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PRINCIPLES

of

METALLOGRAPHY

by ROBERT S. WILLIAMS, S.B., PH.D.
Professor of Physical Metallurgy,
Massachusetts Institute of Technology

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Fourth Edition
NINTH IMPRESSION

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To Henry Fay

A pioneer in the field of Metallography who inspired many men with the love of this new science. To him we dedicate this book in grateful acknowledgment of his unfailing friendship and his helpfulness during the period of our apprenticeship.

PREFACE TO THE FOURTH EDITION

The purpose of this book remains unchanged. It is intended to give to the general reader the fundamentals of Physical Metallurgy and to serve as an introduction to larger and more specialized books.

The text has been extensively revised to include new material that has appeared since the previous edition was published. A new chapter on "The Plastic Deformation and Annealing of Metals" has been added. This chapter was written by Professor Morris Cohen, to whom our sincerest gratitude is due, not merely for the special section, but also for his constant help and friendly criticism throughout the entire revision.

Grateful acknowledgment is made to Professor A. V. deForest for the section on magnetic testing; to Mr. J. D. Edwards for a complete revision of the section on Aluminum; to the American Society for Metals for the use of several diagrams and tables; to Messrs. Epstein, Kehl, and Vilella for illustrations, and to Mr. Otto Zmeskal for several new diagrams, and figures.

ROBERT S. WILLIAMS.
VICTOR O. HOMERBERG.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
CAMBRIDGE, MASS.,
August, 1939.

PREFACE TO THE FIRST EDITION

This little book has been written to meet the needs of those students of General Science or Engineering who do not specialize in Metallography b , who will use it to a limited extent in connection with thei. professional work.

It is hoped that it will be of ervice, also, to the general reader as an introduction to an increasingly important branch of science and as an aid to the better understanding of the more highly specialized books.

Greater emphasis has been laid on the applications of Metallography than on the physico-chemical principles involved but it is believed that the fundamental ideas on which metallography is based have not been neglected.

In the appendix will be found a few of the tables most commonly used by the metallographist, a suggested outline of a brief laboratory course and a descriptive list of the more important books and journals dealing with the subject.

Thanks are due to the authors of many of the standard books on metallography which have been freely used in the preparation of this little volume and grateful acknowledgment is made for the use of a few drawings which have been copied with minor changes from other books.

Special thanks are due to Messrs. Bauer and Deiss from whose book on "The Sampling and Chemical Analysis of Iron and Steel" most of the microphotographs of steel and iron have been taken.

It is a pleasure to express my appreciation for the services of Professor L. F. Hamilton who has helped greatly by his kindly criticism of the proof.

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PRINCIPLES OF METALLOGRAPHY

CHAPTER I

THE SIMPLE ALLOY DIAGRAM

Metallurgy is one of the oldest of the sciences, and until the latter part of the nineteenth century it had been concerned chiefly with the production of metals from their ores and with the various processes used in the manufacture of steel, brass, bronze, and other alloys. Shortly before the beginning of the present century it became increasingly evident that the useful properties of metals and alloys were affected by many things other than the method of production. Their characteristics changed, for example, as a result of heating followed by sudden cooling, or they were changed by rolling, drawing, or other kinds of mechanical work. Today the field of metallurgy is commonly subdivided into the closely allied branches of: (1) *production or process metallurgy*, dealing with the recovery of metals from their ores; and (2) *physical or adaptive metallurgy*, which is concerned with the physical properties of the metals and alloys made from them.

Physical metallurgy, then, is the general study of metals and alloys, their physical and chemical properties, their internal structure, the methods of investigation, and, perhaps most important of all, the study of the mechanical properties, uses, and defects of the commercial alloys.

Many branches of science are necessary for the solution of the problems of the physical metallurgist. The chemical composition must often be determined; the tensile strength, hardness, ductility, or other mechanical properties must be found; the magnetic behavior is sometimes important, and the examination of the alloys by means of the *x*-ray has come to be of the utmost value. Other methods of study are possible, but the group of principles that has done more than anything else to systematize the study of alloys and to make possible the remarkable advances in the use of metals that have taken place in the last thirty years is known as *metallography.* Metallography is one of the most important divisions of the larger field of physical metallurgy and is concerned chiefly with the internal structure of the solid formed when two or more metals are cooled from the molten state and with temperature effects occurring during the cooling or heating process.

If a pure metal is melted under conditions that make it possible to determine the changes of temperature during the cooling and if these changes are indicated in graphical form, a curve of the form shown in Fig. 1 is obtained. The temperature readings are taken at definite time intervals, and in plotting the curve these temperatures are used as ordinates with the corresponding time intervals as abscissas. The solidification of cadmium has been selected as an example. It will be noticed that the curve falls smoothly until the temperature of 320.9°C. is reached, when it breaks sharply and remains horizontal, indicating a constant temperature during an appreciable period. The curve again falls gradually to room temperature without further abrupt changes in direction. The horizontal line represents the transition of the cadmium from the liquid to the solid state. The heat that is necessary to maintain the mass at constant temperature is the latent heat of solidification. Since the amount of heat liberated at this time is proportional to the mass of metal solidifying, it is

evident that, other conditions being equal, the length of the horizontal line is a measure of the amount of material present. This does not hold absolutely in practice, as it is impossible to get ideal cooling conditions, but it is true to such a degree of approximation that the fact is of great value in the thermal study of alloys. The horizontal line has the additional physical significance that it indicates the only temperature at which solid and molten cadmium will stay in contact with each other indefinitely. At any higher

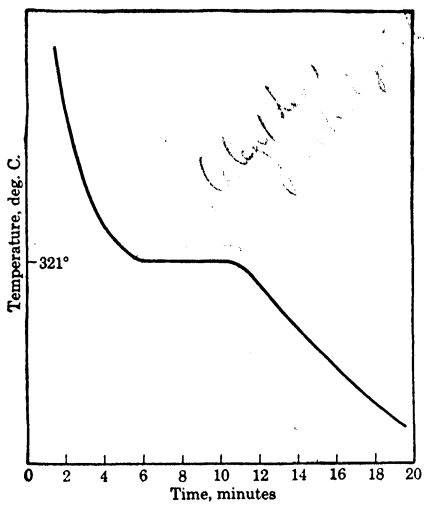


FIG. 1.—Cooling curve of pure cadmium.

temperature solid cadmium will disappear, and at a lower one there will be no liquid. Several other methods of drawing these *cooling curves* will be described later in connection with the laboratory study of the alloys.

Normally, when a molten metal solidifies, crystallization starts at the cooler walls of the containing vessel and at a series of nuclei or crystal centers in the metal itself. The solidification proceeds outwardly from these centers until the growth of each grain is stopped by contact with a grain growing from an adjacent nucleus. The hairlike lines of contact between the grains are the grain boundaries. It

may be said, in general, that the slower the cooling, the larger the grains and that fine-grained cast material indicates rapid cooling. A metal or an alloy cooled in a sand mold is always coarser grained than the same metal cooled in a metal mold (chill cast). The grain structure characteristic of a pure metal is shown in Fig. 9 page 12.

The Eutectic Alloy.—The first type of alloy to be considered is that in which the two metals are completely miscible in the liquid state and completely nonmiscible[1] or insoluble in each other in the solid state. It is a well-known fact that in most cases in which one substance is dissolved in another the freezing point of the solvent is lowered. This phenomenon is illustrated by salt solutions in which the addition of common salt progressively lowers the temperature at which ice forms, the minimum temperature of −22°C. being reached when the solution contains 23.5 per cent salt. Numerous alloys behave in the same way. An excellent example of this relationship is found in alloys of bismuth with cadmium. If a small amount of bismuth is added to molten cadmium, the freezing point of the latter is lowered, and increasing quantities of bismuth still further lower this freezing point. If, on the other hand, a small amount of cadmium, is added to pure bismuth, the freezing point of the bismuth is also lowered and is progressively decreased by the addition of increasing quantities of cadmium. The effect of the addition of each metal to the other is shown in the series of curves of Fig. 2. It is obvious that, since each metal lowers the freezing point of the other, the lines connecting these freezing points must intersect at some point as shown by the dotted lines in the drawing Fig. 2. This point of intersection is one of great interest and importance

[1] No two metals are completely insoluble in each other in the solid state, but in many cases this solubility is too slight to be detected by temperature measurements or microscopic examination and for most purposes may be disregarded.

and has been called the *eutectic point.* The alloy corresponding to the composition at which the two lines intersect is the *eutectic alloy,* and the temperature is the *eutectic temperature.* The *eutectic alloy* then is the lowest melting alloy in a series.

This method of representing the temperature changes in a series of alloys is not satisfactory even in so simple a case, and it becomes impossible in more complicated

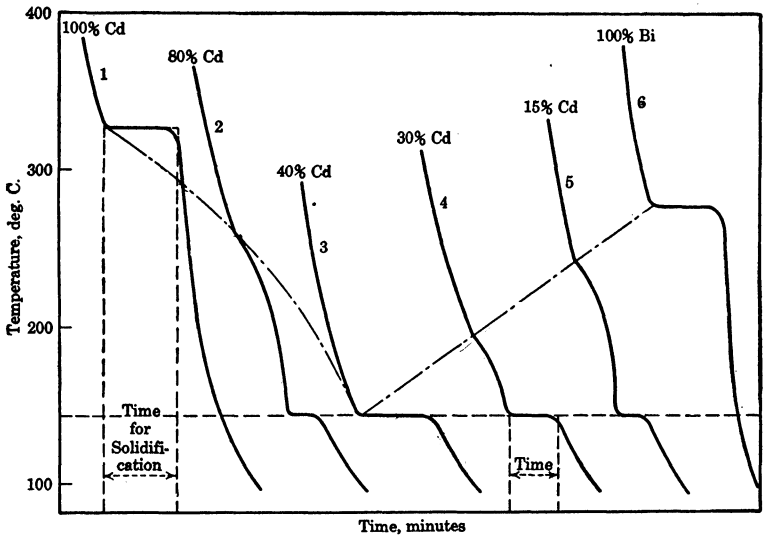


FIG. 2.—Cadmium-bismuth cooling curves.

cases. This has led to the use of a graphical form of representation known sometimes as the *freezing-point diagram* but, more accurately, as the *equilibrium diagram* of the alloys. Disregarding for a moment the time taken for each alloy to solidify, as shown by the length of the horizontal lines in the series of curves, it is evident that the temperature changes may all be indicated on a chart in which the ordinates represent temperatures and the abscissas percentage compositions of the different alloys. Since in the case under consideration the melting point of each metal is lowered by the addition of the other and,

furthermore, since an evolution of heat always occurs at 140°C. regardless of the composition of the alloy, the freezing-point or equilibrium diagram shown in Fig. 3 consists of the V-shaped curve *ABC* through the bottom of which passes the horizontal *DBE*.

