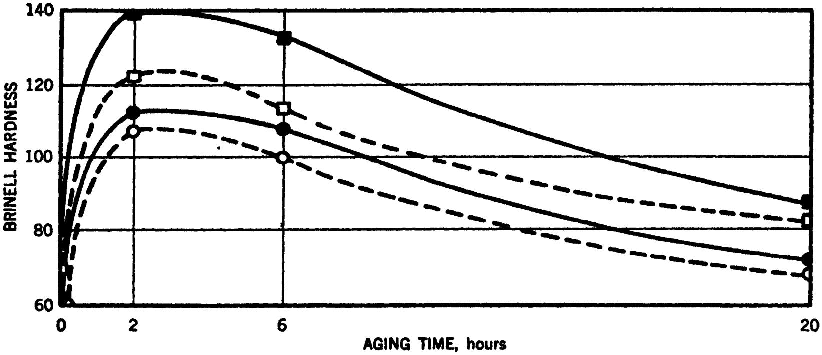

Fig. 613. Effect of aging time on the Brinell hardness of sintered Duralumin compacts (composition: 94.5–4.5–0.5–0.5 Al–Cu–Mg–Mn). Compacts were produced from a mixture of the elemental powders at the pressures indicated, followed by sintering in hydrogen for 16 hours at 500°C. (930°F.) and furnace cooling. One series was repressed at the pressures indicated, and then reheated to 530°C. (985°F.) and water quenched; the other series was directly reheated to 530°C. (985°F.) and water quenched. All specimens were precipitation treated at 120°C. (250°F.) for the time indicated. (The symbols are identified in Figure 612.)

One interesting aspect is given by the possibility of employing master alloy powders together with pure aluminum powder.[170a] By sintering

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[170] G. D. Cremer and J. J. Cordiano, *Trans. Am. Inst. Mining Met. Engrs.*, *152*, 152 (1943).

[170a] Brit. Pat. Applic. 9150/47, (April 16, 1946); see also *Metal Powder Rept.*, *2*, No. 5, 69 (1948).

above the eutectic temperature of about 550°C. (1020°F.), the Duralumin master alloy powder forms a liquid phase that cements the aluminum particles and creates a strong grain boundary constituent. Careful control of the sintering time avoids complete homogenization, which would reduce the alloy concentrations in the grain boundary network. As can be seen from Table 277, compacts from mixtures containing various percentages of the alloy powder—produced by compression at 40 tsi and air-sintering for one hour at 600°C. (1110°F.) followed by water quenching—combine the superior strength of the alloy with the superior ductility of the pure sintered aluminum. The nonequilibrium structure of this type of material appears particularly advantageous for lightweight bearing applications involving both dense and porous products (see also Chapter XXVI).

TABLE 277
Effect of Duralumin Powder Addition to Pure Aluminum Powder Compacts[a]

Composition				
Aluminum, %	Duralumin, %	Treatment	Tensile strength, psi	Elongation, %
100	—	Cast, annealed	10–12,000	30–40
—	100	Cast, annealed	20–30,000	15–25
100	—	Pressed at 30 tsi, sintered at 615°C. (1140°F.) 1 hr. in NH_3	11,850	48
—	100	Pressed at 50 tsi, sintered at 580°C. (1075°F.) 30 min., in air, water quenched	30,000	3
80	20	Pressed at 40 tsi, sintered at 600°C. (1110°F.) 1 hr. in air, water quenched	22,200	20
70	30	Pressed at 40 tsi, sintered at 600°C. (1110°F.) 1 hr. in air, water quenched	24,500	18

[a] Courtesy of P. Schwarzkopf and American Electro Metal Corp., Yonkers, N. Y.

Aluminum–Copper–Nickel–Magnesium. Sintered aluminum-base alloys containing 4% Cu, 2% Ni, and 1.5% Mg were also found by the author to be susceptible to precipitation hardening. Age-hardening curves are shown in Figure 614 for compacts pressed from the mixed meta powders at different pressures, sintered in dry hydrogen (dew point —60°C.; —76°F.) for 16 hours at 500°C. (930°F.) and water quenched and precipitation treated at 120°C. (250°F.). In its fully precipitated state, the highly densified material exhibited a Brinell hardness of 146 a tensile strength of 44,000 psi, and an elongation of 4%.

Aluminum–Silicon. Sintered binary alloys of aluminum and silicon have a potential field in automobile piston applications. High-silicon alloys are extremely desirable because of their excellent coefficients of thermal expansion and low specific gravity, but casting difficulties limit the permissible silicon content to about 15%. However, sintering of these alloys also meets with serious obstacles because of the affinity of the silicon to oxygen, which interferes with diffusion. While master alloys can be used for alloys of comparatively low silicon content, their use is not feasible for alloys containing more than 15% Si. Considerable difficulties have been encountered in the production and use of alloy powders containing 20 to 30% Si, both with regard to fusion and atomizing, and with regard to compaction of the hard and brittle powder. On the other

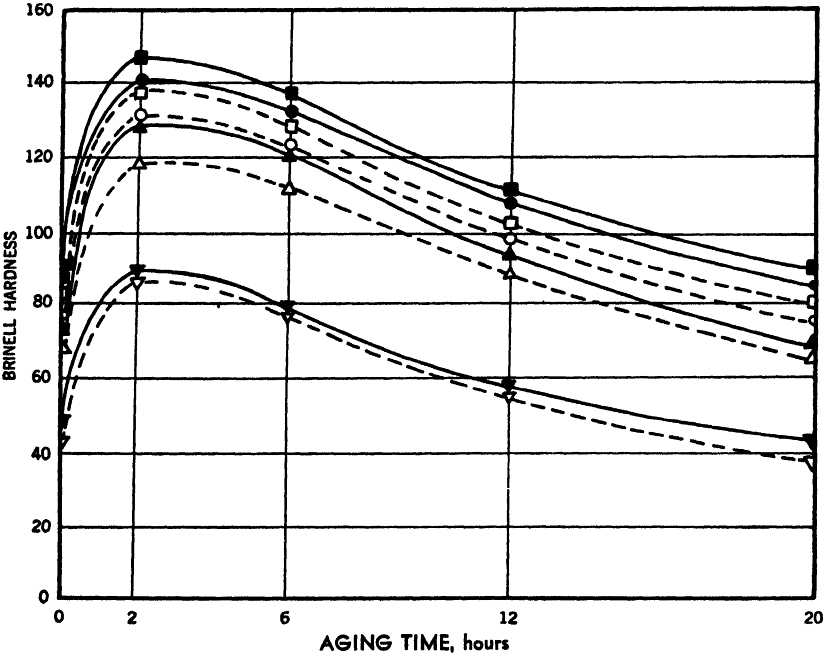

Fig. 614. Effect of aging time on the Brinell hardness of sintered 92.5–4–2–1.5 aluminum–copper–nickel–magnesium alloy. Compacts were produced from a mixture of the elemental powders at the pressures indicated, followed by sintering in hydrogen for 16 hours at 500°C. (930°F.) and furnace cooling. One series was repressed at the pressures indicated, and then reheated to 510°C. (950°F.) and water quenched; the other series was directly reheated to 510°C. (950°F.) and water quenched. All specimens were precipitation treated at 120°C. (250°F.) for the time indicated. (▽) Compacts pressed at 10 tsi; (▼) pressed and repressed at 10 tsi; (△) pressed at 30 tsi; (▲) pressed and repressed at 30 tsi; (○) pressed at 50 tsi; (●) pressed and repressed at 50 tsi; (□) pressed at 70 tsi; (■) pressed and repressed at 70 tsi.

hand, the sintering of mixed powder compacts did not produce uniform materials even if very pure powders were used, and the heat treatment was performed in very dry hydrogen or cracked ammonia. Compacts containing from 20 to 30% Si were found by the author to possess a hardness of only 45 to 50 Brinell units after compaction at 45 tsi and sintering in dry hydrogen at 500°C. (930°F.) for 16 hours. The development of production methods for master alloy powders containing about 50% Si in combined form would undoubtedly further the interest in the piston alloy production by powder metallurgy.

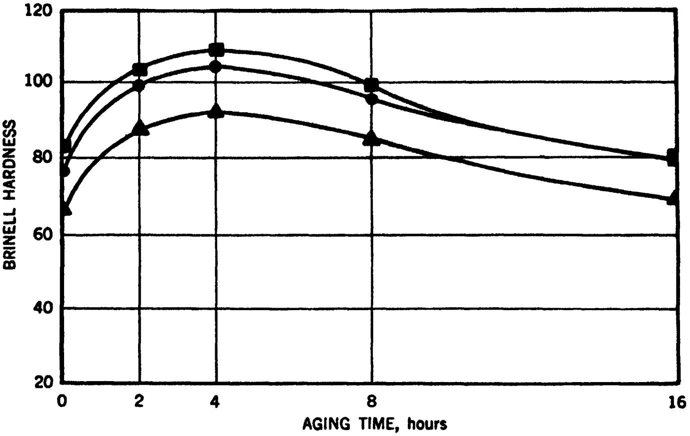

Fig. 615. Effect of aging time on the Brinell hardness of different aluminum–silicon-base complex sintered alloys. Compacts were produced from mixtures of the elemental powders at 65 tsi, followed by sintering in hydrogen for 14 hours at 500°C. (930°F.), repressing at 65 tsi, reheating to 525°C. (975°F.), and water quenching. All specimens were precipitation treated at 175°C. (350°F.) for the time ndicated. (▲) 85.2–12–1–0.8–1 Al–Si–Cu–Ni–Mg; (●) 74.8–21–1.5–1.5–0.7–0.5 Al–Si–Cu–Ni–Mn–Mg; (■) 78.3–14–4.5–1.5–1–0.7 Al–Si–Cu–Ni–Mn–Mg.

The properties of alloys containing 13.5, 20, and 30% Si in a state of only partial equilibrium have recently been studied,[169a] and the results were found generally in agreement with those observed on aluminum–copper alloys (page 723).

Aluminum–Silicon–Copper–Nickel. The powder metallurgy production of more complex aluminum–silicon-base alloys suffers from the same sintering difficulties encountered in the binary alloys. Only prolonged sintering periods, very fine and pure powders, and an extremely well-dried reducing atmosphere produce sufficient homogenization during sintering and solution treating to obtain a precipitation effect. The diagram of Figure 615 represents age-hardening curves for three different alloys containing various amounts of silicon, copper, and nickel, with magnesium and manganese as minor addition elements. All the alloys were produced by compaction at 65 tsi, sintering at 500°C. (930°F.) for 14 hours in hydrogen of a dew point of —60°C. (—76°F.), coining at 65 tsi, reheating at 525°C. (975°F.) for 2 hours, and water quenching. Precipitation hardening was performed at 175°C. (345°F.). From the character of the individual curves it may be concluded that the response of the different alloys to the aging treatment was definitely noticeable, although the numerical hardness values lie below those obtainable with the fused alloys of corresponding analysis.

Aluminum–Zinc. Sintered binary alloys of aluminum and zinc have been investigated[171] but only moderate tensile strengths were obtained by air-sintering at temperatures up to 510°C. (950°F.). By sintering at 570°C. (1060°F.), however, a 90–10 Al–Zn alloy could be produced that would combine good tensile strength (22,000–25,000 psi) with excellent elongation (16–17%). More detailed data for this alloy are given in Table 216, Chapter XXVI.

Aluminum–Zinc–Magnesium. A ternary alloy containing 7% Zn and 3% Mg was investigated,[171] and is described more fully in Chapter XXVI. Sintering in air at 510°C. (950°F.), followed by water quenching, resulted in a tensile strength of 40,000 psi; this figure could be increased to 45,850 psi by aging the compact at 140°C. (290°F.) for 24 hours. These figures are comparable with those obtained by sintering in cracked ammonia, as given in Table 218, Chapter XXVI.

Aluminum–Zinc–Copper. Aluminum alloys containing 12% Zn, 3% Cu, and 0.5% each of Mg and Mn have also been produced by the sintering technique, but their response to precipitation hardening was found to be smaller than that of either the ternary aluminum–zinc–magnesium alloy or the standard zinc-free Duralumin alloy. Aging for 10 days at room temperature produced a maximum hardness value of 70 Brinell, as compared with a Brinell hardness of 44 for the solution-treated alloy.

Aluminum–Magnesium. A sintered binary aluminum alloy containing 10% Mg has been produced[171] by sintering in air at 430°C. (800°F.) for 24 hours. A compact, initially pressed at 55 tsi, had a porosity of only 3.3% and a tensile strength of about 25,000 psi. This alloy has been described more fully in Chapter XXVI. It should meet with considerable interest where weight-saving applications are concerned, owing to its very low specific gravity, which is roughly 90% of that of pure

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[171] L. W. Kempf, in J. Wulff, *Powder Metallurgy*. Am. Soc. Metals, Cleveland, 1942, p. 314.

aluminum, and about 80% of that of aluminum–copper or aluminum–zinc alloys. Additional information on these alloys is given under magnesium alloys (page 741).

Aluminum–Manganese. Aluminum-base powder mixtures, containing approximately 5% of the intermetallic compound Al_5Mn in the form of atomized or pulverized powder, have been compacted at 18 to 28 tsi and sintered in air at 600°C. (1110°F.) for a period up to 72 hours.[172] By the appropriate selection of composition and treatment,

TABLE 278

Density and Hardness of Sintered Aluminum–Lead Alloys[a]

Composition of powder mixture		Sintering temperature,[d]		Sintering time,[d] hr.	Lead loss, % of Pb	Final lead content, %	Density, g./cc.	Brinell hardness
Al,[b] %	Pb,[c] %	°C.	°F.					
90	10	300	570	1	—	10.0	2.79	38.0
				6	—	10.0	2.79	37.0
		400	750	1	0.6	9.9	2.80	36.0
				6	1.2	9.9	2.79	35.0
		500	930	1	1.2	9.9	2.80	29.7
				6	1.7	9.8	2.80	28.4
80	20	300	570	1	—	20.0	3.08	38.0
				6	—	20.0	3.09	36.0
		400	750	1	0.6	19.9	3.06	33.6
				6	0.9	19.8	3.08	32.0
		500	930	1	1.2	19.8	3.07	29.1
				6	1.45	19.7	3.05	27.8
70	30	300	570	1	—	30.0	3.37	37.0
				6	—	30.0	3.39	34.5
		400	750	1	3.65	28.9	3.30	32.0
				6	6.5	28.1	3.31	30.4
		500	930	1	7.15	27.9	3.27	26.5
				6	7.7	27.7	3.28	24.9
60	40	300	570	1	—	40.0	3.73	33.6
				6	—	40.0	3.77	31.2
		400	750	1	11.1	35.5	3.45	28.4
				6	13.8	34.5	3.51	27.2
		500	930	1	15.4	33.8	3.49	23.8
				6	17.5	33.0	3.46	22.8
50	50	300	570	1	—	50.0	4.21	28.4
				6	—	50.0	4.18	23.8
		400	750	1	25.75	37.1	3.61	22.8
				6	28.45	35.8	3.61	21.8
		500	930	1	30.0	35.0	3.54	20.1
				6	32.4	33.8	3.46	19.0

[a] Courtesy Charles Hardy, Inc., New York, N. Y. Data abstracted from Laboratory Report No. 44.

[b] Atomized aluminum powder, −150 mesh.

[c] Atomized lead powder, −325 mesh (sieved).

[d] Compacts sintered in dry hydrogen after compaction at 30 tsi.

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[172] G. Wassermann and R. Weber, *Metallwirtschaft*, **22**, 201 (1943).

a stable state of equilibrium is produced between the liquefied compound in the grain boundaries and the solid aluminum particles. The solidified structure has been found suitable for bearing purposes,[172] and should find potential use as a lightweight bearing material for applications involving aircraft and surface transport machinery. This subject has been discussed further in Chapter XXVII. Sintered binary alloys in only partial equilibrium, containing 2, 10, and 20% by weight of manganese, have recently been investigated,[173] and it was found that the degree of diffusion, as well as that of the purity of the ingredients, affects the ultimate properties.

Aluminum–Iron. Porous sintered aluminum–iron bearing alloys in which the iron is added as powdered intermetallic compound, Al_3Fe, in proportions from 5 to 9%, are produced in a similar manner as given for the aluminum–manganese alloys[172]; they have also been described in Chapter XXVII. Alloys containing larger proportions of iron, *i.e.*, 4, 10, 25, and 50% by weight, have been studied more recently[173]; as in the case of aluminum–manganese alloys, the final properties of the sintered compacts were found to be affected by the uniformity of the duplex structures, and also by the purity of the components.

Aluminum–Lead. Alloys of aluminum and lead have also been used for bearing purposes[172] (see also Chapter XXVII). Because of the wide difference in specific gravity of the two elements and the ensuing segregation in the liquid state, it is extremely difficult to produce these alloys by casting methods; therefore, this case constitutes a natural application for powder metallurgy. Although the bearing properties of these alloys appear somewhat inferior to those obtainable in ordinary Babbitt bearings, there is a potential field of application in aircraft and surface transport engines and in general machinery where weight-saving is a factor. Table 278 shows the density, hardness, and lead loss for alloys with different lead contents that have been sintered under various conditions in hydrogen (dew point —60°C.; —76°F.), and Table 279 shows compressive and tensile properties for alloys of 80–20 and 60–40 Al–Pb compositions.

Aluminum–Thallium. Bearing alloys based on this system have been described previously under thallium alloys.

Aluminum–Tin. Sintered binary aluminum alloys containing from 5 to 8% Sn, and more complex alloys with 6.5% Sn and smaller proportions (about 1% each) of nickel, and copper, with or without silicon (2.5%), have been found to yield bearing properties that are superior

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[173] E. Nachtigall, *Proc. International Powder Metallurgy Conference,* Graz, July 12–17, 1948, Referate No. 30.

TABLE 279

Tensile and Compressive Properties of Sintered and Coined 80–20 and 60–40 Aluminum–Lead Alloys[a]

Composition of powder mixture		Compacting pressure, tsi	Sintering temperature,[d]		Sintering time,[d] hr.	Coining pressure, tsi	Tensile properties			Compression properties		
Al,[b] %	Pb,[c] %		°C.	°F.			Ultimate strength, psi	Elongation in 2 in., %	Reduction of area, %	Ultimate strength, psi	Compression, %	Increase of area, %
80	20	30	300	570	6	—	5,690	0.8	0.75	21,100	23.6	29.8
					6	30	7,330	1.2	1.25	—	—	—
					16	—	6,550	0.8	1.00	27,300	30.3	37.7
					16	30	10,080	1.7	1.75	—	—	—
60	40	30	300	570	6	—	4,750	0.8	0.75	14,900	13.3	27.3
					6	30	6,750	0.8	1.20	—	—	—
					16	—	6,010	0.8	0.90	20,500	24.0	31.9
					16	30	8,330	1.2	1.75	—	—	—

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[a] Courtesy Charles Hardy, Inc., New York, N. Y. Data abstracted from Laboratory Report No. 44.

[b] Atomized aluminum powder, −150 mesh.

[c] Atomized lead powder, −325 mesh (screened).

[d] Compacts sintered in dry hydrogen.

to those of aluminum–lead compositions and that match the best precipitation-hardened aluminum alloy bearings. In fact, if produced by fusion methods, this type of alloy is claimed to combine desirable characteristics of white metal and copper–lead bearing alloys, such as the antifriction and corrosion resistance of the former and the strength and fatigue of the latter.[173a] In contrast to Babbitt alloys, it retains its hardness up to a temperature of 150°C. (300°F.). An additional advantage is the relatively high heat conductivity, which is about three times that of steel and five times that of Babbitt. Tested at increasing speeds—up to 3000 r.p.m.—and at increasing loads—up to 24,000 psi—the relative friction of the aluminum–tin alloys was found to be lower than that of either white metal or copper–lead bearings under identical test conditions; the wear resistance was also better than that of the copper–lead bearings.

Aluminum–Carbon. A 90–10 Al–C composition has been studied recently,[178] and it was found that the aluminum–graphite powder mixture gave fairly good strength values after pressing and sintering at 600°C. (1110°F.); microscopic examination disclosed the formation of the compound Al_4C_3.

Magnesium and Magnesium Alloys

MAGNESIUM

The sintering of magnesium and its alloys presents considerable difficulties; the powder now available commercially is produced by machining or by other comminution methods; it is, therefore, heavily oxidized and has a particle shape not particularly suitable for compaction and for the formation of contact points and sinter bonds. Moreover, magnesium readily absorbs such gases as nitrogen and oxygen at elevated temperatures, making the sintering operation even more difficult. Extremely weak and brittle compacts have resulted from sintering in dissociated ammonia, and vacuum sintering above 550°C. (1020°F.) often causes complete disintegration (possibly due to reactions with surface impurities). Sintering in very dry hydrogen (dew point —65°C.; —85°F.) or in argon at 600°C. (1110°F.) has resulted in fairly strong but brittle compacts (tensile strength 9500 psi, elongation nil). Imbedding of the compacts in a pack of magnesium powder to which an equal part of Al_2O_3, MgO, or BeO is admixed produces a getter action and prevents oxidation during sintering. However, this expedient effects only insignificant changes in physical properties.

[173a] H. Y. Hunsicker and L. W. Kempf, *Quart. Trans. Society of Automotive Engrs., 1,* No. 1, 6 (1947).

Sintered pure magnesium has a potential field as a starting material for wrought products, since the ingots obtained by fusion processes are contaminated with gaseous inclusions and films around the grains. But further development of the powder metallurgy approach must wait for the advent of new techniques of manufacturing the powder to a quality which is better with regard both to purity and to particle shape. While it may be possible to improve the purity of the mechanically comminuted powder by acid pickling or other chemical cleaning, a more suitable particle shape can be produced only by employing other production methods, such as atomizing, condensation from the vapor phase, or electrolysis.

In this connection, some extremely interesting work on sintered magnesium, performed several years ago in Germany, was recently reported.[174] The most significant phase of this investigation is the portion dealing with the properties of extruded crystal aggregates of distilled magnesium. These crystal aggregates were compacted at 6.6 tsi into bars of $^3/_4$-in. diameter and extruded at about 330°C. (625°F.)—without previous sintering—into $^5/_{32}$-in. diameter wire. For comparison, remelted distilled magnesium, cast magnesium of commercial quality, and sintered magnesium from compacted commercial powder were processed in the same way. Duplicate tests on a larger scale were also made on bars, which were cut into hexagonal prisms of 2.5-in. diameter, hot-pressed at a temperature ranging from 280 to 420°C. (535 to 790°F.) (in the extrusion press, by blocking the outlet), and finally hot-extruded into $^5/_8$-in. diameter rods. Some of the extruded material was cold-rolled into 0.1- and 0.05-in.-thick strips and ultimately annealed at 280–320°C. (535–610°F.). The physical properties of the magnesium specimens produced in these various ways are given in Table 280. Corrosion tests carried out on the rolled and annealed strips by immersion in 1% NaCl solution showed that the extruded crystal aggregates were equal to a commercial magnesium–manganese alloy—presumably because of their high purity—while all other magnesium specimens were considerably inferior. Exposure to tap water for 6 weeks produced greater corrosion in the extruded crystal aggregates than in cast magnesium; this may be attributed to inherent porosity in the former, since the opposite behavior was found after bichromate coating.

This work is especially noteworthy in that it points the way toward the production of magnesium components by powder metallurgy that may *surpass* in physical and chemical properties the products now made by conventional casting methods. This point of view is further strengthened by the fact that magnesium can be extracted from sea water in great

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[174] F. Sauerwald, *Arch. Metallkunde, 1*, No. 7/8, 363 (1947).

abundance, so that increased demand for the metal caused by possible new applications based on a newly developed technology can be readily fulfilled. While it is apparent that high-purity powders, such as the distilled crystal aggregates, will yield optimum properties, it has been shown that even such low-class material as swarf can be processed into products having attractive properties. Thus, a potential industrial development in the direction of structural parts and bearings of extremely low specific gravity (less than 2) is indicated.

TABLE 280

Physical Properties of Extruded Magnesium from Powders and Cast Ingots (Sauerwald[174])

Material	Treatment		Properties		
	Processing	Working	Yield strength, psi	Tensile strength, psi	Elongation, %
Distilled magnesium crystal aggregates	Hot-pressed at 280–420°C. (535–790°F.)	Extruded at 320–340°C. (610–645°F.) to 5/8-in. diameter rod	12,000–20,000	24,000–30,000	8.0
		Extruded at 320–340°C. (610–645°F.) to 5/8-in. diameter rod, and rolled	16,400	24,400	5.0
		Extruded at 320–340°C. (610–645°F.) to ribbon, 0.1 in. thick	8,600	21,600	7.5
	Remelted		11,200	22,600	5.8
	Hot-pressed at 280–420°C. (535–790°F.)	Extruded at 320–340°C. (610–645°F.) to ribbon 5/8-in. thick, and rolled	12,200	27,600	5.8
	Remelted		12,200	26,800	9.0
	Cold-pressed at 6.6 tsi	Extruded at 320–340°C. (610–645°F.) to 5/32-in. diameter wire	—	27,800	7.5
	Remelted		—	24,400	4.2
Magnesium powder	Cold-pressed at 6.6 tsi		—	21,000	0.5
Fused magnesium	Cast		—	32,200	7.5
98–2 magnesium–manganese wire	5/32-in. diameter wire, as supplied		—	35,400	3.5

MAGNESIUM ALLOYS

Attempts have been made to alloy magnesium and other light metals (Al, Be), heavy low-melting metals (Zn, Pb, Sn, Cd, Bi, Sb), and some higher melting metals (Mn, Cr). The powdered ingredients have been mixed with magnesium powder to test the formation of alloys under pressure alone. When heating in air, it was found that a number of intermetallic compounds were formed in the solid state.[175] Experiments with magnesium–iron compositions have already been discussed under iron alloys (page 627).

Table 281 reproduces the procedure used and the results obtained by the author in the sintering of a number of typical magnesium alloys. Brinell hardness values obtained on healthy specimens fall within the range found in the cast alloys of corresponding composition.

Part of the aforementioned investigation[174] was concerned with material made from fine grindings and turnings (swarf) of pure Mg and a 91–9 magnesium–aluminum alloy, which were compared with material produced in a similar manner from duralumin or 91–9 aluminum–magnesium alloy swarf. The powdered materials were compacted either into small bar shapes, approximately 2 in. long and $^3/_4$ in. in diameter, at 20 tsi, or into large ingot shapes, 4 to 6 in. long and 2.5 in. in diameter, at 12.5 tsi. Sintering was performed under argon at 250°, 400°, and 550°C. (480°, 750°, and 1020°F.) for 2, 8, and 24 hours, respectively, and was followed by water quenching. Final consolidation was obtained by hot-extrusion of the $^3/_4$-in. diameter bars to $^5/_{16}$-in. diameter rods, and of the 2.5-in. diameter ingots to $^5/_8$-in. rods, the extrusion temperatures being 300°C. (570°F.) for the pure magnesium, 340°C. (645°F.) for the magnesium alloy, and 450°C. (840°F.) for the aluminum alloys. The physical properties of the materials were of the same order as those of the cast alloys; extruded sintered magnesium alloy had a tensile strength slightly superior to that of extruded cast alloy, while the hardness of the sintered alloy was about 25% lower than that of the cast alloy. On the other hand, the compressive strength of the sintered alloys was about 25% better than that of the cast alloy (31,200 psi *vs.* 25,400 psi), while notch impact values were about equal. With increasing sintering temperatures the strength of the magnesium alloy increased, whereas that of the aluminum alloys decreased. Sintering time had no evident effect on the physical properties. Microscopic examination disclosed no appreciable recrystalli-

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[175] G. Masing, *Z. anorg. Chem.*, *51,* 330 (1906); 62, 265 (1909).

TABLE 281

Effect of Sintering Treatment on Properties of Sintered Magnesium Alloy Compacts Initially Compressed at 30 Tsi^{a}

Composition, %						Type of powder^{b}	Sintering temperature		Sintering time, hr.	Gas	Packing mass	Appearance after sintering treatment	Brinell hardness
Mg	Al	Zn	Mn	Be	Cr		°C.	°F.					
90.7	6.0	3.0	0.3	—	—	A	330	625	1	CG^{d}	BeO		—
							400^{c}	750	1	"	"	Warped; partly fused	
							525	975	4	"	"	Melted	—
						B	330	625	1	"	"		50
							400^{c}	750	1	"	"	Slightly bent and expanded	
							525	975	4	"	"	Mostly melted	—
						C	330	625	1	"	"		53
							400^{c}	750	1	"	"	Slightly bent and expanded	
							525	975	4	"	"	Somewhat stained and porous	52
93.7	6.0	—	0.3	—	—	A	415	780	2	CG	BeO	Undistorted; metallic	50
							525	975	4	"	"	Partly fused and distorted	—
						B	415	780	2	"	"	Undistorted; metallic	53
							525	975	4	"	"	Melted and distorted	—
						C	415	780	2	"	"	Undistorted; metallic	55
							525	975	4	"	"	Partly fused and distorted	—
93.7	3.0	3.0	0.3	—	—	A	330	625	1	CG	BeO		40
							400^{c}	750	1	"	"	Metallic; undistorted	
							525	975	4	"	"	Melted	—
						B	330	625	1	"	"		42
							400^{c}	750	1	"	"	Metallic; undistorted	
							525	975	4	"	"	Partly fused	—
						C	330	625	1	"	"		
							400^{c}	750	1	"	"	Metallic; undistorted	44
							525	975	4	"	"	Melted	—

98.0	—	—	2.0	—	—	A	540	1005	2	CG	None	Metallic; locally stained	37
							500	930	4	H_2	None	Metallic; unstained	37
						B	540	1005	2	CG	BeO	Metallic; skin partly peeled off	—
							500	930	4	H_2	None	Metallic; locally pitted	39
						C	540	1005	2	CG	None	Metallic; skin partly peeled off	—
							500	930	4	H_2	None	Metallic; tarnished (yellow)	40
96.0	—	—	4.0	—	—	A	540	1005	2	CG	None	Metallic; partly distorted	39
							500	930	4	H_2	None	Metallic; undistorted	39
						B	540	1005	2	CG	BeO	Metallic; skin partly peeled off	—
							500	930	4	H_2	None	Metallic; undistorted	40
						C	540	1005	2	CG	None	Metallic; skin partly peeled off	—
							500	930	4	H_2	None	Metallic; tarnished (yellow)	44
97.0	—	—	2.0	1.0	—	A	485	905	2	H_2	None	Metallic; undistorted	39
							500	930	4	"	BeO	Metallic; undistorted	40
						B	485	905	2	"	None	Metallic; pitted; tarnished	—
							500	930	4	"	BeO	Metallic; pitted; tarnished	—
						C	485	905	2	"	None	Metallic; slightly discolored	44
							500	930	4	"	BeO	Metallic; undistorted	44
97.0	—	—	2.0	—	1.0	A	485	905	2	H_2	None	Metallic; slightly stained	44
							500	930	4	"	BeO	Metallic; partly stained	44
						B	485	905	2	"	None	Metallic; pitted; tarnished	—
							500	930	4	"	BeO	Metallic; pitted; tarnished	—
						C	485	905	2	"	None	Metallic; slightly stained	50
							500	930	4	"	BeO	Metallic; undistorted	50

[a] Courtesy Charles Hardy, Inc., New York, N. Y. Data abstracted from Laboratory Report No. 157.

[b] Powder A, −50 mesh; powder B, −100 mesh; powder C, −200 mesh.

[c] Follows immediately preceding half of cycle. [d] Cracked city gas.

TABLE 282. Physical Properties of Sintered and Extruded Magnesium, Magnesium Alloy, and Aluminum Alloy Compositions (Sauerwald[174])

Treatment			Properties		
Processing	Working	Alloy	Yield strength, psi	Tensile strength, psi	Elongation, %
Pressed at 12.5 tsi; sintered in argon at 400 °C. (750 °F.) for 2 hr.	Extruded at 300 °C. (570 °F.) to $^{5}/_{8}$-in. diameter	Mg (100%)	20,200	28,700	3.1
	Extruded further at 300 °C. (570 °F.) to $^{1}/_{8}$-in. diameter		21,100	29,100	3.0
	Extruded at 350 °C. (660 °F.) to $^{5}/_{8}$-in. diameter	91–9Mg–Al	28,700	40,400	8.1
	Extruded further at 350 °C. (660 °F.) to $^{1}/_{8}$-in. diameter		39,900	44,800	3.3
	Then annealed for 25 min. at 320 °C. (610 °F.)		30,400	41,400	13.3
	Extruded at 450 °C. (840 °F.) to $^{5}/_{8}$-in. diameter	95–4–1 Al–Cu–Mg	28,000	38,700	9.5
	Extruded further at 450 °C. (840 °F.) to $^{1}/_{8}$-in. diameter		29,700	42,000	9.3
Pressed at 9.5 tsi; sintered in argon at 340 °C. (645 °F.) for 2 hr.	Extruded at 350 °C. (660 °F.) to $^{5}/_{8}$-in. diameter	91–9 Mg–Al	25,400	39,800	9.0
Pressed at 32 tsi; sintered in argon at 340 °C. (645 °F.) for 2 hr.	Extruded at 350 °C. (660 °F.) to $^{5}/_{8}$-in. diameter	91–9 Mg–Al (90%) + 95–4–1 Al–Cu–Mg (10%)	26,000	36,200	7.0
	Then annealed for 24 hr. at 400 °C. (750 °F.)		19,400	20,400	1.6
	Extruded to $^{5}/_{8}$-in. diameter, annealed for 24 hr. at 350 °C. (660 °F.), and extruded at 380–400 °C. (715–750 °F.) to $^{5}/_{16}$-in. diameter		27,400	30,000	1.7
	Extruded at 350 °C. (660 °F.) to $^{5}/_{8}$-in. diameter	91–9Mg–Al (80%) + 95–4–1 Al–Cu–Mg (20%)	26,600	36,800	6.0
	Then annealed for 24 hr. at 400 °C. (750 °F.)		20,200	20,400	1.0
	Extruded to $^{5}/_{8}$-in. diameter, annealed for 24 hr. at 350 °C. (660 °F.), and extruded at 380–400 °C. (715–750 °F.) to $^{5}/_{16}$-in. diameter		25,400	26,000	2.9
	Extruded at 350 °C. (660 °F.) to $^{5}/_{8}$-in. diameter	95–4–1 Al–Cu–Mg	26,400	40,800	12.0
	Extruded at 350 °C. (660 °F.) to $^{5}/_{8}$-in. diameter	95–4–1 Al–Cu–Mg (90%) + 91–9 Mg–Al (10%)	25,800	31,800	2.4
	Then annealed for 24 hr. at 400 °C. (750 °F.)		21,600	23,300	2.0
	Extruded to $^{5}/_{8}$-in. diameter, annealed for 24 hr. at 350 °C. (660 °F.), and extruded at 380–400 °C. (715–750 °F.) to $^{5}/_{16}$-in. diameter		—	22,800	0.0

zation, and no grain growth beyond the original particle boundaries, probably due to the grain growth inhibiting effects of the surface oxide films. Some of the physical properties are given in Table 282.

Another part of the same investigation was concerned with mixtures of the magnesium-base and aluminum-base powdered scrap alloys, the latter being added in amounts of 5, 10, and 20% of the total. In small specimens pressed at 20 tsi to the 2-in. long, $^{3}/_{4}$-in. diameter bar shape, sintered in an argon atmosphere for 3 days at 420°C. (790°F.), and extruded at 350°C. (666°F.) to $^{5}/_{16}$-in. rods, maximum tensile strength of 40,800 psi with an elongation of 7% were obtained. Subsequent heat treatment for 2 days at 370°C. (700°F.) caused a decline in the values to 38,000 psi and 5%. Duplicate tests with the addition of 10% active charcoal gave tensile strength values of 28,000 to 32,000 psi and elongations of 2.5 to 3.5% on the extruded rods, but the values declined sharply after the annealing treatment. Specimens prepared by pressing the larger ingot (2.5-in. diameter) at 32 tsi in the case of the mixtures, and at 9.5 tsi in the case of the plain 91–9 magnesium–aluminum alloy, followed by sintering in argon at 340°C. (645°F.) for 2 hours, extrusion to $^{5}/_{8}$-in. diameter at 350°C. (660°F.), annealing for 24 hours at 400°C. (750°F.) or 350°C. (660°F.), and a second extrusion at 380–400°C. (715–750°F.) to $^{5}/_{16}$-in. diameter, gave the physical properties listed in Table 282. Although these results may not be considered outstanding (probably due to the formation of intermetallic compounds) it is interesting to note that they were fairly constant in spite of the widely varying composition.

Before leaving this subject it might be appropriate to mention that the method of briquetting, forging, and extrusion of magnesium and aluminum turnings (sometimes referred to as "mechanical ingoting") as a means of increasing the yield and economy of light metal production was initiated some time before the war,[175a] and reported in this country in 1943.[175b]

Beryllium and Calcium

BERYLLIUM

Beryllium metal powder is obtained by electrolysis of the fused fluoride or chloride.[176] Melting the powder in beryllia crucibles or vacuum distillation of the fused beryllium ore[177,178] always leads to a

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[175a] Brit. Pat. 540,105; U. S. Pats. 2,299,043; 2,302,980 and 2,302,981.

[175b] M. Stern, *Iron Age, 152,* No. 7, 90 (1943).

[176] A. E. van Arkel, *Reine Metalle.* Springer, Berlin, 1939, pp. 99 ff.

[177] H. A. Sloman, *J. Inst. Metals, 59,* 365 (1932).

[178] W. Kroll, *Metallwirtschaft, 13,* 725 (1934); *Metal Ind., London, 47,* 29 (1935).

brittle metal or condensate, respectively. The fused element in its pure form has not found practical application; it is used mainly as an alloying element to the heavy metals copper and nickel to render them suitable for precipitation hardening. Beryllium powder can be rendered more suitable for sintering by removing oxide films with dilute or concentrated nitric acid just before pressing and sintering.[179] It is advantageous to sinter the metal just below the melting point. Sintered beryllium has been reportedly used as window material for x-ray tubes.[180] The recent interest in beryllium as a "moderator" in nuclear fission work (see page 710) has opened a potential field of application for products of the highest purity produced by sintering, hot pressing, or extrusion.

CALCIUM

Powdered calcium metal has been used effectively as getter material (powder packs) and deoxidizing agent in powder compacts that show a strong affinity to oxygen during sintering.[181] Typical analyses of powder packs are 60–40 Cu–Ca and 60–40 or 85–15 Mg–Ca.[182] The metal is produced either by the electrolysis of fused calcium chloride or by the distillation of calcium from its compounds (*e.g.*, calcium silicide).[183] Alloys of calcium and iron have been described under iron alloys (p. 627). Calcium hydride has been suggested as a deoxidizing agent for strongly oxidizing metals,[184] and is advantageously admixed with the powder prior to compaction and sintering. A useful summary of literature concerned with the preparation and industrial applications of calcium hydride has been given quite recently.[185]

Lithium, Sodium, and Potassium

Because of their instability under atmospheric conditions, none of these metals has gained any significance in powder metallurgy.

Strong Electropositive Metals

The strongly electropositive metals, rubidium, cesium, strontium, and yttrium are not available as powder products. However, combinations of barium with iron, nickel, or copper have been suggested for electrodes for gaseous discharge tubes.[186] Fifty–fifty barium–aluminum master

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[179] German Pat. 704,517.

[180] K. W. Hauser, A. Bardehle, and G. Heisen, *Fortschr. Gebiete Röntgenstrahlen*; *35,* 636 (1926).

[181] C. Hardy, *private communication.*

[182] Brit. Pat. 584,471.

[183] C. L. Mantell and C. Hardy, *Metals & Alloys, 10,* No. 2, 52 (1939).

[184] P. P. Alexander, *Metals & Alloys, 8,* No. 9, 263 (1937); *9,* No. 2, 45 (1938).

[185] E. E. Halls, *Ind. Chem., 22,* No. 262, 680 (1946).

[186] Brit. Pat. 584,270.

alloy powder has been added to thorium and iron oxide (Fe_2O_3) powder mixtures for high vacuum getters.[186a] Radium, in the form of a powdered salt ($RaSO_4$), is mixed with gold and other metal powders,[187] and the mixture pressed, sintered, and rolled into strip (for details see section on gold, Chapter XXVI). The material has been suggested for the discharge of static electricity, for the supply of ionization current in cold cathode tubes, and for the activation of luminous paints.[187]

Rare Earth Metals

Cerium is the only rare earth metal that has received some attention in powder metallurgy. The cerium metal powder is produced by electrolysis of the fused chloride and is alloyed with iron in a ratio of 70–30 Ce–Fe. The alloying can be accomplished readily either by compaction of the powder mixture (in the presence of a protective fluid) and sintering in vacuum at 600°C. (1110°F.) (*i.e.*, below the melting point of cerium) or by vacuum fusion. Cerium–iron is used as a pyrophoric alloy in gas and tobacco lighters.

Another known use of cerium in powder form is in combination with aluminum as a prealloy that is added to thorium in a ratio of about 1:4 for getters ("Ceto"-getters); these getters were developed during the war in Germany, and their production and use have been described recently.[186a]

NONMETALS

Carbon, Silicon, Boron, and Their Compounds

Although these elements are nonmetals, they resemble the metallic elements in many respects and, in combination with the metals, form metallic compounds; therefore, they are often referred to as "metalloids."