In his various papers on Thermic Analysis, Tammann[1] has shown that, in addition to the simple freezing-point diagram just described, the introduction of a curve, or curves, showing the time interval during which the temperature stays constant for each alloy of a series is valuable both in the construction and in the interpretation of these equilibrium diagrams. The time curves are obtained and applied to the diagram as follows: Perpendicular lines are projected from the ends of the horizontal portions of the curves to the time ordinate as shown in Curves 1 and 4, Fig. 2. The time at constant temperature is then read in seconds or minutes, depending on the length of the horizontal. In Tammann's earlier work these time lines were drawn from the horizontal temperature lines to which they referred. This led to a certain amount of confusion, as one set of ordinates had to be used to indicate both time

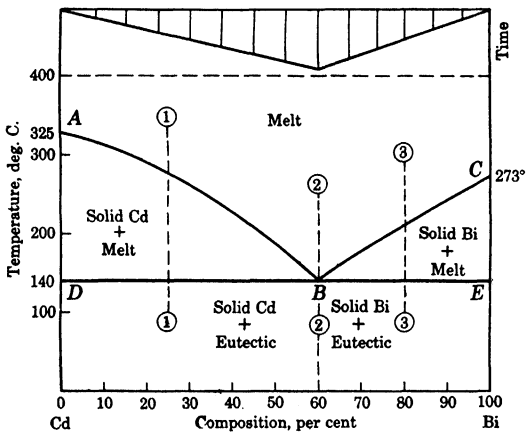


FIG. 3.—Cadmium-bismuth diagram.

[1] *Zt. Anorg. Chem.*, **37** (1903), 303; **45** (1905), 205; **47** (1906), 289.

and temperature. In the more recent work of other metallographers the time curves are made a separate part of the diagram, as shown in Fig. 3.

Since, as was stated on page 2, the time taken for a metal to solidify is proportional to the amount of material present when the cooling conditions are constant, it is obvious that the time of solidification of the eutectic will be greatest when its amount is greatest and will decrease to zero when either cadmium or bismuth is present alone. The triangle that is formed by drawing a line through the ends of the time perpendiculars is useful in several ways. From it may be determined not only how much time will be required for any alloy in the series to solidify, no matter what its composition, but also, what is more important, the percentage composition of the alloy. In order to determine this composition, an equal weight of the unknown specimen is cooled under conditions identical with those used in establishing the diagram, the time interval on its cooling curve is noted, and the percentage composition corresponding to the same time interval on the equilibrium diagram is found. The point at which the ordinate of the time triangle has the same length as the unknown time interval indicates the percentage composition of the alloy. This is the fundamental idea of thermic analysis, and, while the results do not compare in accuracy with ordinary quantitative methods, it is quite possible, in those instances in which it is applicable, to get results rapidly and with a degree of accuracy that is often sufficient for commercial alloy work.

The complete equilibrium diagram makes it possible to predict the physical condition of any alloy in the series at any temperature included in the diagram. This question of the interpretation of diagrams is one of the greatest importance to the metallographer. Consider as an example the physical changes that take place in a few special cases as, for instance, during the cooling of alloys ①, ②, and ③

in Fig. 3. Since the lines *AB* and *BC* were obtained by connecting the beginnings of freezing of the separate alloys, it is evident that the area above these lines represents a temperature range in which everything is in the molten condition. These two lines constitute the *liquidus*. As the temperature of alloy ① falls no change takes place until the line *AB* is reached, at which temperature pure cadmium begins to separate. The result of the separation is to leave a solution richer in bismuth than the original solution and, therefore, one that has a lower freezing point. Pure cadmium continues to separate with the consequent formation of solutions increasingly rich in bismuth and therefore with lower freezing points. The fact that the solution from which the cadmium is crystallizing is of constantly changing composition is the reason for the shape of the cooling curves (see Fig. 2) in alloys of this type. The curve is not a horizontal line as in the case of a pure metal, but, as it represents an infinite number of freezing points, it appears in the form of a change in the direction of the normal curve, or as a *hold*, as it is often called. As the liquid from which the cadmium is separating becomes richer in bismuth, it approaches the eutectic composition indicated by *B* (Fig. 3). Since this represents the lowest possible temperature at which cadmium and bismuth alloys can solidify, it is evident that when the residual liquid finally reaches the eutectic composition it will solidify at this constant temperature. The same reasoning applies to alloy ③ except that in this case the bismuth crystals separate first. The primary separation of bismuth is followed by an enrichment of the remaining liquid with cadmium until the eutectic composition is reached again. At the composition ② no change takes place until the eutectic temperature is reached, when cadmium and bismuth solidify simultaneously in the form of the eutectic mixture. The line *DBE* (the eutectic line) represents that temperature below which the alloy is solid and is therefore called the *solidus*.

To summarize the statements made above, it may be said that any alloy having a composition between D and B shows two heat evolutions on cooling, one which corresponds to the *primary* separation of cadmium and a second which is due to the solidification of the liquid of eutectic composition. The amount of residual material having the eutectic composition becomes greater as the composition approaches that of the point B. Since *primary* cadmium separates along the line AB and *primary* bismuth along the line CB, the point B, which is common to both lines, represents a temperature at which bismuth and cadmium solidify simultaneously from the liquid. The separation of either cadmium or bismuth as one of the eutectic constituents is called a *secondary* separation.

Because of the constant temperature at which the eutectic separates, it was formerly believed that the eutectic was a compound. The microscope shows that this is not the case but that, on the contrary, the eutectic alloy is an intimate mixture of the two component metals. Since the eutectic is a mixture of the two metals, and since, as shown in the diagram, the eutectic line extends from one side of the diagram to the other, it follows that, while cadmium and bismuth are wholly miscible and soluble in each other in the liquid state, they are wholly nonmiscible,[1] or insoluble in each other, in the solid state. That the metals are insoluble in each other in the solid state must be true, as the diagram shows that, however small an amount of either metal is added to the other, there is always the secondary heat effect at the eutectic temperature.

The practical application of the time curves is evident from this diagram. Since the time taken for the eutectic to solidify increases as the composition approaches that of the eutectic, it follows that the time curve has its maximum at the eutectic composition and is zero at the pure metals. This fact is useful in the construction of the diagram of two

[1] See page 4, footnote.

unknown metals. Formerly, the location of the eutectic point was a matter of repeated trials with no advance information as to the probable location of the point. With the introduction of the time line idea the question is much

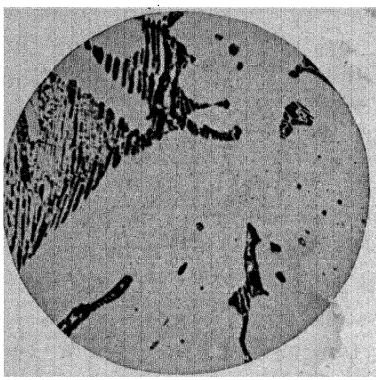


FIG. 4.—Bismuth 90 per cent + cadmium 10 per cent. Primary bismuth (light) embedded in eutectic.

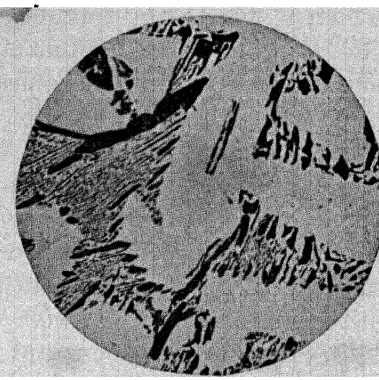


FIG. 5.—Bismuth 80 per cent + cadmium 20 per cent. Primary bismuth (light) embedded in eutectic.

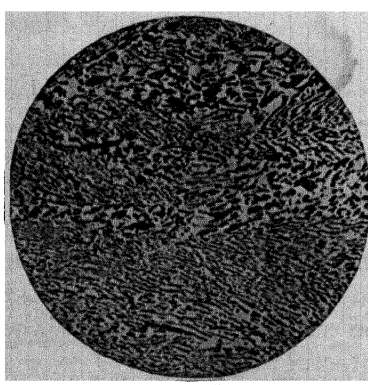


FIG. 6.—Bismuth 60 per cent + cadmium 40 per cent. Eutectic structure.

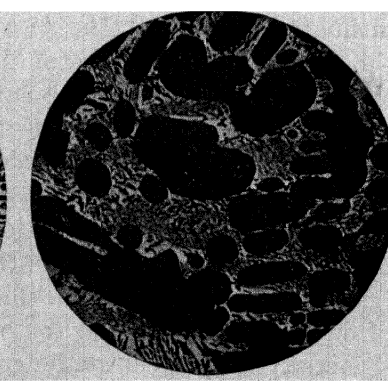


FIG. 7.—Bismuth 25 per cent + cadmium 75 per cent. Primary cadmium (dark) embedded in eutectic.

simplified. It is necessary to determine the time lines for only a few alloys. The time taken for the eutectic to freeze in each case is plotted against the composition, and the intersection of two oblique lines drawn through these points will represent a composition approximately that of

the eutectic, so that its exact determination, if that is desired, is a matter of a very few additional experiments.

After the construction of the diagram, or frequently in practice simultaneously with its construction, a microscopic study of the solid alloys is made. A highly polished surface free from scratches is obtained on which the internal structure of the alloy is brought out by treatment with suitable etching reagents which attack one constituent

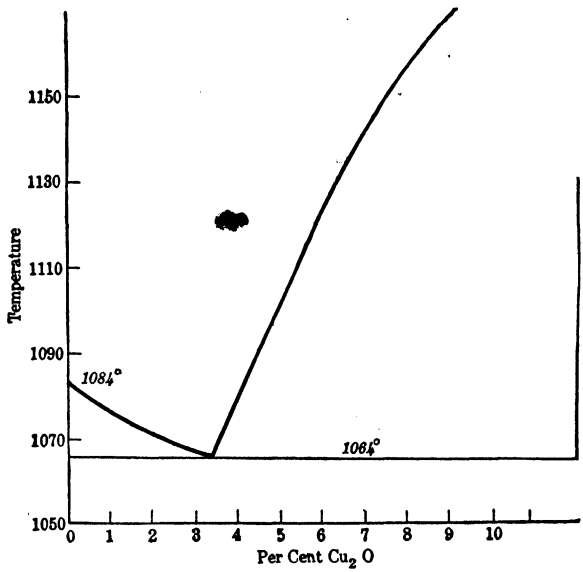


FIG. 8.—Equilibrium diagram of the copper-copper oxide system.

more than the other and produce in this way depressions in the surface, color changes of the constituent attacked, or other differences which are noticeable under the microscope. The method of polishing the specimens and preparing them for microscopic examination will be considered in the section on Laboratory Methods (p. 250).

The miscroscopic structure of these alloys is exactly what would be predicted from the diagram. All alloys from pure bismuth to the eutectic composition show primary bismuth crystals surrounded by more or less of

the eutectic B, depending on the composition (Figs. 4 and 5). Alloys from the cadmium side to the eutectic show primary cadmium crystals embedded in the eutectic (Fig. 7). The alloy having the composition B shows simply the fine-grained eutectic structure without primary crystals

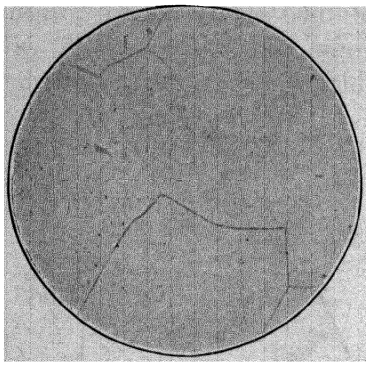


FIG. 9.—Pure copper.

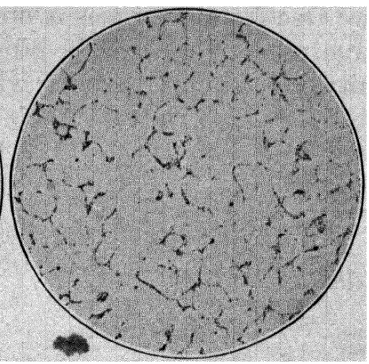


FIG. 10.—Pure copper (light) + eutectic (dark).

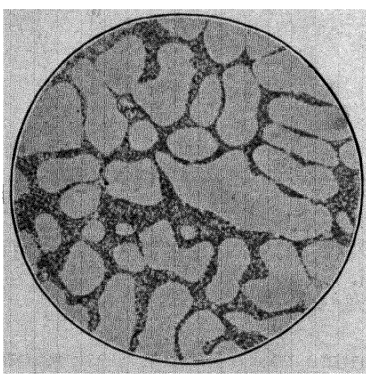


FIG. 11.—Pure copper (light) + eutectic (dark).

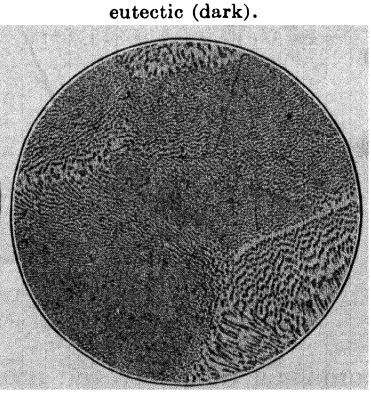


FIG. 12.—Eutectic (copper oxide, dark particles; copper, light).

of either metal (Fig. 6). The cadmium-bismuth alloys are of little commercial importance. Almost exactly the same relationship exists between lead and antimony. Because of the importance of *hard lead*, these alloys are extensively used. Antimony is too brittle to be useful alone but, because of its hardness, it gives to lead properties that are very desirable for certain purposes. The alloys

are used for storage-battery plates, acidproof coatings, type, and light bearings.

Another important series of alloys of the same class are those of the copper-copper oxide system. Figure 8 shows that the eutectic contains 3.5 per cent copper oxide and freezes at 1064°. The photomicrograph of pure copper (Fig. 9) shows the characteristic polygonal structure of a pure metal.

Figure 10 is that of copper containing a small amount of eutectic. Figure 11 shows an increasing amount of the

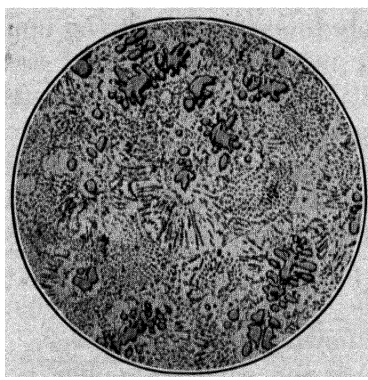


FIG. 13.—Eutectic with excess (dark masses) of copper oxide.

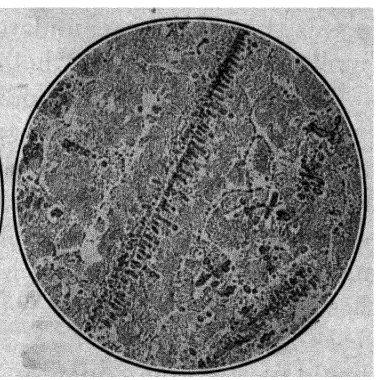


FIG. 14.—Eutectic with excess (dark masses) of copper oxide.

eutectic. Figure 12 shows the eutectic only, while Figs. 13 and 14 show eutectic with an excess of copper oxide, Cu_2O. The presence of copper oxide in copper greatly decreases its electrical conductivity so that the microscopic examination of the metal to determine its purity is of service.

The two examples just given illustrate in a general way the factors that are commonly determined in the study of alloys. Many other types of alloy diagrams have been worked out; these deal with the formation of intermetallic compounds, solutions of one metal in another, transitions of one compound into another, either during the solidification of the alloy or after it has completely solidified, and other possible changes that may take place.

CHAPTER II

THE ALLOY DIAGRAM AND ITS MEANING

In Chapter I the construction of a simple alloy diagram was outlined. This is usually referred to as the *eutectic diagram*, representing graphically the behavior of two metals that dissolve completely in each other in the liquid (molten) state but are wholly insoluble in the solid state.

The Phase Rule.—In addition to this simple type (the eutectic), various other combinations of two or more metals are possible. The relationships are most readily indicated, especially in the more complicated cases, by means of the alloy or equilibrium diagrams. An exceedingly useful principle to help in the interpretation of these diagrams was developed by Willard Gibbs many years ago and is generally known as the *phase rule.* It should be stated in advance that the principle applies in its exact sense only to conditions of complete equilibrium and that such conditions are seldom, if ever, reached in alloy systems. Nevertheless, the phase rule is often so valuable in spite of its limitations that an understanding of it in its simplest form is essential.[1]

The general statement of the phase rule is as follows:

$$P + V = C + 2$$

in which V represents variance or the number of *degrees of freedom*, C the number of *components*, and P the number of *phases*. In the general case, these factors are often difficult to define, but in the application to metallic alloys no such difficulty is encountered. The *components* C

[1] For a detailed discussion see FINDLAY, "The Phase Rule and Its Applications."

are obviously the metals. The *degrees of freedom* are the independent changes that the alloy can undergo, namely, changes of temperature, concentration, and pressure. Since vapor can be neglected with most alloys and since the pressures commonly met in alloy practice are too small to have any appreciable effect, changes in pressure can be omitted, reducing the variables (degrees of freedom) to temperature and concentration. A *phase* is defined as a homogeneous, physically distinct substance. In dealing with alloys, it may be a pure metal, a metallic compound, or a solid solution. In addition, each physical state of the substance, whether solid, liquid, or gas, constitutes a separate phase.

Neglecting the vapor phase and the effect of pressure, the phase rule for alloys may be reduced to the simple form

$$V = C + 1 - P$$

The number of components in a binary alloy is two, so the expression is still further simplified and takes the form

$$V = 3 - P$$

A concrete illustration of the use of the phase rule is given in the following diagram, Fig. 15. A point at X lies in the liquid phase. Substituting 1 in the simplified expression, it becomes, $V = 3 - 1 = 2$. In words, the alloy now possesses 2 degrees of freedom. Both temperature and composition can be varied within the area bounded by AEB and the alloy will stay molten. This field then represents an area of *divariant equilibrium*. At the point X_1 on the line AE, the solid is beginning to separate but is in contact with the liquid. Two phases, solid and liquid, are present, and the expression becomes, $V = 3 - 2 = 1$. The alloy now has only 1 degree of freedom, for any change in temperature is accompanied by a change in concentration along the line AE, and a change in concentration necessi-

tates a change in temperature. The lines AE and BE are therefore lines of *monovariant equilibrium*. At the point E, the eutectic point, or at any other point on the eutectic line CED, two crystal phases, A and B, are in contact with a liquid phase of composition E. (Solid E contains A and B in the form of very fine crystals.) Under these conditions, the expression becomes $V = 3 - 3$ and the system becomes *nonvariant*. Neither the temperature of the

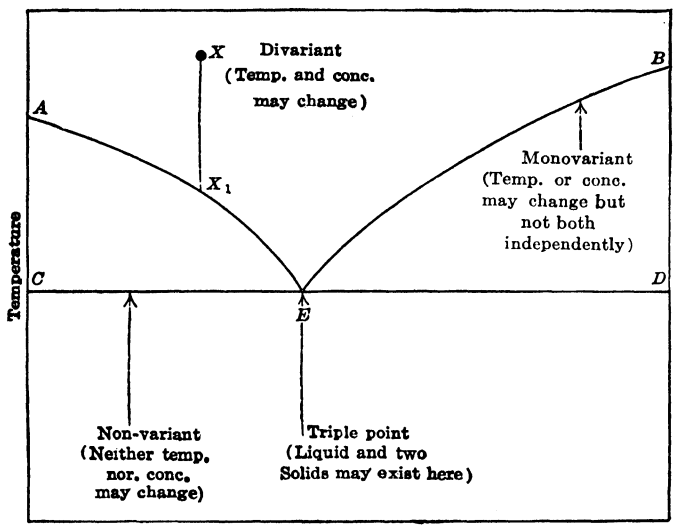


FIG. 15.—Phase-rule diagram for binary alloys.

mixture nor the composition of the three phases can change until one of the three phases has disappeared. The temperature cannot fall until all the liquid phase E has solidified nor can it rise without the disappearance of either A or B. It must not be understood that the *mixture* can have only the composition represented by the point E. It may have any composition along the line CD, but the *composition of each phase* remains the same, the difference in original composition producing changes in the *relative amounts* of the three phases. The line CD, therefore, is a line of nonvariant equilibrium.