CARBON

The production of carbon and graphite products follows closely the powder metallurgy process; these are produced by mixing the carbon powders with organic binders, forming or extruding the mixture, and sintering the product by resistance heating with the aid of a high-amperage current.

Carbon, either as diamond or as graphite, is an essential ingredient of many powdered and sintered products. Its use in diamond-impregnated tools has been discussed in Chapter XXII; its application in the form of graphite as a lubricant in porous bearings has been described in Chapter

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[186a] W. Espe, *Powder Metallurgy Bull.*, *3*, No. 5, 100 (1948).

[187] U. S. Pats. 1,718,899; 2,326,631; 2,462,241; 2,476,644; and 2,479,882.

XXVII, as a friction element in Chapter XXVIII, and as a major component in electric contacts in Chapter XXIII.

As an alloying ingredient, carbon (graphite) has become increasingly significant in its use in sintered steels; it has been evaluated fully in Chapter XXV.

However, the most important application of carbon is probably in combination with the refractory metals, tungsten, titanium, and tantalum, in the form of the extremely hard metal carbides. Chapter XXII is largely devoted to this particular field of application.

SILICON

A suggested use for pure silicon powder has been as a starting material for silicon rectifiers. The production of silicon rectifiers has been described in a British patent,[188] in which highly purified silicon powder is fused in a silica crucible in helium atmosphere and cooled at a controlled rate of 150°C. (270°F.) per minute to obtain uniform advance of the solidification zone. A "conditioning" of the silicon powder by adding 0.1–0.5% silicon carbide has been suggested in the same patent.

Silicon has been used as an alloying ingredient in several powder metallurgy alloys. It combines with iron to form a soft magnetic material that is suitable for low-frequency alternating-current applications (see Chapter XXIV). It combines with aluminum (see above) to form low-density alloys that exhibit a coefficient of thermal expansion desirable for automobile piston applications.

A potential use of silicon is in the form of hard compounds with the refractory metals (silicides). Silicon carbide is a stable refractory compound which is used for various purposes, such as polishing and grinding abrasives, furnace parts, and resistor heating elements (Globar). Silicon carbide has been used in certain phases of research concerned with heat-resistant, high-strength materials for use in turbine blading,[189] recently reported from Germany. Using hot-pressing as the means of consolidation, the investigator was able to produce high-temperature refractory gas turbine blades of low specific gravity from compositions of 84% SiC, 5% TiC, 2% W, 3% Cr, and 6% Co; and 88% SiC, 2% TiC, and 10% Fe.

BORON

Relatively pure boron powder with only 1% impurities, which can be sintered satisfactorily under pressure, can be obtained by reduction of

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[188] Brit. Pat. 590,458.

[189] J. Bingel, *Arch. Metallkunde, 1,* No. 7/8, 309 (1947).

boric oxide with magnesium at high temperatures.[190,191] In spite of its inherent hardness, technical applications have not yet been found for pure boron.

It has been suggested that its compounds with refractory metals be used as contact materials,[192,193] and that its compounds with chromium be used as corrosion-resistant hard surfacing and tool materials.[194]

A recent British patent application[195] has disclosed the manufacture of chromium boride tools by cold- or hot-pressing. The aluminothermically produced boride powder with an average particle size ground to 10 μ and down to below 1 μ is bonded with a preformed 325-mesh alloy powder containing 65–75% Ni, 13–20% Cr, 2.75–4.75% B, and up to 10% Fe, Si, and C. After cold-pressing at 45 tsi, sintering is performed in dry hydrogen (free of nitrogen) for $^1/_2$ to 1 hour at 1140°C. (2080°F.) in the case of a 50–50 mixture of boride and alloy powders; the sintering temperature is raised to 1500°C. (2730°F.) for a 70–30 mixture, and to 1800°C. (3270°F.) for an 80–20 mixture. Presintering at 200–500°C. (390–930°F.) is necessary if paraffin is used as pressing lubricant. Although the alloy binder liquefies at about 1050°C. (1920°F.), it is prevented from oozing out of the compact by the capillary effect caused by the very fine particle size (and therefore pore size) of the chromium boride matrix. At the higher temperatures, superficial alloying of matrix and binder takes place, but shrinkage remains below 1%. In hot-pressing the chromium boride compacts, graphite molds are heated by direct resistance or high-frequency induction to 1200°, 1550°, and 1850°C. (2190°, 2820°, and 3360°F.) for the 50–50, 70–30, and 80–20 mixtures, respectively. A maximum pressure of 1600 psi is applied for 2 to 3 minutes. The hardness of a hot-pressed compact from the 50–50 mixture is Rockwell A-83 up to 380°C. (715°F.) and A-80 at 650°C. (1200°F.). The transverse rupture strength is below that of cemented carbides (especially in the cold-pressed and sintered material), and the material is also more brittle. In many other respects, however, the chromium boride material is supposed to possess the physical properties required of hard metals (based on carbides).

[190] G. Weintraub, *Ind. Eng. Chem., Ind. Ed., 5,* 106 (1913).

[191] A. E. van Arkel, *Reine Metalle.* Springer, Berlin, 1939, pp. 142 ff.

[192] German Pat. 289,864.

[193] German Pat. 651,594.

[194] U. S. Pat. 2,088,838.

[195] Brit. Pat. Applic. 13283/47 (May 22, 1946); see also *Metal Powder Rept., 2,* No. 5, 75 (1948).

Further details about the manufacture of chromium boride with 30% Ni as a binder have recently been reported[196]; the hot-pressed alloy has a hardness of Rockwell A-89 and a transverse rupture strength (modulus of rupture) of 120,000 psi at room temperature, while the hot-hardness is generally inferior to that of conventional types of cemented carbides.

In a co-pending patent application,[197] the use of nickel and cobalt-base high-temperature alloys (such as Hastelloy-B-, Inconel-, and Vitallium-type alloys) in powdered form is suggested as binders for chromium boride, and the resulting material is claimed to be suitable for such applications as steam and gas turbine blades, valve inserts or seats for internal combustion engines, and discharge nozzles and exhaust tubes for jet engines. Certain other refractory elements may also be incorporated into the chromium boride for the purpose of producing a mixed boride base, such as tungsten, molybdenum, tantalum, and columbium. The mixed borides are prepared by fusion at 1800–2500°C. (3270–4530°F.) for 1 to 2 hours followed by pulverizing. Since chromium, molybdenum, and tungsten appear to have deoxidizing effects on chromium boride, up to 1% of these metals may be used for reaction with oxide films on the boride crystals. The metal is added before mixing the boride with the binder by conventional ball milling, followed by a heat treatment. When molybdenum or tungsten is used, the treatment should be carried out in vacuum at 1000–1250°C. (1830–2280°F.) to allow volatile oxides to escape. It is also suggested that titanium hydride or lampblack be used as deoxidizing agents. Shaped bodies are obtained by hot-pressing the mixtures at 2000–3000 psi and 1800–2200°C. (3270–3990°F.) under argon or neon atmosphere, or in a vacuum. In the case of deoxidized chromium boride mixtures containing only a few per cent of chromium, molybdenum, and/or tungsten, hot-pressing is possible at the same pressure and a temperature ranging from 2000 to 2800°C.; (3630 to 5070°F.) without an alloy binder. Subsequent diffusion heat treatment of the sintered or hot-pressed alloys at a temperature of 1000–1400°C. (1830–2550°F.) tends to homogenize the structure.

In another co-pending patent application,[198] the impregnation technique is suggested as an additional method of producing the chromium boride base hard material. By this method a porous compact of the boride

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[196] S. J. Sindeband, *Proc. International Powder Metallurgy Conference*, Graz, July 12–17, 1948, Referate No. 61; *J. Metals, 1,* No. 2, 198 (1949).

[197] Brit. Pat. Applic. 18541/47 (July 23, 1946); see also *Metal Powder Rept.*, **2**, No. 8, 120 (1948).

[198] Brit. Pat. Applic. 13452/47 (May 25, 1946); see also *Metal Powder Rept.*, **2**, No. 5, 77 (1948).

is impregnated with the binder metal to yield an 80:20 ratio of matrix to binder. The properties of the material (high softening temperature of the homogenized material) are supposed to make it useful for valve inserts, valve seats, steam and gas turbine blades, discharge nozzles and exhaust tubes for jet propulsion, etc.

Recently, a number of investigations have been concerned with the crystal structure of the borides of chromium (Cr_2B, Cr_8B_2, CrB, Cr_9B_{11}, and CrB_2),[198a] tungsten and molybdenum (WB and MoB),[198a] columbium and tantalum (CbB_2 and TaB_2),[198a,b] zirconium (ZrB_2),[198a–c] titanium (TiB_2),[198b,d] and vanadium (VB_2).[198b]

Boron carbide is the hardest man-made substance in existence. Known in the trade as Norbide,[199] it is used in powder form for grinding and polishing cemented carbides and other hard substances. It can also be produced in simple shapes (*e.g.*, cylindrical or prismatic) by hot-pressing (usually with the aid of a binder) and has been used in mortars and similar laboratory ware requiring extreme wear resistance.

On an experimental basis, boron carbide has been combined with a number of refractory metals, especially with titanium, tungsten, molybdenum, and iron.[200] In one instance, a mixture of 22 parts boron carbide and 100 parts titanium was hot-pressed above 500°C. (930°F); an exothermic reaction between the ingredients was observed. The resulting material appeared to be a mixture of about 80% boride and 20% carbide, approximately, according to the equation:

$$B_4C + 5\,Ti \longrightarrow 4\,TiB + TiC$$

X-ray diffraction work showed that no boron carbide was present in the end product, but it was indicated that up to 5% free titanium was present. There was also no proof that titanium boride had been formed, since the lattice constants of the latter were not known. In this connection, it is claimed that this method of boride manufacture via boron carbide should have potentialities, since it is simpler and supposedly less costly than the processes based on the elemental boron.

[198a] R. Kiessling, *Acta Chem. Scand.*, *1*, 893 (1947); *3*, 90, 595 and 603 (1949).

[198b] J. T. Norton, H. Blumenthal, and S. Sindeband, *J. Metals*, *1*, No. 10, 749 (1949).

[198c] P. M. McKenna, *Ind. Eng. Chem., Ind. Ed.*, *28*, 767 (1936).

[198d] P. Ehrlich, *Angew. Chem.*, *59*, 163 (1947).

[199] Product of the Norton Company, Worcester, Mass.

[200] Studiengesellschaft Hartmetall, Board of Trade (B. O. T.) German Division (Documents Unit), F. D. 3806/47; see also *Metal Powder Rept.*, *2*, No. 9, 142 (1948).

Phosphorus, Arsenic, and Sulfur

PHOSPHORUS

The pure element has found application in the form of a powdered ingredient in copper-base and silver-base brazing compounds; it is usually added in a proportion corresponding to the eutectic composition (8.4% P in the case of Cu–P), and the powder mixture is directly applied.

In minor proportion (up to 0.5%, max.), phosphorus has been added to brasses with beneficial effect on the ductility of the sintered products (see Chapter XXVI). In the form of an iron–carbon–phosphorus eutectic alloy, it has been used successfully as a binder for hot-pressed powdered cast iron, which could thereby be cemented into a highly densified material of remarkable physical properties[201] (see also Volume I, Chapter XII). In the form of ferrophosphorus, the element has also been added to sintered iron[202] (see also page 627).

ARSENIC AND SULFUR

Neither of these elements has found application in powder metallurgy.

Selenium and Tellurium

SELENIUM

Selenium occurs in the form of selenide in copper, silver, lead, and iron sulfide ores, and is won in the form of a precipitated powder as a by-product from the anode mud of copper refineries, and the lead chamber sludge of sulfuric acid plants (see also Volume I, Chapter VI). It is effective as a red colorizing agent for glass, ceramic, and steel ware; lately, selenium powder has found its principal application in photoelectric cells, where its conductivity is changed when subjected to varying light intensities. Powder made from a fused mixture of selenium and about two hundredths of one per cent of a selenium halide has been recommended for selenium rectifiers.[203] Various methods for applying the selenium, *e.g.*, blowing[204] or extrusion,[205] have been suggested.

TELLURIUM

Tellurium powder is obtained by chemical precipitation of the dioxide from the sludges in copper and lead refineries, and reduced by heating

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[201] W. D. Jones, *Foundry Trade J.*, *59*, 401 (1938).

[202] U. S. Pats. 2,226,520; 2,291,734.

[203] Can. Pat. 436,090.

[204] Brit. Pat. 582,214.

[205] Brit. Pat. 582,385.

with carbon (see also Volume I, Chapter VI). The element forms tellurides readily with many metals and is used as a hardener for lead. In powder metallurgy, it has found no application to date.

Summary

A survey—according to the periodic system—of metals and alloys for potential use in powder metallurgy discloses a number of interesting possibilities. Foremost in our present interest are those alloys that may serve as heat-resistant superalloys for turbine and jet engine blades and buckets. Because of finer grain size and inherent porosity, nickel, cobalt, and chromium-base alloys may exhibit in the sintered state superior hot-strength, hot-fatigue resistance and creep resistance over their cast or wrought counterparts.

One metal of outstanding possibilities as a lightweight structural element is titanium. Because of an excellent combination of properties—strength and ductility matching those of ordinary steels, a specific gravity about one half of that of steel, very good workability above the transformation temperature (880°C.; 1615°F.), and a corrosion resistance comparable to that of stainless steels—the metal may be considered as a natural construction material for aircraft. Present large-scale research on alloying titanium already shows indications of further improvements in the aforementioned properties. Current process metallurgy of titanium is still only partly developed, and the metal must still be considered to belong to the rare element group (this in spite of the overabundance of the ore). There is, however, little doubt that new and less costly methods of producing the metal on a large scale will be discovered soon, and it is in this phase that powder metallurgy procedures may have their part.

In the field of low-melting heavy metals, powder metallurgy appears to have few prospects. The high powder costs and comparatively poor quality of the end product, caused by the mandatory low sintering temperatures coupled with strong oxidation tendencies, offer little incentive toward further development.

In the light-metal field, however, powder metallurgy prospects are bright. Bearings in particular, but also high-strength, lightweight structural parts, will find increasing interest in airplane engine and surface transport machinery. Eventually, extreme savings in weight may be accomplished in products made from suitable magnesium powders.

CHAPTER XXXIII

Stress Analysis of Sintered Metal Structures

A comparison of the physical properties of sintered and fused industrial metals and alloys (Chapter XXXI) has in most instances clearly ndicated marked differences. The sintered materials are generally inferior in such properties as ductility and toughness, while their strength may approach or equal that of fused materials. It appears appropriate to discuss the basic theoretical causes for this phenomenon so that the usually inferior physical properties of powder metallurgy products can be more fully understood. Some time ago, Schwarzkopf[1] developed an nteresting concept on why the mechanical strength and ductility of sintered metals differ from those of reguline metals, and this chapter is written in close conformity with his presentation.

State of Reguline Metals

SINGLE CRYSTAL UNITS

The properties of crystalline materials may be divided into two classes: structure-insensitive and structure-sensitive.[2] The former includes density, specific heat, compressibility, coefficient of expansion, and lattice structure, and is practically the same for single crystals and polycrystalline samples of the same substance. These properties are ittle affected by cold working, annealing, or the introduction of small amounts of various impurities. The latter class includes the mechanical and electrical properties of the crystals, the work hardening of metals, ferromagnetic phenomena, and hysteresis losses accompanying mechanical vibrations; all of these properties may differ from sample to sample even though no such difference is corroborated by x-ray, microscopic, or chemical analysis.

The structure-sensitivity has been attributed[3] to the discontinuity of the internal structure of the crystal which is believed to originate, in

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[1] P. Schwarzkopf, *Powder Metallurgy.* Macmillan, New York, 1947, p. 288ff.

[2] F. Zwicky, *Mech. Eng.*, *55*, 427 (1933).

[3] F. Zwicky, *Proc. Natl. Acad. Sci. U. S.*, *16*, 211 (1930).

general, from disturbances during the crystal growth. No single crystal prepared industrially or in the laboratory possesses complete homogeneity of its lattice structure, and the same is true for the individual grains of the polycrystalline metallic materials. Each crystal, whether a single crystal or a member of a polycrystalline structure, is disrupted periodically by flaws and discontinuities; these are the cause for the existence of a "mosaic" structure. Each of the mosaic blocks between the flaws is estimated to consist of about 50 to 100 atoms (*i.e.*, about $^1/_{20}$ to $^1/_{40}$ of one micron) on an edge; each block differs slightly from the other in orientation and also in spacings. The flaws, when occurring at the surface of the specimen, may act as notches and lower the tensile strength materially. Thus, it has been found that a crystal of sodium chloride if immersed in hot water has the enormous breaking strength of 228,000 psi (160 kg./mm.^{2}), which may be attributed to a smoothing of the surface notches by the water. This value approaches the calculated cohesive strength between atoms across a possible plane of separation, which is about 285,000 psi at room temperature and about 425,000 psi (300 kg./mm.^{2}) under optimum conditions. The drastic effect of the surface imperfections becomes apparent when these figures are compared with the actual breaking strength of 700 psi (0.5 kg./mm.^{2}) as obtained on sodium chloride single crystals fractured in air.[3a] (In this connection, the reader is referred to the work by Smekal[3b,c] as discussed in Chapter XXXV, page 820.)

The fact that the force actually required to produce fracture of a crystal is only one hundredth to one thousandth of the cohesive force calculated from atomic constants cannot, however, be explained solely by the flaws constituting the mosaic structure. Within the domain of a coherent lattice block, weakening of the lattice structure is caused by gaps in the regular space lattice positions, by the irregular placement of individual atoms between regular lattice positions, and by the placement of foreign atoms within the regular pattern.

If we now attempt to compare different materials, the question is whether or not the discrepancy between theoretically calculated and actually registered strength values (caused by the discussed deviation from the perfect structure) can be assumed to be of the same order in the materials compared despite the enormous absolute value of the discrepancy. Although no direct evidence exists as to the effects that

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[3a] A. F. Joffé, *The Physics of Crystals*. McGraw-Hill, New York, 1928.

[3b] A. Smekal, *Proc. International Powder Metallurgy Conference*, Graz, July 12–17, 1948, Referate No. 60.

[3c] A. Smekal communication on "Mechanism of Crystal Growth," *Symposium on the Physics of Powder Metallurgy*, sponsored by Sylvania Electric Products, Inc., Bayside, L. I., N. Y., August 24–26, 1949.

differences in the method of preparing the crystal have on possible diversities in mosaic structure and lattice imperfections, the just cited case of the sodium chloride crystal submerged in hot water strongly suggests a connection. This is suported by the fact that natural rock salt crystals that have grown over a period of thousands of years also display extremely high strength values, possibly because of the complete absence of a mosaic structure and of lattice imperfections.[1] In the case of metals it is believed that the error introduced by neglecting differences in the mosaic structure and lattice imperfections is of no particular significance. Moreover, there exist, as far as known, no practical means of controlling these imperfections and discontinuities in the lattice structure, so that attempts to influence the mechanical properties of metallic substances must concentrate on other factors, such as change of space lattice by alloying or removal of foreign atoms (impurities). In order to simplify our study, we will henceforth consider the individual crystals as regions of uniform lattice structure irrespective of the method of preparation.

POLYCRYSTALLINE UNITS

In practice it is not possible to build up large "single" crystal structures by forming aggregates of equally oriented single crystals, since for this purpose the individual crystals would have to be brought so close together that the distances become of the same order as the lattice distances, *i.e.*, of the order of magnitude of a few angstroms. As a consequence the resulting conglomerate of crystals does not exhibit exactly the same characteristics as the original single crystals, and other factors, especially in connection with the grain boundaries and the grain size, play a very important role. Whereas certain physical properties such as the modulus of elasticity or the electrical resistivity of such aggregate of crystals can be calculated from the corresponding values of the single crystals with due allowances for the differences in crystal orientation, such mathematical relationships cannot be established for other characteristics, including the technically important properties of mechanical strength and ductility.

In reguline metals, the grain boundaries are generated by the well-known process of crystallization (see also Volume I, Chapter XIV). Crystallization starts at various centers during solidification of a molten metal; out of these centers individual crystals develop which continue to grow as long as crystallizable substance and space for further growth are available. When neighboring grains meet and the liquid metal is exhausted, the process of grain growth is concluded. Since the grains differ from one another in their crystal orientation, they cannot unify into a single crystal and remain separated by clear-cut boundary areas. These areas consist of a substance that was present in the melt until the end and that could not be absorbed by the lattice of the growing crystal. The boundary material may easily be of a different nature than the grains themselves; thus it can be solid matter in the nature of an alloying element or an impurity or a combination of impurities or alloying elements with the grain materials. Gases, too, which have been suspended or dissolved in the molten metal and have subsequently been evolved during cooling, may constitute part of the boundary substance, although in fused and solidified metals the major part of the boundary areas is usually in the solid state.

Whereas in the past the solid boundary material of reguline metals was held stronger than the grain material itself because of the predominantly transcrystalline fractures observed at low temperatures, the modern concept is that the grain boundary substance is not generally as strong as the crystal substance. The difference, however, is not sufficient to limit the fracture at low temperature to the boundaries instead of following the line of highest stress concentration, meaning that the fracture at low temperature may be partly transcrystalline and partly intercrystalline. Only at high temperatures does the cohesion of the boundary material become so weakened that an intercrystalline fracture prevails.[1]

The actual strength of the grain boundary areas is composed of the cohesive strength of the boundary material itself and the adhesive strength between boundary substance and grain substance. The cohesive strength of the boundary material is normally quite high, since in most fused metals strong chemical compounds related to the metal constitute the major boundary constituents. On the other hand, the adhesive strength between boundary and grain materials is generally weak and therefore considered mainly responsible for an over-all weakness of the grain boundary areas. Such boundary weaknesses are overcome in high strength materials by the formation of links or bridges between neighboring grains or between grains and coherent boundary material. These bridges constitute a direct bonding of the grains by means of material possessing not only a high cohesive strength but also a strong adhesion to the grain material; the material for the bridges must not necessarily have the same composition as the grain substance itself.[1]

Closely related with the grain boundary effects on strength are the grain size effects. It is well known that strength and particularly hardness increase with diminishing grain size. One of the main effects of metal working, especially if carried out cold, is a reduction in grain size by fragmentation. Fragmentation is also believed to play an important role in work-hardening phenomena,[4] and the degree of fragmentation appears to have a direct relation to the extent of hardening. The smallest grain size that can be obtained practically is in the order of one tenth of one micron (4×10^{-6} in.); in the case of α-iron, for example, the greatest possible fragmentation and thus maximum hardness is reached for a cold-working reduction in cross section of about 95%, the hardness increase being accompanied by a strength increase and by a decrease in ductility.

For metals exhibiting an equiaxed grain structure, the combination of strength and ductility at normal temperatures becomes more favorable with smaller grain size. However, ordinary fusion and casting methods do not lend themselves readily toward the production of fine grain size materials except where subsequent working is possible. The process of crystallization *per se* excludes the genesis of fine-grained products, since the grain size is determined by the number of crystallization centers formed. This number is usually restricted despite the fact that new nuclei form constantly during the life of the melt, while grains continue to grow out of those previously formed. The grain size of the fusion metal, however, can be reduced by undercooling of the melt, but it is difficult to apply this method in most instances.

State of Sintered Metals

The above-described effects of the grain boundary and grain size factors in polycrystalline reguline metals are of equal significance in metals produced by the sintering technique; in that case, however, the pore effects must be added as a third important factor. It may be said without reservation that these three factors are chiefly responsible for the difference in mechanical properties between sintered and fused metals. So far, successes in the production of high quality metals by powder metallurgy techniques (*e.g.*, refractory metal or hard metal products) can be traced essentially to the recognition of the fact that the sintering method offers a possibility of influencing these factors to a greater extent than is possible with casting or other orthodox metallurgical processing methods. The fact that most lower melting metal products produced by sintering today do not compare in strength and ductility with corresponding fusion products only serves to challenge the powder metallurgist to make full use of the processing variables inherent in the powder process.

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[4] N. P. Goss, *Trans. Am. Inst. Mining Met. Engrs., 140,* 337 (1940).

BOUNDARY EFFECTS

In considering the boundary effects in sintered metals, one must distinguish between intergranular boundaries within the particles and interparticle boundaries in the powder compact. Only when the powder is produced by certain methods of solidification of a molten metal or by fragmentation of coarse-grained brittle materials do the particles consist of single crystals so that the two types of boundaries coincide. The particles of powders produced by the important electrolytic or reduction processes are polycrystalline in character (see also Volume I, Chapters III and IV). Since these methods invariably involve a purification process during annealing or reduction treatments, it may be assumed that considerably smaller amounts of impurities are present as boundary materials between the "primary" grains within the particles than would be present in the grain boundary areas in cast metals.

In addition to this intergranular boundary material introduced with the raw material, however, it is also necessary to consider the presence of foreign substances introduced into sintered structures in the form of boundary material *between* the particles ("secondary grains"). This interparticle boundary substance consists essentially of gases and only to a lesser degree of solid matter. The gases filling the interstices between the grains in sintered metals have no binding capacity, and practically any solid bonding material in fused metals would constitute a better bonding agent.

The gases may be adsorbed on the particle surfaces, may be trapped during the molding process, or may be dissolved during sintering and evolved during cooling. Recrystallization and grain growth during sintering tend to replace the original secondary particle boundaries by primary grain boundaries, whereby a large proportion of the gas content in the boundaries is eliminated, provided the sintering cycle prevents premature closing of surface pores or the generation of additional gassing effects. It may also be assumed that the remaining gas volume is more favorably distributed in the boundaries created by recrystallization than would be the case in the interparticle boundary areas. A complete elimination of all gases is possible only if sintering is carried out in high vacuum; so far, this procedure is reserved for certain refractory metals (tantalum) and special compositions (*e.g.*, chromium-containing alloys), or if alternate forging and vacuum-annealing operations are subsequently applied.

As to the solid particle boundary substances, the flexibility of the powder metallurgy technique permits a considerable degree of control of distribution, quantities, and composition of such material. The means of control include: (*1*) selection of powders of closely controlled chemical analysis; (*2*) far-reaching elimination or control of impurities; (*3*) use of alloying elements in the form of prealloyed or coated powders; (*4*) selection of powders of suitable particle structure; (*5*) selection of powders of suitable particle-size distribution; (*6*) selection of suitable sintering atmosphere; and (*7*) selection of suitable sintering cycle with temperatures and times variable over a wide range.

Although this control of the distribution, amount, and composition of the solid boundary material in sintered metals is far superior to that possible in cast metals, it must be emphasized again that in contrast to cast metals, in which a major proportion of the boundary material is solid, solid boundary substances play only a minor role in sintered metals and the matter occupying the boundaries consists predominantly of gases. (Of course this only applies to metals that are sintered in the absence of a liquid phase.)

In sintered metals the previously mentioned bridging effects in the boundary regions also gain specific significance, and the sintering technique appears to offer a distinctive advantage over the casting processes. Because of the effect of the impurities present in the melt, the composition of solid boundary material is difficult to control in reguline metals; however, in sintered metals which can be and, in fact, in many instances are produced from purer raw materials, boundary composition, and thus possibilities of bridge formation, can be controlled with comparative ease. Thus the amount and kind of foreign material can be predetermined and produced under temperature conditions that allow close control of precipitation at the boundaries. Typical examples are sintered tungsten carbide and tungsten–copper products. In the case of the sintered hard metal, the bridge material has the same composition as the grain material itself. The tungsten carbide particles are connected by bridges of WC which had been dissolved by the cobalt binder during sintering, and reprecipitated during cooling (see also Chapter XXII, and Volume I, Chapter XIV). In the case of copper–tungsten contact metals, the bridge material is formed by the foreign metal nickel (see also Chapters XXI and XXIII), and strengthening of the cohesion of the boundary areas is obtained by an increase of the solubility of tungsten in the nickel–copper alloy formed.

GRAIN SIZE EFFECTS

With regard to the effect of grain size on mechanical properties, it may be said that the sintering techniques offer another distinct advantage over the casting processes. In sintered products the grain size can be controlled easily, its final size depending on the powder particle characteristics and the sintering conditions. Thus it is possible to vary the grain size of the finished products from dimensions corresponding to the original crystallites in the polycrystalline type of particles (or the entire particles in the case of single crystal particles) to large single crystal bodies; since powders can be produced that have particle or crystallite sizes in the order of 0.1 μ, it is possible to produce sintered products that have grain sizes of the same order of magnitude as obtained in cast metals by the limit of fragmentation after most severe cold working. A typical example of the beneficial effects of grain size refinement and control in powder metallurgy is given by the sintered Alnico permanent magnets (see Chapter XXIV).

PORE EFFECTS

In the preceding discussion of the grain boundary effects on the mechanical properties of sintered products it has been emphasized that continuous gaseous boundary substances materially lessen the cohesion of the entire structure. Besides these gaseous boundary substances, which are essentially of the nature of very thin gas films, there must also be considered the important effects of gaseous inclusions contained in pores. It has been shown repeatedly throughout this book that porosity is a normal property of all sintered metals and that usually only the quantity and type of pores can be affected by the variables of powder metallurgy processing. Thus, pores may vary from the minutest size—as determined only by ultramicroscopic examination in the grain boundaries—to dimensions resembling blow holes in castings; they may have near-spherical (lenticular) or rugged, sharp-edged outlines; they may be present as isolated cavities or in groups of myriads of equally sized and shaped pores that are interconnected by a labyrinth of channels.

In view of the fact that these gas-filled pores and interstices carry practically no load (except possibly in compression), their detrimental effects on the mechanical properties in sintered metals become obvious. A comparison of the mechanical properties of sintered products of varying degree of porosity shows that, with increasing pore volume (decreasing density), strength as well as ductility and toughness are reduced progressively, with the effect on ductility and toughness being generally more pronounced than the effect on strength. On the other hand, it has been proved that with increasing density of the product the mechanical properties approach normal values, with strength increasing nearly proportionally with density, while ductility and toughness values show drastic improvements only when the density rises to within 1 or 2% of normal. In this connection the reader is referred to the recent study of the effects of density and particle characteristics on the physical properties of sintered iron by Squire,[5,6] who in isolated instances observed extraordinary impact strength values.

When interpreting the effect of pores on mechanical strength it is necessary to consider first the reduction of the effective cross section. In porous materials the load-carrying area of the cross section is reduced by the pore area, thereby causing a reduction in mechanical strength. Experimental evidence, however, shows that for porosities greater than nominal the actually observed decrease in strength—as for instance measured in conventional tensile strength tests representing load divided by *apparent* cross sectional area—often materially exceeds that corresponding to the reduction of the *effective* cross-sectional area. In fact, it has been experienced in certain (brittle) powder metallurgy products that a reduction of only 5% in effective cross-sectional area has reduced the tensile strength by as much as 50%.

This phenomenon appears to be coupled with the previously stated fact that, especially where the basically more brittle metals are involved, the values for ductility (tensile elongation and reduction of area) and toughness (impact resistance) decrease at disproportionally drastic rates with a reduction of the metallic cross section. It is therefore to be assumed that factors other than the plain reduction of the effective cross-sectional area must play an important role in the depreciation of the mechanical properties in sintered metals. Among these are considered the stress concentrations in the neighborhood of the pores which are caused by notch effects, especially in the case of angular cavities.

Stress Conditions in Reguline Metals

NOTCH EFFECTS IN STRESSED SOLID SPECIMENS

The recognition of the fact that notch effects constitute one of the most important causes for brittle failures has inaugurated numerous experimental and theoretical investigations. In this connection the reader is referred particularly to the publications by Gensamer,[7] Frocht,[8] and Nadai.[9] For simple shapes the effects of notches on the distribution of stresses can be explained by mathematical stress analysis. Photoelasticity measurements on models made of transparent plastics have corroborated many of the theoretical findings. The stress distribution in

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[5] A. Squire, *Trans. Am. Inst. Mining Met. Engrs.*, *171*, 485 (1947).

[6] A. Squire, *Watertown Arsenal Lab. Rept. WAL 671/16* (Oct. 1944).

[7] M. Gensamer, *Strength of Metals under Combined Stresses.* Am. Soc. Metals, Cleveland, 1940, p. 19.

[8] M. M. Frocht, *Photoelasticity.* Wiley, New York, 1941.

[9] A. Nadai, *Plasticity.* McGraw-Hill, New York, 1931.

a notched bar subjected to tension forces is reproduced from Gensamer's work[7] in Figure 616, with σ_l, σ_t, and σ_r designating the principal stresses in the longitudinal, tangential, and radial directions, respectively, and τ_{max} designating the maximum shear stress. The curve for σ_l shows the marked increase just below the surface of the root of the notch. The stress concentration increases with increasing sharpness and depth of the notch.

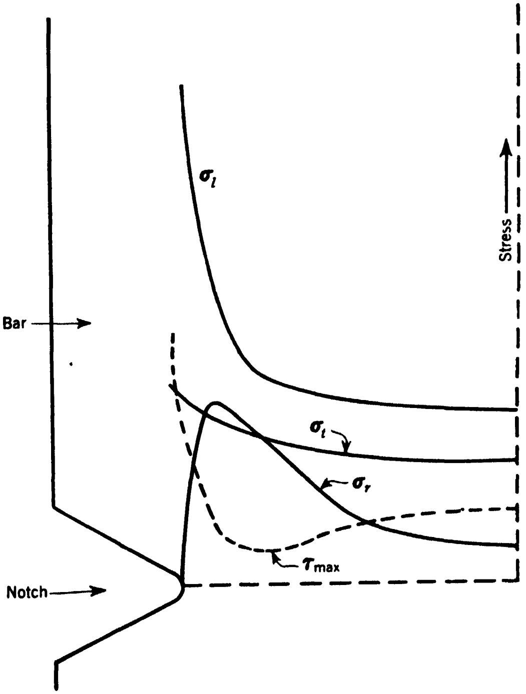

Fig. 616. Variation of state of stress across a notched cylinder in tension from the base of notch to center line (according to Gensamer[7]).

NOTCH EFFECTS IN STRESSED SPECIMENS CONTAINING HOLES

The typical notch effects caused by holes or pores have been demonstrated by Frocht.[8] In Figure 617 a photoelastic stress pattern is reproduced for a bar with a central hole that is subjected to pure tension. In Figure 618 a similar pattern is shown for a bar containing two eccentrically placed holes, the bar being subjected to axial tension. The effects of several holes is not simply additive, since the stress concentra-

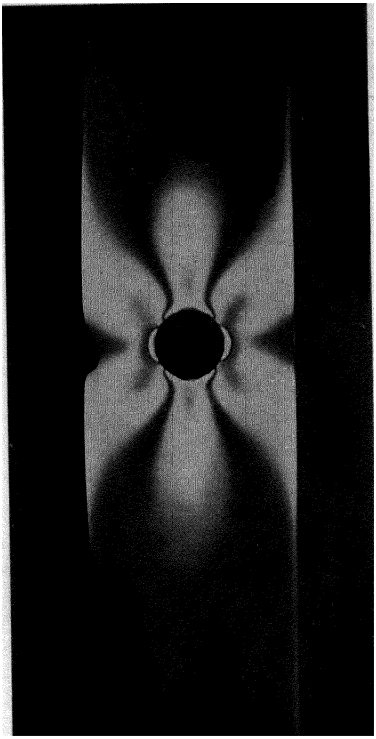

Fig. 617. Photoelastic stress pattern of a bar containing one central hole and subjected to pure tension (according to Frocht[8]). (Reproduced by permission from *Photoelasticity* by Max M. Frocht, John Wiley and Sons, Inc., New York, 1941.)

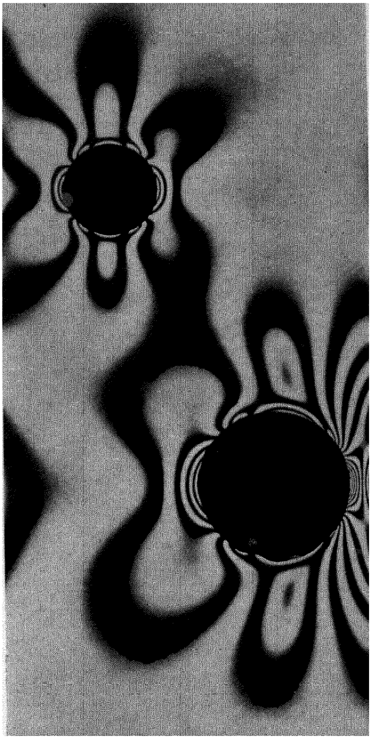

Fig. 618. Photoelastic stress pattern of a bar containing two eccentrically placed holes and subjected to axial tension (according to Frocht[8]). (Reproduced by permission from *Photoelasticity* by Max M. Frocht, John Wiley and Sons, Inc., New York, 1941.)

tion in the immediate vicinity of the notch or hole is always accompanied by a stress reduction in parts farther from the notch. Thus, it is even considered possible that stress concentrations can be substantially relieved by a series of notches placed at regular distances.[10]

Stress Conditions in Sintered Metals

NOTCH EFFECTS IN POROUS SINTERED METALS

Any attempt to apply the results of the simplified notch effect studies to an analysis of the pore effects in sintered metals must, by necessity,

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[10] A. Thum and H. Ude, *Giesserei, 16,* 501 (1929).

be extremely sketchy. It appears to be quite impossible to make either mathematical deductions or experimental studies of the extent of internal stress-raising produced by the pore system. While the proximity of the great multitude of pores may even cause a certain degree of stress relief or stress equalization, the effects of irregularities in the pore shapes and the deformation of the pore outlines under stress complicate matters to such an extent that even an approximate stress analysis appears impossible. All that it is safe to say is that, even taking into consideration possible stress equalization effects, the remaining stress-raising effects will still be predominant—accounting for the generally observed decreases in mechanical properties in excess of those that can be accounted for by the reduction of the effective cross section. As previously indicated, this discrepancy between the values calculated on the basis of the reduced cross section and the actual experimental values observed is considerably greater in the case of ductility and toughness than for the strength values. This leads to the assumption that the notch effects exerted by the pores have a greater influence upon ductility and toughness than upon strength, which is in full agreement with the results of studies made on the relationship of plasticity and brittle failures.[11,12]

PLASTIC FLOW MECHANISM

The flow mechanism in notched or perforated bars is of such complexity that a mathematical analysis is out of the question even for the simple case of a notched bar.[12] All that is known is that the stress concentration caused by a hole or a notch results in premature yielding. The flow distribution depends upon the stress, but at the same time the flow also changes the stress distribution, thus accounting for the complexity of the mechanism. In Figure 619 the region of plastic flow around a single hole is indicated schematically,[11] and the same is shown in a photoelastic stress pattern in Figure 620.[11]

TRIAXIAL STRESS DISTRIBUTION

From the foregoing it is obvious that, in the case of sintered metals containing a network of small irregularly shaped pores and interstices in closest proximity to each other, no definite assumptions can be made as to the mechanism of plastic flow, although it is hoped that the steady advances made in the study of the relationship between notch effects and brittle failures of metals will eventually lead to a quantitative treatment

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[11] A. Nadai, *Plasticity*. McGraw-Hill, New York, 1931, p. 103.

[12] M. Gensamer in "Symposium on Cohesive Strength," *Trans. Am. Inst. Mining Met. Engrs., 162,* 538 (1945).

of the problem. However, any serious approach to the problem must take into account the fact that notches tend to produce triaxial stress distribution. With increasing triaxiality of the stress distribution the ductility of the material decreases, the yield strength approaching the cohesive strength of the metal; complete triaxiality results in complete brittleness. Whether, and to what extent, a triaxiality of the stress distribution is generated in porous powder metallurgy products, is not definitely established, but the generally experienced lack in ductility and impact resistance of these materials points toward such a condition.

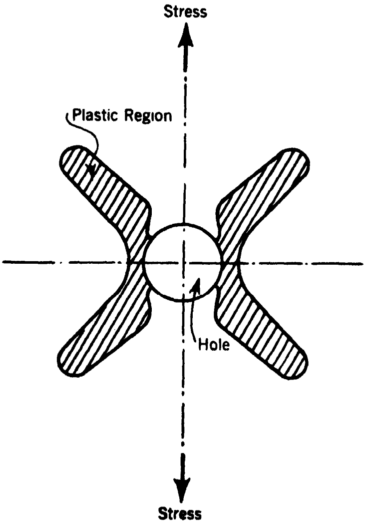

Fig. 619. Schematic presentation of the region of plastic flow around a single hole in a bar stressed in tension (according to Nadai[11]).

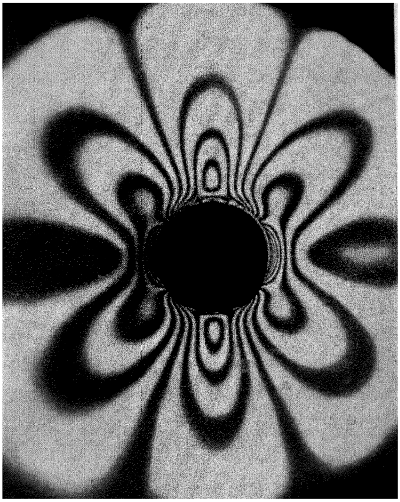

Fig. 620. Photoelastic stress pattern showing region of plastic flow around a hole in a bar stressed in pure tension (according to Nadai[11]).