One of the principal uses of the phase rule is to determine whether or not true equilibrium has been reached. It is evident that, since an alloy with less than 0 degrees of freedom is an impossibility, there can never be more than two solid phases in contact with, or separating from, a two-component liquid metal. Therefore, in a case like that indicated in Fig. 29, page 34, and illustrated in Fig. 30, page 36, the presence of *three* phases, in the microscopic section of the solid alloy, is a positive indication of incomplete equilibrium.

The Solid Solution.—The eutectic type diagram (p. 6) indicates that the metals are soluble in each other in all proportions in the molten state but wholly insoluble after solidification has been completed. Another relationship which may exist between metals is a partial or complete solubility of one metal in the other *in the solid state* as well as in the molten condition. This relation is known as the formation of a *solid solution.* The solid solution differs from the liquid solution simply in its physical condition. Like a liquid solution, it may be homogeneous and may be unsaturated or saturated.

Consider as an example of this class of alloys the important group of lead-tin alloys in which will be found the common solders. Figure 16 gives the diagram of this set of alloys as constructed from the cooling curves. This differs from the simple eutectic diagram shown in Fig. 3, page 6, only in the location of the sloping lines AB and CD, the significance of which is merely that melted lead, having tin in solution, is able to retain about 19.5 per cent of it after solidification and that tin will retain about 2.5 per cent lead. This diagram, like that of the eutectic alloys, may be studied conveniently by considering the changes taking place during the cooling of the alloys ①, ②, ③, and ④ (Fig. 16). When an alloy containing about 15 per cent of tin is at the temperature indicated by ①, it is completely liquid. When the point a is reached

the alloy begins to solidify. The fact, however, that distinguishes the cooling of an alloy which is to form a solid solution from a simple eutectic alloy is that the crystal that first begins to separate, in this case at the point *a*, is not a pure metal but is a solid solution, the composition of which is represented by the point *a'*. It should be noted, in this connection, that at the temperature corresponding exactly to the point *a* there is actually no sepa-

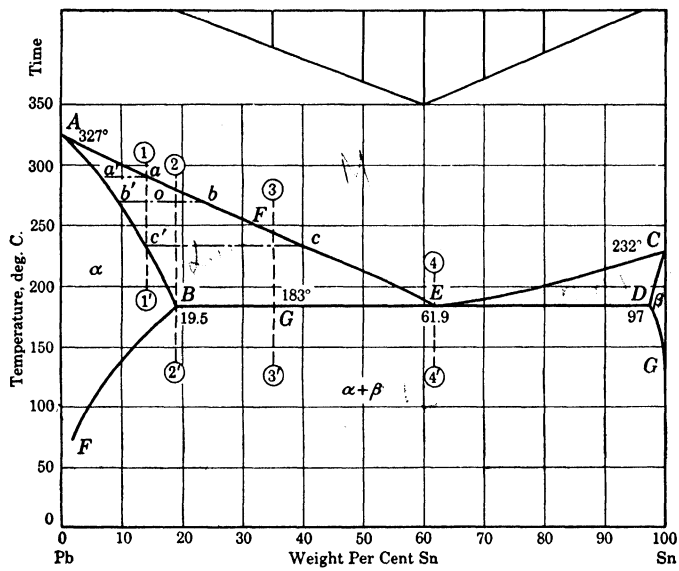


FIG. 16.—Lead-tin diagram.

ration of solid but that when the temperature falls ever so slightly below this point solid begins to form and increases in amount with the falling temperature. Since the amount of solid formed at first is so extremely small, the experimental determination of its composition would be difficult. When the temperature has fallen to the point *b*, enough solid could be separated from the remaining melted metal for analysis. The composition would be found to correspond closely to that indicated by *b'*. As the mass of metal continues to cool, the composition of the

crystals changes along the line *AB*, which includes the points *a'*, *b'*, and *c'*, and that of the liquid along the line *AE* containing the points *a*, *b*, and *c*.

Since the *average* composition of the final solid alloy must be the same as that of the original melted metal ①, it follows that at the point *c'* the last trace of melted metal, the composition of which is *c*, disappears. The relations between liquid and solid just described are often considered in terms of equilibrium. It may be said that crystal *a'* is in equilibrium with liquid *a*, crystal *b'* with liquid *b*, and crystal *c'* with liquid *c*. In other words, at the temperature represented by the line *b'b* crystals of *b'* will stay unchanged indefinitely in a liquid of the composition *b*. This stable relationship between crystals and melt would not exist between *b* and *b'* if the temperature were changed in the slightest degree, nor if the temperature were kept constant could any lead-rich liquid and solid of different compositions from those corresponding to *b*-*b'* exist together. Because of the fact that *a'*, *b'*, and *c'* represent the compositions of the solids in equilibrium with the liquids *a*, *b*, and *c*, respectively, the name *solidus* has been given to the line connecting the points *A*, *a'*, *b'*, *c'*, *B*, *E*, *D*, *C* and *liquidus* to the line *AabcEC*, connecting those points which represent the compositions of the liquids with which these solids are in contact. The liquidus represents the beginning of solidification and the solidus the end.

The perpendicular line *ac'* is one of great importance in interpreting the diagram. It is possible to state the relative quantities of liquid and solid that can exist together at any given temperature within the solidification range. It is evident that the amount of crystal *a'* existing in the presence of the liquid *a* must be infinitely small, as these points represent the beginning of the change from the liquid to the solid form, and it is equally true that at the temperature *cc'* the amount of liquid is infinitely small, as this represents the temperature at which the freezing is

completed. Between these extremes lie all possible relationships between solid and liquid. These relationships, however, are graphically represented by the horizontal lines left and right from the line ac' to any pair of liquid and solid phases in the series. The distance from a to a is zero, indicating that there is no solid; the distance from c' to c' is also zero, showing that there is no liquid; while the distance ob (right from the line ac') shows the relative amount of solid of composition b' as compared with ob', the amount of liquid of composition b.

This diagram will serve as an excellent example of the application of the phase rule. In this connection two rules suggested by Hoyt in his "Metallography"[1] will be found helpful.

"Rule I. In a Field of Heterogeneous Equilibrium, to Determine the Compositions of the Two Phases which are Stable at any Temperature. Draw the temperature horizontal; its intersections with the two conjugate lines bounding the heterogeneous field will give the points representing the compositions of the two phases which are in equilibrium at that temperature.

"Rule II. To Determine the Relative Amounts of the Two Phases. Draw the concentration vertical (or 'Characteristic line') representing the total concentration; the relative amounts of the two phases may be ascertained from the 'lever relationship' using the two intersection points as the points of application of the two loads, and the intersection of the total concentration vertical and temperature horizontal as the fulcrum point. The loads required to maintain a balance, expressed in per cent, as computed for the two lever arms, give directly the relative amounts of the two phases."

In the diagram, Fig. 16, the area above the lines AEC indicates a single phase. There are, therefore, two degrees

[1] HOYT, "Metallography," Part I, p. 12, McGraw-Hill Book Company, Inc., New York, 1920.

of freedom so that both temperature and composition may be varied without changing the physical character of the phase. Lines AE and CE, showing the beginning of freezing, represent a situation in which a liquid phase and a solid phase exist together. The number of phases is now two; the number of degrees of freedom, therefore, is one, and monovariant equilibrium exists. Temperature may change with an associated change in the composition of the two phases, or the composition may change with a corresponding change in temperature, but both temperature and composition cannot change independently. At point E three phases, solid D, solid B, and liquid E, exist together. With two components, lead and tin, and the three phases, the rule shows that there can be no degrees of freedom, so that E represents nonvariant equilibrium.

In the meaning of Rule I, lines AB and AE and lines CE and CD are *conjugate lines*, as they bound the two heterogeneous fields in which liquid and solid exist together. The lines $a'a$, $b'b$, and $c'c$ are the *temperature lines* of Rule I, and the points of intersection with the conjugate lines AB and AE show the compositions of liquid and solid phases that are in equilibrium at the temperatures given.

Rule II may be used to show the amounts of liquid and solid existing at any given temperature. ①–① is the *concentration vertical* ("characteristic line") and the distances ob and ob' show the relative amounts of solid b' and liquid b in accordance with the lever law:

$$\frac{\text{The amount of } b'}{\text{The amount of } b} = \frac{ob}{ob'}$$

The nature of the solidification of a solid-solution crystal naturally determines the shape of its cooling curve. When a pure metal or a eutectic mixture solidifies, the crystal separating and the liquid from which it separates have the same composition, and, following well-established laws, the temperature stays constant during freezing and appears

as a horizontal line on the temperature-time curve. In the freezing of solid solutions, however, the solidifying crystal changes its composition constantly, as does the solution from which it is crystallizing. The solidification, then, is not that of a single solution but of an infinite number of solutions having a corresponding number of freezing points. The effect of this sort of freezing is to produce a curve that shows, not a horizontal line, as in the case of a pure metal, but an oblique line indicating a change in the normal cooling rate during the solidification

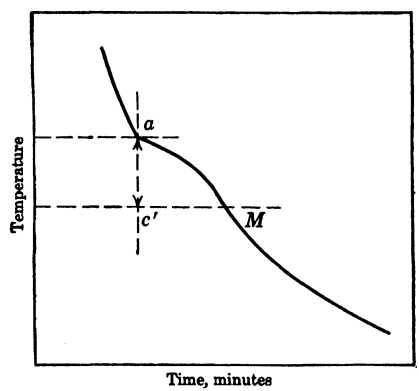


FIG. 17.—Type of solid-solution curve.

interval. The normal curve of a solid-solution alloy is shown in Fig. 17, in which point *a* represents the beginning of the freezing and point *M* the end, after which the normal cooling rate is resumed. The perpendicular distance between *a* and *M* is shown by the line *ac'* and represents the temperature drop during the process of solidification. Point *a*, then, represents one point on the liquidus (Fig. 16), and *M* or *c'* a point on the solidus. By constructing a number of freezing-point curves and determining the temperatures at which freezing begins and at which it ends in each, the liquidus and the solidus can be located.

The mechanism of the cooling of alloy ② (Fig. 16) is the same as that of ①. The solid alloy differs from ① only in

that the lead in ① is capable of dissolving more tin and is therefore an *unsaturated* solid solution, while in ② the lead is not able to hold any more tin in the solid state at this temperature and is therefore a *saturated* solid solution. Alloy ③ starts to solidify in the same manner as alloys ① and ②, and cooling then takes place exactly as in the eutectic alloy. Since, however, it contains more tin than is needed to form the primary saturated solid solution, the temperature falls to that corresponding to *BD* when the remaining liquid solidifies to form the eutectic *E*, one constituent of which is the saturated solution of lead in tin, the other the secondary saturated solid solution of tin in lead. The behavior of alloy ④ is exactly analogous to the freezing of simple eutectic alloys, differing only in that the components of the eutectic are the saturated solid solutions α and β.

The lines *BF* and *DG* (Fig. 16) indicate changes which take place below the eutectic temperature *BED*. In most instances, the solubility of one metal in another in the solid state decreases as the temperature falls. This is indicated in the sloping of the line *BF* toward the left. Alloys on the left of *BF* are lead-rich solid solutions and those to the right contain more or less of the tin-rich solid solution *E* at temperatures below *BED*. If in passing from a high temperature to a low temperature the composition line crosses *BF* at a temperature lower than *B*, a decomposition of the lead-rich solid solution should occur with the formation of a small amount of the tin-rich solid solution and a corresponding reduction in the amount of tin completely dissolved in the lead. This decomposition, since it takes place in the solid state, is often sluggish and in many cases in practice does not occur at all except as a result of extremely slow cooling. The shape of a curve of this kind can best be determined by *x*-ray methods (p. 297).

In some instances the solid solubility of one metal in another does not decrease as the temperature falls but stays constant at all temperatures. In this case the line *BF*

would become straight and perpendicular to the line *BED*. A third condition may exist in which the solid solubility *increases* as the temperature *decreases*. Under these circumstances the line *BF* would slope to the right from *B*. Because of the difficulty in determining accurately the slopes of these solid solubility lines, they are often indicated by dotted lines in alloy diagrams. When these lines have been located definitely, their positions in the diagram are shown by solid lines.

Of the many mixtures of lead and tin used for soldering purposes, three may be taken as typical. That with 38 per cent lead corresponds to the eutectic *E* and because of its low melting point is commonly called *tin solder*. *Plumbers' solder* contains approximately 67 per cent lead (2 parts of lead to 1 of tin) and probably the most common of all solders is one with equal parts of tin and lead. The diagram shows that the alloy ③–③ does not change suddenly from a liquid to a solid as does the eutectic alloy but that it freezes slowly through the temperature interval *FG*, a range equal to about 100°C. In this interval, the alloy is composed of lead-rich crystals carried in melted metal, producing the pasty consistency that makes the plumber's *wiped joint* possible.

The extent of the solid solubility of the metals in each other may be determined in two ways. First, since there is no separation of a second crystal form until the concentrations represented by points *B* and *D* are exceeded, it follows that no evolution of heat will be noticed on the cooling curve at the eutectic temperature (183°C.) until the limit of solubility has been reached. Or, conversely, if a horizontal line is drawn through the points locating the eutectic temperature, the ends of the line will be found at points *B* and *D*, the limits of the solid solution. The second method of locating the limit of solubility in the solid state is by microscopic examination. The microscopic appearance of the lead-tin alloys is exactly what would be expected

from the diagram. From 100 per cent lead to 80.5 per cent lead, the alloys do not pass through a eutectic transformation during equilibrium cooling. From 80.5 per cent lead to 38.1 per cent lead the solid alloys show gradu-

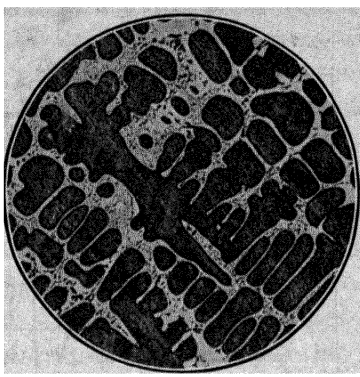


FIG. 18.—Silver 30 per cent + copper 70 per cent. Dark masses are saturated β (copper-rich). Light area with dark spots is eutectic.

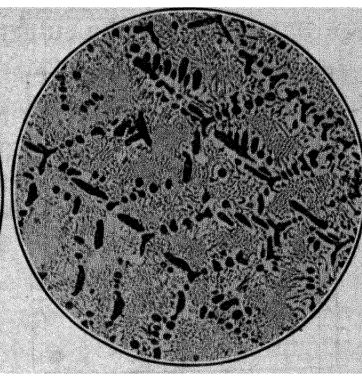


FIG. 19.—Silver 60 per cent + copper 40 per cent. Dark masses are β. Light area with dark spots is eutectic.

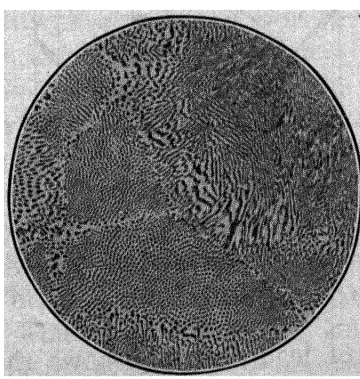


FIG. 20.—Silver 71.9 per cent + copper 28.1 per cent. All eutectic. Dark particles are secondary β in eutectic. Light background is α.

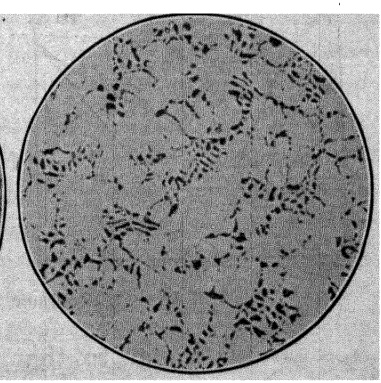


FIG. 21.—Silver 90 per cent + copper 10 per cent. Light is saturated α (silver-rich). Eutectic is dark in contrast to light α.

ally decreasing quantities of the saturated solid solution embedded in the eutectic E. From 80.5 per cent to 2.5 per cent lead the solid alloys show gradually increasing amounts of the saturated solid solution of lead in tin embedded

in the same eutectic E, and from 2.5 per cent lead to pure tin the alloys are once more homogeneous. When the limit of solubility is reached, the addition of the slightest excess of either metal to the other forms an alloy which is no longer homogeneous under the microscope but which will show indications of the eutectic.

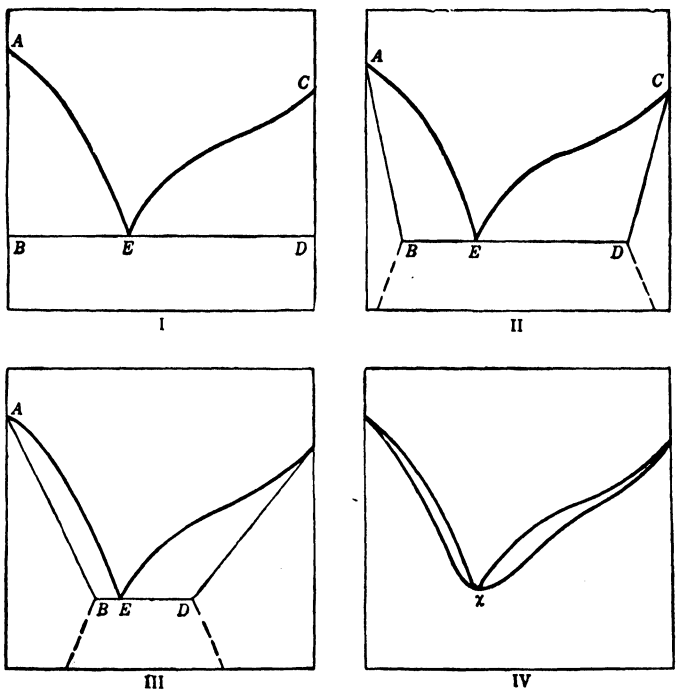


FIG. 22.—Development of the solid solution.

A diagram similar to that of lead and tin shows the relation of copper and silver. The microstructure of the silver-copper alloys is shown in Figs. 18, 19, 20 and 21.

Several of the silver-copper alloys are of commercial importance. American coins and those of several European countries contain 90 per cent silver and 10 per cent copper. British coinage is, however, slightly richer in silver, containing 92.5 per cent. Several alloys of the same type are

known, among them aluminum-tin, bismuth-tin, cadmium-tin, but except for the silver-copper and aluminum-tin, none is of technical importance. Aluminum with a low percentage of tin has been used to a limited extent in making light castings but is unsatisfactory because of the ease with which it corrodes.

The solubility of one metal in another may increase, as shown in the series of diagrams in Fig. 22, until the condition indicated in IV is realized. The line *BED*, representing the secondary or eutectic separation, has gradually shortened with the increase in the mutual solubility of the two metals until in the alloy IV the line has disappeared wholly and *X* represents coincidence of the points *B*, *E*, and *D*, showing that the metals are soluble in each other in all proportions. Diagrams I and IV differ radically in this respect that, although both show the two metals to be soluble in each other in all proportions in the liquid state and although each metal lowers the melting point of the other, diagram I indicates that the two metals are completely *insoluble* in each other in the solid state, while diagram IV shows that the metals are completely *soluble* in each other in the solid state. Alloy *E* in diagram I is as inhomogeneous as possible, while *X* in diagram IV is perfectly homogeneous; it shows clearly that one of the series of perfect solutions has a melting or a freezing point lower than any of the other solid solutions in the series. This is often referred to as the *solid-solution minimum*.

The metals copper and manganese are completely soluble in each other in all proportions in the solid state, but each lowers the freezing point of the other, leading to the formation of a solid-solution minimum like that shown in IV, Fig. 22.

The actual diagram is given in Fig. 23. The method of cooling along the line ① ① and ③ ③ and the changes taking place in the solidification interval between the liquidus and the solidus are exactly similar to those described

in considering the cooling of the lead-rich solid solution in the lead-tin series. The primary separation from alloy ① is a copper-rich crystal, while from alloy ③ it is manganese-rich.

The alloy having the composition ② (copper 70 per cent, manganese 30 per cent) is unique in that it is the only one of the series in which the composition of the crystal first separating is the same as the liquid melt from which

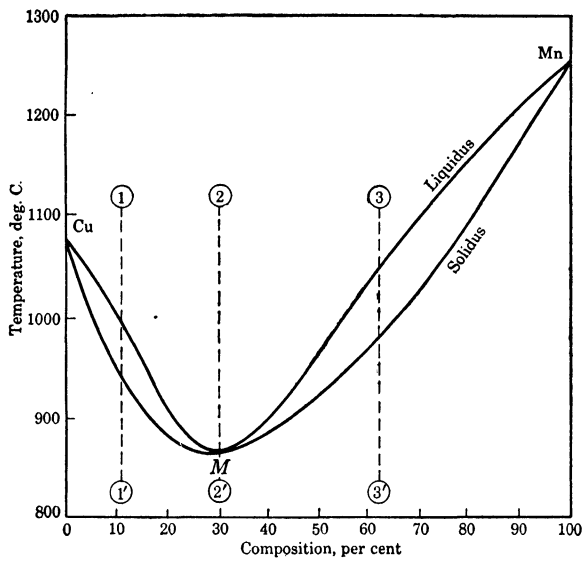


FIG. 23.—Copper-manganese diagram.

it comes. The freezing that takes place at *M* is, therefore, analogous to the freezing of a pure metal, and its cooling curve is represented by two sloping lines connected by a horizontal.