EFFECTS OF SOLID INCLUSIONS

As further supporting evidence of the presence of triaxial stresses in sintered metals we may compare the physical properties of the porous sintered metal with those of the same metal in the cast condition that contains solid inclusions corresponding in amount, size, and shape to the pores in the sintered material. In the case of pure iron or low-carbon steels, for example, we will find that all ductility values, and especially the values for reduction of area, are far inferior in the sintered porous metals. In fact, even for sintered steels of a density in the order of 95%

of theoretical, values for reduction of area hardly exceed the elongation figures and may even fall short of these values (see Table 246, Chapter XXXI); in contrast to these results, steels saturated with slag or other (impurity) inclusions retain practically their customary ductility properties, with values for reduction of area about 1.5 times the elongation values. From these findings one may conclude that the solid foreign inclusions provide a certain load-carrying capacity that makes the material more ductile than the sintered material containing merely gas-filled pores.

EFFECTS OF GASEOUS INCLUSIONS

While it may be assumed safely that notch effects caused by the pores play a major and possibly a deciding role in determining the degree of brittleness of the sintered metals there are undoubtedly still other factors that contribute to the losses in strength and ductility observed in these porous bodies. Such factors are indicated if experimental data obtained with nearly dense material are extrapolated to zero porosity; this applies especially to sintered materials belonging to the class of moderately ductile metals, such as low-carbon steels, for which values for elongation, reduction of area, and impact strength tend to remain short of normal. One of the contributing factors may be an uneven distribution of gas films in the grain boundary regions. Another may be the fact that, often, the gases occluded in the pores or interparticle interstices may be stored under considerable pressures, as, for example, in the case of air entrapped during the compaction of the powder. This gas pressure may not always be completely relieved during the sintering operation, and may impart a state of nonequilibrium between the internal and external stresses, or between the internal stresses in various sections.

ELIMINATION OF POROSITY EFFECTS

From the foregoing analysis it may be deducted that a considerable improvement in physical properties of sintered products can be obtained by a substantial elimination of the pores. As previously discussed (see Volume I, Chapter XIV), several means of reducing porosity are at our disposal. They include processing of the most plastic powders available for each metal, with solid and gaseous impurities kept at a minimum. In molding, the amount of entrapped air must, if possible, be eliminated, and the sintering cycle must be chosen in such a manner that all gases liberated during sintering must be allowed to escape from the interior to the surface of the part before the pores in the surface regions are closed by shrinkage and grain growth. High temperatures and extended times of sintering, as well as sintering atmospheres of very high purity with complete freedom from oxygen and moisture, are also essential. The equivalence of the physical properties obtainable with correctly sintered high density aluminum with those of the fused and wrought metal (see Table 239, Chapter XXXI) is a good example of the quality of pore-free sintered material. Repeated pressing and sintering operations performed in several successive steps on less plastic materials tend to reduce porosity materially, and repressing in coining dies at high pressures has proved to be a valuable expedient both for simple and for more complicated shapes. Repressing, as well as working of ingots or blanks of indefinite shape, is particularly effective if carried out at elevated temperatures at which the metal is more plastic; swaging, rolling, or forging under such conditions makes possible the production of completely dense products of tenacious materials such as high-carbon steels and refractory metals. A repetition of the sintering and repressing or working operation has the advantage of disrupting gas films in the grain boundaries, and of filling the residual pores by plastic deformation and grain growth. Hot-pressing of the powder directly or after the first sintering operation results in similar densification.

As an alternative to the process of pore volume reduction by crystallization effects during sintering or by densification effects through the exertion of mechanical energy during pressing or working, the pore volume can also be neutralized effectively by filling the individual pores with foreign substances that, upon solidification, can act the same way as solid impurity inclusions. This effect is obtained by introducing low-melting metals into sintered products with intercommunicating pore systems. It has been found that if sufficient wetting and also a certain degree of alloying or solubility between the infiltrant and skeleton metal exist the sintering process will resemble that occurring in the presence of a liquid phase. As a result, alloy formation is added to the simple process of filling the pores with a substance that can function as load-carrier after solidification, and amazingly high physical properties, including ductility and toughness, can be obtained by employing such a procedure. As an example, copper-infiltrated iron and steel are cited (see Tables 194 and 196, Chapter XXV).

Summary

While in fusion metals the major part of the boundary material consists of solids aiding in the cohesion of the structure, in sintered metals the substances occupying the boundary regions consist predominantly of gases. These gases have no binding capacity and cause a substantial weakening of the cohesive strength of the material; this weakening is only partly offset by the comparatively small proportions of solid boundary materials that can act as bridges. These solid boundary substances, however, can be controlled more effectively by the powder metallurgy technique—insofar as distribution, amount, and composition are concerned—than would be possible by fusion metallurgy processes. To this possibility of closely controlling the solid phase of boundary materials can be added the advantage of closer control of the final grain size in powder metallurgy products, with both factors working in favor of superior mechanical properties.

The fact that the mechanical characteristics of sintered products are not generally equivalent to those obtained by conventional metallurgical processes can be chiefly attributed to the predominant effects of inherent porosity. It is believed that the individual pores act as stress-raisers and that internal notch effects are the chief cause for the deficiency in ductility and toughness of sintered metals.

Thus, the various techniques of pore elimination have become of great importance in the attempt to improve the mechanical properties of powder metallurgy products. With further developments in sight it may become possible to produce directly to final shape products that are equivalent or perhaps superior in their mechanical properties to their counterparts produced by conventional processing methods. That this goal is not out of reach is indicated by the achievements made in the refractory metal field, in which sintered and subsequently worked products possess physical characteristics that are definitely superior to those obtainable in the same metals produced by fusion methods.

CHAPTER XXXIV

Appraisal of Testing Methods for Sintered Metals

Throughout the latter part of this volume, the physical properties of materials produced by the powder metallurgy process have been examined closely, and in Chapter XXXI these properties have been compared with those of fusion metals. A definite distinction between the characteristics of sintered and fused metals has been apparent in almost all instances, with the powder metallurgy products usually having inferior physical properties. The stress analyses of sintered metal structures presented in Chapter XXXIII have illuminated some obvious causes for this discrepancy, and have indicated the detrimental effects of elements such as the inherent porosity and gaseous films accumulated in the grain boundaries. While various factors are thus responsible for fixing the *absolute* values of the physical properties at levels that are usually below normal, the same factors must also have some effects on the methods of *determining* the exact extent by which these values fall short of normal. Only if this conclusion is fully taken into account can a sound judgment of the quality of sintered metals be made and a basis of comparison with metals produced by conventional methods be found.

There is one other important point that must be borne in mind when dealing with the testing of powder metallurgy products: what are the real properties to be determined by the test? In view of the greater number of variables that influence the test results in the case of sintered metals as compared with bulk metals, it is often quite difficult to evaluate the results of conventional testing methods correctly, and, accordingly, misleading conclusions about the quality of the product are often unavoidable. Therefore, the first question that must be resolved when deciding on a particular test is whether or not the test really does determine the property of which knowledge or control is desired. When this is not obvious, it may be necessary to stabilize or eliminate certain factors which distort the test results, or else it may be necessary to devise a series of superimposed tests which permit elimination of one variable after another.

In accordance with these reflections, an attempt to evaluate different testing methods that are applicable to sintered products appears to be indispensable within the larger framework of a survey dealing with all phases of the powder metallurgy process. This appraisal touches a field which in itself is large and complex in scope, and, in certain respects, only in its earliest stages of development. Therefore, no attempt at completeness has been made in this chapter; it can serve merely as a basis for consideration and as a stimulus for further research.

Destructive Testing Methods

The determination of most physical properties of metallic materials involves destructive methods of testing, dealing with the resistance of crystals to deformation, the cohesion between crystals under the action of an applied force, and the susceptibility of a metal to forming operations. Physical testing provides a means for disclosing the character of a metal on the basis of specific test specimens directly cut from the product or prepared under conditions identical with those of the product. With the exception of tests such as the determination of specific gravity or of electrical or magnetic properties, all physical testing implies destruction of the test specimen, and the properties thereby determined are generally referred to as mechanical properties. Depending on the nature of the force applied during the test, we may distinguish between static and dynamic testing methods.

STATIC TESTING

Hardness. The hardness of metallic objects is conventionally tested by one of the following three methods: (*1*) indentation or impression; (*2*) scratching; and (*3*) rebound. Only the first two methods are both static and destructive in nature and to be discussed here; the third will be briefly mentioned along with other dynamic testing methods, although the method does not necessarily imply destruction of the product.

In the diagram of Figure 621 the most common hardness scales are shown in relation to Mohs' scale of hardness, according to Rose.[1] Included in the diagram are several indentation test scales and also the scale for the dynamic scleroscope test. The respective position of heat-treated steels on these scales and of the standard minerals on the Mohs' scale (circled numbers) are also indicated. To the original chart the respective positions on Mohs' scale of sapphire or corundum, respectively, as well as tungsten and titanium carbides, and a cemented carbide composition containing 3% Co have been added. The reference to Mohs' scale of hardness aids in demonstrating the great hardness of diamond in

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[1] K. Rose, *Metals & Alloys, 18,* No. 6, 1353 (1943).

comparison to synthetic abrasives, hard refractory metal carbides, and their hard metal products, and to hardened steels. When studying this relationship, however, it must be borne in mind that the scales shown are not exactly convertible; a number of factors are introduced by the specific method of determining the hardness, which, although constant for that method, prevent its accurate duplication by another method. The Brinell scale shown is only approximately correct, since it is obtained by a reduction to a corresponding number basis of actual hardness determinations based on other systems of measurements.

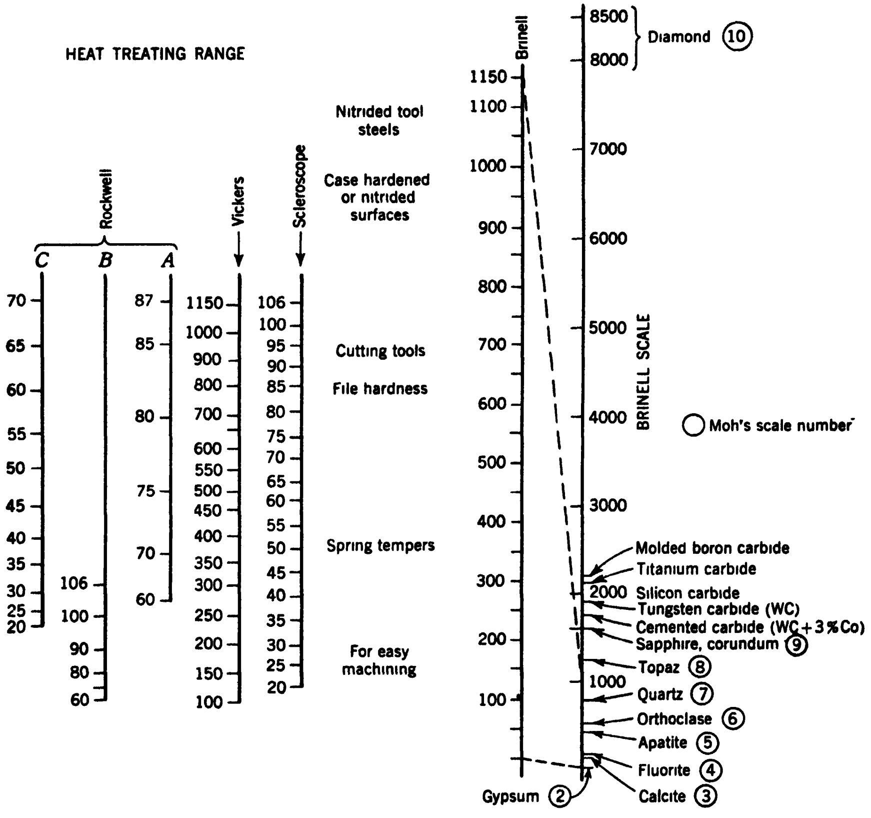

Fig. 621. Comparable scales of hardness (based on original chart by Rose[1]).

A similar comparison between Mohs' hardness scale and the microhardness, as determined by the so-called Knoop hardness tester,[2] is shown

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[2] F. Knoop, C. G. Peters, and W. B. Emerson, *J. Research Natl. Bur. Standards*, *23*, 39 (1939).

TABLE 283

Variations in the Reported Microhardness Values (Knoop Numbers) of Hard Substances (According to a Tabulation by Thibault and Nyquist[3])

Mohs' scale	Substance (as designated in the literature)	Published by members of the staff of the National Bureau of Standards[a–c]	Brodie[d]	McKenna[e]	Winchell[f] (from his Table II)
10	Diamond	8200, 8200–8500; 5500–6950[h], 8000–8500	—	—	—
	Tungsten titanium carbide	—	—	2600	—
	Boron carbide	2265; molded: 2230; 2250–2260	—	—	—
	Tantalum carbide[e]	—	>2200	—	—
	Silicon carbide	2000; 2130; green: 2130–2140 black: 2050–2150	—	about 2150–2250	Green: 2675–2830 Black: 2855–3010
9	"Alundum"	Variety not stated: 1635; 1655; "Regular": 1620–1635; "98": 1670–1680	—	—	—
	Corundum	—	—	—	Synthetic colorless: 1930–2240 light ruby: 1425–2310 dark ruby: 1750–1955
	Spinel	—	—	—	Synthetic blue: 1115–1235
8	Topaz	1250	—	—	985–1230
	Tungsten carbide	—	>2200	WC: about 1950	—
	"Carboloy"	1050; 1050–1500	—	—	—
7	Quartz	710–790	—	—	653–902

[a] C. G. Peters and Frederick Knoop, *Glass Ind.*, *20*, 174 (1939).

[b] Frederick Knoop, C. G. Peters, and W. B. Emerson, *J. Research Natl. Bur. Standards*, *23*, 39 (1939).

[c] C. G. Peters and Frederick Knoop, *Metals & Alloys*, *13*, 292 (1940).

[d] Constance B. Brodie, *Trans. Am. Soc. Metals*, *33*, 126 (1944).

[e] P. M. McKenna, *Automotive and Aviation Ind.*, *91*, 40, 92 (1944).

[f] Horace Winchell, *Am. Mineral.*, *30*, 583 (1945).

[g] V. E. Lysaght, *Bull. Am. Soc. Testing Materials*, No. 138, 39 (1946).

[h] Given by Lysaght[g] as the revised values from the National Bureau of Standards.

TABLE 284

Microhardness of Various Hard Substances (Thibault and Nyquist[3])

Substance	Knoop number[a]	
	Average	Range
Primary boron carbide ("Norbide")	2800	2670-2940
Molded boron carbide ("Norbide")	2760	2580-2900
Gray silicon carbide (Regular "Crystolon")	2460	2250-2680
Gray silicon carbide [Regular "Crystolon" (check)]	2550	2320-2760
Green silicon carbide (Green "Crystolon")	2480	2230-2740
Green silicon carbide [Green "Crystolon" (check)]	2480	2130-2620
Titanium carbide	2470	2350-2620
Tungsten titanium carbide	2190	2050-2320
Alpha-aluminum oxide ("38 Alundum")	2050	1860-2200
Alpha-aluminum oxide (synthetic boule)	1950	1680-2100
Primary (unbonded) tungsten carbide (WC)	1880	1570-2140
Cemented carbide ("Kennametal K6")	1800	1700-1940
Cemented carbide ("Kennametal KM")	1500	1390-1600
Cemented carbide ("Kennametal K12")	1410	1280-1500
Garnet (Barton Mines, New York)	1360	1240-1440
Topaz (Thomas Range, Utah)	1340	1240-1500
Synthetic blue spinel (Linde)	1270	1190-1460
Quartz	820	760- 880
Hardened tool steel, Rockwell C-60.5	740	730- 760

[a] Determined at 100-g. load (K_{100}); random crystal orientation.

TABLE 285

Hardness Conversion Table for Sintered Carbides (Scott and Gray[3a])

Diamond pyramid hardness[a]	Rockwell "A" scale[b]	Rockwell "C" scale[c]	Diamond pyramid hardness[a]	Rockwell "A" scale[b]	Rockwell "C" scale[c]
1750	92.4	80.5	1250	88.5	73.0
1700	92.0	79.8	1200	88.1	72.2
1650	91.7	79.2	1150	87.6	71.3
1600	91.3	78.4	1100	87.0	70.4
1550	90.9	77.7	1050	86.4	69.4
1500	90.5	77.0	1000	85.7	68.2
1450	90.1	76.2	950	85.0	66.6
1400	89.7	75.4	900	84.0	64.6
1350	89.3	74.6	850	82.8	—
1300	88.9	73.8			

[a] 50-kg. load.

[b] 60-kg. load, Brale penetrator.

[c] 150-kg. load, Brale penetrator.

for various hard substances in Table 283, while in Table 284 the position of several cemented carbides is shown in relation to the pure carbides and other hard compounds on the microhardness (Knoop hardness) scale, according to Thibault and Nyquist.[3] (A practical hardness conversion chart for sintered carbides, comparing the Vickers diamond pyramid hardness with the Rockwell "A" and "C" scales, is reproduced in Table 285, according to Scott and Gray.[3a])

Indentation tests by which the resistance to the penetration of an indenter is measured and expressed in conventional units, comprise various specific methods. The Brinell test, in which a hardened steel ball is pressed into the surface being tested at a fixed load, and the Brinell hardness number is expressed as the ratio of load to area of the surface of the impression; the Vickers test, which is similar in principle but uses a diamond indenter in the shape of an inverted square-based pyramid; the microhardness test, which is similar in principle, except that very small indenters and test loads are used, and the point of indentation is selected through a cross-hair lens of a microscope; the Rockwell test, in which a hardened steel ball or a diamond cone is pressed under a fixed load into the surface—with the depth of the impression being measured automatically after removal of the load.

Indentation hardness testing of powder metallurgy products is generally unreliable because the bulk of these products are characterized by residual pores in the surface being tested, and also frequently by nonuniformity in density and structure throughout the cross section. Also, it must be understood that the abrasion resistance of a material depends much more upon the microstructure of the material than upon its density. Thus, for example, hardened sintered steel may be fully martensitic, but its hardness may only register 30 to 40 on the Rockwell "C" scale. Hence, density and microstructure must be taken into account when evaluating indentation hardness data. It is obvious that quite different values can be obtained, depending upon whether the indenter hits a metal grain, a pore, or a metal grain that bridges a cavity. If a small indenter hits a grain, the value will approach the hardness of the particular metal and will therefore be higher than that corresponding to an over-all hardness and performance of the material. If it hits a pore, the value will be zero. A subnormal hardness value will be obtained if the indenter hits an area consisting partly of metal and partly of pore volume, or if a full grain is hit which can be pushed into adjacent pore voume. This latter effect will be more pronounced the higher the applied load. Essentially the same arguments apply to duplex structures of higher density, such as infiltrated composite products in which the pores are replaced by copper or silver, which are considerably softer than the refractory metal skeleton.

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[3] N. W. Thibault and H. L. Nyquist, *Trans. Am. Soc. Metals, 38,* 271 (1947).

[3a] H. Scott and T. H. Gray, *Trans. Am. Soc. Metals, 28,* No. 2, 399 (1940).

The testing of microhardness offers an interesting approach toward determining the true hardness of the metal phase in the sintered product.[4] A comparison of the microhardness measurements and Rockwell "F" readings is shown in Figure 622, in which the hardness numbers for various densities are plotted against density of sintered iron. Both curves will intersect at 100% density if extrapolated, thereby giving a good indication of the accuracy of the testing method.

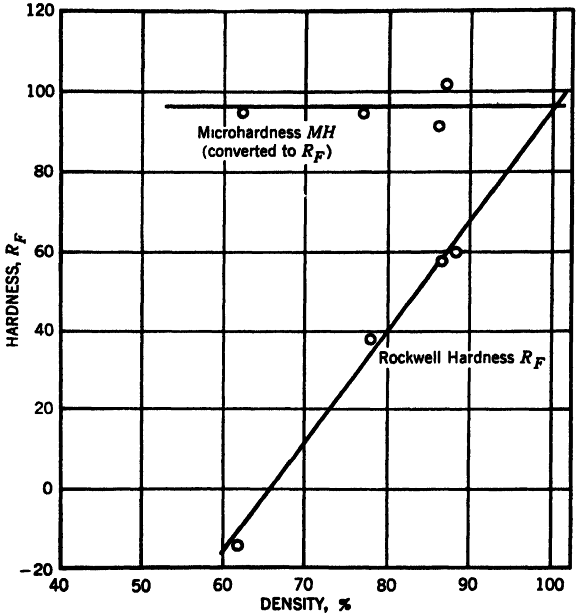

Fig. 622. Effect of increasing density of a sintered powder compact on the Rockwell hardness, measuring a composite of metal structure and pores, and on the microhardness, measuring only the metal structure (according to Steinitz[4]).

When hardness testing serves the purpose of quality control of production items, the microhardness test would tend to give a distorted picture, since it does not take into account the pore volume and pore distribution, and therefore gives values above the over-all hardness. An equally incorrect result, though in the opposite direction, is obtained when the pore effect is unduly magnified by applying high loads, giving too low values.

The observations made by Steinitz have recently been carried further

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[4] R. Steinitz, *Metals & Alloys, 17,* No. 6, 1183 (1943).

by Bückle,[5] Mitsche,[6] and Onitsch.[7] Microhardness as well as macrohardness are load-dependent in accordance with Meyer's law:

$$P = ad^n$$

where P is the applied pressure, a the counterforce, d the diameter of the impression, and n the so-called Meyer exponent which lies below 2 (limiting values are nearly 2 for very soft metals, such as lead, and about 1.25 for very hard metals, such as multiple carbides). Although errors amounting to as much as ±20% were found, Bückle,[5] working with sintered iron and aluminum, could confirm his theoretical findings that the microhardness can be extrapolated to macrohardness when plotting the straight-line function (on log-log paper) of hardness *vs.* load. It was definitely proved that n is a function not only of the material constants, but also of the history of the specimen, and of the degree of work hardening occurring during indentation. A variation of n during pressing and sintering of metal powder compacts can be followed by comparing a set of Meyer curves.[7] Strictly speaking, microhardness refers only to single crystals, while the hardness of a polycrystalline section represents its macrohardness and is dependent on the deformation of the crystals and also on the relative movement of the crystals or the particles.[6]

Therefore, it may be concluded that conventional indentation hardness tests employing *low* loads and indenters with a *large* effective surface area give a fair average picture reflecting the over-all hardness of the material to be tested. Experience has actually shown that indentation values obtained by such procedures reflect best the actual service performance, as for instance in wear applications.

The correct way of specifying the hardness of sintered materials would be to give the actually measured values (*e.g.*, the Brinell 500-kg. load, 10-mm. ball test, or the Rockwell "H" and "F" scales for soft materials; or the Rockwell "A" scale and the Rockwell superficial "15-N" scale for hardened steel or similar materials), and then convert to hardness scales used conventionally with bulk material (*e.g.*, Rockwell "C" scale). In case of such conversion it must be pointed out that the given values are not those actually obtainable on the conventional scale, but rather represent the values of standard engineering materials, which in actual service would correspond to the sintered products specified.

In many respects, file and scratch hardness tests simulate service

[5] H. Bückle, *Proc. International Powder Metallurgy Conference*, Graz, July 12–17, 1948, Referate No 19.

[6] R. Mitsche, *Proc. International Powder Metallurgy Conference*, Graz, July 12–17, 1948, Referate No. 35.

[7] E. M. Onitsch, *Proc. International Powder Metallurgy Conference*, Graz, July 12–17, 1948, Referate No. 36; *Mikrochemie*, *2*, 131 (1947).

conditions better than indentation tests. While file hardness tests constitute a crude method of quality control for hardened sintered steels primarily, the scratch hardness is a more accurate method. It employs a diamond point which is subjected to a certain load and is drawn over the surface of the metal to be tested. For a given load, the width of the scratch is a measure of the hardness of the material; also, the load required to produce a scratch of a standard width may be taken as a measure of the hardness. In order to compensate for soft phases or pores in the surface to be tested, a progressive load increase with proceeding scratch appears advantageous, since in such method the resultant triangular impression can be measured and evaluated more accurately.

One factor common to both the indentation and scratch methods is that the metal is deformed during the test, and the deformation in turn increases the hardness of the metal. Therefore, metals that work-harden rapidly will give higher hardness values than those which do not, especially if the pore structure is such as to permit ready deformation of the metal grains.

Tension. Conventional tension testing is applicable to sintered products, but certain allowances must be made in view of the specific character of the material. First to be considered is the method of obtaining a test specimen. With the exception of the large-size products produced in the refractory metal field, the finished sizes of powder metallurgy parts are generally too small for machining standard tensile test pieces, and extremely small specimen sizes would have to be used. But even then, the merit of such a procedure remains questionable, since many parts, especially if of more complex shape, are nonuniform in density and structure throughout their cross section. The latter argument, however, holds equally true for the case in which special test specimens are prepared parallel with the commercial products—and by identical techniques. The prismatic test specimens will hardly display the identical distribution of internal stresses caused by residual pores or phases as found in the custom-molded parts. Moreover, it must also be realized that there may be a certain variation in stress distribution from one test piece to another, since each specimen is produced individually, and that testing of duplicates prepared by identical procedures from the same raw material may show quite considerable variations in properties.

Kieffer and Hotop[7a] have recently reported the successful use of a special machine developed by Chevenard[7b] in testing microtensile specimens cut from sintered iron and steel parts.

[7a] R. Kieffer and W. Hotop, *Sintereisen und Sinterstahl*. Springer, Vienna, 1948, pp. 324–328.

[7b] M. P. Chevenard, *Rev. Mét., Mémoires, 38,* No. 12, 317 (1941); *39,* No. 2, 33; No. 3, 65 (1942).

The stress analysis in sintered metals undertaken in Chapter XXXIII has indicated that the residual porosity has a profound effect on the mechanical properties of the material, and that especially cohesive strength and ductility can be materially impaired if the pore volume becomes pronounced. Aside from the internal notch effects produced by the residual pores, the actual reduction of the *effective* cross section of the test bar must be considered. It is apparent that large tensile specimens with standard gage length in definite relation to the cross section lose their significance, since the apparent cross section obtained by direct measurement can be taken only with due allowance for incomplete density. Difficulties in determining the true density in the cross-sectional area at which fracture occurs also prevent the accurate determination of the value for reduction of area (which is so significant as a criterion for ductility).

Recognition of these circumstances has led to the suggestion that a special small tensile specimen be used that resembles the dumb-bell shape standardized for concrete and similar brittle materials.[7c] This specimen would be suitable for determining the tensile strength, but the narrow section in the middle where the cross section is reduced causes a sharp concentration of all stresses at that point, and leads to distorted elongation values. Therefore, this type of specimen is recommendable only for brittle products in which ductility data have no significance. Where, on the other hand, ductility is an important property requiring control, tensile specimens of standard gage length must be used—in spite of the error encountered because of the inherent porosity effects—since ductility can at least be observed qualitatively in the standard bar by elongation and reduction-of-area measurements.

Tensile testing in the elastic range and determination of the modulus of elasticity in metals sintered to different states of consolidation has been suggested recently by Bartels[8] as a means of routine quality control. The method is applicable to different metal systems (*i.e.*, single metals such as iron) or alloys that sinter either in the absence of a liquid phase (system Fe–Mo) or in the presence of a liquid phase forming solid solutions (system Fe–Al) or duplex structures (system Fe–Cu).

Compression. Powder metallurgy products are generally more adaptable to compression stresses than to tension stresses, since compression tends to diminish the pore volume. However, unless entirely surrounded by a mold, the sintered specimen is liable to fail in the compression test because of the tension and shear stresses acting on the

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[7c] F. Sauerwald and St. Kubik, *Z. Elektrochem.*, *38*, 33 (1932).

[8] H. J. Bartels, *Proc. International Powder Metallurgy Conference*, Graz, July 12–17, 1948, Referate No. 29.

circumferential fibers of the test cylinder. The compression fracture is usually cone-shaped—similar to the fracture of brittle materials such as cast iron.

For the purpose of practical quality control the cylindrical compression specimen has been replaced by cores or sleeves corresponding to actual form pieces produced on a production scale. The method used widely in porous bearing manufacture is known as the radial break test; a hollow cylinder is crushed radially between two plates of a press. The maximum load withstood by the bushing before break is taken as a basis for the compressive strength of the part. Correctly speaking the specimen fails not in compression but in the tension and shear to which the sections at right angles to the axis of applied stress are subjected.

A test method using $^1/_2$-in. diameter cores whose length may range from $^3/_4$ to $1^1/_2$ in. has been suggested by Baëza.[9]

Transverse Rupture. The cohesive strength of very brittle and hard materials cannot be determined readily by ordinary tensile testing methods, since special gripping devices would be required to hold the test pieces; also, the use of specimens of standard gage length design would be nonsensical. Therefore, materials such as cemented carbides or hardened sintered steels are usually tested for transverse rupture strength. This test provides for simple prismatic test bars which can be obtained by direct molding and sintering and require only finish-grinding. Conventional sizes for cemented carbides are rectangular bars, 0.250 by 0.1825 in. in cross section and of sufficient length to allow room for supports $1^1/_2$ in. apart,[10] or 0.375 by 0.200 in. in cross section and long enough for supports $^9/_{16}$ in. apart.[11] The test bar is supported on its flat side on knife edges. The breaking load is applied midway between the fixed line centers of the supports, which must be placed to prevent failure through shear. The ultimate load and deflection that the specimen can withstand before breaking are taken as criterion of the quality of the material. Since load plus deflection depends on the span and size of the cross section as well as on the material, specimen sizes are varied according to the characteristics of the material. In order to exclude the specimen size factor, the results should be calculated to the "transverse modulus of rupture," according to one of the following expressions.

Rectangular bar: $S_r = 3lP/2wh^2$

Cylindrical bar: $S_r = 2.546lP/d^3$

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[9] W. Baëza, *A Course in Powder Metallurgy*. Reinhold, New York, 1943, p. 100.

[10] E. W. Engle, in J. Wulff, *Powder Metallurgy*. Am. Soc. Metals, Cleveland, 1942, p. 444.

[11] P. M. McKenna, in J. Wulff, *Powder Metallurgy*. Am. Soc. Metals, Cleveland, 1942, p. 457.

where S_r is the modulus of rupture, l is the length of span, P is the ultimate or breaking load, w is the width of the bar, h is the height of the bar, and d is the diameter of the bar.

There is no constant relationship between tensile strength and transverse modulus of rupture. The modulus is the higher of the two values and usually increases with increasing tensile strength, though not in the same proportion.

The transverse rupture test has lately been also suggested as a means of determining the cohesive (green) strength of unsintered powder compacts.[11a]

Bending. In the case of the more ductile sintered metals, the transverse testing method can be used as a bend test, with maximum deflection before appearance of visual cracks and resulting bending angle used as criteria for the ductility of the material. Specimens suitable for this test are preferably rectangular in cross section, with a width at least three times the thickness. The length of the span between the supports may vary according to the thickness and must be sufficient to prevent shear failure. The tensile strength in bending, based on the stress in the outermost fibers of the specimen may be calculated according to the expression:

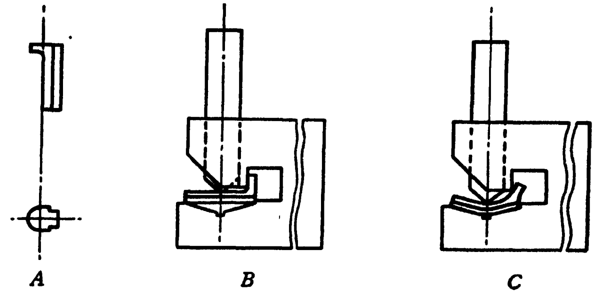

Fig. 623. Fixture designed to test the ductility of a powder metallurgy component (according to Lenel[13]): *A*, design of component; *B*, test fixture with inserted component; and *C*, deformation without fracture of component during testing with static load.

$$S = 3Pl/2wh^2$$

where S is the bend strength, P is the load, l is the length of the span, w is the width of the specimen, and h is the height of the specimen. A standard gage over which the elongation is to be measured is generally specified as 0.3 in. for specimens from $^1/_4$ to $^1/_2$ in. in thickness[12]; it

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[11a] J. P. Scanlan and R. P. Seelig, *Powder Met. Bull.*, *4*, No. 4. 128 (1949).

should be located at the section of maximum bending and in the center third of the width of the specimen.

A deviation from this procedure provides a simple bend test around a mandrel by steady application of a static load or by hammering until rupture occurs, or, for control purposes, until a definite bending angle, say 60, 90, or 180°, is attained. The diameter of the mandrel is usually made to equal the thickness of the specimen. (For bend test results by this method obtained with sintered copper, see Figure 598, Chapter XXXII.)

In actual production control work it may be desirable to test the ductility of the manufactured products directly; this can be accomplished easily with the aid of simple fixtures, as, for example, the one shown in Figure 623.[13] The piece shown (Fig. 623*A*) is molded with the long section in the direction of pressing—pressure being applied from opposite ends. It will have its lowest density, and therefore its lowest strength and ductility, in the middle of the long section, and the performance of the piece at this central section is a criterion of the quality of the part. The test fixture (Fig. 623*B*) allows the piece to be bent to a specified degree at which the material must not fracture (Fig. 623*C*); simultaneously, it imposes a bending moment on the joint between the flangelike and the long sections by bending the former.

Shear. If the span between the knife edge supports of the transverse testing fixture is narrowed to twice the thickness of the test specimen, the material will fail in shear. The ultimate load applied before fracture may then be used to calculate the double-shear strength.

There are a number of other shear testing methods suitable for testing rectangular powder metallurgy specimens, either in single or in double shear. One of these procedures provides for the use of three ringlike dies with square holes through their axes to receive the test piece. While the outer- and innermost dies are supported, the middle die receives the load and causes a short section of the specimen to shear.

While shear strength and shear modulus are properties specific for each material, they are in rough relation to the tensile strength. Sintered steels behaving like cast iron have a ratio of shear strength to tensile strength of about 0.5–0.9 in the case of single shear and 1.0–1.8 in the case of double shear.

High Temperature Testing. Recent developments in the high-temperature metals field, utilizing sintered or hot-pressed refractory metals and superalloys, have introduced the conventional high-temperature testing methods into powder metallurgy. With the exception of hot fatigue testing, these methods are all of the static type and include the short-term hot tensile strength and the long-term stress rupture and creep tests. Hot hardness testing (Rockwell or Brinell) has been employed as an auxiliary means of determining the resistance of the materials to deformation at elevated temperatures.

In view of the fact that this subject is only of very recent interest, little information is yet available, and an intelligent analysis of the testing procedure in relation to the powder metallurgy products is not possible. Let it suffice to say that the problems of inherent porosity as well as those connected with resistance to oxidation and erosion are likely to assume considerably greater importance with the sintered refractory metals than would be the case with dense fusion products. Consequently, greater difficulties may be encountered in analyzing the causes for failure of the material. It is interesting to note, however, that it has recently been suggested that the creep test—with its high structure sensitivity—be used as a method of investigating the variables of the powder metallurgy process.[14] In support of this suggestion, reference is made to the quantitative analysis of the creep process by Nowick and Machlin.[15] Since the creep of metals may be considered to be a process that passes potential barriers, Eyring's theory of rate processes would apply; the application of this theory to the dislocation mechanism of Taylor results in a relationship which indicates that highest resistance to creep can be expected in those metals possessing the highest moduli of rigidity. The modulus of rigidity, in turn, is related to the modulus of elasticity, as expressed by the formula:

$$G = E/2(1 + \mu)$$

where G is the modulus of rigidity, E is the modulus of elasticity, and μ is Poisson's ratio. Thus, the analysis of Nowick and Machlin confirms the conclusions drawn elsewhere in this volume (Chapters XXXII and XXXVI) that the high melting metals and metal-like compounds of the refractory and hard metal groups with their very high moduli of elasticity should prove to be excellent materials for high-temperature, high-stress applications, provided, of course, that the valuable physical properties of these materials are adequately protected from deterioration by chemical or corrosive attack. Late reports on the properties of heat-resistant cemented titanium carbide materials seem to prove this point.[16,16a] In this connection the inherent porosity in the sintered products deserves special attention, since the exposed surface area is enlarged many times over by an intercommunicating pore system. As far as the mechanical performance at high temperatures of a porous refractory metal under exclusion of chemical attack is concerned (*i.e.*, in an inert atmosphere

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[14] W. E. Kuhn, *Canadian Metals, 10,* No. 6, 27 (1947).

[15] A. S. Nowick and E. S. Machlin, National Advisory Committee for Aeronautics, *Tech. Note No. 1059* (1946).

[16] Anonymous, *Materials & Methods, 26,* No. 6, 85 (1947).

[16a] J. C. Redmond and E. N., Smith, *Trans. Am. Inst. Mining Met. Engrs., 185,* 987 (1949).

or in the case of a stable material), little is known to date and little can be deducted from theoretical considerations. Pfeil,[17] however, has directed attention to the fact that sintered porous platinum has a higher creep resistance than cast dense platinum; the same has also been found true for wires made from these materials.[17a] It has also been found that some of the heat-resistant superalloys (*e.g.*, Vitallium and Hastelloy B) have given similar results on an experimental scale.

DYNAMIC TESTING

Hardness. One method of testing the hardness of metal objects, which gives good comparative results without penetrating the surface to be tested, is the scleroscope hardness test. The scleroscope measures the height of rebound of a tiny, diamond-tipped hammer after it falls upon the surface of the specimen. The chief reason why this method—in spite of its simplicity and nondestructive character—has not been adopted widely for powder metallurgy products lies in an apparent inconsistency of results obtained that must be attributed to surface conditions. A smooth surface of the specimen is very essential for the test, since, otherwise, serious fluctuations and generally too low values will be found in the rebound readings. Much the same undesirable effect can also be noticed in sintered specimens whose surfaces are porous or pitted.

Impact. Tests that determine the resistance to shock and sudden impact constitute the principal destructive dynamic testing methods readily applicable to powder metallurgy products. The standard Izod and Charpy impact tests, which attempt to simulate sudden shocks in service, require simple rectangular specimens that can be directly processed (except for the V and keyhole notches, which must be machined). Depending on the specific method, the specimen is either gripped at one end only, with the pendulum striking the free end immediately above the notch, or supported on both ends, with the pendulum striking the specimen opposite the notch midway between the supports. The arc traveled by the pendulum after fracture indicates how much of the initial energy of the pendulum is absorbed in fracturing the specimen; this figure, reduced to the area of the fracture, indicates the notch toughness of the material. The principal objection to this type of test lies in the brittle character of most sintered metals, which results in very low impact values that cannot be measured very accurately with standard testing equipment. But this situation can be considerably improved if unnotched specimens are used. In order to differentiate between specimens of different degrees of brittleness, and to be able to establish trends, impact testers of high sensitivity

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[17] L. B. Pfeil, *Conference on Metallic Creep,* Royal Soc., London, Feb. 1946 (unpublished).

[17a] A. B. Middleton, L. B. Pfeil, and E. C. Rhodes, *J. Inst. Metals, 75,* 595 (1949).

in the low range must be used; such equipment has recently been developed for the plastics industry.

Other methods of dynamic testing that are equally valuable in evaluating the shock resistance of sintered metals include tension-impact testing, which also requires special equipment and machined specimens, and compression-impact testing by means of a simple gravitational hammer. The latter method is very primitive and gives results that have but little significance; the simple cylindrical shape of the test specimen, however, represents an advantage for this method.

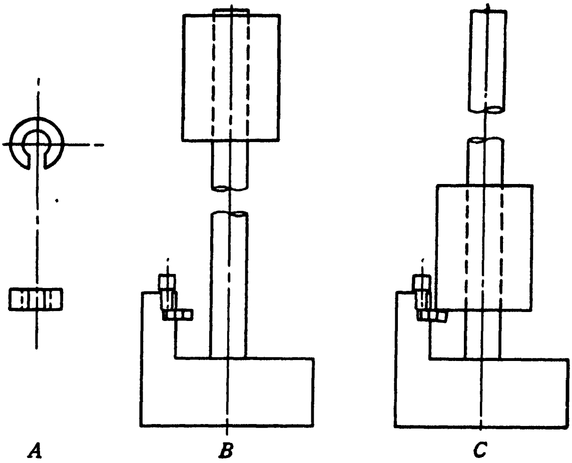

Fig. 624. Fixture designed to test the shock resistance of a powder metallurgy component (according to Lenel[18]): *A*, design of component; *B*, test fixture with attached component; and *C*, deformation without fracture of component during impact testing.

Often, it has been found appropriate to devise special testing fixtures to test the shock resistance of production parts. Generally, it has been found that impact strength and ductility in sintered products parallel each other, and that a material poor in elongation and bending is also very brittle and sensitive to shock. A typical shop fixture used to test the shock resistance of a mass production part requiring good toughness is sketched in Figure 624.[18] The slotted ring piece (Fig. 624*A*) is clamped in a vise in such manner that one side of the slot is flush with the edge of the vise (Fig. 624*B*); thus, slightly more than half of the part protrudes into the path of a small drop hammer of specified weight. Specifications would imply that for a given height the part must withstand the hammer impact without fracture (Fig. 624*C*); for a lower height, the piece must arrest the hammer without showing any cracks.

Fatigue. All of the known fatigue-testing methods require special test specimens which must be machined to accurate size. The most common method of determining the endurance limit involves the rotation of a cylindrical specimen with a standard gage length, loaded either as a simple beam or as a cantilever. At any time the fibers at the top of the specimen are in tension and those at the bottom in compression; after the specimen has rotated 180° the stresses are reversed. The number of stress reversals that the material can endure in the case of different stresses is a criterion of the quality of the metal.

The method less frequently used applies repeated alternating tension and compression stresses at both ends of the specimen; the stress reversals can be produced either mechanically or electrically, with amplitude and cycle adjustable over a specified range. The specimens for this test may be rectangular, and may therefore be processed directly from powders without subsequent machining, but the testing machinery is more complicated.

In any case, fatigue testing requires long periods of testing, and is not suitable for production quality control. However, as a research tool in the investigation of the properties of sintered metals, fatigue tests have been used with good success.[18,18a]

MISCELLANEOUS TESTING

Metallography. Because of its paramount importance, metallographic testing deserves brief mention. As in common metallurgical practice, sections are prepared both from test specimens and from production samples. Generally speaking, conventional polishing and etching techniques are applicable to the powder metallurgy products. Because of the inherent porosity of most of the materials produced during sintering, however, extreme caution is necessary: (*a*) in polishing, to avoid tearing or dislocating of particles, which would give a distorted picture of the structure; (*b*) in etching, because of the ready absorption of the etchant by the capillary action of the pores, which would result in internal corrosion; (*c*) in electrolytic etching, because of similar effects caused by the penetration of the electrolyte. With a large pore volume in the compact the preparation of good metallographic specimens becomes exceedingly difficult, though not impossible. Even presintered or unsintered compacts can be sectioned, polished, and etched if the necessary skill is employed. Sintered and molded sections are preferably mounted in plastics (*e.g.*, Bakelite or Lucite), while powders or powder particle agglomerates can

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[18] C. G. Goetzel and R. P. Seelig, *Trans. A.S.T.M.*, *40*, 746 (1940).

[18a] M. Hempel and H. Wiemer, *Arch. Metallkunde*, *3*, No. 1, 11 (1949).

be either mounted in plastics or cemented with sodium silicate on to a suitable base specimen.

In this connection, several recently published techniques for metallographic mounting of powders and porous specimens may be mentioned. According to Simister,[19] a mold is made from a brass tube that is cemented to a glass slide, and the specimen is placed into it with the face to be polished resting on the glass. The mold is then filled with Bakelite cement, and all air bubbles are removed in a vacuum desiccator. A release of the vacuum results in a filling of the pores with Bakelite. The solvent of the cement is driven off by heating to 60–70°C. (140–158°F.) for several hours, and the Bakelite is then set in a drying oven at 110°C. (230°F.). The mounting is readily removed from the brass mold due to a slight shrinkage during setting of the Bakelite. A similar method which uses sodium silicate as mounting medium was mentioned by Kingston[20]; another one for mounting loose or compacted iron powder in Lucite and polishing with the aid of a chromic oxide abrasive was described by Jamison and Byron.[21] A mounting technique, recently developed by Wachtell,[21a] for the purpose of preserving the edges of porous compacts is based on the infiltration of pure Bakelite resinoid.

Electron Microscopy. The very large magnifications (×20,000–100,000) that can be obtained with the electron microscope permit observations in a range of resolution that lies between that of the optical metal microscope and that possible only by x-ray techniques. Thus it has been found possible to examine particles from 0.01 to 0.2 μ in size with the electron microscope and also to make profile studies of larger particles; more recently, electron microscope studies have been extended successfully to recrystallization and sintering phenomena in powder metallurgy specimens. Of greatest importance in electron microscopy is the preparation of suitable samples with an adequate dispersion of the particles. Kahler[22] reports that by applying ultrasonic waves (of 100–500 kilocycles frequency) to a suspension of the powder sample in an inert liquid, a separation of the agglomerate without danger of attrition of the individual particles is possible. In the case of substances of comparatively low melting point or high sorptive capacity, the action of the electrons may cause local heating and possible recrystallization that may lead to incorrect conclusions. Electron microscope studies on a number of nonmetallic

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[19] E. Simister, *Metal Progress, 49, No.* 1, 128 (1946).

[20] W. Kingston, *Proc. International Powder Metallurgy Conference,* Graz, July 12–17, 1948, Referate No. 62; also *private communication.*

[21] H. M. Jamison and E. S. Byron, *Metal Progress, 51,* 437 (1947).

[21a] R. Wachtell, *Powder Metallurgy Bull., 4,* No. 4, 126 (1949).

[22] F. Kahler, *Proc. International Powder Metallurgy Conference,* Graz, July 12–17, 1948, Referate No. 33.

powders have been reported by Harvey[23] (who worked with carbon and magnesium oxide) and Kahler[22] (who studied MgO, $MgCO_3$, and Fe_2O_3); metallic specimens examined by the same investigators were silver and iron. The possibility of oxidation of tungsten and molybdenum powder samples in high vacuum while being held in the electron microscope was established by Schmidt.[23a] A series of truly magnificent electron micrographs of particles of tungsten powder, and especially of carbonyl nickel and iron powders, was recently published by Delisle.[23b]

X-Ray Diffraction. Modern investigations of the state and constitution of many sintered alloys and, especially, the hard metal compounds, have been carried out with the aid of x-ray testing known as the Debye-Scherrer or powder method.[24–30b] The method involves photographic recording of the diffraction pattern of the metal crystals that are contained in powder particles in a random or preferred orientation. The method enables the researcher to explore the nature and constitution of the material under investigation, and to give evidence of the type of alloy and the number of phases present.

The powder to be used in the test must be truly representative of the sintered metal. While a great deal of the x-ray diffraction work is carried out on the surface of the sintered specimen which usually contains the necessary fine grains in approximately random arrangement to fulfil the conditions for diffraction, circumstances frequently require the removal of a powder sample from the part before examination. In this event, the powder must be severed from the compact specimen in such a manner that segregation and contamination (*e.g.*, by the oxygen of the air), as well as work hardening, other than already present in the compact, is avoided. When this is not possible, the powder must be especially treated to restore the state in which the particles were prior to their separation from the compact specimen.

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[23] G. G. Harvey, in J. Wulff, *Powder Metallurgy.* Am. Soc. Metals, Cleveland, 1942, p. 234.

[23a] R. W. Schmidt, *Kolloid Z., 102,* No. 1, 15 (1943).

[23b] L. Delisle, *J. Metals, 1,* No. 3, 228 (1949).

[24] W. Trzebiatowski, *Z. physik. Chem., A169,* 91 (1934); *B24,* 75 (1934).

[25] E. A. Owen and L. Pickup, *Proc. Roy. Soc. (London), A149,* 282 (1935).

[26] A. G. Metcalfe, *Metal Treatment, 13,* 127 (1946).

[27] A. Carter and A. G. Metcalfe, *Symposium on Powder Metallurgy,* The Iron and Steel Institute, Special Report No. 38, London, 1947, p. 99.

[28] W. Trzebiatowski, H. Ploszek, and J. Lobsowski, *Anal. Chem., 19,* 93 (1947).

[29] H. Nowotny and R. Kieffer, *Metallforschung, 2,* 257 (Sept. 1947).

[30] F. Regler, *Proc. International Powder Metallurgy Conference,* Graz, July 12–17, 1948, Referate No. 40.

[30a] H. Hendus and H. Nowotny, *Proc. International Powder Metallurgy Conference,* Graz, July 12–17, 1948, Referate No. 66.

[30b] A. Neth, *Proc. International Powder Metallurgy Conference,* Graz, July 12–17, 1948, Referate No. 41.

The x-ray diffraction method permits the study of a number of factors that may influence the properties of sintered metals. In the loose and compacted powders, the degree of work hardening and the orientation of the individual crystallites can be investigated by an analysis of the diffraction patterns. As an example, Figure 625 shows photograms of three different types of iron powder compacts investigated by the back reflection method.[31] In fact, it may even be possible under favorable circumstances to determine how severe cold-working effects grow from the contact points between particles to the interior of the particles with progressing compaction. In the sintered compact, recovery and recrystallization can be traced by the diffraction pattern.

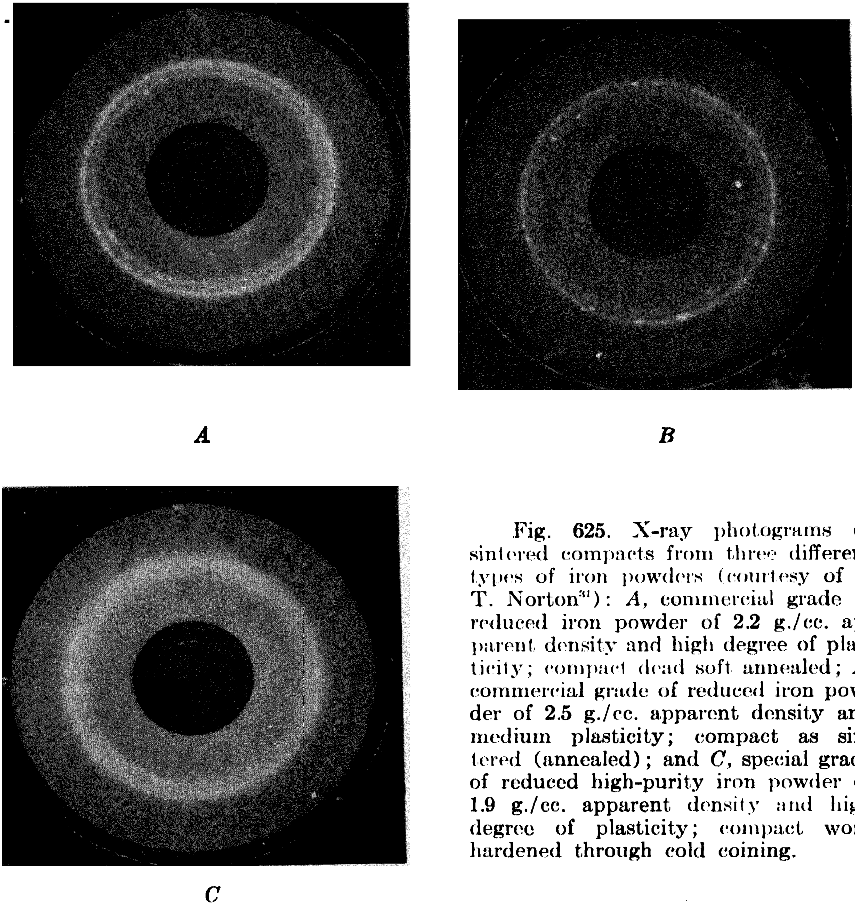

Fig. 625. X-ray photograms of sintered compacts from three different types of iron powders (courtesy of J. T. Norton[31]): *A*, commercial grade of reduced iron powder of 2.2 g./cc. apparent density and high degree of plasticity; compact dead soft annealed; *B*, commercial grade of reduced iron powder of 2.5 g./cc. apparent density and medium plasticity; compact as sintered (annealed); and *C*, special grade of reduced high-purity iron powder of 1.9 g./cc. apparent density and high degree of plasticity; compact work hardened through cold coining.

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[31] J. T. Norton, *unpublished data.*

In this connection it is interesting to note that the Geiger-Müller counter can be used to measure the intensities of reflections from the x-ray spectrometer. The estimation of tungsten carbide and other substances in metal powders by x-ray diffraction analysis using this instrument has been reported.[32] It is claimed that an x-ray analysis can be completed with the instrument in 35 minutes.

Neutron Transmission. Most recently, the transmission of monoenergetic slow neutrons has been described for the first time on metal powder specimens in support of x-ray diffraction testing. Experimenting with powdered solid solutions and mechanical mixtures of titanium carbide and tungsten carbide, Sidhu[33] found that factors such as crystallinity, crystallization, grain size, order-disorder, orientation, strain, solubility, etc., which all cause changes in the lattice, affect the scattering cross sections, since the wavelengths of the neutrons are comparable to the interplanar lattice spacings of the carbides.

Nondestructive Testing Methods

Testing of metals is not restricted to the exploration of their physical characteristics by means of destructive testing methods, but also includes the determination of the homogeneity and soundness of the product as a whole. While the character of the metal itself is established and controlled by physical testing of samples, testing for soundness is concerned with the structural continuity of the actual part, and may involve 100% inspection of the final product. A discontinuity of the structure, as manifested by pores, cavities, cracks, or nonmetallic inclusions, must therefore be determined without destroying the part. A variety of testing methods of nondestructive character have been developed, including permeability, radiographic, electrical, and magnetic methods. Their applicability to powder metallurgy products will be surveyed briefly.

TESTING OF DENSITY

Powder metallurgical products distinguish themselves from ordinary metal products by one important peculiarity, the predominant pore volume. In contrast to the case of defect castings, these pores do not constitute local discontinuities of the structure, but rather do they form an integral whole with the structure. Thus, the presence of porosity in sintered metals cannot be taken *per se* as a criterion for unsoundness, and it is rather the *volume* and *distribution* of the pores throughout the part which must be determined and controlled. The determination of the

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[32] E. S. Kopecki, *Iron Age, 157,* No. 9, 48 (1946).

[33] S. S. Sidhu, *J. Applied Phys., 19,* 639 (1948).

(relative) density of the entire part or of certain sections thereof constitutes a fundamental step.

The density of porous sintered parts is customarily determined by immersion in water of the part after it has been impregnated with a water-repellent fluid, such as oil. The density value is calculated from the formula:

$$\rho_r = A/(B - C)$$

where ρ_r is the (relative) density in grams per cubic centimeter, A is the weight in grams of the part weighed in air before impregnation, B is the weight in grams of the part after it has been impregnated with oil, and C is the weight in grams of the impregnated part in water. The weights A, B, and C must be determined to within 0.05% of each weight, which for small parts necessitates weighing on an analytical balance to the nearest milligram.[33a]

Two methods of oil impregnation are conventionally used. The part may be impregnated .by immersion for a minimum of 4 hours in oil of a viscosity of approximately 200 sec. saybolt at 100°F. (38°C.) which is held at a temperature of 180 ± 10°F. (82 ± 5°C.); the part is then cooled to room temperature in the oil. In the alternate method the part is immersed in low-viscosity oil at room temperature; the pressure over the oil is reduced to an absolute pressure of not more than 2 in. Hg (50 mm. Hg) for a minimum of 30 minutes; the part is left in the oil for at least 10 minutes after atmospheric pressure has been reestablished. After impregnation, care must be taken that all excess oil is removed. During weighing the part in water, the effect of the surface tension of the latter may be lessened by adding a small quantity of a wetting agent.

Where simple prismatic parts are involved, the determination of the volume by direct measurement may be more expedient. This method may merely require the determination of the weight in air and the height of the part, where sintering conditions imply a closely controlled shrinkage of the radial or lateral dimensions, which are kept constant before sintering by the contours of the die cavity.

When the axial dimension is also closely controlled during molding and sintering, the density of the part may be determined simply by measuring the weight of the accurately dimensioned part. Since modern methods of determining accurate weights can handle large-scale volumes at great efficiency, the last procedure can be used readily for production control work and can even be used for 100% inspection.

[33a] U. S. Army Ordnance Dept., *Tentative Specification AXS-1067* (March 4, 1944).

TESTING OF POROSITY

Permeability for Liquids. The proportion of interconnected pore volume in the total volume of porosity within the sintered part can be determined by measuring the quantity of a water-repellent liquid that can be absorbed by capillary action of the interconnected pores and then by bringing the calculated value into relationship with the value for the relative density of the part.

The interconnected porosity can be expressed as:

$$P_i = \frac{B-A}{(B-C)\rho_0} \times 100$$

where P_i is the interconnected porosity (in volume per cent), ρ_0 is the specific gravity of the liquid impregnant (in grams per cubic centimeter), and A, B, and C are in their order the weights in air (in grams) of the part before impregnation, after impregnation, and after immersion in water. This value can then be related to the total porosity volume by the formula:

$$P_p = \frac{P_i}{1-(\rho_r/\rho)}$$

in which P_p is the proportion of the interconnected pore volume in the total pore volume (in per cent), P_i is the interconnected porosity (in volume per cent), ρ_r is the relative density of the part (in grams per cubic centimeter), and ρ is the theoretical density of the metal.

In addition to its use in the determination of the size of the interconnected pore volume, the impregnation procedure lends itself to the study and control of the *character* of this porosity. More specifically, the method permits certain deductions as to size, shape, and location of the individual pores or agglomerations of pores by testing the permeability of the structure for liquids of different viscosity, surface tension characteristics, or wetting properties. Various procedures for testing the permeability for liquids have been developed for porous metals and, in particular, for products that have to serve as filters, membranes, and the like. Principally, they may be divided into methods measuring a reduction in pressure and into methods measuring the flow of the liquid. In the first instance the frictional forces acting at the walls of the pores and channels cause a drop of the pressure of the liquid from the entrance face to the exit face of the porous section. This pressure drop is more pronounced the smaller and the more irregular the pores. It can be measured by simple manometer readings. In the second case the flow rate of a specific liquid through the porous structure is timed, the flow being impeded less by a few large and simple-shaped pores and channels than by a multitude of small and odd-shaped pores which cause greater friction losses. Timing is conveniently and accurately conducted with an electric clock by forcing a mercury column between two contacts ahead of the liquid impregnant, and by allowing the mercury to close an electrical circuit. Where there is no possibility of forming amalgams with the sintered metal, the mercury itself can be used as impregnant. One of the most interesting examples of a mercury flow test is the permeability control of the porous sintered nickel spacer cup used in the mercury safety switch of the U. S. Navy's V-T proximity fuze.[34]

Duwez and Martens[35] have made a major contribution to the study of permeability of porous sintered bodies in connection with their search for a material suitable for heat-exposed engine components that may be protected by "sweat cooling" (see Chapter XXVII). The physical principles determining the flow of fluids through porous media were formulated by Darcy in 1856, and it was found that the rate of flow of water through a unit area of a porous material is directly proportional to the pressure drop per unit length of the material. Darcy's law may be expressed by the following equations for liquid and gaseous fluids, respectively:

Liquid:

$$\frac{Q}{(P_1-P_0)/L} = \alpha\frac{\rho_0}{\mu}$$

Gas:

$$\frac{Q}{(P_1^2-P_0^2/L)} = \alpha\frac{\rho_0}{2P_0\mu}$$

Q is the weight rate of flow per unit area (in lb./sq. in sec.), P_1 is the pressure at the entrance side of the porous metal (in psi), P_0 is the pressure at the exit side of the porous metal (in psi), L is the thickness of the specimen (in inches), ρ_0 is the weight of the fluid per unit volume at P_0 (in lb./in.^{3}), μ is the viscosity of the fluid (in lb. sec./in.^{2}). and α is the permeability coefficient (in in.^{2}). The permeability coefficient is a constant for a given material and is independent of the liquid or gas used as a fluid. However, Darcy's law is valid only for viscous laminar flow. The limiting rate of flow at which the flow ceases to be truly laminar can be expressed in the case of a porous medium, just as in pipes, by a critical Reynolds number. Whereas it has been found in experiments with compacted sand that the critical Reynolds number above which Darcy's law is not satisfied is generally between 1 and 10, and in the case of packing of spheres of equal diameter or of a granulated material

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[34] Anonymous, *Steel, 118,* No. 16, 84 (1946).

[35] P. Duwez and H. E. Martens, *Trans. Am. Inst. Mining Met. Engrs., 175,* 848 (1948).

having a narrow range of particle sizes it is possible to define an average grain diameter and a characteristic length, in the case of porous sintered metals it is very difficult to define the characteristic length that enters into the expression of the Reynolds number. (In spite of careful study of the structure of the porous metals, Duwez and Martens could not arrive at a reasonable interpretation of an average pore size which would lead to an evaluation of a Reynolds number.) The permeability coefficient, however, was found by Duwez and Martens to hold for the flow of certain fluids (kerosene, nitrogen, hydrogen) through porous stainless steel specimens, but not through porous bronzes in which the porosity was varied by the particle size of the powder instead of by different quantities of pore creating agents (ammonium bicarbonate).

Permeability for Gases. Gases may substitute for liquids in the permeability test in all those cases in which the porosity characteristics would impose the use of great pressures to overcome the friction forces, *e.g.*, where the total pore volume is small, where the proportion of interconnected to total pore volume is low, or where the pores and interstices are extremely irregular in shape. Common gases, such as air, nitrogen, and hydrogen, can serve as penetrating media. Again, as in the case of liquid impregnants, the pressure drop or the flow rate of the gas can be measured by manometer or electric timing devices. Since the gases used in this type of test are likely to be less contaminating to the metal structure, both during the actual test and afterward when a certain volume of the impregnant remains absorbed by the pore structure, the gas permeability test is often more suitable for production control purposes. A prominent example of this type of test is again the permeability control of the porous nickel cups for the V-T fuze, which involves 100% inspection of the permeability of the sintered product in a nitrogen pressure-loss test.

TESTING OF VOLUMETRIC CHANGES

Volumetric changes in sintered metals are a composite of the effects of shrinkage, growth, stress relief, and the thermal expansion of the metal. The mechanism concerned with the shrinkage and growth in the compacts has been described in Volume I, Chapter XIV, and is also summarized in Chapter XXXV. The effects of these processes are usually studied on the basis of measurements made on the compacts *before* and *after* the sintering operation; in order to know how the volume changes *during* the sintering treatment, dilatometric measurements are necessary. These tests, however, concern themselves with a *net* volume change at any particular temperature level and permit no differentiation between the processes of pore volume reduction, pore volume increase, and metal lattice expansion. In order to segregate these different phenomena, a graphical presentation of the change in length with rising temperature is most convenient. By superimposing the normal thermal expansion curve for the particular metal over the curve obtained from actually observed dilatometer readings, it is possible by subtraction to obtain a curve representing the combined shrinkage and growth changes in the compact at any particular temperature. While it is not possible to produce separate curves for shrinkage and growth, the combined curve establishes a trend and permits deductions as to which gross volume changes are predominant at any particular temperature level. Dilatometric measurements on metal powder compacts have been described by Kalischer[36] who worked with iron, nickel, cobalt, and silver; by Duwez and Martens during their previously mentioned research[35] on porous stainless steel and nickel–molybdenum–iron, and, more recently, on copper, iron, copper–nickel, and copper–zinc[36a]; by Duwez[36b] during his work on sintered copper–gold compacts; by Silbereisen[36c] during his studies of the sintering of iron, copper, and aluminum; and by Dawihl and Rix,[37,37a] who worked with cobalt and copper; expansion measurements on tungsten powder compacts and loose powders have also been suggested as a quality index for incandescent lamp filaments.[38]

TESTING FOR STRUCTURAL CONTINUITY

The detection of structural discontinuities in sintered metals, such as local regions of high porosity, interstices in the grain boundaries, or gradients in pore concentration in any direction, is quite difficult and requires testing methods more elaborate than those adequate for the determination and control of the over-all pore volume (density tests) or the nature of the pore structure (permeability tests). Among testing methods worthy of consideration are chiefly radiographic, electrical, and magnetic methods.

Radiographic Testing. Electromagnetic rays of short wavelength

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[36] P. R. Kalischer, *Symposium on Powder Metallurgy,* A.S.T.M., Philadelphia, Pa., 1943, p. 31.

[36a] P. Duwez and H. E. Martens, *J. Metals, 1,* No. 9, 571 (1949).

[36b] P. Duwez, communication on "The Sintering of Copper–Gold Alloys," *Symposium on the Physics of Powder Metallurgy,* sponsored by Sylvania Electric Products, Inc., Bayside, L. I., N. Y., August 24–26, 1949.

[36c] H. Silbereisen, *Arch. Metallkunde, 2,* No. 9, 305 (1948).

[37] W. Dawihl and W. Rix, *Z. Metallkunde, 36,* No. 8, 197 (194).

[37a] W. Dawihl and W. Rix, *Z. Metallkunde, 40,* 115 (1949).

[38] D. E. Tesen, *Office of Military Govt. for Germany (U. S.).* Field Information Agency, Technical (F.I.A.T.). Final Rept. No. 413, p. 7.

(x-rays), penetrate solid matter and reveal variations in density on a fluorescent screen or a photographic plate; the degree of absorption of the x-rays being about proportional to the atomic density of the substance. As a consequence, the x-rays are less penetrative the higher the atomic number of the element; on the other hand, they are highly penetrative in the case of low-density nonmetallic inclusions or cavities and cracks that show up on the photographic film as intensely darkened patterns. With the aid of high-voltage x-ray equipment it is thus possible to detect flaws in the interior of metal objects without their destruction, and the technique is being used widely in the inspection of castings and welded structures.

In powder metallurgy, little use has been made of radiographic testing. This may be chiefly attributed to the circumstance that most mass production parts are either very porous or complex in shape. In the first instance, the detection of nonmetallic inclusions or large cavities is nearly impossible; in the second, sudden changes in cross section prevent correct and rapid interpretation of the radiogram or the fluoroscope image. But, there are cases where radiographic testing has been successfully employed; among these are cases in which gross changes in the concentration of pores exist between one section and another or in which components consist of joint sections from different metals. In this connection, the inspection for soundness and freedom from cracks of the tips and welds of tungsten-base electrodes and contacts is significant.

One possible application of the radiographic method (not yet investigated extensively) is in its use as a research tool in the study of the change of pore structure during sintering. By interpreting radiograms of compacts sintered for various intervals under otherwise constant conditions it is reasonable to expect an increase of the metal phase at the expense of the gradually diminishing over-all volume. By employing the same technique it should also be possible to obtain an indication as to whether or not diffusion and shrinkage effects during prolonged sintering cause a change in the porosity distribution.

The use of radiograms in the determination of the density distribution in compressed powder cylinders[38a,b] has been described in Volume I, Chapter VIII.

Magnetic Testing. Two important methods of nondestructive testing of metallic objects are based on the fact that discontinuities at the surface or in the interior of the metal cause a marked change in a magnetic field. In the first method, a heavy direct current is passed through the metal. This will produce a magnetic field which, in turn, will induce a current in a wire coil that is moved alongside the object; variations in current density caused by flaws can then be noted. In the second

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[38a] R. Kamm, M. A. Steinberg, and J. Wulff, *Trans. Am. Inst. Mining Met. Engrs.*, *171*, 439 (1947).

method, the nonhomogeneous object is magnetized and its surface coated with iron powder or powdered magnetic iron oxide; the particles will collect in distinct patterns at the discontinuity due to an intensified field. However, neither of the methods lends itself too well to powder metallurgy products, the first being used exclusively for the testing of bulk steel products (*e.g.*, steel rails), and the second, generally known as the Magnaflux method, being restricted to steel products with *superficial* discontinuities, since the sensitivity of the method decreases rapidly with the distance of the defect below the surface.[39]

Electrical Testing. It appears evident that, in principle, electrical conductivity testing may be an effective method of determining the structural homogeneity of powder metallurgy products. Unfortunately, however, the conductivity is seriously affected by impurity films present in most commercial powders, rendering the method impractical as an indicator for the continuity of the structure.

A novel method of nondestructive testing of steel parts, which is readily adaptable to certain control work on a mass production basis, employs a special high-frequency oscillator known as a cyclograph, whose output is governed by magnetic and eddy current losses. The method lends itself to a correlation of the high-frequency core losses with internal stresses that may be caused by cold-working or quenching, and can also lead to a prediction of fatigue failures.[40] However, attempts to utilize the core-loss measurement for nondestructive testing or control of the ductility of iron powder metallurgy products have been successful only to a limited extent. The apparent reason for this is the number of variable factors that influence the readings simultaneously, such as work hardening, oxide films, gas inclusions, etc. Since the determination of each of these factors would require a specific frequency and sensitivity range of the cyclograph, the method is only sensitive, where all factors except one are stabilized or eliminated—a condition that does not usually exist in production work.

Mechanical Testing. -A testing method of increasing interest in the study of brittle materials deals with the damping capacity of metals subjected to mechanical vibrations. In cast alloys, and especially cast irons, the damping capacity, *i.e.*, the resistance to resonant vibrations such as created by slight impacts, is generally high; the material rapidly absorbs the vibrations caused by shock by absorbing a large amount of the vibration energy during each stress cycle. Because of certain similarities in mechanical properties of brittle castings and sintered metals, it may be assumed that the latter, too, display similar damping characteristics,

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[39] F. T. Sisco, *Mining and Metallurgy*, *27*, No. 476, 442; No. 477, 478 (1946).

[40] P. E. Cavanaugh, *Trans. Am. Soc. Metals*, *36*, 137 (1946).

especially since the inherent porosity will tend to enhance the damping capacity of the part. Based on this assumption, it has been suggested that testing methods involving the observation of damping and transmission of mechanical vibrations may give an indication of the internal friction and thereby of the degree of stability of the intercrystalline boundaries.[41] While the apparatus necessary to excite the test piece is relatively simple, the evaluation of the test results appears extremely difficult, thus rendering the method impractical for general use.

Acoustic Testing. The utilization of sound waves for a rough testing of metals dates back to the earliest days of metal making. Deep-going imperfections, such as cracks or large cavities, reflect sound waves of a different wavelength than the metal itself; solid impurities in the form of isolated inclusions or included in the metal in uniform or varying concentration tend to absorb sound waves. However, the exact determination of the type of imperfection is possible only if ultrasonic waves are produced whose wavelength is in the order of magnitude that produces resonance in the imperfection. To the author's knowledge, nothing is known to date about any possible successful application of acoustic testing in powder metallurgy research or production control.

Summary

The testing of metal powder products belongs to one of the most difficult and controversial phases of the art. Certain typical characteristics, such as the inherent porosity, the brittle character of the structure, and the like, make conventional testing methods unsuitable in many instances. Rather, they demand special procedures which make allowances for the unusual properties involved. This makes it very important to analyze carefully the real properties that must be determined by the test, and also whether the type of test conventionally used is just as necessary or satisfactory in the case of sintered metals.

This problem is very obvious in the case of simple hardness testing, where, depending upon whether the object of the test is the true hardness of the metal phase or the over-all resistance of the body to indentation, entirely different hardness readings can be obtained. When testing static and dynamic properties, the direct measures for strength, ductility, and impact resistance also give an unfair picture, since they are based on the apparent cross section of the test piece which usually includes a major volumetric proportion of pores.

Measurements of density and porosity represent the principal nondestructive methods of testing and are extremely helpful in control of the

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[41] A. Reis, *unpublished communication.*

product as well as in properly evaluating the mechanical testing data. Other nondestructive testing methods, such as permeability and radiographic methods have found specific use in certain products, while procedures based on electrical, magnetic, mechanical, or acoustic principles are only of academic value at present.

CHAPTER XXXV

Theories of Bonding and Sintering—Summary

Inasmuch as the powder metallurgy method is based predominantly on the mechanism of bonding and sintering between the individual powder particles, the underlying theories for this process are of greatest interest and importance. It is the author's belief that no book that is to deal broadly with the *art* of powder metallurgy can afford to by-pass a detailed survey of the existing *theories* of the fundamental processes.

In order to retain the logical organization of this treatise, it was necessary to present the principal theoretical aspects of the processes when dealing with the technology of the powder metallurgy method. Thus, in Volume I, Chapter VIII, the mechanism of bonding during compaction was described in considerable detail, and in Chapter XIV a similar treatment was given to the principles of sintering of compacted powders at elevated temperatures. While the material presented in these sections appears adequate for the purpose of familiarizing the reader with the theory to an extent that enables him to understand the process in its broader respects (both as to potentialities and limitations) further discussion of the subject seems desirable for the benefit of those readers who are particularly interested in the physics and metallurgy of the process and who care to give this subject further thought.

The summary given here will lead to certain unavoidable repetition, but this was considered preferable to having the reader burdened with the necessity of constantly referring to cross references to other sections of this work.

This chapter deals with the subject in its entirety and embraces the recent summarizing surveys by Skaupy,[1] Schwarzkopf,[2] and Rhines.[3] The student of the theoretical aspects of the powder metallurgy process is advised to refer to Volume I, Chapters VIII and XIV in addition to the perusal of this chapter, so that he may obtain the most complete picture possible.

[1] F. Skaupy, *Metallkeramik*. 3rd. ed., Verlag Chemie, Berlin, 1943, p. 83 ff.
[2] P. Schwarzkopf, *Powder Metallurgy*. Macmillan, New York, 1947, p. 273 ff.
[3] F. N. Rhines, *Trans. Am. Inst. Mining Met. Engrs., 166,* 474 (1946).

HISTORICAL DEVELOPMENT OF THEORETICAL CONCEPTS

Although the art of powder metallurgy enjoys a long history and an impressive renaissance around the turn of the century, most interest remained centered around the metallurgy of the refractory metals during the first two decades of this century. However, the possibility of applying the powder technique to other than refractory metals was seen by Guertler[4] as early as 1912, and the reason for a delay of about ten years in following his suggestions may be blamed, at least in part, on the lack of a thorough understanding of the underlying principles of the sintering process as supported by experimental evidence. This situation may be fully appreciated if we realize that until about 1920 the theoretical concepts regarding physical processes such as recrystallization and grain growth were rather indefinite, and, therefore, no clear understanding of even the most simple principles connected with the sintering process could be formulated.

THEORIES BY SAUERWALD

A first attempt to formulate a theoretical concept was made by Sauerwald[5] in 1922 on the basis of compaction and sintering experiments with a variety of metals. His first publication was followed by a series of additional papers[6-16] reporting on extensive experimental work that he had conducted with a number of collaborators over a period of more than twenty years. While slight modifications were introduced in the successive papers, the main concepts of Sauerwald's original theory remained as outlined in his first publications. It may be stated here that most scientists and researchers concerned with the theoretical aspects of the powder metallurgy processes have leaned heavily on Sauerwald's theory, and that especially the German school of thought has been predominantly based on Sauerwald's classic revelations.

Briefly stated, Sauerwald's theory of sintering embodies the following point of view. During sintering, there exist two distinct successive

[4] W. Guertler, *Metallographie I.* Bornträger, Berlin, 1912, p. 173.

[5] F. Sauerwald, *Z. anorg. allgem. Chem.*, *122*, 277 (1922).

[6] F. Sauerwald, *Z. Elektrochem.*, *29*, 79 (1923).

[7] F. Sauerwald and E. Jaenichen, *Z. Elektrochem.*, *30*, 175 (1924).

[8] F. Sauerwald, *Z. Metallkunde*, *16*, 41 (1924).

[9] F. Sauerwald and G. Elsner, *Z. Elektrochem.*, *31*, 15 (1925).

[10] F. Sauerwald and E. Jaenichen, *Z. Elektrochem.*, *31*, 18 (1925).

[11] F. Sauerwald, *Z. Metallkunde*, *20*, 227 (1928).

[12] F. Sauerwald and J. Hunczek, *Z. Metallkunde*, *21*, 22 (1929).

[13] F. Sauerwald and St. Kubik, *Z. Elektrochem.*, *38*, 33 (1932).

[14] F. Sauerwald and L. Holub, *Z. Elektrochem.*, *39*, 750 (1933).

[15] F. Sauerwald, *Metallwirtschaft*, *20*, 649, 671 (1941).

[16] F. Sauerwald, *Kolloid Z.*, *104*, 144 (1943).

stages: *adhesion* and *crystallization*. In the adhesive stage, increased cohesiveness of the compact is due to mutual attraction of surface atoms alone, which is supported, however, by surface tension effects. Upon reaching a certain characteristic temperature—about three-fourths of the absolute fusion temperature of the particular metal—rapid shrinkage is caused by a "spontaneous" interchange of atoms between adjacent particles. This spontaneous crystallization effect is paralleled by a significant increase in grain size.

The fact that bodies formed by compaction of metallic powders have a certain degree of coherence indicates that surface forces are effective between the individual particles or crystallites. These forces are of the nature of those causing the adhesion between smooth surfaces. The effect of increasing compacting pressure is to improve the coherence of the body by increasing the proximity as well as the area of contact between neighboring particles. In order to increase the contact area it is necessary to flatten the crystallites at the contact points unless flat and parallel surface areas exist initially. This flattening is caused by an elastic and plastic deformation during compaction; for a metal of given plasticity it is more pronounced the greater the pressure that is applied to the powder mass.

The mechanism of adhesion is believed by Sauerwald to be based on forces acting in a direction normal to the surface of the particles, while the surface tension forces—increasingly active with rising temperatures—promote atomic activity in a direction tangential to the surfaces of the particles. With increasing temperature, increased thermal agitation of those opposite atoms of contacting particles takes place which previously had been too far apart to be joined; consequently, new atomic linkages are created with a corresponding increase in adhesiveness, and, in effect, with an increase in the total contact area.

Sauerwald's theories are characterized by the concept that the chief forces promoting the consolidation of the compacted powder during sintering are *adhesive* forces, with recrystallization processes playing only a minor part. However, when analyzing the prerequisites for the adhesive attraction between the particles, concepts such as atomic mobility and place changes are used, which would refer equally well to recrystallization.

Of particular interest is Sauerwald's discourse on grain growth ("crystallization") in the powder compact. In his first experiment,[6] the temperature of beginning grain growth was observed by metallographic study; it was found to be characteristic for each metal examined, but was apparently independent of the compacting pressure. The constancy of the grain growth temperatures observed for different pressures in these experiments gave cause to assume that no deformation takes place during compaction, since otherwise increased deformation caused by increased compacting pressures should lower the temperature of incipient grain growth. In the following publication[7] Sauerwald admits the existence of work-hardening effects produced during the compaction of the powder. In a modification of the original theory, it is recognized that cold work lowers the temperature of incipient grain growth according to the degree of particle deformation produced. But the revised concept is still dominated by the original theory, and the work-hardening effects are believed to be only of minor significance.

Sauerwald's contention that recrystallization can take place in sintered metals without previous plastic deformation would mean that a basic difference exists between the recrystallization process in sintered and fused metals, since the latter metals do not usually exhibit recrystallization without preceding plastic deformation. According to Sauerwald; this difference can be explained by the presence of impurities in the grain boundaries of the reguline metal which prevent the exchange of atoms between adjacent crystal surfaces. In sintered metals, on the other hand, this atomic exchange at the crystal boundaries can proceed unhampered, since no foreign phases cause interference and recrystallization can take place readily.

In his more recent publications, Sauerwald analyzes the effects of internal stresses caused by the compacting pressure,[14] that of deformation of the crystallites during compaction,[15] and that of irregularities in the surfaces of the individual particles.[16] In the first instance, Sauerwald concludes on the basis of a comparison of compacted and uncompacted powders that internal stresses in the compacted powders promote recovery of the metal at a low temperature, but that recrystallization only occurs at a higher temperature—comparable to that observed in uncompacted powders. The temperature of sintering as indicated by marked increases in strength and hardness, however, is believed to lie above that of recrystallization.

In the study of the pressure effects, Sauerwald distinguishes three cases. (*1*) Low pressures, which are believed to cause only elastic deformations; with rising temperature, density and hardness increase, but reach significant values only for the higher temperatures. (*2*) Medium pressures, which cause a limited degree of plastic deformation at the particle surface irregularities; with rising temperature, the density increases, but the hardness decreases because of annealing of the work-hardened structure. (*3*) High pressures, which cause intensive deformation involving entire particles; with rising temperature, density and hardness decrease, chiefly because of a loosening of the structure by gas evolution, a relief of internal stresses caused by the severe cold deformation or by an expansion due to grain growth. In the case of medium pressures the local plastic deformation of the surface irregularities causes an increase in contact areas between the particles, and the adhesion forces are enhanced, while recrystallization is believed limited to the areas of deformed surface irregularities and therefore insignificant. In the case of high pressures the deformation comprises entire particles, and the recrystallization during sintering is widespread. Because he observed the "recrystallization" temperature (the temperature at which effective annealing after cold-working of the sintered compact was indicated) to be below the "sintering" temperature (the temperature at which marked increases in strength and hardness were found), Sauerwald maintains that the sintering mechanism is *not* affected by recrystallization caused by recovery from cold work, it being completed at a lower temperature. Only in the case of very high pressures does he agree that recrystallization caused by recovery from cold work becomes a predominant factor that can precipitate spontaneous grain growth. From his diversified studies Sauerwald concludes that except for very high pressures the consolidation of a powder compact during sintering is due to adhesion and not to recrystallization. The clear distinction between these two phenomena is based on the observation that the "sintering" temperatures are higher than the recrystallization temperatures, though lower than the temperatures at which spontaneous grain growth occurs. The adhesion between particles is increased with rising temperature by increasing the atomic mobility and the amplitude of the atomic vibrations, and also by a flattening and smoothening of surface irregularities through plastic deformation. In his most recent paper[16] the sintering concept is extended by the inclusion—next to adsorptive adhesion and atomic migration—of grain growth in sintering without a liquid phase and solubility equilibria in sintering with a liquid phase.

Sauerwald's theoretical explanations, and particularly the concepts referring to the grain growth temperature, have been seriously criticized from various quarters. Smithells, Pitkin, and Avery,[17] initiated the criticism by publishing the results of sintering experiments with tungsten. From measurements of dimensional changes and electrical properties it was observed that grain growth commenced at 1227°C. (2240°F.) in compacts pressed at 8 tsi and at 927°C. (1700°F.) in compacts pressed at 32 tsi—as contrasted with Sauerwald's stipulated grain growth temperature of 2500–2700°C. (4530–4900°F.) (three-fourths of the absolute melting temperature of tungsten)—independent of the compacting pres-

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[17] C. J. Smithells, W. R. Pitkin, and J. W. Avery, *J. Inst. Metals*, *38*, 85 (1927).

sure. Sauerwald's reaction, that photomicrographic evidence as presented by Smithells, Pitkin, and Avery is inconclusive and suggests the possible influence of factors other than a change in pressure, has remained unchallenged, leaving the controversy undecided. But the general conclusions concerning grain growth in sintered metals have also been seriously criticized by others, notably Trzebiatowski (see below) and Bal'shin (p. 803), who emphasize the importance of recrystallization.