Microscopic Appearance.—The microscopic appearance of solid solutions is often misleading but is readily explained. If perfect equilibrium conditions are reached, the solid solution should, and does, resemble a pure metal. Consideration of the method of freezing makes it clear that, unless time is allowed for the readjustment of the varying

crystal concentrations during freezing, the crystal has an inhomogeneous rather than a homogeneous structure. In the case of manganese-copper, rapid cooling of a copper-rich mixture produces an alloy showing leaf-like masses of a copper-rich alloy embedded in a ground mass of manganese-rich material. In cases of this kind in which not enough time has been allowed during the solidification period for the solid-solution alloy to become completely homogeneous, *dendritic segregation* or *coring* is said to have occurred; the inhomogeneous masses are called *dendrites*. This condition is shown in Fig. 68 (p. 84), Fig. 77 (p. 97), and Fig. 128 (p. 140). A true solid solution can always be made homogeneous by annealing, *i.e.*, heating for a suitable period of time at some temperature below its melting point, so that opportunity is given for the concentrations of the duplex crystals to equalize each other by diffusion.

A limited use has been found for copper-manganese alloys of high copper concentration in firebox stay bolts. An alloy containing 82 per cent copper, 15 per cent manganese, and the rest nickel and iron is the interesting alloy, **manganin,** which has a high electrical resistance and a temperature coefficient of almost zero.

A second type of solid-solution diagram that might be expected would be one in which the addition of each metal to the other *raised* both melting points, producing a solid-solution curve with a maximum. This type has been found in only a few rare metal alloys of no industrial importance.

A third and very important type of solid solution includes that class of metals that are mutually soluble in all proportions, but the diagrams of which show neither a maximum nor a minimum. A relation of this sort is shown in the copper-nickel alloys (Fig. 24). The mechanism of cooling is exactly the same as in the case of the copper-manganese alloys, except that there is no alloy in the series that on crystallizing has the same composition as the liquid

from which it separates. These copper-nickel alloys are of great importance. Some compositions are used for copper coins, an alloy containing 20 per cent nickel is used for capping rifle bullets, one with 30 per cent nickel known as **cupronickel** is used in making condenser tubes, and the alloy 60 per cent copper and 40 per cent nickel has high electrical resistance and a low temperature coefficient. Under the name **constantan** this latter is often used for electrical purposes and, coupled with copper or iron wire, forms an excellent thermocouple. One of the important

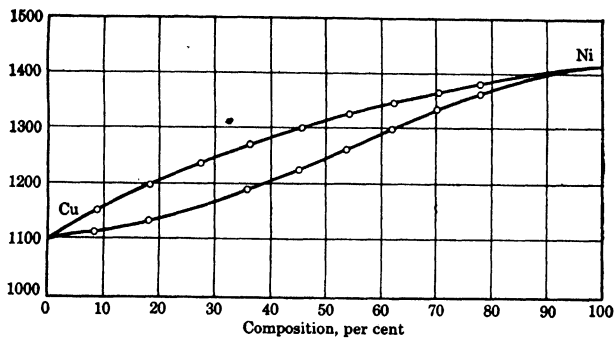


FIG. 24.—Copper-nickel diagram.

Canadian ores is of such a composition that smelting produces a copper-nickel alloy containing about 67 per cent nickel, 28 per cent copper, and a small amount of iron, manganese, and cobalt. The alloy is known as **monel metal**[1] (Figs. 25, 26) and is characterized by its marked resistance to corrosion and by the fact that it retains its strength at high temperatures to a remarkable degree. In this respect, it is better than any other copper-base alloy and much better than common steel. After it has been rolled and annealed, it has a tensile strength of 65,000 lb. per square inch, or better, with an elongation of 40 per cent. At 600°C., its tensile strength is still about 40,000 lb.; a low-carbon steel will decrease in strength to 16,000 lb.

[1] Several monel metal alloys are now available. The properties vary with the amounts of other elements added to standard monel.

under similar conditions. Monel metal is used for valves, pump rods, pump liners, fittings for use with high-pressure steam, and to a large extent in hospital and restaurant tables, sinks, and other equipment. Because of its corrosion resistance, it has been used in the form of circular disks to mark traffic lines on city pavements.

That group of alloys in which the constituents show more or less complete solubility in each other includes by far the greater number of the technically important alloys. Steel, brass, and the bronzes all belong in this class and will be

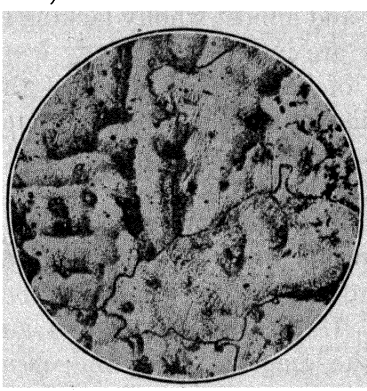


FIG. 25.—Cast. Shows marked dendritic structure due to rapid cooling.

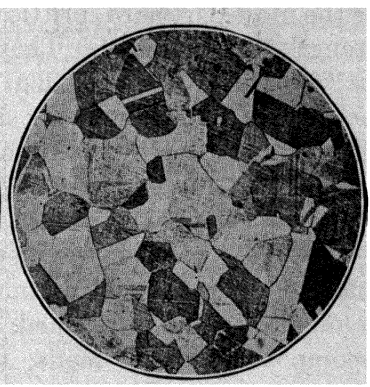


FIG. 26.—Rolled and annealed. Shows twinned crystals (see p. 78).

discussed in detail in later chapters. Brief reference must be made here to a few of the less commonly used alloys of this class which are, nevertheless, important technically. Gold, with dissolved silver, is the basis of gold coinage and jewelry. **White gold** is an alloy of gold with about 18 per cent of nickel or with about 10 per cent of palladium. Of interest to the chemist are **palau,** the palladium-gold alloy used as a substitute for platinum; **nichrome** or **chromel,** the highly resistant nickel-chromium solid solution much used in triangles for laboratory use, for crucible tongs, in heating coils for electric-furnace work, and for heat-resisting containers for various purposes; and **stellite,**

the cobalt-chromium alloy, which, because of its remarkable nonrusting properties, finds varied uses in the manufacture of cutlery, surgical instruments, and the like. Stellite containing tungsten and iron is also used in making metal-cutting tools, since it retains its hardness at high temperatures.

Intermetallic Compounds.[1]—A large number of alloys contain or consist of definite intermetallic compounds of which more than 300 have been found. With few exceptions, these alloys are technically unimportant, as they are for the most part hard, brittle, and almost wholly lacking in strength and ductility. They are interesting chiefly from the viewpoint of the student of valence, as many of the compounds, while relatively simple, show valence relations differing greatly from those that have been generally accepted, as, for example $NaZn_{11}$.

The effect of the existence of a compound on the shape of the equilibrium curve depends on whether the compound does or does not decompose into its elements before its melting point is reached. If the compound does not decompose before it melts, the diagram is of the *open-maximum* type. If it does decompose before the melting point is reached, the diagram is said to show a *suppressed-maximum* or to be of the *transition* type.

The Open Maximum.—The alloys of tin and magnesium illustrate the first type. Tin and magnesium unite to form the compound Mg_2Sn. This compound, which is homogeneous and behaves in every way like a pure metal, is completely miscible both with magnesium and with tin in the molten state but wholly insoluble in both in the solid state. In such a case two systems of the simple eutectic type as shown in Fig. 27*A* and *B* must be considered.

If these two simple diagrams are combined as in *C*, Fig. 27, the result is a typical compound diagram showing a

[1] DESCH, "Intermetallic Compounds," Longmans, Green & Company, New York, 1914.

maximum at a point corresponding to the compound Mg_2Sn. In laboratory practice, there are four indications of the existence and composition of a compound of this type. Representing the two metals as *A* and *B* and the compound as AmBn and assuming that AmBn does not dissolve either *A* or *B* to form a solid solution, it will be seen that:

1. The compound AmBn lies at the maximum of the liquidus curve.

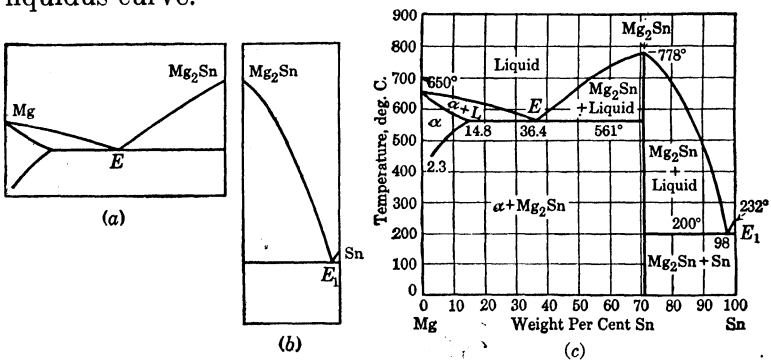


FIG. 27.—Development of open-maximum type diagram. Magnesium-tin diagram. (*Grube.*)

2. The eutectic temperature-hold corresponding to a eutectic between AmBn and *A* becomes zero at *A* and at the composition AmBn.

3. The eutectic between AmBn and *B* also disappears at AmBn.

4. The alloy corresponding to AmBn is the only one that is microscopically homogeneous.

Unfortunately, the methods of locating the compound are seldom as exact as in this case. Far more often the compound will dissolve one or both of the metals from which it is made, to form solid solutions, as indicated in Fig. 28. Under these circumstances, criteria 2, 3, and 4 disappear, as neither eutectic E_1 nor eutectic E_2 ends at the composition AmBn, and the alloy is homogeneous not only at AmBn but also throughout the entire range between *D* and *F*. In

such a case, the intersection of the maximum curve with its tangent, drawn parallel to the concentration axis, indicates the composition of the compound. This point will invariably be found to lie at, or very near, a composition corresponding to a simple atomic relationship. The portions of the solidus below the eutectics shown in Fig. 28 are indicated by dotted lines, as in many cases of this type the actual slope has not been determined.