THEORY BY TRZEBIATOWSKI

In an impressive study of the sintering of fine copper and gold powders at various compacting and heating conditions, Trzebiatowski[18-21] has definitely established that recrystallization takes place during the initial stages of sintering. With the aid of x-ray diffraction, density, hardness, and electrical conductivity measurements, signs of work hardening and subsequent recovery and recrystallization could be observed at temperatures that would indicate no changes in the microstructure. In hot-pressed compacts, very strong work-hardening effects accentuated by the ultrafine particle size of the powders resulted in hardness values considerably in excess of those generally observed with severely cold-deformed fused metals.

The decreases in density observed by Sauerwald during sintering of highly pressed compacts are confirmed by Trzebiatowski and are explained by the evolution of gases that have been occluded during compaction. While entrapped or dissolved gases can escape readily at low sintering temperatures in loosely compacted powders, the gases tend to expand in the densely compacted powders and the agglomerated structure is disrupted, causing an increase in volume and sometimes the formation of blisters.

Trzebiatowski's observation of work-hardening and recrystallization effects on material produced at extremely high pressures (up to 200 tsi) has been corroborated essentially by other investigators who, however, worked with lower pressures. The observations made by Schlecht, Schubardt, and Duftschmid,[22] Grube and Schlecht,[23] Kikuchi,[24] and Dawihl[25]

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[18] W. Trzebiatowski, *Naturwiss.*, *10*, 205 (1933).

[19] W. Trzebiatowski, *Z. phys. Chem.*, *A169*, 91 (1934).

[20] W. Trzebiatowski, *Z. phys. Chem.*, *B24*, 75 (1934).

[21] W. Trzebiatowski, *Z. phys. Chem.*, *B24*, 87 (1934).

[22] L. Schlecht, W. Schubardt, and F. Duftschmid, *Z. Elektrochem.*, *37*, 485 (1931).

[23] G. Grube and L. Schlecht, *Z. Elektrochem.*, *44*, 367 (1938).

[24] R. Kikuchi, *Tôhoku Imp. Univ. Science Repts.*, Ser. I, *26*, No. 1, 125 (1937) (in English).

[25] W. Dawihl, *Stahl u. Eisen*, *61*, 907 (1941).

all prove that work hardening during compaction and subsequent recrystallization must be taken into account not only when high compacting pressures are involved, but also when working within pressure ranges that are common in practical powder metallurgy processes.

THEORIES BY BAL'SHIN

The mechanism of bonding and sintering has been studied intensively by Bal'shin, who has advanced a number of new concepts in his five highly theoretical publications.[26-30] When concerned with a theory of powder compaction, Bal'shin develops a mathematical expression for the relationship between pressure and volume of the compressed powder compact[29] which is based on an analogy with the elastic deformation of a metal body subjected to a compressive load. Accordingly, the height and volume of a compact decreases in arithmetic progression if the pressure increases geometrically. In a series of excellently conceived experiments, Bal'shin has attempted to prove his theory, but his experimental results showed significant deviations from the theoretical relationship. These deviations have been attributed mainly to the initial properties of the powder and the change of these properties during the pressing operation. Bal'shin's work is characterized by the emphasis placed on the variables encountered in metal powders, and in his experiments he is not satisfied with investigating only one type of powder for each metal.[27-29]

In Bal'shin's theory three reasons are advanced for energy expenditure during compaction: (*1*) for overcoming the adhesion between the powder particles; (*2*) for deformation and fragmentation of the particles; and (*3*) for overcoming elastic and residual stresses. The first is of particular interest, since it implies that compaction must occur *against* the action of the adhesive forces that unite the particles, a concept contradictory to Sauerwald's viewpoint. There appears to be justification in such an assumption as long as the pressure is still very small at the beginning of compaction, since changes in the relative positions of the particles must be extensive and initial adhesive bonds are likely to be disrupted. With progressive compaction, however, particle dislocations and disruptions of adhesive bonds will lose their significance, and, instead, the adhesive bonding forces will become the predominant factors. Bal'shin neglects to consider the energy *liberated* by the formation of the new, final adhesive bonds. Thus, his theoretical concept appears incomplete

[26] M. Yu. Bal'shin, *Vestnik Metalloprom.*, *16*, No. 17, 87 (1936).
[27] M. Yu. Bal'shin, *Vestnik Metalloprom.*, *16*, No. 18, 82 (1936).
[28] M. Yu. Bal'shin, *Vestnik Metalloprom.*, *16*, No. 18, 91 (1936).
[29] M. Yu. Bal'shin, *Vestnik Metalloprom.*, *18*, No. 2, 124 (1938).
[30] M. Yu. Bal'shin, *Vestnik Metalloprom.*, *18*, No. 4, 89 (1938).

and the mathematical approach of doubtful value. The experimental data produced in conjunction with the theoretical formulations, however, are of great significance in the study of the principles underlying the compacting and bonding process.

In his theoretical discussion of the sintering process,[26,30] Bal'shin's concepts are not so controversial and are generally well conceived and supported by experimental data. In contrast to Sauerwald's theory, Bal'shin maintains that the absence of intergranular (impurity) films in sintered metal structures is bound to *lower* the temperature of incipient grain growth. The relative weakness of the adhesive forces between the particles and the presence of interstices within and between these particles represent a typical condition inherent in the sintered powder compact as contrasted to a fused metal. The strong boundary bonds between the grains of fused metals and the comparative continuity of the metal structure restrict structural changes to the growth of one grain at the expense of another. In sintered powder compacts the much weaker boundary bonds are more easily disrupted and particles can grow into the pore volume without affecting the adjacent particles. As a consequence, recrystallization of sintered metal structures is not only signified by grain growth in the conventional sense, but also by phenomena such as change in particle shape without growth and displacement of boundaries or interstices.

Bal'shin distinguishes three independent processes that take place during sintering:[26] (*1*) a change in the relative position of the powder particles; (*2*) an individual, internal change of the powder particles within the respective particle boundaries which may be connected with a change in shape of the particles; and (*3*) a collective, external change of the powder particles that exceeds the boundaries of the individual particles and involves a change in particle size.

As principal factors influencing the sintering process, Bal'shin enumerates: plastic deformation of the powder particles ("secondary particles"); transformation of the internal structure of the particles from aggregates of crystallites ("primary particles") to single crystal particles by internal grain growth; atomic migration at the particle surface boundaries; external grain growth encompassing a number of neighboring particles; release of residual stresses by recoil ("elastic afterworking") of highly compressed crystallites.

Bal'shin also attempts to classify the sintering processes into those which promote shrinkage (and which are predominant under normal processing conditions) and those which promote swelling, but comes to the conclusion that in almost all instances the processes can act in both directions.[26] While it is believed that adhesive forces will always act favorably in the direction of shrinkage, recrystallization can cause either shrinkage or expansion, depending on the location of the centers of recrystallization. When these centers are located at points of mutual contact between the particles, the effect will involve more than one particle and will usually result in grain growth and shrinkage (increase in density of the compact). On the other hand, when the centers of recrystallization are located irregularly and away from the points of contact, intraparticle recrystallization will occur, which has a tendency to produce equiaxial particle shapes, and thereby leads to swelling (decrease in density of the compact). The effect of internal stresses may also be in either direction. If the elastic stresses are opposed to the direction of compression the particles will tend to move apart, causing expansion of the over-all dimensions of the compact; if the stresses act in the same direction as the forces of compression, they favor closer contact among the particles and work in the direction of shrinkage. A similar double effect on size change of the compact during sintering is believed to be caused by temperature fluctuations. Shrinkage may result from a reduction of the size of the contact interstices because of mutual attraction, and growth from an enlargement of these interstices because of mutual repulsion. Solid or gaseous impurities in the particle interfaces will generally tend to obstruct the closest contact between the particles and cause expansion; in the case of oxide films, however, sintering in a reducing atmosphere may produce fresh metal surfaces that will tend to draw the adjacent contact surfaces together and cause shrinkage.

Perhaps of greatest interest in Bal'shin's theory of sintering is his concept that the sintering phenomena are the results of the counteraction of *groups* of forces rather than of individual forces. Corroborated by experimental data, the increase in dimensions of coarse powders during sintering serves as a typical example. Because of the comparatively small effective surface, the growth of compacts during sintering cannot, in the case of very coarse powders, be attributed to the evolution of adsorbed or occluded gases. Instead, Bal'shin explains the phenomenon with local stress concentrations caused by work hardening at the contact points between neighboring particles which result in an irregular location of the centers of recrystallization. In the case of fine powders the selective work hardening during compaction followed by a selective recrystallization during sintering results chiefly in flattening of the surface irregularities and, therefore, shrinkage; in the case of large powder particles with small specific surface areas, intraparticle recrystallization becomes predominant. As mentioned before, the latter will tend to produce equiaxial particles and cause growth as a cumulative effect of the changes in shape and size. Thus, particle size is advanced as a criterion for the change in size and properties of the sintered compact.

In a belated publication on the relation of shrinkage and physical properties of single-phase and multi-phase powder compacts (*e.g.*, iron, iron–copper, etc.) to their density (porosity), Bal'shin[30a] has essentially confirmed his earlier findings and theoretical postulations (see also page 818).

Recently, Bal'shin has summarized his theoretical work in book form[30b]; in it, he has brought up to date his discussions of the physicochemical processes associated with powder mixing and cementing, pressing, and sintering.

THEORIES BY JONES

A detailed analysis of the processes occurring during pressing and sintering is given by Jones,[31] who also discusses in great detail the earlier theories by Sauerwald and Trzebiatowski. Jones' theory is based essentially on experimental evidence of adhesion between surfaces of massive metal bodies; this concept is favored over the one that explains the connection of the particles during pressing and sintering by a pressure welding effect at the contact points. The adhesion between smooth surfaces can be observed readily at low temperatures on massive metals and also on glass, provided the contact-forming surfaces are free from contaminants. Oxide films (as well as grease films and other foreign matter), so predominant in fine metal powders, tend to interfere with the formation of contact areas. If only slight oxide films are present they can be punctured, spheroidized or partly eliminated by mechanical motion of the particles relative to each other. A rise in temperature and thus an improved plastic deformability enlarges the contact areas and thereby the cohesion of the compact.

Jones summarizes the following four factors as mainly influencing the mechanism of metal powder compaction. (*1*) The forces effective for the welding of the contact points between the particles are chiefly determined by the plasticity of the metal, and therefore influenced by both temperature and time. (*2*) Applied pressure accentuates the effect of plasticity. (*3*) The contact areas are diminished by oxide films and the adhesion is lessened by the presence of certain gases and vapors. (*4*) Relative motion of the adjacent particle surfaces increases the contact areas through removal of interfering oxide layers. The sum of the contact areas between the particles is considered a measure for the effectiveness of the compaction and sintering processes. It is related to the pores

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[30a] M. Yu. Bal'shin, *Zhurn. Teknicheskoi Fiz.*, *18*, No. 9, 1179 (1948).

[30b] M. Yu. Bal'shin, *Theoretical Powder Metallurgy.* Metallurgizdat, Moscow, 1948.

[31] W. D. Jones, *Principles of Powder Metallurgy.* Arnold, London, 1937.

and interstices between the particles and gives special significance to size and shape of the particles.

Jones, perhaps somewhat arbitrarily, distinguishes certain major processes that are the *causes* for the transition from the loose powder (characterized by its large pore volume) to a densely compacted body from other processes that are the *effects* of the externally applied pressure. Among the former are: (*1*) a breakdown of the cavities created by arching of the particles; (*2*) a realignment of the particles through slipping and torsional movements; and (*3*) a filling with small particles of the cavities formed by the larger particles.

On the other hand, processes such as the movement of particles into cavities, the deformation of particles so that they fit more closely together, and the flattening of microscopic and submicroscopic surface projections, are considered by Jones to be microscale effects of the external pressure. The factors contributing to these effects are given as deformation and work hardening of the particles, internal or elastic stresses, abrasion of the particle surfaces, surface films, slip prevention due to very fine grain size or to surface films, and special lattice properties of such fine particles. The behavior of the powder under external pressure is closely related to the nature of the powder, to the size and shape of the particles, to the presence of gases in the powder, to the form and size of the die, and to the relationship of the latter to the size and shape of the particles. The finer or the more brittle the powder, the more difficult becomes the translation of the pressure effects throughout the interior of the compact. This phenomenon (undesirable in practice), according to Jones, is overcome by expedients such as limitation of size of the compact, sintering in successive thin layers, use of multiple molding dies, use of hydrostatic pressure, and use of lubricants.

Special attention is paid by Jones to the effects that gases and vapors contained in the initial powders have on the performance of the compact during pressing and sintering. The distinction is made between *volume* effects (*i.e.*, on porosity and density and the properties influenced thereby), *physical* effects (*i.e.*, of sorbed gases and vapors on the development of the adhesion forces), and *chemical* effects (*i.e.*, reactions between the metal surfaces and gaseous or oxide films). Jones concludes that gases in general are usually quite harmful to the pressing and sintering processes, but their existence must be taken into account in all powders that are not produced in vacuum. However, the effects of the gases can be minimized by a number of expedients, such as wide clearance between the molding tools, elimination of gas-producing solid contaminants (*e.g.*, oxides and carbon), sintering in vacuum, absorption of gases by solid addition agents (*e.g.*, aluminum powder and other deoxidizers), short sintering cycles preventing evolution of the major portion of the gas, an compression of gases under high pressure. Gases that are dissolved in th metal under the action of the high pressure and that remain dissolve throughout the sintering cycle are not usually harmful, except when the affect adversely the ductility of the metal (tantalum and titanium).

In his analysis of the sintering process, Jones correctly repudiate earlier contentions that sintering is dependent on the presence of a liqui phase[32] or an allotropic change,[33] although there is little doubt that bot will have definite influence on the sintering mechanism. Rather, he make the distinction between the forces that cause sintering and the condition which facilitate or obstruct their range of action, *i.e.*, which conditio their effectiveness. The actual forces that effect sintering are the norma cohesive forces within the metal which determine its theoretical strength These forces are known to *diminish* with increasing temperature, wherea the sinter bond itself and the strength of the aggregate *increase* wit temperature. In other words, with rising temperature the effectivenes of the sintering forces becomes greater despite the decrease in the orde of magnitude of the forces, which can only be explained by a decreas of the obstructions in the way of sintering at a still more rapid rate. Th principal obstructive effects include: (*1*) incomplete contact betwee surfaces; (*2*) reduced contact due to action of surface films; (*3*) reduction in sintering forces by chemical action of gases; and (*4*) insufficien plasticity of particles.

The plasticity factor is given particular attention by Jones, and i is held that one of the most important causes for the progress of sintering can be found in the increase of plasticity with rising temperature This becomes apparent when a comparison is made between the sintering of oxides and metals. While oxides become plastic and sinter to hig density only at temperatures very near the melting point, a much large temperature range usually exists when metals are very plastic and ca sinter effectively. However, this concept does not entirely preclude th possibility that in principle strong and dense metal compacts can als be produced without plastic properties. In this case the particle siz distribution of the powder must be such that after compaction a maximum of free surfaces in the powder agglomerate lie in the field of th effective surface forces of neighboring particles. With rising temperatur the amplitude of vibration of the surface atoms increases to an exten that an approach to the vibrating atoms of the adjacent free surfaces becomes possible, resulting in the promotion of sintering. However, there is no reason for disagreement with Jones' concept that the in-

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[32] K. Endell, *Metall u. Erz, 18,* 169 (1921).

[33] R. C. Smith, *J. Chem. Soc.* (London), *123,* 2088 (1923).

crease of plasticity with increasing temperature can be considered to be mainly responsible for the favorable temperature effect during sintering.

THEORY BY BALKE

According to Balke[34] the sintering mechanism is based on the action of surface tension forces that smoothen the deep crevices formed during compaction of the powder. Proceeding in a circular way from the points of contact, the surface tension forces enlarge the contact areas during sintering in a zipperlike fashion and constitute the basis for shrinkage of the entire powder mass. While the compacting process can rupture the interfering solid or gaseous surface films, fragments of these impurities remain in the surface regions and may in turn be trapped during sintering by the closing of the metal "zippers." Balke, in agreement with Jones, holds that the main function of an increased sintering temperature is to increase the plasticity of the metal. Only if this property is of significant magnitude can the surface tension forces become sufficiently effective within practically feasible periods of time.

THEORY BY DAWIHL

Dawihl[35] has given close attention to the sintering forces and the shrinkage effects that characterize the sintering process. In dealing with the first, his concept follows essentially that advanced by Jones (p. 808); otherwise, his and his coworker's[36] hypotheses follow those postulated by Sauerwald (p. 798 ff.). The forces that promote strength and shrinkage during sintering are free, molecular forces at the surfaces of the powder particles which are unsaturated toward the outside; they are fundamentally the same forces that control the strength of fused metals. Since the strength of all substances diminishes with rising temperature, the same must be true for the forces effecting sintering. If, regardless, experience has shown that metal powder compacts increase in strength with rising temperatures, it must be concluded that at low temperatures obstacles (*e.g.*, gas or oxide films) are in the way of sintering, which are only removed at higher temperatures by the increased mobility of the atoms.

In his theoretical discussion of the shrinkage process, Dawihl takes a view opposite to that of Bal'shin (p. 804) in attributing it mainly to changes in shape of the particles, *i.e.*, a transformation of irregular surfaces into more equiaxed crystal surfaces, a factor which Bal'shin believes

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[34] C. C. Balke, *Iron Age, 147,* No. 16, 23 (1941).

[35] W. Dawihl, *Stahl u. Eisen, 61,* 907 (1941).

[36] W. Dawihl and W. Rix, *Z. Metallkunde, 36,* No. 8, 197 (1944); *Proc. International Powder Metallurgy Conference,* Graz, July 12–17, 1948, **Referate No. 2.**

to be one of the chief causes for expansion. Dawihl's concept of shrinkage is based solely on the increased atomic mobility caused by increased temperatures. He draws attention to the following processes.

(*1*) When a sufficiently high temperature level is reached the mobility of the atoms becomes of an order that permits purely mechanical slipping of the particles into densest packing.

(*2*) The surfaces of the particles which, depending on the history of the powder, are of different degree of irregularity, undergo change of form at higher temperatures. Recrystallization within the individual particle produces more regular crystal faces and thus a reduction in the external space demand of the particle. As a consequence of the latter, slippage of the particles into a closer packing becomes possible. (As an example of this process the spheroidizing of iron oxide particles[37] is mentioned.) The temperature of incipient particle form change probably coincides closely with that of recovery after work hardening and initial shrinkage.

(*3*) After certain temperatures are exceeded, the recrystallization and particle form change phenomena encompass a group of adjacent particles and result in grain growth. The tendency toward smoothing the irregular surfaces of the particles causes further reduction of the external space required, thus leading to further shrinkage.

(*4*) Allotropic changes in the crystal structure and chemical reactions also work in favor of shrinkage, since they produce particularly increased mobility of the atom.

Dawihl assumes that the possibility of a particle form change depends largely upon a state of instability inside as well as at the surface of the particle. Inasmuch as this state of instability is dependent on the method of production and treatment of the powder, the shrinkage process during sintering at a given cycle, and consequently the density and physical properties of the sintered compact, are primarily controlled by the nature of the powder.

THEORIES BY HÜTTIG

One of the most intensive studies of the sintering processes has been recently conducted by Hüttig and his coworkers.[38–46] In an impressive

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[37] J. A. Hedvall, *Z. Elektrochem.*, *37*, 482 (1931).

[38] G. F. Hüttig, *Kolloid Z.*, *97*, 227, 281 (1941); *98*, 6, 263 (1942); *104*, 161, 189 (1943).

[39] G. F. Hüttig, C. Bittner, R. Fehser, H. Hannawald, W. Heinz, W. Hennig, E. Herrmann, O. Hnevkovsky, and J. Pecher, *Z. anorg. allgem. Chem.*, *247*, 221 (1941).

[39a] G. F. Hüttig, *Z. anorg. allgem. Chem.*, *249*, 134 (1942).

[40] G. F. Hüttig and K. Arnestad, *Z. anorg. allgem. Chem.*, *250*, 1 (1942).

[41] G. F. Hüttig and H. H. Bludau, *Z. anorg. allgem. Chem.*, *250*, 36 (1942).

[42] G. F. Hüttig and W. Hennig, *Z. anorg. allgem. Chem.*, *251*, 260 (1943).

[43] G. F. Hüttig and T. Freitag, *Z. anorg. allgem. Chem.*, *252*, 95 (1943).

[44] W. D. Jones, *Metal Treatment*, *13*, 265 (1946).

[45] G. F. Hüttig and H. Rainer, *Powder Met. Bull.*, *3*, No. 3, 48 (1948).

[46] G. F. Hüttig, *Proc. International Powder Metallurgy Conference*, Graz, July

series of experiments, the temperature effects were observed on the changes of properties such as: (*a*) adsorption capacity for methanol vapor; (*b*) adsorption capacity for dyes; (*c*) chemical reactivities; (*d*) catalytic activities; (*e*) solubilities; (*f*) electromotive forces; (*g*) electrical conductivities; (*h*) apparent densities; (*i*) pycnometric densities; (*j*) x-ray diffraction patterns; (*k*) microstructure; and (*l*) mechanical properties.

In comparing these properties for different metals, Hüttig makes use of Tammann's temperature factor α, the ratio between the particular temperature and the melting point temperature, expressed in absolute values. In the main the results support the concept that with rising temperature a periodic change of the properties takes place in conjunction with the decrease of the specific surface area of the compacted powder. Different ranges of α appear to correspond to certain elementary processes at the surface and in the interior of the powder particles; these are of significance for the progress of the sintering mechanism as well as the properties of the resulting compacts that have been heated to the particular temperature indicated by the α range. The individual temperature zones are characterized briefly as follows.

1. First temperature range $\alpha = 0$ *to* 0.23. Period of adhesion at lowest temperatures, determined merely by adherence of the particles to each other. As a consequence, an increasing "coverage" is effected with rising temperature through closest alignment of the surfaces of neighboring particles which causes a reduction in surface area available for such processes as adsorption. No noticeable shrinkage occurs.

2. Second temperature range $\alpha = 0.23$ *to* 0.36. Period of surface diffusion, resulting in activation of the surfaces of the particles through rearrangements on a molecular scale, loosening or evolution of superficially sorbed gases, and increase of the adsorptive capacity. The surface mobility causes the metal atoms to move into the most narrow crevices between the particles thereby producing linkages, consolidation, and shrinkage.

3. Third temperature range $\alpha = 0.33$ *to* 0.45. Period of grain boundary displacements by growth of one crystallite at the expense of others, in which the growing one is not necessarily the larger crystallite at the beginning of the process. Stabilization and deactivation of the surfaces takes place due to ending of rearrangements of surface molecules. A strong decline of adsorptive capacity is observed.

4. Fourth temperature range $\alpha = 0.37$ *to* 0.53. Period of lattice diffusion, resulting in atomic movements throughout the entire cross section of the crystallites. As a consequence of the activations in the interior of the crystallites, gaseous substances contained in the lattice are expelled. These processes have little effect on the adsorptive capacity, but produce strong bonding tendencies between neighboring particles.

5. Fifth temperature range $\alpha = 0.48$ *to* 0.8. Period of formation of new crystallization centers, resulting in complete recrystallization at high temperatures. Grain growth causes a reduction in surfaces, and continued lattice diffusion causes a deactivation. As a consequence the adsorptive capacity decreases further.

6. Sixth temperature range $\alpha = 0.8$ *to 1.* Period of excessive grain growth. Possibly new activations occur in preparation of fusion processes.

This classification of the different temperature zones is the basis for Hüttig's two "elementary" processes: (*1*) changes which a single crystallite suffers during the period of gradually increasing temperature; and (*2*) processes that lead to a coalescence into a single crystal of (primary) crystallites in contact with each other, whose causes are (*a*) adhesive forces, (*b*) surface diffusion, (*c*) lattice diffusion, and (*d*) recrystallization processes. Hüttig's concept that the single crystal represents a thermodynamically stable end-product of the sintering process, can only be suscribed to with reservations, however, in view of the strong experimental evidence that for any particular temperature a final state of equilibrium exists that involves a definite polycrystalline size distribution.

Essentially in agreement with the earlier investigations on copper powder surface phenomena is a work phase concerned with the magnetic properties of iron powders as affected by changes in the surface conditions of the particles.[45] (The reader interested in Hüttig's work is referred to this paper because of the valuable description of the procedure employed, and an extensive bibliography appended.)

Most recently, Hüttig[46] has given a comprehensive account of his theoretical investigations, toward a fundamental theory of the sintering processes in metallic powders. The survey covers a study of the behavior of a single crystal during the course of a rise in temperature, of the behavior of two or more contacting crystals of the same substance with increasing temperature, and of the sintering of mixed powders.

The first takes into consideration such phenomena as thermal vibrations and self-diffusion, both in the interior and at the surface of the crystal; it leads to fusion phenomena, and indicates the possibility that surface fusion may take place even at a temperature level of $\alpha = 0.7$. Deviations from the ideal case may be encountered because of such anomalies as allotropic changes, thermodynamic irreversible disturbances of the crystal lattice, presence of foreign matter such as sorbed gases or oxide layers, and disturbances of the homogeneity of larger crystals by mosaic structures.

The second analyzes the thermodynamic and kinetic principles that are the basis for the sintering of a number of crystals or particles of the same metal. The polycrystalline aggregate has the tendency to pass from the state of thermodynamic nonequilibrium to that of equilibrium as represented by a single crystal, and such elementary processes as adhesion and self-diffusion at the crystal surfaces and in the crystal interior are subordinated to this tendency. The division of the sintering process at different temperature stages as derived from extensive experimental work with sorptive reagents is again emphasized.

The third deals with powder mixtures that either do or do not form chemical compounds. Both cases have the first three stages in common: reduction of the accessible surface; activation through hybrid molecules and molecular films formed by atomic migration of the more mobile component; and deactivation of the molecules and molecular films. The process continues only if a chemical compound is formed, and three further stages can be distinguished: a renewed activation caused by internal diffusion of the more mobile component into the less mobile; formation of semi-ordered crystal aggregates of the addition compound; and, finally, the perfection of the crystal structure of the compound.

Hüttig's theoretical and experimental work during the war has been summarized by Jones[44]; his postwar work was covered in a recent address given in this country.[46a] His comparison of the different key theories of sintering as they relate to atomic migration is given elsewhere (p. 831 ff.).

THEORIES BY HEDVALL

In conjunction with Hüttig's theoretical contributions, the reader's attention is drawn to the work of Hedvall,[47,47a] who has linked surface physics and surface chemistry with powder metallurgy processes. As with catalysts and adsorbents, the peculiar activity and mobility of surface materials are subject to controls. Structural changes in alloys coincide with maximum activity in some directions, and alloying and recrystallization may take place more readily in mechanical mixtures than in corresponding solid solutions. Catalytic activities change in nickel and iron powders at the Curie points, and in copper, brass, and steel powders when exposed to ultrasonic waves. Surface tension, recrystallization, rate of transformation, and reactivity are influenced by soluble gases, as shown by Hedvall's and Hüttig's work on SiO_2, Al_2O_3, and Fe_2O_3 in which nitrogen and oxygen were dissolved. (The facilitating of powder

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[46a] G. F. Hüttig and W. E. Kingston, communication on "The Fundamental Problems of Sintering Processes," *Symposium on the Physics of Powder Metallurgy,* sponsored by Sylvania Electric Products, Inc., Bayside, L. I., N. Y., August 24–26, 1949.

[47] J. A. Hedvall, *Proc. International Powder Metallurgy Conference,* Graz, July 12–17, 1948, Referate No. 48.

[47a] J. A. Hedvall, *Arch. Metallkunde, 1,* No. 7/8, 296 (1947).

reactions by lattice disturbances was also observed by Fricke[48] and Heuberger.[48a])

THEORY BY WRETBLAD AND WULFF

In describing the process of sintering, Wretblad and Wulff[49] analyze it as being fundamentally a mechanism of bonding by atomic forces, with particular emphasis placed on the role played by plastic deformation and recrystallization. In substantial agreement with the previous theories of Jones, Dawihl, and others, it is recognized that the atomic forces cause adhesive bonding even at room temperature, especially if plastic deformation has increased the areas of contact at which the attractive forces can act. When the powder compact is heated to temperatures at which recrystallization occurs, the atomic mobility is greatly increased, and in fact a movement of the atoms across grain boundaries may be effected. However, the latter requires that the thermal energy of the atoms together with the potential energy produced by the lattice distortions from previous cold working exceed a certain critical value. These recrystallization processes facilitate sintering, as indicated by an increase in density and strength, even if they are associated with grain growth. In contrast to Bal'shin's concept, growth of individual crystallites inside polycrystalline particles is given only minor significance, but full agreement is voiced with Bal'shin's and Trzebiatowski's criticism of Sauerwald's concepts regarding the temperature of spontaneous grain growth. Plasticity is held to be the principal temperature effect during the advanced stages of sintering, with its importance believed to surpass that of increased diffusion rates.

Special attention is paid by Wretblad and Wulff to the changes that the porosity undergoes during the sintering process and which, as can be generally observed, involve a transition from an extensive network of thin channels to spherical or near-spherical caverns of like volume. These changes in the pore characteristics are attributed to surface tension forces which cause either diffusion of the metal atoms along the surfaces of the pores or plastic flow of bulk metal into the sharpest angles and crevices, simultaneously filling the narrow chasms and enlarging the central regions until complete spheroidizing of the cavity has taken place.

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[48] R. Fricke, *Proc. International Powder Metallurgy Conference,* Graz, July 12–17, 1948, Referate No. 3.

[48a] J. Heuberger, *Festskrift tillägnad J. Arvid Hedvall,* Göteborg, 1948, p. 241. See also R. A. Hetzig, *Metallurgia, 38,* 169–171 (1948).

[49] P. E. Wretblad and J. Wulff, in J. Wulff, *Powder Metallurgy.* Am. Soc. Metals, Cleveland, 1942, p. 36.

Rhines[50] takes issue with this concept to the extent that a mechanism of simply transferring metal from one part of a pore to another until the cavity is spheroidized fails to explain the shrinkage of pores as evidenced by numerous investigations. Of the two possibilities of the metal to diffuse or flow bodily inward to fill up the pore, Rhines holds that it is difficult to visualize plastic flow under the prevailing conditions and diffusion is the more likely mechanism. Taking as a basis the lately advanced vacancy migration theory[51] which supposes that diffusion of the atoms progresses by way of occupying vacancies in the crystal lattice (which in turn drift about in the metal), Rhines advances the thought that the "holes" themselves diffuse in a preferred direction, from the porosity to the external surface of the metal, resulting in the movement of the metal atoms inward. Thus submicroscopic voids might form at the surfaces of the pores where the surface tension is highest and dissipate at the surface of the compact where the surface tension forces are low. This mechanism would also explain why during progressive sintering very small pores with their greater surface tension forces (on account of the sharper curvature of their surfaces) would shrink and disappear faster than large pores that remain or even grow in size.

The significance of the type of pore structure, incidentally, has also been discussed by Shaler,[52] who maintains that in solid metals such as copper the rate of sintering is not so much dependent on particle size and size distribution as on the size and distribution of the voids between the particles.

THEORY BY FRENKEL

The theory advanced by Frenkel[53] is essentially a mathematically founded discourse on the theme previously advocated by Balke,[54] which holds that the sintering of metal particles is caused by the action of surface tension forces. Frenkel shows that, under the influence of these "inner" forces, crystalline (metallic) bodies can display a viscous flow similar to that of amorphous bodies and that it is possible to explain in this way the phenomena of the "cold welding" (sintering) of crystalline powders as well as the formation of crystalline faces on an originally spherical crystalline body, as recently observed by Lukirsky.[55] The viscous type of flow of an amorphous or crystalline substance is due chiefly to diffusion of individual cavities of an atomic order of magnitude,

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[50] F. N. Rhines, *Powder Met. Bull., 3,* No. 2, 28 (1948).
[51] H. B. Huntington and F. Seitz, *Phys. Revs., 61,* 315 (1942).
[52] A. J. Shaler, *Trans. Am. Inst. Mining Met. Engrs., 185,* 796 (1949).
[53] J. Frenkel, *J. Phys. U.S.S.R., 9,* 385 (1945) (in English).
[54] C. C. Balke, *Iron Age, 147,* No. 16, 23 (1941).
[55] P. Lukirsky, *Compt. rend. acad. sci. U.R.S.S., 46,* 300 (1945).

in contrast to the ordinary plastic flow that is a specific property of crystals and is due to some kind of orderly slipping of entire atomic layers in certain crystallographically fixed directions. In the process of sintering of crystalline (metal) powders at high temperatures below the fusion point into a crystalline body the cavities which formed a multiconnected space initially are finally separated from each other by a compact crystalline substance and gradually decrease in size until they are fully closed. Since the powder particles and their crystallites have different and generally uncontrollable shapes, the rate of their sintering together cannot be calculated exactly, but Frenkel distinguishes two separate stages of the processes. During the first stage the contact surface between adjacent particles is increased until the pores become disconnected; during the second stage these residual pores are gradually closed. However, the latter process can be arrested by gases leaving the solid matter and accumulating in the cavities, if the pressure of the gas—which, if of constant quantity, increases with a decrease of the radius of the cavity—becomes equal to the capillary pressure.

In a second paper, Frenkel[56] published a discourse on the natural roughness of crystalline faces and the motion of individual surface atoms. In it the concept of a crystalline face as an ideally even plane with an orientation corresponding to a small value of the surface tension is shown to be incorrect, and processes involving variations of the size and shape of crystals are interpreted on the basis of a mechanism of motion of individual surface atoms. Frenkel found that neighboring faces—presumably (according to the principles of statistical mechanics) initiated as the result of thermal fluctuations—which are inclined with respect to the basic face have only a slightly higher surface tension. These neighboring faces can be treated as "terraces" formed on the basis of the main face, and the latter thus acquires a natural roughness which increases with temperature. The boundaries of these terraces are not stationary, but advance and retreat because of the motion of individual atoms. The moving atoms can be considered as an adsorbed "two-dimensional" gas phase on the surface of the terraces and as a "one-dimensional" gas phase along the boundaries. A variation of the size and shape of the crystals is attributed by Frenkel to the gradual transition of atoms from the *condensed* two-dimensional phase (corresponding to an individual terrace) through the linearly adsorbed phase into the two-dimensional *gas* phase, and *vice versa*. The theory represents a generalization of the concept (by Kossel) that evaporation and dissolution are caused by successive removal of the atoms forming the end step of a horizontal edge of a terrace, and accounts not only for changes in volume but also for

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[56] J. Frenkel, *J. Phys. U.S.S.R.*, *9*, 392 (1945) (in English).

variations in shape. The kinetics of the process can be treated mathematically by considering the advance and retreat movements of the terraces to be analogous to a Brownian movement. Frenkel suggests as an application for his theory the formation of crystal faces on initially spherical single-crystalline particles or bodies.

A third paper by Frenkel[56a] deals with a theory of electric contacts between metallic bodies which quantitatively accounts for the dependence of the conductivity on the field strength (Poole's law and Schottky effect); it also accounts for the observation that fine metallic powders and thin films show an increase of conductivity with temperature according to a law analogous to that controlling the conductivity of semiconductors. In the theory an electric contact between two metals is treated as a gap through which electrons pass by the mechanism of thermoelectric emission. Image forces, acting on the electrons, lower the potential barrier, and thus increase the thermoelectric emission by an amount inversely proportional to the width of the gap.

Shaler and Wulff[57,57a] have recently extended Frenkel's calculations of the coefficient of viscosity and the rate of contraction of single pores by including the presence of foreign gases inside the pores and outside the aggregate of crystals (p. 823). The results were checked experimentally by sintering regularly packed, uniform spherical copper particles both in argon at 1 atmosphere and in vacuum. While it was found that the rate of shrinkage agreed qualitatively with the mathematical results, the viscosity coefficient based on the surface tension value for copper (1200 dyne/cm.) was higher than it should be according to the established value for the heat of activation of self-diffusion of copper (57,000–61,000 cal.). The answer to the question of whether this discrepancy lies in an inaccurate value of the surface tension or of the self-diffusion constant for copper, or in a basic error in Frenkel's theory of viscous flow, will have to await supplementary experiments with other metals.

THEORY BY PINES

The theory developed recently by Pines[58,58a] in Russia is analogous to some of the ideas expressed by Rhines in this country[59] (see p. 822) and is based on a conception of sintering as a process of diffusion of

[56a] J. Frenkel, *J. Phys. U.S.S.R.*, *9*, 489 (1945) (in English).

[57] A. J. Shaler and J. Wulff, *Phys. Revs.*, *72*, 79 (1947).

[57a] A. J. Shaler and J. Wulff, *Ind. Eng. Chem.*, *Anal. Ed.*, *40*, 838 (1948).

[58] B. Ya. Pines, *Ukrain. Phys. Tech. Inst. and State Univ. Sci. Publ.*, Jan. 15, 1946 (translated into English by G. C. Kuczynski, Sylvania Electric Products Co., Bayside, L. I.).

[58a] B. Ya. Pines, *Zhurnal Teknicheskoi Fiziki*, *16*, 737 (1946).

[59] F. N. Rhines, *Powder Met. Bull.*, *3*, No. 2, 28 (1948).

molecular voids through solid structures (vacancy migration process[60]). In contrast to the mechanism envisioned by Frenkel (page 816), which presents the voids as being filled by slow viscous creep of the crystal, that of Pines visualizes sintering as filling of the voids atom by atom—thereby *quasi* moving the voids out from the body. With the aid of a mathematical explanation, Pines shows that in the initial stages of the sintering process metal atoms activated during heating would transfer from the particles to near points or areas of interparticle contact until a state of "saturation" between particles and voids is reached. Thereafter, sintering proper would commence—with the voids diffusing through the body toward the outer surface of the compact. The rate of shrinkage would depend upon the difference in concentration between the local and average voids in the structure. Three stages of sintering may be distinguished—uniform, nonuniform, and sharply nonuniform—which are functions of the temperature and could therefore transmute one into the other.

The mechanism of sintering as conceived by Pines leaves no room for the action of other fundamental processes in closing or displacing the voids. The statement that surface diffusion and the process of evaporation from one place and condensation at another (page 816) cannot change the density of a compact has been corroborated by Ivensen,[60a] and has found further support by Shaler and Wulff.[57a]

THEORY BY IVENSEN

Ivensen[60a] established on the basis of experimental evidence that, in the sintering of different single-phase metal or compound powders of widely varying apparent and compact (green) densities, a constant relative decrease in pore volume accompanies the increase in density. Tests with different grades of copper, nickel, iron, cobalt, tungsten carbide, and titanium carbide powders were used for the computation of a coefficient of relative decrease in pore volume. This coefficient expresses the ratio of pore volume before sintering to pore volume after sintering, and also includes a factor which represents the activity of the powder during sintering. Together with values for compact density and reguline density, the coefficient serves as a mathematical estimation of the density obtained during sintering. Bal'shin[60b] criticizes this analysis as limited in validity—it holds only for the special case of a linear correlation between shrinkage and density (porosity)—as compared with his own findings some ten years earlier, which established a more universally valid relationship between shrinkage and density (see also page 803 ff.). However, Jordan and

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[60] H. B. Huntington and F. Seitz, *Phys. Revs.*, *61*, 315 (1942).

[60a] V. A. Ivensen, *Zhurnal Tekhnicheskoi Fiziki*, *17*, No. 11, 1301 (1947).

[60b] M. Yu. Bal'shin, *Zhurnal Tekhnicheskoi Fiziki*, *18*, No. 10, 1332 (1948).

Duwez,[60c] working on the densification of copper powder compacts in hydrogen and vacuum, have established a correlation between density of the compacted and sintered specimens which is similar to the one presented by Ivensen. A densification parameter σ is defined as the difference of the density after sintering (ρ) and before sintering (ρ_0) divided by the difference of the density of the solid metal (ρ_∞) and the density before sintering (ρ_0).

THEORY BY NABARRO

The concept advanced by Nabarro[60d] postulates that the forces acting in the surfaces of a specimen alter the concentrations of lattice defects (Schottky or Frenkel defects) which would be present in thermodynamic equilibrium near these surfaces. The concentration gradient thus formed results in a diffusion of the defects through the lattice from one part of the surface to another. Thus, the process is analogous to the one described by Pines. Nabarro, however, demonstrates by means of a model consisting of three rows of atoms in a material under a shear stress that a homogeneous stress exerts no force on a vacant lattice site or interstitial ion. If a hole migrates in the intermediate row from one end to the other, a displacement of the intermediate row with respect to both the top and bottom rows will take place, but the top and bottom rows will remain fixed in their positions relative to each other. The assumption that this mechanism of vacancy migration results in a shear of the top row with respect to the bottom row, advanced by Kauzmann,[60e] and used by Frenkel[53] as one of the chief suppositions for his "viscous flow" theory, is therefore held erroneous. For perfect crystals, Nabarro's concept leads to a rate of strain which, for a given stress, depends on the size of the crystal. As to the motion of holes in crystals containing dislocations, Nabarro shows that edge-type dislocation lines can move in a direction perpendicular to the glide plane by diffusion of holes or interstitial ions. There exists also the possibility that holes disappear entirely in a perfect crystal, leaving an imperfection of a lower energy.