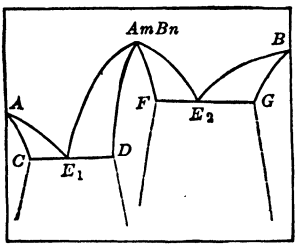


FIG. 28.—Open-maximum type with solid solutions.

The Suppressed Maximum or Transition Type.—This is perhaps one of the most difficult of all alloy types to understand, and, because of experimental difficulties to be referred to shortly, its diagram is

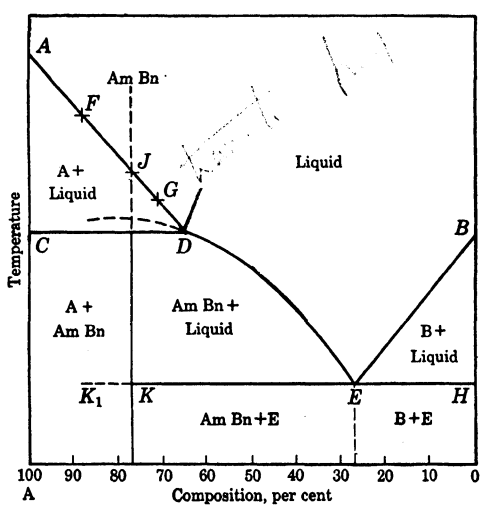


FIG. 29.—Diagram showing concealed maximum.

unsatisfactory to construct. An ideal case is illustrated in Fig. 29.

The metals *A* and *B* unite to form a compound AmBn, but, instead of melting as a homogeneous alloy, the com-

pound decomposes into its elements at a temperature *CD* below its melting point. The result is that, instead of passing directly from a solid compound into a molten metal, it changes at the temperature *CD* into a liquid of composition *D* and a solid of different composition from the original solid, namely, the metal *A*. Conversely, when a mixture of the composition AmBn is cooled from the liquid state, the temperature falls normally until the point *J* on the line *AD* is reached. Here, as the diagram shows, pure *A* begins to separate, and the concentration changes in the usual way until the point *D* is reached. The temperature has now fallen to that point at which the compound AmBn can exist and the tendency for it to form is so great that a reaction takes place between the solid crystals of *A*, which are in suspension, and the liquid of the composition *D*. Since the crystals *A* are obviously far *poorer* in *B* than is the compound and since the liquid *D* is much *richer* in *B* than the compound, a reaction between the two to form the compound causes the complete disappearance of both. If the original mixture has a composition *F*, richer in metal *A* than the compound, not all of the *A* crystals can be used up by the liquid *D*, and the solid alloy is a mixture of *A* and AmBn. If, on the other hand, the original mixture has the composition *G*, containing less *A* than corresponds to the compound, it follows that the *A* crystals which separate first along the line *AD* will be wholly dissolved by the liquid *D* and a certain amount of excess liquid will be left. Crystallization then proceeds along the line *DE* until the eutectic is reached, when the eutectic (a mixture of AmBn and *B*) separates.

Since *D* represents that point at which the pure metal *A* reacts with the liquid and is transformed into the compound AmBn, *D* is often called a *transition point* and AmBn a *transition product.* This type of reaction is often called the *peritectic* type with the temperature of transformation described as the *peritectic* temperature.

As was the case with the open maximum, there is no difficulty in locating the compound in the ideal type of concealed maximum just considered, because the temperature change corresponding to the eutectic E is 0° at the composition of the compound and because, as in the first case, the compound is the only homogeneous alloy in the series. The time during which the temperature stays constant, while the transformation on the line CD is taking place, is longest under ideal conditions at the composition of the compound, dropping to zero at points C and D.

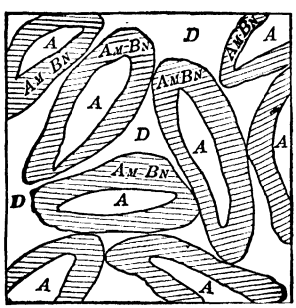


FIG. 30.—Sketch illustrating the phenomenon of "surrounding."



FIG. 31.—Antimony 50 per cent + tin 50 per cent. Shows SbSn inclosing crystals of antimony. The black ground mass is a tin-rich solid solution.

Solid solutions complicate the suppressed-maximum diagram as they do the open-maximum diagram, but there is the additional serious difficulty of incomplete transformation at the point D. This is readily understood from the nature of the reaction taking place at this point. The pure crystals of A begin to dissolve in liquid D to form the compound. This formation takes place on the surface of the crystal, and not infrequently the compound forms a coating around the crystal protecting it from further reaction with the solution D as indicated diagrammatically in the sketch (Fig. 30) and actually in the photomicrograph (Fig. 31).

This phenomenon is known as *surrounding* and makes the location of the compound exceedingly difficult for several reasons. First, the time during which the temperature remains constant at the transition point is normally longest at the composition of the compound but is greatly reduced if the transformation is incomplete, and, instead of decreasing regularly to the left and right of the compound, changes so irregularly that the time curve is of no value. Second, since more of the liquid is left than corresponds to true equilibrium, the eutectic line *HEK* (Fig. 29) extends to the left of its normal limit in some such way as is indicated by the dotted line KK_1. Finally, the alloy, even though it corresponds to the compound, may show three structural elements (Fig. 31). In a case of this sort, practically all that can be done to locate the compound is to anneal a series of alloys in the neighborhood of the compound and determine which one of the series becomes homogeneous.

The hardness of the intermetallic compounds is their most useful property and is made use of in the technical alloys in which they are found. In bearing metals, for example, where a small amount of hard material not easily worn down by abrasion is desired, the compound Cu_3P is found in phosphor bronze and the compounds SbSn and CuSn[1] in Babbitt metal (see p. 45). By far the most important of these compounds is the iron-carbon compound Fe_3C, which occurs in the iron-carbon alloys to be considered later.

Changes in the Solid Alloy.—The diagrams that have been considered so far have dealt with changes that occur when the alloy passes from the liquid to the solid state or vice versa. Some of the most valuable technical alloys, notably steel, acquire their properties or modify them materially by changes which take place in the solid state.

[1] This compound was formerly believed to be Cu_3Sn.

Iron, for example, is known to exist in several allotropic forms, two of which are of great technical importance. Below 768°C. it is known as α-iron and above 906°C. as γ-iron. These two forms differ in many ways. α-iron dissolves carbon only to a limited extent, while an amount of carbon up to about 1.7 per cent will dissolve in γ-iron. γ-iron is either nonmagnetic or paramagnetic, while α-iron is strongly magnetic. The electrical resistance of γ-iron is about ten times that of α-iron, and in other ways the differences may be detected.

In the temperature range between 768 and 906°C., much doubt exists as to the condition of the iron. It is believed by many to be a distinct form of iron and has been called β-iron. The evidence for its existence is a slight temperature effect at about 768°C. and a marked change in the magnetic properties of pure iron at the same temperature. A discontinuity in the tensile properties and in the specific heat of iron is said to have been detected at the temperature associated with β-iron. As against the assumption of the existence of β-iron may be cited the fact that neither in its crystalline form nor in its internal structure as determined by x-ray analysis does it differ from α-iron.

Whether β-iron does or does not exist is at present largely of academic interest and has no bearing on the properties or on the heat treatment of steel. A fourth form, δ-iron, exists just below the freezing point of iron.

More important than changes due to the allotropism of a single metal are those changes which come from the decomposition of a solid solution at temperatures below its freezing point. All the changes that can take place when a liquid solution freezes may also occur when a solid solution decomposes. It may change to a eutectic-like mixture or to another solid solution more or less complete, or it may decompose to form one or more compounds. Some of these possible changes are indicated in the sketch (Fig. 32). The most important of these transformations in

the solid state is that shown in I of this sketch, as many of the valuable properties of steel, given to it by heat treatment, are due to a decomposition of this sort. Although the details will be given later, it may be said that the transformation from a solid alloy of the solid-solution type to one of a different character requires a definite amount of time, and that, by shortening the time, this transformation can be partially or wholly suppressed. For example, by suddenly cooling (quenching) an alloy from the temperature indicated by 1 in Fig. 32,I, it is possible to prevent

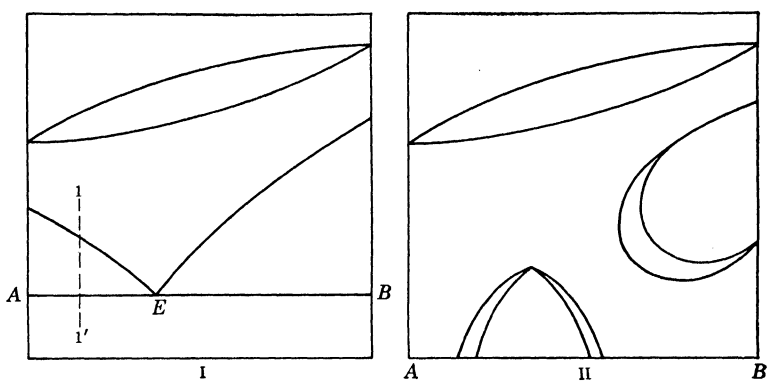


FIG. 32.—Types of changes which may occur in the solid state.

the transformation along AE of the solid alloy into that represented by 1′ with the result that at ordinary temperature the alloy exists in the condition that it had at the higher temperature 1. The physical properties of a solid solution are so different from those of a eutectic-like mixture that the mechanical properties of the alloy can be profoundly modified and can be controlled within fairly definite limits by more or less completely checking the change from 1 to 1′. The alloy represented by the point E, Fig. 32,I, has all the characteristics of the eutectic mixture that separates from a liquid solution. Since the separation takes place from a *solid* solution, however, the name *eutectoid* is commonly given to it.

Many binary diagrams of a much more complex character might be discussed, but all of them are combinations of the simpler ones and can be constructed or interpreted without difficulty. It is necessary only to break down the complex diagrams into the simpler elements of which they are composed in order to make them perfectly clear. Examples of complex diagrams are the Al-Cu system (p. 100) and the Cu-Sn system (p. 95).

Ternary Alloys.—The alloys of three or more metals form a large and, to a great extent, an undeveloped field of metallography. The experimental work, while no more difficult than for the binary mixtures, is much more expensive and time consuming because of the larger number of experiments needed to establish the relationships. The study of ternary systems will be extended in time and will, doubtless, lead to the discovery of other interesting and commercially important alloys.