[60c] C. B. Jordan and P. Duwez, *Trans. Am. Inst. Mining Met. Engrs.*, *185*, 96 (1949).

[60d] F. R. N. Nabarro, *Conference on Strength of Solids*, Univ. of Bristol, 1947, The Physical Society, London, 1948, p. 75.

[60e] W. Kauzmann, *Trans. Am. Inst. Mining Met. Engrs.*, *143*, 57 (1941).

THEORY BY SMEKAL

Smekal[61–61b] has advanced the concept that solid phase reactions at the contact points result in a liquid or plastic interface. While pressure is an essential prerequisite for initiating this phenomena, its magnitude depends on the type of material to be considered. In certain favorable cases, ordinary gravity may be responsible for formation of the interface, *i.e.*, this type of bonding may be observed in loosely heaped powders. In his work with such nonmetallic crystals as rock salt, quartz, and other minerals, Smekal was able to estimate closely, with the aid of a simple mechanical scratch test, the magnitude of the chemical cohesion in contact areas below one micron. Tensile forces of 600 tsi for glass and 60 tsi for a resin agreed fairly well with both the chemical valence forces and the mechanical equivalent of the heat evolved. The temperature at the point of contact was found to increase to well above 700°C. (1290°F.).

The experimental and theoretical work by Bowden *et al.*[62–62d] is in support of Smekal's hypothesis that the bonding of powder particles is facilitated, if not caused entirely, by interfaces (surface cements) that are liquefied at points where fraction produces extreme heat. Both in the case of metals and nonmetals, surface irregularities on a molecular scale are always present, and even if highly polished surfaces are brought in contact they meet only at isolated points at which local pressures of considerable magnitude develop. These pressures may be sufficient to cause a metal to flow plastically (the pressure in the case of mild steel may be as much as 100 tsi). In sliding (as, for example, when powder particles are compacted), friction energy is released in the form of hot spots. Bowden measured the temperature of such hot spots with a cathode-ray oscillograph or a high-frequency galvanometer by using the two sliding metal surfaces as a thermocouple. The number of hot spots that can be observed depends upon the respective heat conductivities of the two materials in sliding contact; the temperature, however, may easily reach the melting point of one or both of the metals, although this temperature

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[61] A. Smekal, *Proc. International Powder Metallurgy Conference,* Graz, July 12–17, 1948, Referate No. 60.

[61a] A. Smekal, communication on "Mechanism of Crystal Growth," *Symposium on the Physics of Powder Metallurgy,* sponsored by Sylvania Electric Products, Inc., Bayside, L. I., N. Y., August 24–26, 1949.

[61b] A. Smekal, *Powder Metallurgy Bull., 4,* No. 4, 120 (1949).

[62] F. P. Bowden and K. E. W. Ridler, *Proc. Roy. Soc.* (*London*), *A154,* 640 (1936).

[62a] F. P. Bowden and T. P. Hughes, *Proc. Roy. Soc.* (*London*), *A160,* 575 (1937).

[62b] F. P. Bowden and D. Tabor, *Australia Council Res., Bull.* No. 145, pp. 7–38, 39–59; No. 155, pp. 1–24 (1942).

[62c] F. P. Bowden, J. N. Gregory, and D. Tabor, *Nature, 156,* No. 3952, 97 (1945).

[62d] F. P. Bowden, *Science News,* No. 4, 139 (July 1947).

can only be retained for a few ten-thousandths of a second. According to Smekal, the areas of these hot spots may average one-half of one micron in diameter. On the basis of these observations, Bowden concludes that, in polishing, the effectiveness of the abrasive is dependent entirely on its melting point relative to that of the abraded material, and not upon its greater hardness. In intermetallic friction processes the surface effects are influenced by the bulk properties of the two sliding materials in accordance with the rule that the coefficient of friction is approximately proportional to the shear strength and inversely proportional to the pressure that produces material flow.

Despite the very high temperatures that apparently prevail at the contact points of sliding surfaces in general, little evidence of their existence has been shown so far in compacted metal powders, probably owing to the great difficulties in connection with accurate experimental work involving such a complex proposition as a multicomponent metallic powder in the state of compaction. While the heat of the contact points is conducted off immediately, an over-all increase in temperature of the compact may result under certain conditions; that this effect remains insignificant for all practical purposes has already been demonstrated in Volume I (pages 268 and 269 and Table 31).

THEORY BY HEUBERGER

A concept advanced by Heuberger[62e,f] suggests that sintering is caused mainly by relaxation of lattice disturbances which are produced in the manufacture of the powder or during the compacting. Simplifying his analysis of the bonding and sintering processes by starting from spherical powder particles, Heuberger arrives at the following analysis. Under compression, conical fields of work hardening are produced in the contact areas. The radial extension of these fields determines the compressibility of the powder. (The frequently encountered inferior pressing qualities of very fine powders, or of dendritic powders, are given as an example for this phenomenon.) In subsequent sintering the contact areas provide nuclei for recrystallization due to their state of maximum lattice disturbance. Surface tension forces cause contraction of the areas, and impurities are expelled from the interior of the crystallites into the gaps formed between neighboring particles. As a result, an over-all increase in tensile strength takes place, which, however, may be coupled with an increase in the electrical resistivity—as in repeated pressing, especially when the

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[62e] J. Heuberger, *Festskrift tillägnad J. Arvid Hedvall,* Göteborg, 1948, p. 241.

[62f] J. Heuberger, discussion of A. Smekal, *Proc. International Powder Metallurgy Conference,* Graz, July 12–17, 1948, Referate No. 60.

direction of pressing does not remain exactly the same. Repressing, on the other hand, may increase the areas of lattice disturbance, resulting in a greater number of nuclei for recrystallization during subsequent sintering.

THEORIES BY RHINES

A major contribution to the understanding of the underlying principles of the sintering processes has been made by Rhines, who has analyzed the subject at a recent seminar session[63] in an excellent summary of experimental data available and theoretical concepts advanced to date. In view of the attendant complications in the processes dealing with the sintering of mixed or alloyed powders, including sintering in the presence of a liquid phase, the survey has been solely concerned with the sintering of monometallic powders. Because of the fundamental nature and wide scope, this part of Rhines' theoretical contributions is treated separately in a subsequent part of this chapter (page 835 ff.).

In earlier investigations Rhines and coworkers[64,65] had studied the sintering of certain homogeneous alloy systems with a particular interest in the nonequilibria conditions in these alloys; the broader aspects dealing with the mechanism of the sintering of alloys were also briefly summarized by Rhines[66] (see also p. 854 ff.).

In discussing more recently the physical principles underlying the formation and spreading of bonds between powder particles during the sintering process, Rhines[66a–b] describes a mechanism consisting of the sum of three overlapping steps. First, initial bonds or point-welds form at the contact points between the particles through a process considered to be probably one of surface diffusion. Second, the bonds spread beyond the established initial welds, and the particles coalesce into a coherent body, while the pores between the particles tend to spheroidize. In this phase, surface tension is considered the most important process. In the third step, a continual decrease in the number of pores takes place, although some individual pores *grow* at the expense of others (as established by experimental work by Rhines *et al.*[66b]). This phenomenon is explained by a diffusion process, involving occupying vacancies in the crystal lattice by the metal atoms, which is superimposed

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[63] F. N. Rhines, *Trans. Am. Inst. Mining Met. Engrs.*, *166*, 474 (1946).

[64] F. N. Rhines and R. A. Colton, in J. Wulff, *Powder Metallurgy*. Am. Soc. Metals, Cleveland, 1942, p. 67.

[65] F. N. Rhines and R. A. Meussner, *Symposium on Powder Metallurgy*. A.S.T.M., Philadelphia, 1943, p. 25.

[66] F. N. Rhines, communication on "Principles of Sintering," *Powder Metallurgy Colloquium*, New York University, May 24, 1946.

[66a] F. N. Rhines, *Powder Metallurgy Bull.*, *3*, No. 2, 28 (1948).

[66b] F. N. Rhines, C. E. Birchenall, and L. A. Hughes, *Trans. Am. Inst. Mining Met. Engrs.*, *188*, 378 (1950).

over the surface tension process causing shrinkage of the small pores. Thus, while the smallest pores are shrinking (because of their greater surface tension) slightly larger neighboring pores of smaller surface tension grow due to the movement of the metal particles by diffusion to fill the smallest pores, and vacant lattice sites and minute voids are conceived as diffusing. This process continues until all the smallest pores have diminished in size to the point of complete disappearance. The small pores near the surface of the compact are lost to the system by "reverse" movement into the "infinite" pore, the atmosphere surrounding the sintered compact.

The sintering process is accelerated by three factors, *i.e.*, pressing the powder into compacts, raising the temperature, and controlling the sintering atmosphere. The first increases the number of metal-to-metal contacts, and, together with the second, increases the rate of sintering (since sintering is essentially a process of diffusion). The effect of a gaseous atmosphere is in general one of retarding the sintering process; gases that do not diffuse readily delay the elimination of the pores to a marked extent, but this is not the case for gases such as hydrogen having a high diffusion rate and strong capacity to reduce the oxide films on the particle surfaces.

In applying the vacancy migration theory (see also page 815) to the mechanisms of shrinkage and sintering, Rhines takes a contrary view to the viscous-flow theory advanced by Frenkel (page 815 ff.) and Shaler and Wulff (see below), according to which every pore would shrink continuously during sintering, and shrinkage would be independent of the mass of powder.

THEORY BY SHALER AND WULFF

Shaler and Wulff,[67] in a recent searching analysis of the physics of sintering, have extended the theoretical work of Frenkel (page 815 ff.) by including the presence of foreign gases inside and outside of the aggregate of crystals. The authors deal experimentally and mathematically with the rate of volume change that occurs during sintering of uncompacted copper powder aggregates containing a multitude of pores of uniform size. It is shown that neither evaporation plus condensation nor surface diffusion processes can account fully for the rate of volume change observed in the copper powder at 800–900°C. (1470–1650°F.). Based on the assumption that shrinkage of the pores is caused by the flow of metal moved by surface tension forces, the authors calculated (along the lines indicated by Frenkel for the case of self-diffusion) both the rate of

[67] A. J. Shaler and J. Wulff, *Phys. Revs.*, *72*, 79 (July 1947); *Ind. Eng. Chem., Anal. Ed.*, *40*, 838 (1948).

shrinkage of the pores and the opposing effect of entrapped indiffusible gases; they found the value of the coefficient of viscosity derived from sintering the copper in argon at atmospheric pressure, or hydrogen at lower pressure, to be of the same order as that resulting from self-diffusion. Three effects are distinguished when inert gases are entrapped: (*1*) the shrinkage of pores below a certain critical size may be accelerated; (*2*) the effect is insignificant on pores of critical size, *i.e.*, the gas pressure balances the counterpressure introduced by the surface tension; and (*3*) after a certain period of time an expansion of the pores beyond the critical size occurs. This finding is of particular interest in connection with experimental results on sintered hollow cylinders that underwent simultaneous radial contraction and longitudinal expansion. A calculation of the effect of a vacuum during sintering on the entrapped gas (which is either at atmospheric or at reduced pressure) shows that all the volume changes occur after the same period, which is governed by the pore size, while the internal gas pressure controls the direction and extent of the volume change.

Shaler and Wulff also considered briefly the case of sintered powder compacts. This differs from the foregoing mainly by the fact that compaction reduces the size of the pores while simultaneously increasing the pressure of the entrapped gases. Thus, it can be expected that if originally spherical pores are flattened by the compaction, the combined action of surface tension at the edges of the pores and an increased gas pressure at the flat sides produce shrinkage and expansion effects in preferred directions.

In a subsequent publication,[68] the prevailing experimental evidence is explained by a mechanism of sintering which may be considered an analogy to the preferential orientation of interstitially dissolved atoms in metals under stress. Thus, it is held that: stress application also results in a preferential distribution of pairs of vacant lattice sites; the rate of orientation is related to the heat of activation for diffusion; and the relaxed orientation of vacancy pairs is perpendicular to a tensile stress. This concept would be in agreement with the authors' earlier theory that the rate of sintering is determined by the viscous flow of metal under the influence of surface tension.

Of some practical significance is a correlation of pore shape and mechanism of shrinkage.[68a] In compacts of plastic metal powders pressed at high pressures the voids are squeezed into flakelike, lenticular shape. The radius of the curvature in the direction of pressing is much larger than in a direction perpendicular to it. Although the gas pressure is hy-

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[68] A. J. Shaler and J. Wulff, *Phys. Revs.*, *73*, 926 (April 1948).

[68a] A. J. Shaler, *Trans. Am. Inst. Mining Met. Engrs.*, *185*, 796 (1949).

drostatic, the surface tension force is not. As a consequence, the pores may first shrink in the lateral direction without marked change in the axial direction; only at a later time they may expand in the direction of pressing while then remaining unchanged in the lateral direction. Thus, after only a short sintering period, the length of a cylindrical compact would be unchanged while its diameter would have shrunk; after a longer time of sintering, the length might increase, while the diameter would undergo no further change. In such a case a denser product would be obtained after a short sintering time than after a long one, and the change of at least one dimension (*i.e.*, the axial one) could be held to a minimum.

Further understanding of the operating mechanism of the sintering process was also achieved by experimentation and mathematical analysis of the surface tension of solid copper (wires)[68b] and of the volume changes of artificially produced longitudinal holes in such wires.[68c]

THEORY BY KUCZYNSKI

The mechanism of sintering was also studied by Kuczynski.[68d–f] Experimenting with spherical copper particles, 5–80 microns in diameter, which were sintered to a flat copper surface at temperatures ranging from 400° to 1000°C. (750° to 1830°F.) for varying periods of time, he observed (using a microscope) changes of the curvatures of the junction formed between the spheres and the flat surface. At a given temperature, time of heat treatment is proportional to the fifth power of the fraction of the radius of the curvature at the junction over the original radius. This finding seems to disprove the concept that sintering takes place by viscous flow under the action of surface tension, as suggested by Frenkel (page 815) and accepted by Shaler and Wulff (page 823), as the viscous-flow mechanism indicates a second-power relationship. Neither does it agree with the concept that sintering is affected by evaporation and condensation processes, as these mechanisms would indicate a third-power relationship; nor can sintering be considered to be exclusively a surface diffusion process, as this would mean a seventh-power relation-

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[68b] H. Udin, A. J. Shaler, and J. Wulff, *Trans. Am. Inst. Mining Met. Engrs.*, *185*, 186 (1949).

[68c] A. J. Shaler, communication on "The Rate of Shrinkage of Synthetic Pores in Copper," *Symposium on the Physics of Powder Metallurgy*, sponsored by Sylvania Electric Products, Inc., Bayside, L. I., N. Y., August 24–26, 1949.

[68d] G. C. Kuczynski, *Bull. Am. Phys. Soc.*, *23*, No. 7, 25 (1948).

[68e] G. C. Kuczynski, *Trans. Am. Inst. Mining Met. Engrs.*, *185*, 169 (1949).

[68f] B. H. Alexander and G. C. Kuczynski, communication on "Relationship Between Diffusion and Viscous Flow During Sintering," *Symposium on the Physics of Powder Metallurgy*, sponsored by Sylvania Electric Products, Inc., Bayside, L. I., N. Y., August 24–26, 1949.

ship. An analysis of Kuczynski's experimental results suggests that sintering of metallic particles is caused by volume and surface diffusion, with the latter predominant for smaller particles and lower temperatures.

THEORY BY SCHWARZKOPF

In a contribution to the theory of sintering, Schwarzkopf[69] holds that interatomic forces are ultimately responsible for both cohesion and surface tension. Going beyond the concepts of Frenkel and Shaler on plastic flow, and of Pines on vacancy migration, the combined effect of interfacial tension and surface tension on the deformation of solids is emphasized in accordance with the concepts by Smith.[70] The sintering mechanism consists of three stages: (*1*) the formation of point contact bonds conditioned by surface forces; (*2*) lateral growth of the point bonds assisted by plastic flow; and (*3*) disappearance of isolated pores due to surface diffusion rather than to lattice diffusion. Plastic flow and surface diffusion occur in all three stages and are also interdependent. Because it cannot be assumed that the reactions involved take place independently of each other and may be complicated further by gas solution or sorption effects, it was not found possible to present an exact mathematical treatment of the processes.

THEORY OF MACKENZIE AND SHUTTLEWORTH

In their recent phenomenological theory of sintering Mackenzie and Shuttleworth[70a] lend strong support to the concept that plastic flow participates in the sintering mechanism. Neither the effects of volume diffusion, as maintained by Kuczynski, nor those of viscous flow, as postulated by Frenkel and Shaler, seem to account fully for the high rate of density increase that occurs generally during sintering. Here, densification is assumed to occur through surface tension, and according to a correlation between the rate of shear strain of the metal and the shear stress at constant sintering temperature.

THEORY OF HERRING

In contrast to the foregoing, Herring's[70b] theoretical treatment of the processes that may motivate sintering considers it unlikely that

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[69] P. Schwarzkopf, *Proc. International Powder Metallurgy Conference,* Graz, July 12–17, 1948, Referate No. 50; see also *Powder Met. Bull., 3,* No. 4, 74 (1948).

[70] C. S. Smith, *Trans. Am. Inst. Mining Met. Engrs., 175,* 15 (1948).

[70a] J. K. Mackenzie and R. Shuttleworth, *Proc. Phys. Soc., B62,* 833 (1949).

[70b] C. Herring, communication on "Surface Tension as a Motivation for Sintering," *Symposium on the Physics of Powder Metallurgy,* sponsored by Sylvania Electric Products, Inc., Bayside, L. I., N. Y., August 24–26, 1949.

plastic flow enters as a major force. Instead, a volume diffusion mechanism is favored which, however, differs from the mechanisms postulated by Kuczynski and others by its consideration of atom transport by grain boundary diffusion. The concept, which is closely related to the mechanism of deformation suggested by Nabarro,[60d] perceives that surface forces produce a concentration gradient of the lattice defects thus resulting in a diffusion of the defects from one part of the grain surface to another.

THEORY BY KINGSTON

Another theory of sintering has been advanced by Kingston[71,71a] who holds the viewpoint that the mechanism of sintering during the successive powder metallurgy processing stages—with the compaction process merely the first stage of the sintering process—can be explained fully by a continuous process of self-diffusion induced by lowering of the total free energy of the system. This process involves nucleation, recovery, recrystallization, and grain growth as progressive stages, and the respective rates are a function of the nature of the metallic surfaces engaged. Accordingly, particle shape, particle size distribution, and average particle size have specific effects upon the different self-diffusion phenomena. Except for interferences caused by the evolution of gases, the mechanism of sintering is analogous to that of fusion; but the rate of reaction and the nature of the grain boundaries are decidedly different.

The phenomena of self-diffusion are followed schematically through the pressing operation and sintering process in Figure 626. At the beginning the surfaces of three randomly placed particles show a disorderly arrangement of the surface atoms resulting in a surface roughness of the first order (Fig. 626*A*). During compaction, high unit pressures and a correspondingly high free energy are created at the contact points; these in turn cause self-diffusion and nucleation to take place (Fig. 626*B*) —processes that are aided by the temperature of compaction (293°K.). With prolonged time of pressing, growth of unstressed crystals at the contact points takes place (Fig. 626*C*). As the cold-pressed powder compact is heated, self-diffusion continues and increases exponentially with temperature; eventually, a level is reached at which the size of the unstressed crystals grown from the stable nuclei become comparable with the deformed regions of the particles, and stress relief can be observed by

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[71] W. E. Kingston, *Proc. International Powder Metallurgy Conference,* Graz, July 12–17, 1948, Referate No. 62; also *private communication.*

[71a] G. F. Hüttig and W. E. Kingston, communication on "The Fundamental Problems of Sintering Processes," *Symposium on the Physics of Powder Metallurgy,* sponsored by Sylvania Electric Products, Inc., Bayside, L. I., N. Y., August 24–26, 1949.

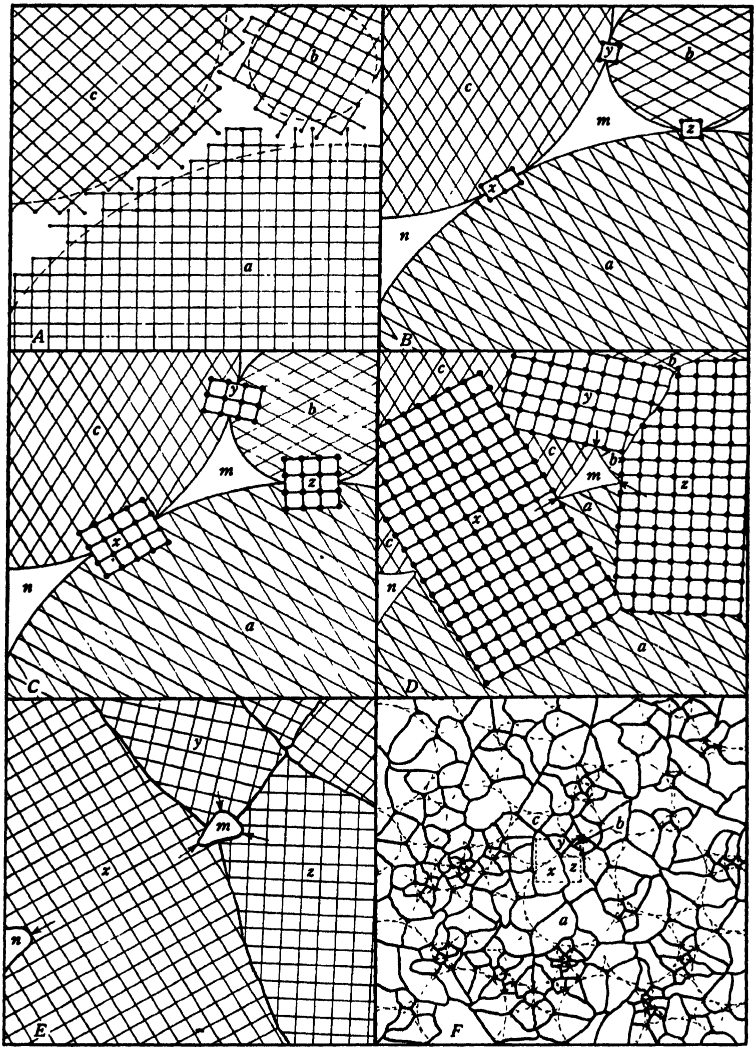

Fig. 626. Schematic presentation of the mechanism of sintering as manifested by progressive self-diffusion with increasing powder compactness and rising temperature, according to Kingston[71]: *A,* loose adherence of three metallic particles *a, b,* and *c* the surfaces of which show a disorderly arrangement of the surface atoms; *B,* establishment of surface contact points of high stress concentration *x, y,* and *z* upon compaction of the three particles, resulting in the formation of nuclei with atoms from both adjacent particles; *C,* growth of nuclei into crystals at the contact points and reduction of volume of interstices *m* and *n* through plastic deformation with time of exerted pressure; *D,* accelerated crystal growth at the contact points and reduction and spheroidization of void volume through surface tension forces with rising temperature; *E,* complete absorption of the original particles into the newly formed unstressed grain structure through progressive self-diffusion and pore shrinkage and spheroidization at high sintering temperatures; and *F,* grain structure of *e* at a reduced scale, before substantial grain growth has taken place.

physical measurements (Fig. 626*D*). Upon further increase in temperature, the newly formed crystals progressively absorb the balance of the originally deformed matrix, simultaneously growing in size to an order visible by conventional microscopes (Fig. 626*E*). Spheroidizing and shrinkage of the interparticle voids—caused by the massive flow of the particle matrices under the influence of surface tension forces—are parallel phenomena. With further advance of temperature and time, self-diffusion—now mainly manifested by grain growth—continues in a logical manner. In Figure 626*F* (a reduction of Figure 626*E*) the grain structure is shown before appreciable grain growth has taken place, and the original particles as well as the newly formed grains are indicated.

Kingston's theoretical discussion is corroborated in part by experimental work, which is chiefly concerned with a metallographic study of the sintering of molybdenum powder compacts (see also Fig. 314, Chapter XXI). Unfortunately, however, one of the mainstays of the theory, namely, the occurrence in comparatively high melting metals of nucleation, self-diffusion, and recrystallization at or near room temperature, is not clearly evident from this experimental work. Nor is it evident from the large volume of original work published over the years by other investigators. Thus, Kingston's logically developed theory remains hypothetical until such time as further experimental proof (perhaps with the aid of x-rays and electron microscopy) is brought forward.

MISCELLANEOUS THEORIES

The concept advanced by Reis[72] attributes the sintering mechanism mainly to crystallization processes. Microstresses and recrystallization effect a material transport over microscopic and submicroscopic distances; this transport is influenced by certain factors that act either as obstacles or as stimuli. To the former belongs lack of contact between metallic faces as caused by interstices or foreign substances; to the latter belong conditions of instability, such as cold working effects, surface energy effects, phase changes, concentration gradients and states of structural nonequilibrium. The effects of cold working are assumed to proceed from the contact points toward the interior of the particles; therefore, at the contact points, recrystallization may be expected to commence at lower temperature. Reis, in putting the "effective" sintering temperature above the low recrystallization temperature of the work-hardened powder compact, holds that the sintering process is not so much influenced by the recrystallization process itself, but by the conditions of instability (*e.g.*, structural nonequilibrium) that prevail at temperatures above recrystallization.

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[72] A. Reis, cited in P. Schwarzkopf, *Powder Metallurgy*. Macmillan, New York, 1947. p. 282.

In a recent discourse on theoretical physics, Koch[72a] has postulated that when electricity flows through a metal the electrons fill lattice vacancies without losing contact with their respective atoms, *i.e.*, there would exist no free electrons. This concept was suggested as a foundation for the understanding of the nature of metallic bonding between adjacent surfaces, such as in the sintering of metal powders.

According to a theory developed by Balarew,[72b] crystalline substances are formed for thermodynamic reasons on conglomerates with large internal surfaces on which impurities are concentrated. Whereas the interiors of the crystals have a typically crystalline structure, the exterior parts (*i.e.*, surfaces, corners, or edges) have, to a varying degree, stoichiometrically different vitreous structures. The well-known process of caking of metal and nonmetal powders at elevated temperatures is used as proof for the theory, and experiments with lead chloride, lead bromide, magnetite, and tungsten trioxide corroborate the theoretical concept. It is held that in metals the grain boundary substance is produced by the expulsion of internally sorbed impurities.

May[72c] has developed the theory that the shrinkage process constitutes the combined effect of atomic mobility and surface cohesion forces. However, attempts to calculate the shrinkage of single-phase systems from data available for these two forces failed to agree quantitatively with experimental results obtained on carbonyl and mechanically disintegrated iron powders. The experiments indicated that particle shape has a profound influence on the magnitude and the direction of the dimensional change, and may determine whether the shrinkage in the direction of compacting is larger or smaller than that in the direction perpendicular to it. For this reason, density determination is considered a more sensitive test than dilatometric measurements. Expansion phenomena observed in binary systems are explained by May as being due to differences in solubilities and diffusion rates of the components. An analysis of May's work seems particularly interesting in view of the contributions of Bal'shin (pages 804, 805) and Ivensen (page 818).

In a theory advanced by Mazzoleni[72d] a critical grain size for powdered metallic materials is emphasized and its peculiar effect on various properties is traced by mathematical analysis. When the dimensions of the particles or grains become extremely small, the increment of their internal energy (due to the marked increase of their surface compared to

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[72a] M. Koch, *Proc. International Powder Metallurgy Conference,* Graz, July 12–17, 1948, Referate No. 70.

[72b] D. Balarew, *Proc. International Powder Metallurgy Conference,* Graz, July 12–17, 1948, Referate No. 1.

[72c] K. May, *Arch. Metallkunde, 2,* No. 10, 154 (1948).

[72d] F. Mazzoleni, *La Metallurgia Italiana, 39,* 86 (March–April 1947).

the volume) attains magnitudes comparable to an analogous increment produced by a considerable increase in temperature. Among the properties that appear affected are the solution potential of the substance, the vapor pressure, allotropic transformations and Curie points, and tempering constituents and grain boundary precipitates. Variations in these properties frequently exhibit a "threshold effect," that is, a discontinuity which depends on the order of dispersion of the initial powder.

THEORIES ON ATOMIC MIGRATION DURING SINTERING

In view of the large—and in part rather controversial and confusing—volume of theoretical postulations recently published and treated in the foregoing section, it appears wise to summarize the principal theories related to the atomic movements believed to take place during sintering. The following discussion, based primarily on recent presentations by Hüttig,[71a,72e,f] considers merely the *ways* in which a transport of atoms

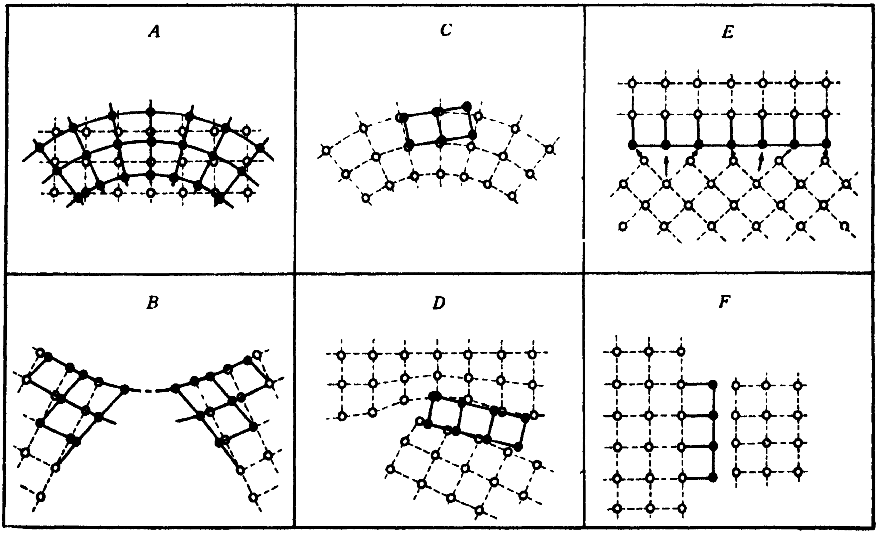

Fig. 627. Schematic presentation of the ways of displacement of a single atom within the region of its immediate neighbors, according to Hüttig[71a]: *A*, lattice distortions within one domain of atomic coherence caused by stresses; *B*, same, at the junction of two such domains; *C*, relief of lattice distortions in the interior of the crystal; *D*, same, at the contact area of two crystals; *E*, crystal growth at the contact area of two differently oriented crystals; and *F*, same, at the junction of two equally oriented crystals.

[71a] G. F. Hüttig, *Proc. International Powder Metallurgy Conference*, Graz, July 12–17, 1948, Referate No. 22.

[72f] G. F. Hüttig, *private communication.*

takes place; thus, the picture unfolded is purely a geometric one, independent of time (transport rates) and driving forces (free energies). Moreover, only those mechanisms will be considered that involve space filled with matter, not empty space. Movements of empty spaces (*e.g.*, lattice distortion gaps, pores, etc.) can only take place with *corresponding* movements of atoms or atomic aggregates, and are therefore closely connected with such processes as lattice distortions and lattice self-diffusion (see below).

Four elementary ways of atomic rearrangement may be distinguished, namely: (*1*) displacement of a single atom within the domain of its immediate neighbors; (*2*) self-diffusion; (*3*) movement of entire aggregates of rigidly arranged atoms; and (*4*) movement of entire atomic aggregates superimposed over displacements of individual atoms within the aggregates. The first course is shown schematically in the diagrams of Figure 627; the other three are presented similarly in the diagrams of Figure 628. It must be assumed that, in general, all four defined types of atomic rearrangements coexist, and the observed cumulative effect constitutes an overlapping of the elementary processes. However, the share of each of these processes varies with different conditions, and especially with temperature, so that, for instance, at specific temperature levels one or the other elementary process of atomic migration becomes predominant to the extent of being practically solely effective.

DISPLACEMENT OF ONE ATOM WITHIN THE REGION OF ITS IMMEDIATE NEIGHBORS

Lattice Distortions. Two cases of such distortions may be distinguished, namely, those occurring *within* one domain of atomic coherence (*e.g.*, mosaic blocks), and those occurring at the *junction* of two such domains. Lattice distortions of the first type are caused by tensile, compressive, bending, or elastic rebound stresses (Fig. 627*A*). Distortions of the second type (Fig. 627*B*) take place when, at the contact area of two-crystal aggregates, the atoms shift in such a manner that they associate themselves with both aggregates simultaneously. This process may be considered as a first step toward the processes of spheroidizing and eventual complete sealing of pores (theories of Shaler and Rhines).

Relief of Lattice Distortions. This phenomenon, too, manifests itself by two processes, namely, nucleation—followed by recrystallization—in the *interior* of the crystals or particles (Fig. 627*C*); and nucleation at the *contact points* (Fig. 627*D*). The first is considered as part of the classic mechanism of recrystallization (theories of Tammann). The second is based on the concept that contact points of pressure-compacted powder particles are predestined for nucleation due to high energy concentration (theory of Kingston). It is even held possible that this process may apply to loosely heaped powder particles as well (theory of Smekal).

Crystal Growth. Again, two different cases may be distinguished, namely, crystal growth at the contact area of two *differently* oriented crystals, and at contact points of two crystals of *like* orientation. In the first instance (Fig. 627*E*), it is held that the one with the more stable crystallographic contact face attracts and incorporates atoms of the less stable face of the neighboring crystal; constant repetition of this process results in complete integration of the second crystal in the first [Sauerwald's mechanism of grain growth and germination (Sammelkristallisation)]. In the second instance, a similar mechanism is possible whereby the atoms in the surface of the larger crystal due to a smaller specific surface energy are able to draw in atoms from the surface of the smaller crystal (classic concept of grain growth by Ostwald).

SELF-DIFFUSION

This process may be characterized as a propulsion of an individual atom from its environment, followed by its going astray *aperiodically* within the crystal lattice until it becomes bound by the force field of an atomic configuration. If the distance of this aperiodic migration of the atom is very small, *i.e.*, the atom is immediately upon propulsion from one force field caught by a neighboring one, the process may be considered merely an exchange of places of the atom (Platzwechsel). The atomic migration may take place along four different paths (theories of Kuczynski and Smekal): (*1*) within the crystal, (*2*) in the free surface, (*3*) along the borders of a domain of coherence, and (*4*) through the gas phase.

Lattice Self-Diffusion. The process of self-diffusion within the crystal lattice (Fig. 628*A*) occurs at comparatively high temperatures, at which the rate of diffusion throughout the entire cross section of the crystal increases rapidly to become the predominant process of sintering. It replaces, but also partly counteracts, the processes essentially completed at lower temperature levels such as diffusion in the free surface or along crystal boundaries.

Surface Self-Diffusion. The process of self-diffusion at the free surfaces of the crystals (Fig. 628*B*) may be considered to precede directly that of lattice self-diffusion, as it is virtually consummated at a lower temperature level. Thus, for example, surface diffusion may be virtually halted upon filling the surface crevices in the case of a junction of a large and a very small crystal, whereas lattice diffusion will go on until the small crystal is completely integrated into the larger one.

Boundary Self-Diffusion. The process of self-diffusion along the boundaries of domains of coherence—which include mosaic blocks, crystallites, or complete grains—is considered to take place either concurrently or somewhat ahead of the surface diffusion process, and, therefore, at a low, if not the lowest temperature level (Fig. 628*B*). The process is generally designated by the term *adhesion* (theories of Sauerwald and Bal'shin); with rising temperature the magnitude of the adhesion forces diminishes, but the amplitudes of the atomic vibrations in the surfaces and boundary regions increase, resulting in an enhanced effectiveness of the atomic bond.

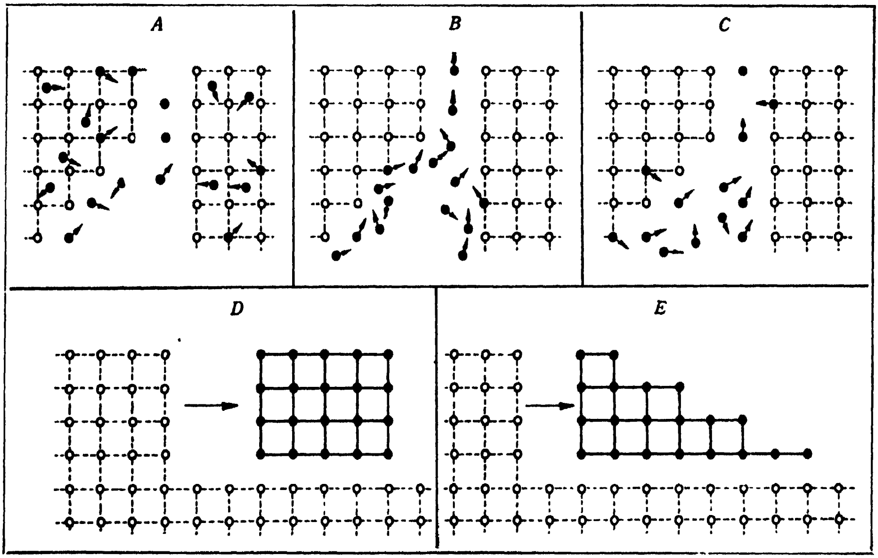

Fig. 628. Schematic presentation of the processes of self-diffusion and movement of entire aggregates of atoms, according to Hüttig[71a]: *A*, self-diffusion within the crystal; *B*, same, at the free crystal surfaces and along the boundaries of domains of atomic coherence; *C*, same, through the gas phase; *D*, movement of aggregates of rigidly arranged atoms; and *E*, movement of aggregates of individually displaced atoms.

Diffusion through the Gas Phase. This process (Fig. 628*C*) is one of sublimation and resublimation. Small crystals have a higher vapor pressure than larger ones, causing a gradual absorption of the former by the latter. In this case, the distance between the crystals may be quite large, especially if the temperature is high.

MOVEMENT OF AGGREGATES OF RIGIDLY ARRANGED ATOMS

Two processes of this kind can be distinguished, where entire atomic aggregates move relative to their environment but where the atomic arrangement within the aggregate remains unchanged (theories of Wretblad and Wulff and Pines), namely, sliding phenomena and shrinkage phenomena (Fig. 628*D*).

MOVEMENT OF AGGREGATES OF INDIVIDUALLY DISPLACED ATOMS

This process (Fig. 628*E*), in which the movement of the aggregate is superimposed over displacements of individual atoms within the aggregate, is considered one of viscous flow (theories of Frenkel and Shaler and Wulff) analogous to that of convection currents in fluids. Atomic migration of this kind predominates where sintering takes place in the presence of a liquid phase.

COMPOSITE THEORY OF BONDING AND SINTERING PURE METAL POWDERS

One of the chief causes for the slow development of a science of powder metallurgy lies in the fact that the experimental evidence is in many respects extremely scarce; in other instances, where abundant, the results constitute data of interest only for specific applications and often are insufficiently organized for scientific research and theoretical conclusions. In spite of the obvious lack of certain pertinent experimental material, Rhines[63] has made an impressive attempt to analyze the theoretical aspects of the sintering process as a whole, thus laying the foundation for a truly scientific approach to the subject. Rhines' statement, that any satisfactory and complete theory must be capable of explaining *all* of the established and uncontested facts, can only be wholeheartedly subscribed to by the author. These facts must be based on a scrutiny of the mass of experimental results that have been reported in the published literature over the last twenty-five years. Since, in the author's opinion, Rhines has succeeded admirably in accomplishing this very task—thereby presenting a basic and solid appraisal of the bonding and sintering processes in pure metal powders without giving himself to hypothetical or even speculative suppositions—the following section is largely based on his presentation. Its instructive value is believed further enhanced by the inclusion of some of the pertinent references published after release of the original communication.

Summary of Experimental Observations

BONDING AT ROOM TEMPERATURE

Uncompacted State. Metal powder particles, like massive metals adhere to each other to a limited extent at room temperature without application of external force.[73] (The same phenomenon can also be observed for certain nonmetallic powders.[72b]) Tin powder particles with clean surfaces form a weakly coherent mass, the strength of the cake increasing with time; clean surfaces of gold particles as well as of nickel[74] and other substances also adhere to each other when light contact is established, in particular under vacuum.

Effect of Pressure. The strength of the bond between the particles is increased progressively with rising compacting pressure until a pressure limit is reached above which no substantial improvement of the bond is obtained.[73] At very high pressures the reverse effect is observed, which may be attributed to the expulsion of entrapped gases.

Establishment of Contact Points. Contacts between opposing surfaces of neighboring particles are limited to points because of the uneven character of the surfaces on a microscale as well as on a coarse scale.[75] Based on electron microscope observations it is presumed that even after considerable compaction contacts are confined to points. Weak electric currents causing a temperature rise of only a few degrees have been observed to increase appreciably the strength properties of compacted powders, presumably due to sintering at the points of contact.[76]

Thermal Effects of Compaction. The bonding of powders at room temperature does not require localized melting at the contact points[77]; the early contentions that "cold" welding of powders is produced by the heat of friction at the contact points[78,79] has been disputed.[73] However, some evidence points in the direction of extremely high temperatures caused by friction which may result in fusion[79a]; the contact areas displaying such hot spots are not believed to be in excess of one-half micron in diameter.[79b]

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[73] W. D. Jones, *Principles of Powder Metallurgy*. Arnold, London, 1937.

[74] R. Holm and B. Kirschstein, *Wiss. Veröffentl. Siemens-Werken, 15,* 122 (1936).

[75] F. Sauerwald, *Kolloid Z., 104,* 144 (1943).

[76] E. Schwarz-Bergkampf, *Proc. International Powder Metallurgy Conference,* Graz, July 12–17, 1948, Referate No. 46.

[77] F. Sauerwald and E. Jaenichen, *Z. Elektrochem., 31,* 18 (1925).

[78] K. Endell, *Metall u. Erz, 18,* 169 (1921).

[79] C. Hardy, *Metal Progress, 35,* No. 2, 171 (1939).

[79a] F. P. Bowden, *Science News,* No. 4, 139 (July 1947).

[79b] A. Smekal, *private communication.*

Effect of Particle Plasticity. The bond between the particles is stronger and the coherence and density of the powder compact greater the more plastic the metal.[73] At a given pressure, basically hard or work-hardened powders produce weaker and more porous compacts than do soft or annealed powders; for comparable properties of the compact, higher pressures must be applied in the case of the less plastic powder.

Effect of Particle Size. The strength and density of the compact are dependent on the size distribution of the powder[73,80]; the finer powders require increasing compacting pressures to produce a given density, indicating that the true geometrical mechanism of packing, whereby fine particles of uniform size pack to the same density as coarse particles, is upset by other factors such as interfering foreign phases. In the compacted powder, the size of the remaining pores decreases with the particle size; the over-all pore volume, however, is decreased only if different powder sizes are mixed to give a definite particle size distribution.

Effect of Particle Shape. The strength and density of the compact are also influenced by the shape of the particles.[73] It is difficult to establish an exact relationship between the shape factor and the properties of the compact because of serious complications due to the large range of shapes possible for any one metal, variations in shape within a given type of powder, and changes in shape through plastic deformation during compaction. As a rule, flaky and very feathery particles yield the lowest density, and irregular and slightly porous particles the highest; the strength of the compact is greater the greater the amount of contact area produced, meaning that spongy and dendritic particles are superior to solid spherical or flaky powders. (A reported[62f] inferiority of dendritic powders in compaction, which would contradict this statement, cannot be considered in accordance with the bulk of the available experimental evidence.)

Effect of Interfering Gases. Bonding is detrimentally affected by gases adsorbed on the surface of the powder particles.[73,80a] Large volumes of gas can usually be removed from metal powders by treatment in vacuum.[81] The adherence of clean nickel faces is greatly improved under vacuum as compared to conditions in which the metal is surrounded by hydrogen[74]; gold, too, adheres more readily in vacuum than in air despite its resistance to oxidation. The beneficial effect of vacuum conditions

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[80] C. J. Leadbeater, L. Northcott, and F. Hargraves, *Symposium on Powder Metallurgy*. The Iron and Steel Institute, London, Special Report No. 38, 1947, p. 15.

[80a] G. F. Hüttig, *Proc. International Powder Metallurgy Conference*, Graz, July 12–17, 1948, Referate No. 22; also W. D. Jones, *Metal Treatment, 13,* 265 (1946).

[81] R. Ruer and J. Kuschmann, *Z. anorg. u. allgem. Chem., 173,* 233 (1928).

during pressing is particularly significant in the case of fine powders presenting a very large surface. Compaction in vacuum is reported to be performed with greater ease and with less risk of producing pressing laminations.[82]

Effect of Interfering Solids. Bonding is seriously impaired by solid films, such as oxides, that cover the surfaces of the powder particles.[73,75,83] With increasing thickness and tenacity of the film the bonds become increasingly weak. Thus, lead powder, which forms oxide films most readily, is compressed at a given pressure into a much weaker compact than an equally soft gold powder, which forms no oxide films.[83] Although clean metal powders result in stronger compacts, oxidized powders can usually be bonded by compression, just as oxides themselves. The strength of compacts made from oxidized powders is more nearly similar to that of compacts from full oxides than from pure metals.[84,85]

Effect of Binders and Lubricants. The density reached with a given compacting pressure may be increased when the powder is mixed with a liquid binder such as water and, after drying, the compact may possess a higher strength than when pressed dry at the same pressure.[86] A similar effect is produced by other substances such as paraffin[87] or stearic acid,[73] which all function as lubricants.

Effect of Pressing Temperature. The use of subnormal temperatures during compressing reduces the strength of the compact,[87a] as do lower pressures at room temperature.[88] Unless increased pressures are used, compacts of lower density are produced. On the other hand, raising the pressing temperature above room temperature has the opposite effect—that of lowering the pressure required to obtain a given density.[89–91]

Properties of Compacts. The strength and hardness of powder compacts produced at room temperature increase with density.[92] While the strength rarely approaches that of massive metal, the hardness increases more rapidly and may even exceed that of cold-worked metal in

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[82] C. Hardy, *Steel, 110,* No. 3, 84 (1942).

[83] C. C. Balke, *Iron Age, 147,* No. 16, 23 (1941).

[84] F. Sauerwald and G. Elsner, *Z. Elektrochem., 31,* 15 (1925).

[85] J. A. Hedvall, *Z. phys. Chem., 123,* 33 (1926).

[86] F. Rollfinke, *Z. Ver. deut. Ing., 84,* 681 (1940).

[87] C. J. Smithells, *Tungsten.* 2nd ed., Chapman and Hall, London, 1936, p. 49.

[87a] R. P. Seelig, communication on "Fundamentals of Pressing of Metal Powders," *Symposium on the Physics of Powder Metallurgy,* sponsored by Sylvania Electric Products, Inc., Bayside, L. I., N. Y., August 24–26, 1949.

[88] W. D. Jones, *Light Metals, 5,* No. 51, 95 (1942).

[89] F. Sauerwald and J. Hunczek, *Z. Metallkunde, 21,* 22 (1929).

[90] G. J. Comstock, *Metal Progress, 35,* No. 6, 576 (1939).

[91] C. G. Goetzel, in J. Wulff, *Powder Metallurgy.* Am. Soc. Metals, Cleveland, 1942, p. 340.

[92] W. Trzebiatowski, *Z. phys. Chem., A169,* 91 (1934); *B24,* 75, 87 (1934).

the case of soft metals such as copper. The electrical conductivity also increases with increasing density.

SINTERING AT ELEVATED TEMPERATURE

Temperature Effect on Structure. With rising temperature, bonding between the particles becomes increasingly effective, and at a temperature usually associated with the recrystallization temperature major structural and property changes become apparent,[73,93] which are the result of a very rapid rate of sintering. By recrystallization temperature is generally understood that temperature at which visible grain growth in the powder compact takes place; it is considerably higher than that observed in cold-worked massive metals. Early concepts that sintering does not occur below the recrystallization temperature must be attributed to insensitive testing procedures.[94] The effects of temperature on the sintered structure of metal powder compacts are analogous to those on the oxides, except that, in the latter case, temperatures of rapid sintering and recrystallization are appreciably above those for the corresponding metals.[84,85] Accordingly, oxidized metal powders require higher temperatures for effective sintering than clean metal powders. Analogous to bulk pieces of metal that lose their sharp corners when held at high temperatures below their melting point, individual powder particles tend to spheroidize at high temperatures, which, however, may be considerably below their melting points.[75,83]

Temperature Effect on Density. With certain exceptions the density of compacts increases with rising sintering temperatures.[95] This is particularly true for loosely compacted powders, for compacts produced by vacuum pressing and vacuum sintering, and for powders of high purity, such as hydrogen-reduced tungsten, molybdenum, and iron. Differences in density throughout the cross section of the compact tend to equalize with increasing sintering temperature.[86,96] An initial decrease in density with rising temperature is observed for most metals in the temperature range immediately above room temperature, *i.e.*, up to 200°C. (400°F.).[96] A second, sometimes very marked, decrease in density is frequently observed at or above the recrystallization temperature, especially in compacts molded at very high pressures.[92,97]

Temperature Effect on Volume. Thermal expansion and crystal-

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[93] R. Kieffer and W. Hotop, *Stahl u. Eisen, 60,* 517 (1940).

[94] P. E. Wretblad and J. Wulff, in J. Wulff, *Powder Metallurgy.* Am. Soc. Metals, Cleveland, 1942, p. 36.

[95] G. Grube and H. Schlecht, *Z. Elektrochem., 44,* 367 (1938).

[96] M. Yu. Bal'shin, *Vestnik Metalloprom., 16,* No. 18, 82 (1936).

[97] C. J. Bier and J. R. O'Keefe, *Trans. Am. Inst. Mining Met. Engrs., 161,* 596 (1945).

lographic transformations produce normal volume changes in loose powders as well as in compacts; these changes are modified by the density changes connected with sintering during the temperature rise.[98,99] The volume changes caused by crystallographic transformations alter the density permanently, as observed on iron sintered just above 900°C. (1650°F.), which exhibits a large decrease in density that is undiminished after cooling.[99,100] The decrease in density produced during sintering at or near the recrystallization temperature is associated with an increase in volume; for powders of similar particle size distribution, the expansion is greater the lower the apparent density of the powder[101]; for powders of dissimilar particle sizes, the expansion is greater the coarser the powder.[96] When expansion occurs throughout the entire temperature range of sintering, it may be attributed chiefly to the effects produced by the evolution of dissolved or occluded gases, sometimes in conjunction with the furnace atmosphere. Repulsive forces disrupting the sinter bonds have been advanced as another possible explanation.[102] Relief of stresses set up during compaction is also believed to be an important cause of expansion.[102a]

Temperature Effects on Properties. With initial increases in temperature, *i.e.*, up to 200°C. (400°F.), there are first indications of an increase in the adhesion between loose powder particles as well as in the strength of compacts for all metals except the refractory type,[92,95,103,104,104a] despite the frequently observed decrease in density.[96,105] The observation that loose powders of various metals, including zinc, copper, and iron, all begin to show strong adhesive tendencies within the same narrow temperature range of 140–148°C. (284–298°F.) indicates that this effect is caused by a factor not closely connected with the melting point and other characteristics of the individual metal, but rather with a more independent factor such as the evolution of adsorbed gases.[103] Other properties such as hardness and electrical conductivity have also been found to increase with temperature, up to 200°C. (400°F.),[92,95] and this effect has been found unaltered by the degree of

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[98] P. R. Kalischer, *Symposium on Powder Metallurgy*. ASTM, Philadelphia, 1943, p. 31.

[99] J. Libsch, R. Volterra, and J. Wulff, in J. Wulff, *Powder Metallurgy*. Am. Soc. Metals, Cleveland, 1942, p. 379.

[100] F. Sauerwald, *Metallwirtschaft, 20,* 649, 671 (1941).

[101] J. E. Drapeau, Jr., in J. Wulff, *Powder Metallurgy*. Am. Soc. Metals, Cleveland, 1942, p. 323.

[102] M. Yu. Bal'shin, *Vestnik Metalloprom., 16,* No. 17, 87 (1936).

[102a] R. Kamm, M. A. Steinberg, and J. Wulff, *Trans. Am. Inst. Mining Met. Engrs., 180,* 694 (1949).

[103] G. Tammann and Q. A. Mansuri, *Z. anorg. allgem. Chem., 126,* 119 (1923).

[104] B. Garre, *Z. anorg. allgem. Chem., 161,* 152 (1927).

[104a] G. Durst, *Metal Progress, 51,* No. 1, 97 (1947).

[105] J. Hampel, *Z. Elektrochem., 48,* 82 (1942).

previous cold working of the powder.[96] As far as the second decrease in density associated with the recrystallization temperature is concerned, this may be accompanied by a reduction in cohesive strength of the compact. Generally speaking, the physical properties, particularly strength and ductility, are benefited by an increasing temperature, with the exception of hardness, which decreases at the recrystallization temperature because of recovery from work hardening. Sintering at very high temperatures, approaching the melting point, may impart to the compact physical properties not very different from those of the massive metal.

Time Effect on Structure. For a constant temperature the rate of sintering is most rapid at the beginning, but proceeds at a decreasing rate[85,97,101,106]; the progress of sintering, however, is not always regular. With increasing time, structural changes can be observed in the powder compact provided that the temperature reaches a level at which recrystallization can take place. At higher temperatures, grain growth proceeds with time.

Time Effect on Density. Experimental evidence points to a general increase in density with time for any given temperature,[101,106] except initially, when a temporary decrease in density may occur. The effect of time appears to be more pronounced at low temperatures of sintering than at high. Frequently, a saturation value is reached: in iron compacts sintered at low temperature, this value is in the order of several hours, but is considerably less if the sintering temperature is higher.[99]

Time Effect on Volume. Following the changes in density with time, the volume undergoes corresponding changes. Often, an initial period of expansion precedes a period of marked shrinkage; finally, another period of expansion may follow.[101]

Time Effects on Properties. The physical properties are not regularly affected by the rate of sintering. For sintering temperatures coinciding with the recrystallization temperature, strength and ductility increase with time until a saturation value is reached. For higher sintering temperatures the strength does not necessarily increase with time; depending upon whether the shrinkage or grain growth factor is predominant, the strength may either increase or decrease.[100] Ductility, however, does increase steadily with time even for very high temperatures. Hardness, after an initial drop due to recovery of the structure, reaches a constant value irrespective of the level of temperature. Electrical conductivity increases with time in accordance with the changes in density and grain size.[95]

Effect of Initial Pressure on Consolidation. Sintering proceeds

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[106] F. C. Kelley, in J. Wulff, *Powder Metallurgy*. Am. Soc. Metals, Cleveland, 1942, p. 60.

in loose powders without the application of pressure beyond that exerted by gravity,[75,100,107] and its rate is more rapid the finer the powder[108]; but it is generally proceeding at a slower rate than that of compressed powder compacts. Work hardening of the powder produces sintering at a slightly accelerated rate. Although, in general, the work hardening of a powder by previous milling appears to be more effective than that caused by compaction,[102] the sintering rate may serve as an indication of the degree of work hardening during pressing[102,108]; another criterion for work hardening would be a lowering of the temperature of recrystallization.[109,110]

Effect of Initial Pressure on Density and Physical Properties. With constant sintering conditions the density and associated physical properties increase with rising compacting pressure up to a certain limit[86,95]; beyond this pressure limit the density and associated properties may decline.[92,100,102,106,111] Irrespective of the pressure applied, compacts pressed from different types of powders of the same metal sinter to the same density if they are initially pressed to the same density[102]; on the other hand, when compacted at the same pressure, the density increase during sintering is greater the lower the initial density of the compact,[102] especially in the case of the softer metals.[92,100,106] The decrease in density for high compacting pressures may be attributed to degassing effects, and also possibly to phase changes and stresses arising from thermal gradients.[111a] The latter may be expected to be particularly pronounced in the axial direction, where relief of residual stresses due to the initial pressing operation may cause axial expansion. Moreover, the radial stresses at the top and bottom of a compact being practically zero, the longitudinal stresses on the side wall are tension stresses and vary from top to bottom[111b] (for iron, they are approximately one half as great in magnitude as the yield point of solid iron), meaning that the center of the compact is in compression.[111c] Consequently, on heating, the surfaces are first relieved of stress, and in time, the residual compressive stresses expand the compact—a process that may lead to bursting of the compact if the rate of heating exceeds a critical value. Swelling due to an expansion

[107] L. Schlecht, W. Schubardt, and F. Duftschmid, *Z. Elektrochem.*, *37*, 485 (1931).

[108] L. Delisle, *Trans. Electrochem. Soc.*, *85*, 135 (1944).

[109] C. J. Smithells, W. R. Pitkin, and J. W. Avery, *J. Inst. Metals*, *38*, 85 (1927).

[110] W. Dawihl, *Stahl u. Eisen*, *61*, 909 (1941).

[111] J. Groom and W. D. Jones, *Metal Ind., London*, *52*, 131 (1938).

[111a] P. Duwez and H. E. Martens, *Trans. Am. Inst. Mining Met. Engrs.*, *175*, 848 (1948).

[111b] J. Wulff, *Trans. Am. Inst. Mining Met. Engrs.*, *166*, 504 (1946).

[111c] R. Kamm, M. A. Steinberg, and J. Wulff, *Trans. Am. Inst. Mining Met. Engrs.*, *180*, 694 (1949).

of gases trapped during pressing may be considered superimposed on the axial expansion.[111c]

Effect of Simultaneous Pressure and Temperature. The simultaneous application of pressure and heat produces a denser and stronger compact than is obtained when the same pressure and temperature are applied successively[89,90,112]; but densities approach the theoretical limit only when relatively high pressures are used at temperatures within the normal hot-working range.[112-114] Below the recrystallization temperature the effects of hot pressing are insignificant.[115] Hot-pressed compacts that are sintered undergo less volume changes than do compacts initially pressed at room temperature.[112]

Effect of Successive Pressure. The density and associated physical properties are improved substantially by repressing after sintering and a subsequent resintering treatment may produce densities and properties closely approaching normal values; for example, copper treated in this way can attain the properties of the wrought metal.[116] Cold and hot working of the compact subsequent to sintering further improves the quality of the metal whose density may approach the theoretical maximum value.[117,118]

Effect of Solid Foreign Substances. In general, foreign solid matter tends to impede sintering,[83] regardless of whether composed of oxides, other impurities, or addition elements. But on the whole the interference of oxide films with sintering is less serious than usually assumed, primarily due to the reducing capacity of the sintering atmosphere.[75] Only when the oxides resist ready reduction by the furnace atmosphere, as in the cases of Al_2O_3, MgO, etc., do they constitute serious obstacles to sintering and may cause a depreciation in strength and density of the compact. On the other hand, it has been observed in cases where less stable oxides are found that substantial sintering and consolidation of the compact can be achieved by sintering or hot-pressing in air,[119] especially in the case of certain noble metals.[115] Oxide inclusions contained within the powder particles are reduced less readily by the sintering atmosphere than are films; their reduction requires higher temperatures or higher gas pressures, and frequently is accomplished only at the expense of

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[112] C. G. Goetzel, *Trans. Am. Soc. Metals, 28,* 909 (1940).

[113] C. G. Goetzel, *Trans. Am. Soc. Metals, 30,* 86 (1942).

[114] C. G. Goetzel, *Trans. Am. Inst. Mining Met. Engrs., 161,* 580 (1945).

[115] F. R. Hensel and E. I. Larsen, *ibid., 161,* 569 (1945).

[116] C. G. Goetzel, *J. Inst. Metals, 66,* 319 (1940).

[117] C. G. Goetzel, *Wire and Wire Products, 16,* 217, 274 (1941); *18,* 329, 394, 457 (1943).

[118] J. Tyssowski, *Trans. Am. Inst. Mining Met. Engrs., 143,* 335 (1941).

[119] W. D. Jones, *Metal Ind., London, 56,* 69, 225 (1940).

losing the sinter bonds formed earlier; as a result, the compact expands during the late stages of sintering.[120]

Effect of Gaseous Foreign Substances. The evolution of adsorbed and absorbed gases as found in the atmosphere, but notably oxygen in combined form,[81] causes serious interferences with sintering by disrupting the bonds and expanding the entire structure.[73,86,92,94,105,120] The rate of gas evolution under vacuum, already substantial at room temperature,[81,121] is further increased with temperature and becomes very high at the recrystallization temperature.[121] By sintering copper in vacuum, higher density can be obtained than by sintering in hydrogen,[100,122] in spite of the frequent development of an intertwined pore pattern as a result of the escape of trapped gas at a late stage of sintering.[122] The release of gases has generally been held as the main factor contributing to the growth of compacts during sintering.[92,94,105,115,120] However, gases may also affect the metal powder compacts in other ways, such as by changing the rate of grain growth in tungsten.[109]

Effects of Sintering on Grain Structure. The temperature of recrystallization is lower the greater the degree of cold work imparted to the powder by milling or compaction[86,100,109,110,123]; in other words, annealed powders, loose or pressed, tend to exhibit a higher recrystallization temperature than do milled or otherwise work-hardened powders. Since cold work in compacted powders is concentrated at the interparticle contact points, it is reasonable to assume that recrystallization first occurs in the interparticle boundary areas; this phenomenon is believed responsible for the moving of the recrystallized grain boundaries away from the interparticle boundary, as observed quite generally in all metals. After sintering at a high temperature, grain growth occurs across the original interparticle boundary.[75,100] This effect has been observed even with loose powders that have not been in a cold-worked condition; it is not believed to be necessarily the result of recrystallization.[100] The temperature of rapid spontaneous grain growth, in contrast to that of recrystallization, has been observed to be independent of the degree of preliminary cold working of the powder at approximately two-thirds to three-quarters of the absolute melting temperature of the metal.[86,100,124,125] Grain growth may be impeded by such factors as impurities or porosity. The ultimate grain size is also affected by the size of the initial particles, with

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[120] C. W. Balke, *Symposium on Powder Metallurgy*. A.S.T.M., Philadelphia, 1943, p. 11.

[121] G. Tammann, *Z. anorg. allgem. Chem.*, *114*, 278 (1920).

[122] C. G. Goetzel, *Metals & Alloys*, *12*, No. 1, 30 (1940); *12*, No. 2, 154 (1940).

[123] F. Sauerwald and R. Holub, *Z. Elektrochem.*, *39*, 750 (1933).

[124] F. Sauerwald, *Z. anorg. allgem. Chem.*, *122*, 277 (1922).

[125] F. Sauerwald, *Z. Metallkunde*, *16*, 41 (1924).

the coarser powders yielding finer grain sizes in such metals as tungsten and iron[99,102,126]; this effect is attributed to a lower temperature at which recrystallization occurs in fine powders[100] that are believed to be more severely deformed during compaction; it is also possible that grain growth proceeds at an accelerated rate in compacts from fine powders.[109]

Effects of Sintering on Pore Structure. Extended sintering periods or high temperatures promote a change in the shape of pores from an angular to a spherical form,[97,105] similar to a spheroidizing of solid impurities such as irreducible oxides. Extended sintering times at high temperatures cause shrinkage in size of the individual pores and may even lead to complete disappearance of the pores; small pores appear to reduce in size faster than larger voids. The shape of the pores formed during pressing of plastic metals (*e.g.*, copper) is believed responsible for a pronounced radial shrinkage of cylindrical compacts.[111c] After pressing, the pores are all lenticular, with their minor axis in the direction of pressing. These pores tend to widen in the pressing direction at the expense of shrinkage in the radial direction, when relief of internal stresses or gas causes expansion in the axial direction. At the same time, the greater curvature still in existence at the periphery of the expanded lenticular pores results in a more rapid rate of sintering and shrinkage in the radial direction.

Effects of Sintering on Physical Properties. The strength of a compact as tested in a tensile, compressive, or bend test increases together with the density up to a temperature at which rapid grain growth becomes apparent; for higher temperatures the strength either decreases or increases, depending on which of the opposing factors of grain growth and shrinkage is predominant.[86,100,127,128] All of the lower melting metals exhibit a decrease in strength which is attributed to grain growth; in iron this decrease is observed directly below the point of alpha–gamma transformation.[128] The ductility of a compact as measured by the tensile elongation tends to increase with sintering at a much slower rate than other mechanical properties; it continues to show an increase with time at a given sintering temperature after the other properties have approached saturation values.[99] The slow improvement of the ductility has been attributed to its greater sensitivity to shapes and sizes of pores which function as centers of stress concentration.[129] The hardness increases only insignificantly at the early stages of sintering, except in hot-pressed compacts[112-114] in which values can be reached in excess of those

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[126] W. P. Sykes, *Metal Progress*, *25*, No. 3, 24 (1934).

[127] F. Sauerwald and E. Jaenichen, *Z. Elektrochem.*, *30*, 175 (1924).

[128] W. Eilender and R. Schwalbe, *Arch. Eisenhüttenw.*, *13*, 267 (1939).

[129] P. Schwarzkopf, *Powder Metallurgy.* Macmillan, New York, 1947, p. 294 ff.

observed in the cold-worked massive metal. With the onset of recovery and recrystallization, the hardness falls rapidly to normal values. Hardness and tensile strength do not regularly coincide in their course as is the case in most massive metals, and hardness is the only mechanical property that can reach values exceeding those in other forms of the same metal[73] with the exception made by the refractory metals tungsten, tantalum, and molybdenum, in which the wrought sintered metal is stronger than the fused metal.[120] Changes in electrical conductivity appear to follow closely those that the density undergoes during progressive sintering.[73]

Composite Theory of the Mechanism of Bonding and Sintering

Rhines[130] has successfully combined in a composite theory a number of theories of bonding and sintering which individually have covered only part of the experimental observations cited. In this composite theory all factors have been included that are beyond dispute and some that are still controversial. The inclusion of the latter factors was deemed necessary to give the composite theory a logical construction. In view of its excellent reasoning and completeness, the essential points of Rhines' presentation are given in the following section.

THE INITIAL BOND

At room temperature a certain initial bond exists between adjacent particles in a loosely heaped metal powder. This bond appears spontaneously at the points of metal-to-metal contact. It is of the same kind as the cohesive forces that fix the atoms in certain positions in a metal crystal and are responsible for the strength of solid metals. It is also the same kind of bond that exists in sintered metals, except that it is of a different order of magnitude due to the comparatively small total area of interparticle contacts and possible distortions of the crystal lattice in the vicinity of the contact points.

If clean surfaces are brought into close contact, cold-welding phenomena can be observed with little or no external pressure applied. Because the surfaces of most metal powder particles are rough on a microscale, contact may be established at only a few isolated points. Therefore, the cold-welding bonds must by necessity be small in their total effect. Whereas a rise in temperature, especially if it leads to melting of the surface regions, tends to increase the strength of the bond, this is by no means a prerequisite for the establishment of the bond. Any type of foreign phase, either in the form of solid films of oxides on the particle surfaces or in the form of surface layers containing adsorbed gases, reduces

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[130] F. N. Rhines, *Trans. Am. Inst. Mining Met. Engrs., 166,* **474** **(1946).**

the effectiveness of the bond, since it constitutes interference with the metal-to-metal contacts.

THE INCREASE OF THE BOND DURING COMPACTION

Compaction of the metal powder by applying pressure increases the bond by increasing the number of contact points between adjacent metal surfaces as well as by enlarging the individual areas of contact. The externally applied pressure promotes a closer packing of the particles, partly by redistribution of the different sizes and partly by plastic deformation in the direction of increasing the conformity of opposing surfaces. The deformation and abrasion of the surfaces during compaction may also increase the number of interparticle contact points by causing the rupture or dislocation of interfering surface films of oxides, adsorbed gases, and other foreign matter.

The increase in the number and size of the areas of contact permitting cold-welding bonds becomes evident in the increased strength of the molded powder compact with rising compacting pressure. In accordance with the decrease or increase of the number and size of the contact areas as controlled by the plastic deformability of the metal at the particular pressure and temperature conditions, the bonding effects caused by pressure are lessened at subnormal temperatures and enhanced at elevated temperatures. For the same reason they are also diminished in powders consisting of hard particles and increased in those consisting of soft particles. The strength of the bond is also affected by the size and shape of the powder particles through their effects on the total surface area, their plastic deformability, and their ability to align themselves in such a way as to produce greatest conformity of opposing surfaces. A rearrangement of the particles toward greater conformity of adjacent surfaces is also assisted by lubricants—with denser and stronger compacts resulting.

THE INCREASE OF THE BOND DURING HEATING

Heating of the metal powder increases the bond through lateral growth of the initial contact areas or points. This enlargement of the contact sites is accomplished by a transfer of metal which is obtained through the action of plastic flow or of surface diffusion or of both acting in concert under the influence of the energy of surface tension as the major driving force. The transfer of metal proceeds more rapidly the narrower the space adjacent to the contact points. The deep crevices and sharp angles in these regions coincide with areas of greatest surface curvatures at which surface tension forces would reach their greatest intensity and thus act most effectively toward leveling the curvature. Surface diffusion will result in a transfer of metal from adjacent regions into the crevices, and plastic flow in an enlargement of the areas of conformity through mutual abutting. The actions of surface diffusion and plastic motion are more impeded the larger the size of the voids, the greater the gas pressure in the pores, and the heavier the layers of interfering foreign substances. With rising temperature either action intensifies at an accelerated rate, while the rate is diminishing with time. Above a certain temperature level, bonding will become so pronounced that it becomes obvious on a macroscale; it is then commonly referred to as sintering in its narrow, technical sense.

The described mechanism of growth of the bond area is consistent with the increased rate of shrinkage and the increase of density generally observed with rising sintering temperature; the described action of surface diffusion and plastic flow is in agreement with observations of pronounced sintering as expressed by grain growth and similar signs of atomic movements; and the described mechanism actuated by surface tension forces is supported by the observations at high temperatures of the spheroidization of individual metal particles. The reasoning that sinter bonds are established without additional pressure beyond that necessary to produce some initial metal-to-metal contact points is borne out by the common experience that loose powders sinter to coherent masses at elevated temperatures. The statement that the transfer of metal to the contact regions is facilitated by a diminishing size of the voids is in agreement with the general observation that the sintering process is accelerated by the initial application of pressure, by repressing and resintering, or by hot-pressing. The fact that diffusion rates are increased by cold work is a logical explanation for the observation that cold-worked powders undergo an accelerated sintering process. The progressive reduction of surface tension forces with a rounding of the sharp angles in pores explains the decrease in the rate of sintering with time. The impeding of diffusion and plastic flow through interfering foreign substances is consistent with the common experience of a retarded sintering of powders exhibiting particles with oxide films or high pressure gas inclusions.

REACTIONS DURING HEATING

The mechanism of sintering so far described takes into account only a reduction of the powder volume; increase in volume must be explained by processes not directly connected with bonding and sintering. The action of gas pressure appears to be one of the major causes for the expansion of the compacted powder mass. At low sintering temperatures gases initially adsorbed on the surfaces of the particles are liberated and build up an increasing gas pressure; at the same time, the pressure of gases trapped in between the particles during the initial compaction is also increased. With rising temperature this action causes a steady expansion of the interparticle interstices until escape corridors are opened for the gases at the expense of the continuity of the bonding surfaces. At higher temperatures, similar effects are produced by gaseous reaction products originating from the reduction of surface oxide films or by gases initially dissolved by the metal particles and now given up due to a reduced solubility. At very high temperatures, growth of the compact may be exaggerated if extensive plastic flow has sealed the channels connecting the pores, especially in the case of those gases which do not diffuse rapidly through the metal. In such an event a marked increase of the gas pressure results that is relieved only by spontaneous expansion of the interparticle interstices. The formation of blisters on the surface of the compact is another frequent symptom of this effect. Other possible causes of swelling of a compact include stresses caused by irregular relief of work-hardening stresses imparted to the particles during milling or compaction, stresses introduced by the irregular occurrence of crystallographic transformations, and stresses introduced by irregular temperature changes.

Because of their exceedingly large total surface, powders exposed to the atmosphere always contain on their particle surfaces very considerable quantities of adsorbed gases and also gases combined with the metal in the form of oxides or other compounds. Therefore, at elevated temperatures the volume of gases directly released or produced by reaction with reducing agents is also very considerable. The interference of this action with the sintering process is evidenced by pronounced expansion under circumstances which under gas-free conditions should favor rapid sealing of the interconnected pore pattern, as, for instance, when very high initial pressures were used, when sintering is conducted at the highest temperatures, and when sintering is allowed to proceed over very long periods of time. These expansion processes are assisted by the tendency of the pores to spheroidize with progressive sintering, whereby the connecting channels are sealed off, and by the reluctance of compact oxide inclusions in the interior of the particles to reduce completely at the early stages of sintering, thus providing a potential source of reaction gases until the sintering process is far advanced.

STRUCTURAL CHANGES DURING HEATING

In metal powder compacts, recovery, recrystallization, and grain growth proceed in a manner that differs from normal only in degree due to the effects of the special geometrical factors inherent in the powder material. After compaction the particles are most severely cold-worked on their surfaces at points of metal-to-metal contact at which plastic deformation has taken place. Therefore, recovery and nucleation will begin in favored locations near the points of particle contact, resulting in the formation of recrystallized grains common to two adjacent particle surface regions which will grow across the original particle interfaces, and also resulting in an uneven relief of the stresses imparted in the particles. The initial powder particle size influences the amount of interparticle surface area that can become effective and also the range of cold working from the surface to the core of the particle. The shape of the particles and the characteristics of the metal have similar effects. The rate of grain growth remains small until sintering has progressed sufficiently to form substantial junctions between the particles; then grains larger than the original particles may develop, but rapid grain growth, common in solid metals at high temperatures, is impeded by the network of voids. Although apparently coincident with the temperature of rapid sintering, that of spontaneous grain growth should not be influenced by preceding cold work whose effects are eliminated at considerably lower temperatures. The rate of grain growth is influenced by the compacting pressure only to the extent that sintering can progress at an accelerated pace in more densely compacted powders. In the advanced stage of the sintering process a bulk diffusion of metal takes place from the exterior surface of the compact or loose powder mass into the spheroidized pores. The driving force for the metal transport toward the pore is derived from the difference between the low surface tension energy of the exterior surface having a small curvature and the high surface energy of the pore having a sharper curvature. Accordingly, those pores located near the surfaces of the compact may be closed before those of the center; also, small pores having the highest surface energy will be sealed at a more rapid rate than larger pores. With progressive sintering, unreduced oxides and other foreign solid inclusion will tend to spheroidize in a manner similar to that for the pores.

The temperature of recrystallization is sensitive to pressing conditions, but the temperature of rapid grain growth is not. It usually coincides with the temperature of rapid sintering; but this temperature is generally above the temperature of rapid grain growth observed in massive metals. The influence of particle size on the final grain size is evidenced by the observation that for tungsten large grains develop from fine powders and small grains from coarse powders; in the case of the fine powders with their correspondingly small interparticle voids, the pores are closed earlier, thus restricting the rate of nucleation and promoting the growth of the resulting fewer grains. The process of more rapid sealing of the pores in the surface regions of the compact is corroborated by a common experience with inflated compacts in which gases contained within pores in the core region are trapped by the hermetic enclosure of the surface, giving cause for considerable gas pressures.

PROPERTY CHANGES DURING HEATING

The changes in physical properties of metal powder compacts during sintering are directly associated with the structural changes described. Therefore, they do not fall within the actual scope of a theory of the mechanism of bonding and sintering but rather serve as supporting evidence for the processes treated. They have been discussed as such earlier.

THEORETICAL CONCEPTS OF SINTERING ALLOYS

The Diffusion-Controlled Mechanism of Sintering

Since the mechanism by which alloying proceeds during sintering is primarily that of diffusion, a brief consideration of the underlying principles appears to be in order. The processes of diffusion involve the transport of atoms or molecules from points of high concentration to points of lower concentration, with the concentration gradient determining the driving force for the movement of the material. Diffusion can occur between substances in like or unlike states of aggregation: gases can diffuse into gases, into liquids, or into solids; liquids can diffuse into liquids or solids; and solids can diffuse into solids. In the sintering operation, gas-to-gas and liquid-to-liquid diffusions play no part. Gas-to-liquid and liquid-to-solid diffusions, however, are of considerable interest when sintering of alloys takes place in the presence of a liquid phase. The diffusion of gases into solids is of major importance for the sintering of both metals and alloys. The diffusion in the solid state constitutes one of the principal processes on which the mechanism of sintering of pure metals and of alloys is based.

DIFFUSION OF GASES

The important role played by the diffusion of gases into solids has already been discussed in the preceding section. The processes of gas diffusion in metals has been the subject of intensive study,[181] especially in view of finding means of degassing the metals in the solid state.[182] The laws governing these processes are essentially the same in the case of sintering metal powder compacts, except that conditions are consider-

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[181] F. N. Rhines, *Trans. Am. Inst. Mining Met. Engrs., 156,* 335 (1944).
[182] F. J. Norton and A. L. Marshall, *ibid., 156,* 351 (1944).

ably exaggerated by the enormously large total surface area of the particles, which gives rise to more widespread contact between the gas molecules and the metal. Therefore, sorption energies and free energies involving chemical reactions such as those of the reducing furnace atmosphere with oxide films on the particle surfaces constitute important factors in addition to the diffusion coefficient.

The diffusion of gases into liquid metals, although proceeding at a more accelerated rate, is of importance only as far as the degassing of the metal during solidification and cooling is concerned. In the sintering of alloy systems in the presence of a liquid metal phase, gas diffusion is more pronounced the larger the concentration of the liquid phase, the higher the sintering temperature above the melting point of the liquid phase, and the longer the time during which the liquid phase is exposed to the gas. Thus, alloy compacts containing a minor proportion of a liquid phase of transitory character, which solidifies with progressing sintering by diffusion into the major solid constituent, will suffer less gassing than compacts that retain the liquid phase over a large temperature range throughout the sintering operation, until advanced cooling causes solidification of the liquid phase.

DIFFUSION IN THE SOLID STATE

The process of diffusion in the solid state is based on a material transport at a certain temperature level. The atomic migration follows either one of these mechanisms: atoms of a foreign metal may change places with atoms in the lattice of the base metal; they may diffuse through interstices in the lattice of the base metal; they may diffuse by way of unoccupied positions in the lattice of the base metal.[133] Although all of these mechanisms are possible, the last, which may be considered as vacancy migration because the unoccupied positions constantly change place, is the most likely if vacancies are present in the crystal lattice.[134]

The process of alloy formation by diffusion of metals in the solid state is based on the tendency of the structure to attain an equilibrium of concentrations. According to Fick's fundamental law of diffusion, the diffusion coefficient is dependent upon the concentration gradient; it is an exponential function of the absolute temperature, thus causing the diffusion to increase at an accelerated rate with temperature. Accordingly, the rate of diffusion of one metal into the lattice of another metal is higher the closer the temperature approaches the melting point of the first metal. In a binary system the metal of lower melting point will diffuse more rapidly at a given temperature.

[133] F. Seitz, *Physics of Metals*. McGraw-Hill, New York, 1943, p. 183.

[134] H. B. Huntington and F. Seitz, *Phys. Revs., 61,* 315 (1942).

As far as the diffusion of metal powders during sintering is concerned, the same laws apply. However, the process is usually accelerated by the greater difference in concentration between neighboring particles of different metals. On the other hand, the diffusion rates may also be impeded by such adverse factors as interparticle voids and solid stable films of impurities. Moreover, in the reactions between the solid particles not only the quantity of the involved surfaces (surface contact areas) but also their quality (surface activity) are of great significance. A relative maximum of reactivity is found in a material when it is in a state of transformation or uncompleted structural development. According to Hedvall,[185] the reactivity *in statu nascendi* plays an even more pronounced role in solids than in liquids or gases. (Solid solutions of cobalt and nickel, for instance, are prepared best and most rapidly by reducing a mixture of the respective oxides in a stream of hydrogen, *i.e.*, under conditions that permit the interaction of the metals *in statu nascendi.*) In general, high reactivity of the surfaces is observed in the temperature range of thermal transformations, but changes in magnetic, electrical, and irradiation conditions, or exposure to ultrasonic waves. also have positive effects.

DIFFUSION IN THE PRESENCE OF A LIQUID METAL PHASE

Since all crystal lattices break down at the melting point and the atoms become unbound, diffusion rates in liquid metals are considerably more rapid than those involving metals in the solid state; in fact, they are of an altogether different order of magnitude. In alloying fused metals, a state of equilibrium is obtained readily by such simple means as stirring or high-frequency induction currents. However, the sintering process by definition can endure a liquid metal only along with a solid constituent that must be sufficiently potent to permit retaining the shape of the compact at the temperature at which sintering takes place. Therefore, the solid phase must be predominant in proportion and must possess a melting point considerably above the sintering temperature; conversely, the liquid phase must only be a minor constituent which functions as a cement. The degree of increased diffusion obtained by sintering in the presence of a liquid phase depends upon a number of variables, such as the intimacy of contact as obtained by the process of wetting the solid surfaces by the liquid metal, the rate of solubility of the solid metal particles (especially of the smaller sizes) in the liquid phase, the presence of gaseous or solid foreign substances that interfere with a direct contact

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[185] J. A. Hedvall, *Arch. Metallkunde, 1,* No. 7/8, 296 (1947); *International Powder Metallurgy Conference,* Graz, July 12–17, 1948, Referate No. 48.

of the metal phases, and the rate at which these interfering substances can be dissolved by the liquid metal.

The Sintering of Homogeneous Alloy Systems

Alloying during sintering can be achieved by two principal methods: (*1*) the use of alloy powders in which each individual particle consists of the desired alloy concentration and (*2*) the sintering of mixtures of the metal powders or of master alloy powders in the proportion required by the desired alloy composition. The use of alloy or master alloy powders obtained by a preliminary fusion process or a diffusion treatment in the solid state is most advantageously applied when long periods and high temperatures are required for complete diffusion of the alloying ingredients. However, these powders are generally characterized by a reduced plasticity which results in poor compactibility. For this reason, the sintering of alloys from mechanically mixed pure metal powders is preferable in many processes and is the method most commonly used. Often, for practical reasons, the diffusion process is not carried out to a state of complete equilibrium; it is materially advanced when a liquid phase is generated during the sintering operation.

THE PROCESS OF HOMOGENIZATION

During sintering of compacts from mixed metal powders the rate of homogenization of the structure depends, according to Rhines and Colton,[136] upon the particle size, which determines the distances between maximum and minimum concentrations. The rate of alloying is, according to Rhines,[137] inversely proportional to the square of the distance between unlike centers of particles or domains; for example, if the average diameter of the particles is doubled for a given powder mixture, it will take four times as long at the same temperature to achieve the same extent of alloying. The rate is also sensitive to the composition of the powder mixture, reaching its highest value at a 50–50 ratio of the components.[138]

Rhines and Colton[136] have proved mathematically the commonly experienced fact that in a mixture of given proportions homogenization is attained most rapidly when particles of the minor constituent have a smaller size distribution. Also, it can be expected generally that the minor component of a binary powder mixture will alloy more rapidly

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[136] F. N. Rhines and R. A. Colton, in J. Wulff, *Powder Metallurgy.* Am. Soc. Metals, Cleveland, 1942, p. 67.

[137] F. N. Rhines, communication on "Principles of Sintering," *Powder Metallurgy Colloquium,* New York University, May 24, 1946.

[138] F. N. Rhines, *Powder Met. Bull.,* *3,* No. 2, 28 (1948).

than the major constituent. During the diffusion process, layers of different concentration will form envelopes around the particles of the minor constituent.

The actual rate of alloying in powder mixtures cannot be determined in general despite the fact that diffusion coefficients have been measured for many metal combinations. But it is known that the rate always increases at an accelerating pace with rise in temperature. Most diffusion-controlled processes follow the rule of doubling their rates for every increment in temperature of 10°C. up to the melting point, when a very large increase in the rate occurs.[137] A mathematical approach, wherein the distribution of metallic powder in a given space is expressed by means of a triple series—which is used to obtain the solution of the diffusion equation—has recently been given by Weinbaum.[138a] The expressions obtained for the concentration of individual metals in certain binary alloys prepared by sintering give concentration as a function of space, time, temperature, and particle size. At least in one instance, namely, a copper–nickel alloy in a one-to-one atomic proportion, it was possible to establish a general agreement between sample calculations and experimental data.

The process of homogenization has been analyzed by Rhines and his coworkers for one binary alloy system of continuous solubility (copper–nickel)[136,139] and for two binary systems of partial solubility (copper–zinc and copper–tin).[137,138] The first instance represents one of the simplest cases of alloy sintering possible. But even under these simple conditions the course of homogenization could not be mathematically determined on the basis of the laws of diffusion. Apparently the geometry of the boundaries is already too complex to permit a mathematical treatment. The boundaries, and especially gas films contained therein, tend to reduce the rate of homogenization to an unpredictable degree, and complete homogenization frequently requires the elimination of all gas content in the compact.

If the alloying process involves a binary system in which compounds as well as solid solutions can be formed by the two metal components, an even more complicated diffusion and homogenization process results. If the mixture is held for some time at a temperature below the melting point of the low melting constituent, a number of intermediate layers corresponding to the number of intermediate single phases stable in the alloy system at that particular temperature will form at the contact surfaces between the particles of the two metals. All compositions rep-

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[138a] S. Weinbaum, *J. Applied Phys., 19,* 897 (1948).

[139] F. N. Rhines and R. A. Meussner, *Symposium on Powder Metallurgy.* A.S.T.M., Philadelphia, 1943, p. 25.

resented in one-phase regions of the constitutional diagram at the diffusion temperature will appear in these layers and in the order given by the phase diagram. With progressing diffusion the intermediate layers grow at the expense of the pure metal phases in the interior of the particles until the metal of minor proportion is completely absorbed by the alloy phases, and eventually the equilibrium phase encompasses the entire structure.

In studies of the formation of powdered binary copper alloys with nickel, zinc, and tin by diffusion sintering, Duwez[140,140a] could essentially confirm the aforementioned theory. With the aid of thermal expansion measurements during heating and x-ray diffraction patterns the structure of these alloys was determined, and the homogenization followed. In accordance with the constitution of the alloy system (copper–zinc and copper–tin) most phases noted could be explained by the equilibrium diagram. Diffusion of zinc—and to a lesser extent of tin—into the copper was found accompanied by unusual expansions (similar to observations made by the same investigator with the diffusion of silicon into tungsten, molybdenum, and other powders).

The observation that when intermediate phases are present in the constitution diagram of two metals some of these phases may form during sintering was confirmed by Duwez[140b] for the copper–gold system, where below a certain temperature range an intermediate phase is in pseudo-equilibrium with one of the two constituents and the rate of further homogenization at the temperature becomes negligible. It was found that in compacts containing 25 atom per cent of gold ($AuCu_3$) the ordered AuCu phase forms first, and at a temperature of 315°C. (600°F.) the system comes to a pseudo-equilibrium between AuCu and copper. In order to reactivate the diffusion process and carry on the homogenization, it was found necessary to increase the temperature above the critical temperature of the order–disorder transformation of AuCu (424°C.; 795°F.).

The diffusion of carbon in sintered steels was recently studied by Seith,[141] who found that the diffusion constant of carbon in steel is reduced and diffusion impeded by a number of alloying elements, in the following order of effectiveness: cobalt, nickel, manganese, copper, tungs-

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[140] P. Duwez, *Proc. International Powder Metallurgy Conference,* Graz, July 12–17, 1948, Referate No. 69.

[140a] P. Duwez and C. B. Jordan, *Trans. Am. Soc. Metals, 41,* 194 (1949); *Powder Met. Bull., 4,* No. 5, 144, No. 6, 168 (1949).

[140b] P. Duwez, communication on "The Sintering of Copper–Gold Alloys," *Symposium on the Physics of Powder Metallurgy,* sponsored by Sylvania Electric Products, Inc., Bayside, L. I., N. Y., August 24–26, 1949.

[141] W. Seith, *Proc. International Powder Metallurgy Conference,* Graz, July 12–17, 1948, Referate No. 7.

ten, silicon, vanadium. With increasing concentrations of cobalt, nickel, or tungsten to the vicinity of the austenitic range, however, the diffusion constant rises again. In general, Seith holds that knowledge of diffusion constants might be useful in estimating sintering times, though no values could be given for the contact surface area, and the increase in the rate of diffusion caused by interrupted contacts. Diffusion generally is believed to proceed faster at the surface than in the interior, and still faster at the grain boundaries.

Basically, the same principles apply if mixtures of more than two components are considered, except that in such case it is more difficult to analyze the process.

If the sintering temperature is raised above the melting point of the lower melting metal, other mechanisms besides diffusion come into play —such as interfacial and surface tension forces. This has lately been emphasized by Lenel[142] in an extensive review of the available information on the processes of sintering homogeneous alloys in the presence of a transitory liquid phase. In support of this view, certain microstructural and density changes are cited which occur during sintering of the commercially important porous bronzes and iron–nickel–aluminum permanent magnet alloys—selected as key examples for the sintering of alloy systems in which the liquid phase forms during the sintering process, but the amount present decreases with time at the sintering temperature or during heating.

THE PROCESS OF INCOMPLETE HOMOGENIZATION

It is apparent that the ultimate structure and, therefore, properties of the sintered alloy depend not only on the composition selected but also on whether alloying is complete, or, if incomplete, at which stage it is stopped. If homogenization is carried through to essential completeness, the structures of the sintered alloys do not differ from those of cast alloys of like crystal lattice, except for grain size. But by controlling the temperature and time of diffusion, many nonequilibrium structures can be produced that are not normally obtainable, and as a result, unique properties may be produced. The relationship between physical properties and metallographic structure in alloys can be expressed by certain rules; the one referring to the continuous phase is most significant:[187] in an alloy structure the properties of that phase which is physically continuous predominate in the over-all properties. Thus, widely differing properties can be obtained by arresting the alloying process at stages at which certain phases are continuous in the sintered metal structure. For ex-

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[142] F. V. Lenel, *Trans. Am. Inst. Mining Met. Engrs., 175,* 878 (1948).

ample, it is possible to produce by a controlled heat treatment in a 70–30 Cu–Ni alloy transient maximum strength, hardness, and electrical resistance values greater than those natural for such alloy, and approaching those normally found in a 50–50 alloy, because there is a time during the treatment when there is a large amount of 50–50 material present in the structure.

In the case of more complex alloys, in which intermediate phases can form, Rhines[138] has not yet advanced to a point where a complete description of the mechanism of homogenization and corresponding changes in properties can be given for any one alloy. Certain preliminary findings, however, are of considerable interest and seem to indicate that laws established for the isomorphous copper–nickel system apply. In copper–zinc mixtures of the 70–30 brass composition heated just below the melting point of zinc (*e.g.*, 400°C.; 750°F.) only the ductile phases copper (alpha) and zinc (eta) are present at the beginning of the treatment. With progressing diffusion, the brittle gamma and epsilon phases appear in increasing quantity, with a logical effect on the physical properties of the alloy (increase in hardness and decrease in elongation). As homogenization advances, the gamma and epsilon phases decrease in amount, while the more ductile beta phase becomes dominant. At this stage the maximum number of five stable phases possible in the system are present simultaneously in the structure. As diffusion continues, alpha replaces beta as the predominant phase, and the alloy eventually converts completely into alpha. The complete homogenization process, however, is very lengthy and has not yet been traced very far.[138] Early results indicate that the changes in the mechanical properties of incompletely homogenized copper–zinc alloys are in accordance with expectations. Copper–tin alloys, on the other hand, are more complex in their constitution, and preliminary studies by Rhines[138] indicate the existence of several cycles of rising and falling properties, presumably corresponding to the transient dominance of one phase after another as diffusion progresses.

In practice, this principle of incompletely homogenizing alloy structures is unwittingly employed in most processes involving alloying from powder mixtures, since complete alloying requires high temperatures and extended periods of time. Sintering is usually interrupted when the desired properties are reached; in certain instances, a careful selection and control of the sintering cycle might yield products of exceptional physical properties that are better or more desirable than those in the completely homogenized alloy.

The Sintering of Heterogeneous Alloy Systems

Generally speaking, the theoretical concepts dealing with heterogeneous alloy systems do not introduce any concepts that are fundamentally different from those discussed for sintered pure metals or homogeneous alloys. Only the fact that the sintering and diffusion process is more complicated in these alloy systems invites a separate treatment of the topic.

SINTERING IN THE ABSENCE OF A LIQUID PHASE

The mechanism of sintering heterogeneous alloy systems without partial liquefaction involves adhesive forces between particles of different metals in addition to the cohesive bonding forces between the particles of the same metal. The degree of solubility of the constituents in each other has a marked effect on the diffusion rates, and mutually insoluble substances exhibit no measurable diffusion. According to Umstätter[143] the solubility may be considered as a harmonizing of molecular vibrations whose amplitude and wavelength increase with temperature, and whose frequency depends upon the surface tension and molecular weight of the respective substances. Thus, it is considered possible that the use of relatively small amounts of capillary-active substances for varying the surface tensions would facilitate adhesion between otherwise nonadhering powder particles.

SINTERING IN THE PRESENCE OF A LIQUID PHASE

If sintering causes the liquefaction of one phase, diffusion processes, such as alloying, and adhesion processes, such as wetting, become more pronounced. This is especially noteworthy for systems that produce a partial solubility of the solid constituents in the liquid phase. In this instance a preferential solution of small particles of the solid component in the liquid phase may be followed upon cooling by a precipitation of the dissolved material on the surface of larger particles, especially near the contact areas. As a result, a strong cementing bond is created between the particles of the main constituent, and the structure becomes of extremely uniform grain size.

Kieffer and Benesovsky,[143a] in an up-to-date review of the mechanism of sintering while introducing the liquid phase through infiltration of porous skeleton bodies, have stressed some of the fundamentals that deviate from those met in the sintering of compacted mixtures of the components. Of special significance appear the understanding and control of reactions that either enhance or inhibit such important processes as wetting, solubility, pore volume filling by capillary action, gas evolution,

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[143] H. Umstätter, *Arch. Metallkunde, 1,* No. 7/8, 299 (1947).

[143a] R. Kieffer and F. Benesovsky, *Berg- u. Hüttenmännische Monatshefte, 94,* N. 8/9, 284 (1949).

and volume- or fluidity-affecting reaction or diffusion processes. Attention is also drawn to the specific nature and pattern of the grain structure—spheroidized skeleton grains, macrodispersion of components, formation of diffusion zones and borders—and their bearing on the effectiveness of solution and precipitation treatments.

Lenel[142] in his comprehensive survey gives prominence to the sintering processes that occur at a temperature between liquidus and solidus of the alloy system, *i.e.*, where the liquid phase is present for the entire time the alloy is at the sintering temperature. Referring especially to the tungsten–nickel–copper ("heavy alloy") and cemented carbide systems, Lenel stresses the importance of diffusion and solubility rates on the structural and density changes that occur during sintering. However, in a subsequent publication dealing with the results of experiments with alloys of the iron–copper system, Lenel[143b] expands his analysis by including other factors such as interfacial and surface tension forces, as possible influences on this type of sintering mechanism.

In this connection, reference is made to the work by Smith[144] on the effects of these two types of forces that are responsible for the particular and varied spatial arrangements of grains and phases that are observed in microstructures. Using a qualitative approach, Smith develops the logical and simple concept that many microstructures result from an attempted approach to equilibrium between phase and grain interfaces whose surface tensions geometrically balance each other at the points and along the lines of contact. In this process the surface contact angle formed between the liquid and a solid surface, together with the relation of the different interfacial tension forces (*e.g.*, solid–liquid interface *vs.* interface between two solid grains), govern the distribution, pattern, and shape of the phases (especially the minor and lowest melting), and have a predominant effect on such phenomena as "wetting" of grains by a liquid metal, and extent of solubility of a solid grain structure in a liquid phase.

The contact angle appears to be of particular significance, too, in connection with the penetration of a molten metal into a solid one of higher melting point. If there is a slight solubility of the solid metal in the liquid, solution will commence and be most rapid at the grain boundaries. If the angle of the liquid against the grain boundary of two solid crystals—designated as the "dihedral" angle Θ—is greater than zero but less than 90° penetration will proceed only until the particular dihedral

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[143b] F. V. Lenel, communication on "Sintering with a Liquid Phase," *Symposium on the Physics of Powder Metallurgy*, sponsored by Sylvania Electric Products, Inc., Bayside, L. I., N. Y., August 24–26, 1949.

[144] C. S. Smith, *Trans. Am. Inst. Mining Met. Engrs., 175,* 15 (1948).

angle is reached, with further solution only occurring under conditions that maintain this angle. As long as Θ is below 60°, penetration will occur linearly along grain edges; it will spread progressively over the grain faces as the angle approaches zero. If the dihedral angle is zero, all the grains tend to be enveloped by the penetrating liquid as it is being carried inward by capillary action. As a result, the liquid pries apart the individual grains and eventually completely disintegrates the solid structure. According to Smith, stresses accelerate this disintegration and may even cause continuous penetration if the dihedral angle if somewhat greater than zero.

Smith explains the common observation of a liquid wetting the grains of the solid phase with which it is in equilibrium in cases where pure metals or alloy systems having extensive solid solutions or intermetallic compounds exist, and where the liquid does not differ widely in composition from the solid. The interfacial tension of the solid–liquid interface is less than *half* of that between the solid grains, and the dihedral angle of the liquid *vs.* grain boundary is *zero.* Thus, for example, copper with a zero contact angle spreads indefinitely over an iron or steel surface (be it the macrosurface in the case of brazing or the microsurface of an iron grain), while silver, with a small but positive contact angle, will not spread indefinitely on a plane iron surface, but will spread on a grooved surface (the more readily the more acute the angle at the root of the grooves).[145] With an increasing contact angle, coverage and spreading of the liquid on solid metal surface become progressively limited until a complete stop is reached for 90° and beyond.

The significance of the aforementioned principles in connection with the processes of sintering—based on the presence of a liquid phase—and metallic infiltration of higher melting skeleton bodies is obvious, and has been summarized by Smith[144] as follows:

> "The principles discussed should be of practical value to the powder metallurgist. It is well known that the interstices of a porous solid compact will be filled with a liquid if the surface contact angle is less than 90°. The dihedral angle against a grain boundary is equally important. A mass of polycrystalline lumps will be disintegrated, not sintered together, by a liquid of zero dihedral angle, though capillary action will hold the mass as a whole together. A liquid of positive dihedral angle will act very differently from one with $= 0$. In the case of a two-phase solid alloy made by powder metallurgy methods, the area of contact across which diffusion can occur will vary greatly with the dihedral angle. The chance for grain growth will be greatly affected by impurities. The production of an alloy with connected channels, as in porous bearings, or with a continuous network of a given constituent, is possible only with the proper dihedral angle. It should be possible to produce porous bearings equivalent to the powder metallurgy product by displacing the liquid from a fine-grained alloy made by conventional casting methods, or by annealing a fine-grained worked alloy above its solidus."

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[145] E. R. Parker and R. Smoluchowski, *Trans. Am. Soc. Metals, 35,* 362 (1945).

CHAPTER XXXVI

The Future of Powder Metallurgy

It appears appropriate to close this treatise with an outline of the future of powder metallurgy, which must be considered both in terms of expansion of the present types of products and of development of fundamentally new materials and processes.

Present Status

In broad terms, this comparatively young branch of applied metallurgy has developed in two directions, namely, in the production of materials or products that can *only* be accomplished by the powder technique, and in the manufacture on a *competitive* basis of certain products that are also produced by other methods.

In adopting this convenient though abritrary and not too strict division for a résumé of the present status of the art, we can include in the first class such industrially important commodities as:

(*1*) Refractory metals, such as tungsten and molybdenum products for incandescent lamps, electronic and x-ray tubes, furnace heating elements, and tantalum products for chemical appliances and surgical instruments, whose production has been achieved by developing the metals in ductile form.

(*2*) Sintered hard metals for cutting tools and wearing parts, whose production has been made possible by cementing the extremely hard and brittle refractory metal carbides with ductile auxiliary metals.

(*3*) Diamond tools, such as wheel dressers and grinding laps, whose development has been made possible by bonding the diamonds in sintered matrix metals.

(*4*) Sintered contact metals, such as switch contacts, whose production has been achieved by physically combining refractory metals, metal compounds, or nonmetals with low-melting, highly conducting metal binders.

(*5*) Porous products, such as self-lubricating bearings or metallic filters, whose production has been accomplished by controlling the porosity of the metal during forming or sintering.

(*6*) Friction products, such as metallic clutch facings and brake linings, whose production has been made possible by bonding the friction-producing ingredients in a suitable metal matrix.

(*7*) Dental amalgams, whose production has been achieved by developing plastic, self-hardening metal compositions.

The second class is less clearly defined, since it refers to a phase which by its very nature is more in a state of flux and which is subjected to constant economic and technologic changes. At present, the following commodities can be classified here:

(*1*) Permanent magnets of the Alnico type for which a sintering technique has been developed that produces a finer grain size and greater strength on an economic basis in small sizes.

(*2*) Soft magnetic parts for direct current applications which have been developed from commercial iron powders in competition with machined or stamped products.

(*3*) Sintered iron, steel, and brass parts for the machine industry which have been developed in competition with orthodox production methods.

(*4*) Chemically pure metals and alloys which are particularly suitable for the vacuum technique.

Expansion of Types of Products Exclusively Produced by the Sintering Technique

It may be expected that the refractory metals will find increased use in the lamp and electronic industries, including radio, television, and radar. Tungsten and molybdenum may be used increasingly for high-temperature furnace elements and parts from these metals will appreciably increase in size. Ductile titanium and zirconium may come into being as material for the vacuum technique or for chemical ware. Improvements may be anticipated in methods and materials for glass-to-metal and metal-ceramic joints and seals.

New applications for sintered carbide hard metals for high-speed cutting tools appear to be exhausted (except that new mechanical techniques of fastening the carbide to steel supports under elimination of brazing are anticipated), but their field of application in wear-resistant parts is wide open and will extend from dies, gages, and guides to rolls, grinding equipment, percussion hammers and anvils, rock drill bits and bearings.

The expansion of the field of diamond-impregnated tools will be closely connected with the carbide developments, but further impetus may also be derived from such applications as mining and dental drills.

In view of the fact that many contact problems remain unsolved to date, it may be expected that the uses of composite contact metals may undergo still further expansion and that materials will be developed that show an optimum combination of conductivity and wear resistance or hardness. Combinations of refractory metal carbides or borides with silver or copper may be developed to fulfill extreme requirements.

Developments in the field of porous bearings will center around iron-base and brass alloys in a drive to replace the bronzes by more economical materials. The demand for metallic filters for chemical apparatus, fuel refinery, and refrigeration appliances will increase, and sizes and shapes will become more varied; nickel and stainless steel, as well as brass and bronze powders of suitable particle characteristics, are now available.

Metallic friction products find their most intriguing potential application in liners for automotive brakes. Their development in the direction of ever larger compounded assemblies for brake linings and clutch facings in modern airplanes is indicated. The substitution of corrosion-proof iron-base compositions, with low-cost, silica-rich, and incompletely reduced iron powder as principal raw material, may make these larger assemblies particularly interesting from an economic point of view.

In dental amalgams, no further advance is expected because of increased popularity of silicates and other dental cements.

Expansion of Types of Products Not Exclusively Produced by the Sintering Technique

A large-scale expansion of the production of sintered permanent magnets appears likely now that the sintered Alnico magnet—like the cast—can be heat-treated (cooled) in a magnetic field, with the directional treatment yielding much superior magnetic properties which permit a drastic reduction in size. Also, sintered magnets of progressively increasing size can be expected to be produced economically. Permanent magnets of very small size may in the future be advantageously produced from colloidal magnetic powders (here, some time ago, some quite unique properties were found in a powder metallurgy product consisting of a single metal, the properties being limited to powders below a certain critical particle size, and being completely *opposite* to those of the solid metal).

The future expansion of the production of pressed and sintered soft magnetic parts will much depend on the development of manufacturing methods for compound elements in which the soft iron pole pieces are joined integrally with the permanent magnet during processing. Until this is accomplished by technically and economically sound means, sintered iron magnets will remain restricted to armatures, pole pieces, bridges, shunts, and the like for low-voltage electrical circuits in transportation, communication, phonograph, and related applications.

The ascent of the powder metallurgy production of structural, so-called custom-molded, parts from brass and iron powders, is expected to continue, though perhaps at a slower pace than during the war years. American industries that require parts in lots of hundred thousands or millions per year represent ideal customers for this type of product, and much room for growth of this branch is left on account of the nearly inexhaustible demand for mass production parts in the automotive, bicycle, household appliance, business machine, toy, hardware, and similar industries. The degree and rate of expansion of the powder metal parts business, however, are considerably affected by economic and technical factors. Besides minimum quantity requirements below which costs for tools and process engineering cannot be absorbed, current and future market values of the part, and comparative cost analyses for the conventional production methods, the most careful study of all processing steps is essential for a true evaluation of the economic prospects of the powder approach. Here, a great deal of room is left for improvement with an eye to cheaper and more formable powders, greater densities at lower pressures, precision sintering, and labor saving by mechanization of material transport and auxiliary operations. Last but not least, the development of the sintered parts business will depend on improvements in quality of the sintered products and their performance as compared with the conventionally made parts they are designed to replace.

Development of New Methods to Improve Economy

The future development of powder metallurgy is much dependent on the reduction of raw material costs, which, today, is above that of ingot or stock metals in nearly all cases. Metal powders, however, are not exceptions to the basic rule of economics whereby the price is set by the laws of supply and demand. Thus, it can be expected that the price of powdered iron, copper, brass, stainless steel, and aluminum will drop closer to the level of ingot metal as soon as the market for these powders has increased sufficiently to warrant huge capital investments for installation of new facilities and for streamlining of present processes of powder production. The powder markets, on the other hand, can be expected to increase only *after* powder costs have stabilized at new, lower levels. Thus, a serious impasse results from the fact that neither powder producer nor powder user can carry the economic burden of the interim period during which prices are adjusted and additional, large-scale business is secured. Confronted with this difficulty, we may do well to look for a solution in the direction of a concentration of powder production, or at least powder refinement, and parts production in one organization. This approach has been adopted since the industry's earliest beginnings by the refractory metal and hard metal producers throughout the world. During the war, it has proved of value in the manufacture of shell driving bands in Germany, where raw material specifications were kept rather lenient, and many large and small parts producers refined the raw and inexpensive iron powder by milling, annealing, or reducing, to very rigid specifications, governed by the particular processing methods employed. By adopting this approach more widely, not only will we overcome the temporary difficulties connected with a turn-back of powder prices but we will also make a tremendous step toward establishing close technical liaison between powder production and use.

Although the powder price is important, it is only one of the factors that require improvement. In the field of parts in competition with machined bar stock or castings the machining costs that may be reduced are equally decisive. With a general trend toward increasing, or high level-stabilizing, wages throughout all industrial countries, the amount of labor savings that can be achieved by adopting the powder method may be an enormous incentive. Here, powder metallurgy processes are still in their earliest stage of development and much may be expected from the introduction of transport conveyors that couple molding presses and sintering furnaces, standardization of powder mixing procedures, and mechanization of finishing operations and inspection. Moreover, there may develop a cost-reducing trend toward extending the genuine powder metallurgy operations in the direction of heat-treating and subassembly work. As a consequence, the introduction of complete, self-sustaining powder metallurgy plants as independent operational units within larger industrial metal manufacturing works becomes of increasing interest. By applying the so-called "captive plant" principle to the powder metallurgy process, full advantage can be taken of the labor-saving and scrap-reduction possibilities inherent in the process, while a more favorable rate of overhead can be arrived at than would be possible if the parts production remained in the hands of the smaller independent manufacturer.

Turning now to the actual processing steps, much can be said about necessary improvements of their technological features. Starting with the raw material, much work remains to be done in improving the uniformity and compactibility of those powders needed for mass production purposes. The supply of powders to which a lubricant has been appropriately added during powder production may do much to overcome inherent molding difficulties. The beneficial effect of powder grading on compact densities and dimensional control during sintering is indicated, and may eventually lead to artificial agglomeration of fine powders to coarse granular raw materials, but many scientific and production data must yet be produced to substantiate this view.

Closely connected with a demand for more precise control of the raw materials are the problems of simplifying and making the molding and sintering techniques less costly. The advent of the vibratory, quick-acting hydraulic press will go far in producing compacts of uniform density at a reduced molding pressure. It will enable the production of larger sizes on an economical basis, since capital investment and depreciation costs are reduced by the smaller press capacity, and tool and die consumption is reduced by the application of lower pressures. Furthermore, increased uniformity of particle concentration in the compact will make possible closer control of the dimensional accuracy during sintering, which is particularly important in the case of complicated shapes. Such precision sintering may be expected to reduce or entirely eliminate subsequent coining, sizing or machining operations, and thus further favor the economy of the process.

Because metal powders do not follow the laws of hydrodynamics when subjected to pressure, the production of parts of intricate design or of excessive height or length remains one of the most difficult problems to be handled. The urge to lower the costs of such production by reducing the technical difficulties has led to a number of interesting and promising expedients, which have met with a certain amount of success both here and abroad and may be expected to find more uses in the future. Parts of intricate shape or considerable height, for example, can be produced efficiently with a uniform density by first pressing and sintering smaller parts or sections and then assembling these component parts and uniting them in a second sintering operation by bonding with the aid of binder materials or of a static load application. Parts of considerable length may be produced advantageously by filling steel tubes with the powder and then drawing the tubes on a drawing bench or squeezing them on a profiling rolling mill. In this way the powder would be compressed radially to an extent sufficient to cohere into a solid body during sintering. The incorporation of steel mandrels in the powder fill would make it possible to produce profiles with concentric holes which may serve as bearings. While in this case the original steel tubing may be utilized as backing material, it would have to be detached in the case of cylindrical or profiled porous filter rods.

Development of New Methods to Improve Quality

Even if the powder metallurgy products produced on a mass production scale compete with their conventionally made counterparts, they do not compete in so far as many of their properties are concerned. In fact, some of these properties fall far short of those exhibited in the ordinary materials—as, for example, ductility and impact resistance. Here, very considerable improvements are in order.

The lack of ductility and shock resistance properties in sintered metals may be attributed chiefly to internal stress concentrations. The stress-raising effect can be attributed only to a minor extent to impurity films and inclusions in the grain boundary area. Its main origin appears to be the notch effect produced by the residual pores. An exact stress analysis involving many pores of different shapes is not possible at present. On the basis of a qualitative analysis it may be expected that the stress concentrations and triaxial stresses produced by notches will affect ductility and shock resistance to a larger extent than strength. Since this agrees with experimental observation, the assumption that the poor ductility and impact values of sintered products are due mainly to residual porosity appears to be justified.

The problem of the effects of residual porosity constitutes one of the most important yet unsolved in connection with the powder metallurgy process. After fifty years of industrial development of the art, there is now a definite demand for scientific research on this problem. An earnest attempt toward a solution—perhaps with the aid of such modern tools as x-rays and the electron-microscope—should benefit the entire field. Unquestionably, it would go a long way in advancing our knowledge about the fundamentals of the sintering process, and research concerned solely with the problem of pore elimination might well become a foundation on which a *science* of powder metallurgy could be built. In conjunction with such theoretical studies of the mechanism of the notch effect in the sintered products, a continuation of the presently conducted investigations of the distribution of density, frictional force, and stresses in the powder compacts during the molding process would be of tremendous value.

On the basis of the foregoing assumption, attempts to improve the mechanical characteristics of sintered products would have to be concentrated on methods and means to eliminate residual porosity, that is to say, to increase the density as far as possible. The principal methods resulting in elimination of pores are mechanical densification by pressing or working, preferably hot, and metallurgical densification by shrinkage or filling of the pores with a low-melting metal cement. Of these methods, only hot-pressing and low-melting metal infiltration permit retention of the shape to close enough dimensional accuracy to be of interest in the production of molded parts. Both methods are bound to develop into commercially important processes.

Hot pressing, performed either before or after sintering, results in far-reaching elimination of residual pores through increased plastic flow under pressure and disruptions of harmful gas films. At the same time, appreciably lower pressures can be utilized which may even be less than one-tenth of those required for molding at ordinary temperature. This aspect appears particularly interesting for the future development of the larger parts business, which to date has been greatly handicapped by excessive requirements in press capacity and by the unfavorable economics resulting therefrom. The future of hot pressing, however, is much dependent on the development of satisfactory die materials and integrated processes that permit high production rates and pressing and handling of the material under protective atmosphere conditions. All of these requirements remain to be worked out.

The infiltration process appears more simple and particularly promising at the present stage. Here, the primary pore system created during cold pressing is not objectionable but rather desirable, since it forms the reservoir for the liquid cementing materials injected during sintering. The cementing metal, once lodged in the pore system, tends to fill the internal notches, thereby improving the shock resistance and ductility of the compact; when alloying between the cementing metal and the matrix takes place, a substantial increase in strength also results. Since the technique appears to be workable not only in the case of nonalloyable or partially soluble metals but also, though with greater difficulties, with systems in which complete mutual solubility exists between the infiltrant and the base metal, infiltration powder metallurgy holds great promise as a method by which superior properties can be achieved by economical means for a variety of alloys. If a comparatively large difference in melting temperature exists between the matrix metal and the infiltrant, temperature control is not critical, and presently available commercial furnace equipment can be utilized for silver- or copper-base infiltrants. By controlling the raw material closely it will also be possible to control closely the size of the product during and after infiltration-sintering. Thus, the foundation is laid for consolidation *without* sacrifice in dimensional accuracy, a most important criterion for the development of high-strength precision parts.

Development of New Materials

In conclusion, some remarks should be devoted to the possible development of new powder metallurgy products; a systematic survey of the periodic system in search of potential sinter metals has been given in the text.

The powder metallurgy of the refractory metals indicates that in a comparison of the physical properties of sintered and worked products with those of castings a distinct superiority of the former can be found; more recent work with lower melting metals such as iron, copper, or aluminum have left little doubt that if correctly processed to an adequate density, plain sintered ingots may exhibit physical properties which are either equivalent or superior to those of cast ingots. With improvements in the methods of controlling purity, pore volume, grain size, and possibly structural equilibrium to be anticipated, the production of ingots of nonrefractory metals by the sintering technique becomes a definite possibility. Typical examples of cases where ingot production by powder metallurgy would be of interest are carbon-free stainless steels, oxide-free silicon steels, or gas-free aluminum and magnesium. All of these, on account of their higher purity, their presumably superior workability, and their possibly unique physical properties, would then fall into the noncompetitive class of powder metallurgy products. Since their eventual production on an economical basis is largely dependent on location, type of raw material supply, and scale of operation, sintered ingot manufacture may well grow into a big industrial undertaking.

The production of lightweight structural engineering alloys based on the metal titanium constitutes another development of great potentialities for powder metallurgy. Because of an unusual set of physical and chemical properties, alloys of this type are bound to be a "natural" for the aircraft industry, and await only a markedly reduced production cost. It may be quite possible that powder metallurgy succeeds in contributing to this picture, whether by offering improved ways and means of manufacturing the powdered raw material, or by facilitating working practices for some of these titanium alloys through improved or controlled alloy structures.

The powder metallurgy of aluminum and magnesium is another extremely interesting and promising prospect. With the modern trend in air and ground transportation directed toward faster speeds at greater economy, a maximum possible weight saving is desirable. Precipitation-hardened sintered aluminum alloys give an even more favorable strength–weight ratio than their fused counterparts, owing to their inherent porosity. They are expected to find increased use as porous bearings and dense stressed parts in replacement of the heavier and mechanically inferior die castings now employed. Their chief development, however, is expected to be in the direction of strip and sheet obtained by rolling from sintered ingots. Because of their low specific gravity, high heat conductivity, and stability against galvanic reactions caused by the oxidation of oil, dense thin-sectioned aluminum-base bearing layers molded directly on to steel strip and integrally bonded during sintering are believed to make excellent lightweight substitutes for the presently used Babbitt and main bearings in automobile and aircraft engines. Another potential outlet for precipitation-hardened sintered aluminum lies in clutch facings for automobiles, where a reduction of the kinetic energy by the lighter weight would tend to prolong the clutch life appreciably. The replacement of aluminum by magnesium not only for products such as lightweight bearings and friction elements but also for lightweight structural members is anticipated with the development of fine grades of high-purity magnesium powders and specially adapted hot-working techniques. With the oceanic magnesium winnings forming the most potential source, the production of ductile magnesium *via* the powder metallurgy technique appears bound to be a success over the presently employed casting techniques with their resulting undesirable gassing effects.

Another materials' development that the powder metallurgy of the future is expected to solve refers to soft magnetic parts for alternating current applications which possess adequate permeability at a minimum of eddy current losses at moderate frequencies. In adopting the directional construction of the presently employed laminated sheet assemblies, multiple-layer molding techniques may be developed into products of satisfactory magnetic properties, with the economy of the process mainly dependent on the mechanization of the molding process. Other prospective developments may include the effective molding of flake iron powder; the introduction of insulations by preferential internal oxidation of particle coatings or particle strata composed of metals forming stable oxides, such as aluminum; or the formation of iron alloys, especially with nickel, chromium, or cobalt, during sintering at high temperatures.

Highly stressed structural and power engine parts may eventually be produced economically by employing the infiltration process in conjunction with stainless and alloy steels and precipitation-hardenable alloy infiltrants, and subjecting the products to appropriate heat treating. Materials of unusual or directional properties can develop from the same approach, with facings or layers of extreme hardness or abrasion resistance being integrally joined with tougher backing metals. Parts of complicated contours, which are not moldable by ordinary powder metallurgy processes, may be produced effectively on an industrial scale by joining individual sections into one compounded part during the infiltration process.

Finally, we must consider the almost unlimited potentialities that lie in the production of alloys of specific, carefully controlled nonequilibrium structures which, in many an instance, will result in unique combinations of physical and chemical properties. In this, powder metallurgy can be expected to perform superbly.

Development of Superalloys

Probably most intriguing of all the potential products that the powder metallurgy of the future is capable of developing are the wear-resistant and heat-resistant superalloys. The trend in modern engineering developments is characterized by a continued increase in speed, not only of transportation, but more generally of all types of machine operations, whereby the efficiency and economy of mechanized processes are improved. This increased speed of machine operations produces increasingly higher stresses and greater wear, making imperative the development of materials with higher wear resistance. In engines and prime movers, this trend is overshadowed by another tendency toward progressively higher working temperatures and the rapidly increased efficiency of the engine obtained thereby. This demand for greater efficiency, and therefore more power, has led to the evolution of the power engine from wind and cold water impellers to steam engines, combustion engines, steam turbines, gas turbines, and now jet turbines, and will eventually progress to the utilization of atomic energy.

The necessity of operating at progressively higher working temperatures puts great demands on the available construction materials, since they must exhibit a combination of mechanical strength, wear resistance, and resistance to deformation at the operating temperature. Since all engines used today operate in corrosive atmospheres, such as steam, combustion gases, or hot air, mixed with salt or metal vapors, corrosion resistance is an additional requirement.

However, the increase in efficiency gained by the use of higher temperatures may be nullified by the deformation of the structural members at operating conditions. Thus, the efficiency of jet engines and gas turbines is dependent on the accuracy of the shape of the bladings, buckets, and diaphragm vanes, and the retention of this accuracy during the entire life of the engine. Therefore, resistance to creep is just as important a requirement as are hot strength and resistance to fatigue stresses at service temperatures. The presently employed production methods for these components (castings or forgings) *per se* are contrary to this need of retaining the shape during operation, since the presently practicable casting and working techniques are performed in approximately the same temperature range that applies for service later on; in other words, the material cannot very well be expected to be formable into the required shape at the same temperature at which it is then to be stabilized during service under stresses that may approach or even surpass those exerted during forming. Conventional metallurgy of the superalloys offers an effective expedient in precipitation hardening above service temperature, but this brings improvement in a limited temperature range only.

Indications based on experimental evidence and theoretical reflections are that, for wear-resistant and high-temperature applications, only those materials can be expected to show satisfactory performance which have very high melting and boiling points and which soften only at temperatures considerably above the ultimate service temperatures at which the power engines will operate. Moreover, it is believed that if metallic creep at elevated temperatures is a rate process explainable in terms of the so-called dislocation theory, then the modulus of elasticity is the most important physical constant of a pure metal, and metals having high moduli of elasticity also have high creep strength. This suggests very strongly that the elements tungsten and molybdenum, with their high moduli of elasticity, should be major components of heat-resistant alloys. Unfortunately, however, these metals—which we conveniently designate by the generic term of refractory metals—can only be added in comparatively small amounts, lest they interfere seriously with the conventional manufacturing methods of the alloys. But powder metallurgy—depending on cold- or hot-forming of a powder compact and sintering and alloying this compact without substantially melting it, and without depending on such problems as fluidity and workability, which are so decisive in the orthodox techniques—offers to take fullest advantage of the refractoriness of these materials. It is therefore the logical choice as manufacturing method for the superalloys, the more so since the production of refractory metals and alloys by the powder metallurgy technique is by now a well-founded art which can readily serve as a basis for a production method for heat-resistant superalloys.

Most refractory metals, however, are unstable in oxygen and corrosive atmospheres at high temperatures. Furthermore, most of these metals have a higher specific gravity than steel, which, however, is offset by their considerably higher strength, so that the strength–weight ratio may be somewhat more favorable. Also, lower stresses may be expected at the higher temperatures due to the lower running speeds at which the turbines will operate. On the other hand, there are indications that the resistance to deformation at high temperatures (the creep resistance) is generally somewhat lower in pure metals than in alloys. Thus, even such newly investigated metals as pure titanium and zirconium, which have a far more favorable strength–weight ratio than alloy steels, must be considered as not too suitable from the standpoint of creep resistance; moreover, these metals appear also unsuitable as far as resistance to oxidation and absorption of gases at high temperatures is concerned.

In general, alloys and compounds of the refractory metals suffer from the same handicaps as the pure metals. Thus, tungsten-base alloys with nickel and cobalt are too heavy for their comparatively moderate strength. Cemented carbides are excellent as far as wear resistance is concerned. However, they are only slightly lighter than the "heavy metal" type of alloy and much less stable against burning and severe corrosion at high temperatures.

One of the possible ways of approach to the problem may lie in combinations of these refractory alloys or compounds with light, refractory ceramics. While at present these composite structures lack adequate bonding and ductility at high temperatures, and resistance to sudden heat shocks, improvements in sintering and bonding techniques may well bring surprising results.

Another approach involves the replacement of the carbides by other compounds of the refractory metals which are closely related to them in mechanical and physical characteristics, but which are of reduced specific gravity and exhibit in addition corrosion resistance at very high temperatures. Alloys containing such compounds as the refractory metal borides are now in the developmental stage, and the same principles on which the production of the cemented carbides is based can also be applied to these substances.

Carrying this approach further, powder metallurgy offers great promise as a workable process of producing complex alloys which we know can be forged, but which are difficult or ordinarily impossible to be cast into sound ingots. Alloys of this kind—usually containing the refractory metals tungsten, molybdenum, tantalum, columbium, titanium, etc. in substantial proportions—are believed to be very important as construction materials of *immediate* interest where increased fatigue strength and resistance to creep at operating temperature levels now encountered are demanded.

Still another approach involves the production of present analyses of the superalloys by the powder technique, with indications pointing toward sintered products of superior hot strength and creep resistance because of their better controlled grain size and grain boundary conditions, greater purity, and inherent porosity. Thus, it will be interesting to see such materials as the precipitation-treated, cobalt-base "Vitallium" type, the nickel-base "Nichrome" and "Inconel" types, or the recently developed chromium-base alloys (containing molybdenum or tungsten and iron as minor alloying elements) duplicated by the sintering process and tested for their properties and performance under actual service conditions.

But of greatest possible interest will be a change of the conventional analysis in the direction of increasing the amount of refractory metal phase or substituting part or all of the refractory metals tungsten, molybdenum, titanium, zirconium, or chromium by their metalloidal type of compounds. It is this kind of complex sintered structure that in the final analysis may prove to be the only type of material that can withstand the extremely severe service conditions that the power engine of the near future holds in store.

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