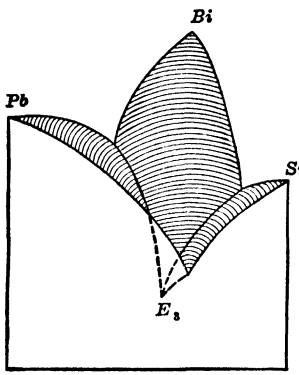


FIG. 33.—The ternary model. (The intersection of the dotted lines E_3 is the ternary eutectic.)

Anything like a complete discussion of ternary diagrams is beyond the scope of this book, but a single example will be considered to show the methods of representing these alloys and the way in which the diagrams are constructed from experimental data.

It is evident that the relation of *three* metals cannot be represented in a plane as in the case of the binary alloys. The easiest way to visualize these relationships is, perhaps, in the form of a space model (Fig. 33) on a triangular base, the corners of which represent the three component metals, while the perpendiculars to this triangular plane represent the temperatures. Such a method of representation has many disadvantages. It is difficult to construct mechanically and is unsatisfactory in that it shows only the

liquidus, *i.e.*, the surface on which solids begin to form, and gives no idea of the changes that take place beneath the surface. A more satisfactory method consists in the projection on a triangular surface of a series of contour lines indicating temperature changes. Such a figure, together with a series of triangular diagrams showing the conditions

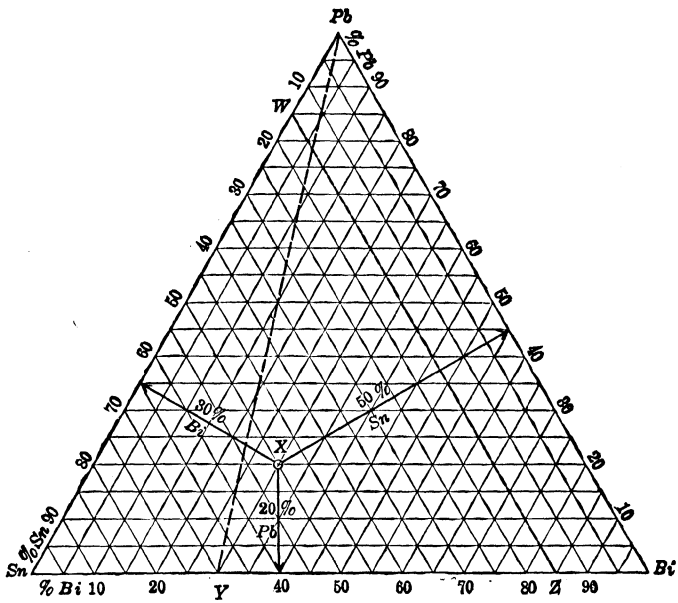


FIG. 34.—Method of showing the composition of ternary alloys.

existing at varying stages of the crystallization, will usually be enough to indicate the various products formed.[1]

In the graphic representation of a ternary alloy, the first step is a method of showing the composition of any given mixture. This is done most easily by the use of plotting paper with triangular coordinates. An example of a simple ternary alloy is the series composed of lead, tin, and

[1] An excellent discussion of ternary alloys will be found in GULLIVER, "Metallic Alloys," 2d ed., p. 340, from which much of the following material is taken and in MARSH, J. S., "Principles of Phase Diagrams," McGraw-Hill Book Company, Inc., New York.

bismuth. In the diagram, Fig. 34, the three corners represent the pure metals. The base of the triangle of which each metal is the apex represents, therefore, zero concentration of that element. For example, the line Pb-Sn represents 0 per cent Bi, the line Pb-Bi 0 per cent Sn, and Bi-Sn 0 per cent Pb. Starting with these lines as bases and approaching the element whose percentage is desired, each line parallel to the base indicates 1 per cent, assuming, as is usually the case, that the triangle is divided by 100 parallel lines in each of the three directions. Point *X* in the figure therefore represents 20 per cent Pb, 50 per cent Sn, and 30 per cent Bi.

A study of the geometry of this figure shows two other facts that are of importance in the actual construction of these diagrams. A line drawn from any corner to any point of the opposite side represents a series of alloys in which the proportions of two of the metals remain constant while the percentage of the third metal varies. *Pb-Y*, for example, is a line on which the ratio of tin to bismuth is always 7:3. A line parallel to one side of the triangle represents a series of alloys in which one metal has a constant percentage while the other two vary. On *WZ*, tin is always 15 per cent, while the lead increases from 0 per cent at *Z* and the bismuth from 0 per cent at *W*.

The next step in the construction of the model would be to erect three plane figures on the three edges of the triangle corresponding to the three binary alloys. The sketch (Fig. 35) shows the appearance of such a space model.

If lead is then added to the binary eutectic of bismuth-tin, the melting point of the mixture is lowered. The same effect is noticed when tin is added to lead-bismuth and when bismuth is added to lead-tin. Since these three lines all slope downward, their intersection must lie at a point lower than the melting point of any of the binary eutectics. This point is shown at E_3, Fig. 33 (p. 40), and is the ternary eutectic. The shape of the space model for an alloy of this

type will be apparent from the considerations just outlined. The three lines connecting the single ternary eutectic with the three binaries form the lower edges of the three valleys made by the intersections of the three curved surfaces composing the liquidus.

If this surface is projected onto its triangular base and contour lines are drawn, representing the intersections of a series of parallel horizontal planes with the space model, a figure of the shape shown in Fig. 36 results. These contour lines, which are naturally isothermals (lines of constant temperature), show that the surfaces above the binary eutectic valleys are convex.

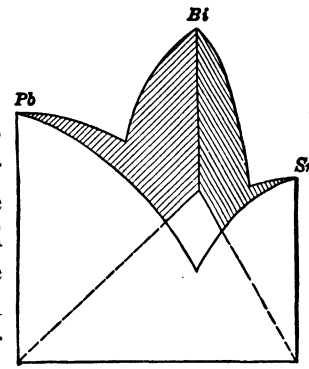


FIG. 35.—Combination of the binary surfaces—lead-tin, tin-bismuth, and bismuth-lead.

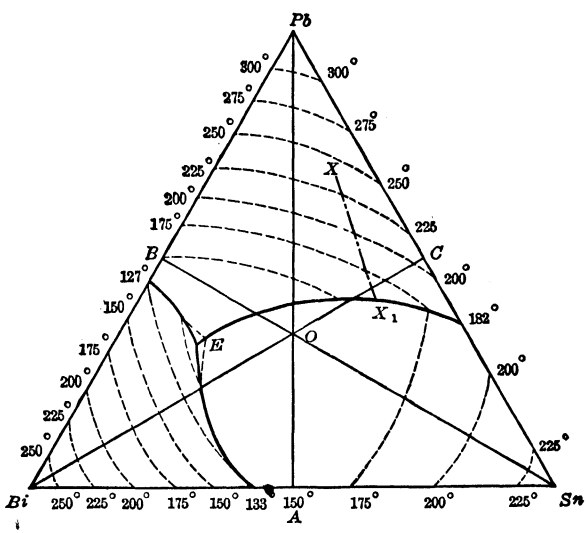


FIG. 36.—Ternary diagram with contour lines. (*Charpy.*)

Consider, next, the changes that take place on cooling such an alloy as is represented by X in the diagram. As

the temperature falls, pure lead separates along the line X-X_1, the relationship of bismuth and tin staying constant. At X_1 enough lead has separated so that lead and tin are in the eutectic ratio, and the two metals crystallize together along the bottom of the binary eutectic valley until the composition E is reached, at which point the remaining liquid solidifies as the ternary eutectic. Although, accurately defined, a eutectic should be of constant melting point, the binary mixtures of eutectic composition vary in melting point with the amount of the third element. As a matter of simplicity, however, the mixtures of binary eutectic composition are usually referred to as *binary eutectics*. If a number of ternary alloys of Pb, Sn, and Bi are studied and the points determined at which the binary eutectics begin to form, planes drawn through these points will give the *binary eutectic surface*. This is found to consist of six twisted surfaces, each intersecting its neighbor in such a way that there will be three ridges, the binary eutectic lines, and three valleys, the projections of which connect the ternary point E with the three corners of the triangle. Since all alloys of the series become solid at the temperature of the ternary eutectic, the *solidus* is a horizontal plane through the ternary eutectic point E.

In the actual construction of these ternary diagrams, the common practice is to study a number of vertical sections from which the space model or its projection can be assembled. In the lead-tin-bismuth series, for example, a fairly complete study of the alloys of the compositions represented by the lines *Pb-A*, *Sn-B*, and *Bi-C*, Fig. 36, gives a general idea of the shape of the model, and the necessity for further study in the area *Bi-O-B* is apparent.

Referring again to Fig. 34, it will be seen that a series of alloys starting with the composition represented by X and with gradually increasing percentages of bismuth (section *X-Bi*) will give much additional information with regard to conditions in the eutectic area. This series might

be followed by another section in which the percentage of bismuth is kept constant at 50 per cent, while lead and tin are varied. By studying several sections in this way, it is soon possible to construct the space model accurately.

Microscopic Appearance of Ternary Alloys.—The microscopic study of these alloys is not satisfactory. The primary crystals are perfectly normal, but the binary eutectic separations occur so slowly and over so considerable a temperature range that segregation generally takes place and the normal eutectic structure is lost. The ternary eutectic is usually so finely divided and so intimate a mixture that the component elements can be found only by careful double etching and then with much difficulty.

In the class of technically important ternary alloys are included **Babbitt metal** and **nickel silver** (formerly called **German silver**). The composition of Babbitt metal varies over a considerable range but it is usually an alloy of tin, antimony, and copper. A common composition is tin, 85 per cent, antimony, 10 per cent, and copper, 5 per cent. Microscopic examination shows the alloy to consist of crystals of SbSn and CuSn embedded in a tin-rich ternary eutectic. Babbitt metal is an antifriction alloy; because of relatively low tensile strength it is commonly used to line bronze, steel, or aluminum-alloy bushings, the backing metal giving the needed strength and the Babbitt the low frictional resistance. The microscope is of great use in controlling the manufacture of Babbitt-lined bearings, as by its aid it is possible to detect segregation in the metal and also to determine the size of the SbSn crystals. Large crystals, due to very slow cooling when the Babbitt is cast, and exceedingly fine crystals, due to a sudden chilling of the molten metal, both produce unsatisfactory bearing surfaces. A temperature of approximately 100°C. for the mold has been found to give satisfactory results. The pouring temperature depends on the composition of the Babbitt metal but is in the range from 280 to 320°C. Lead is often added

to Babbitt metals and in the *lead-base* Babbitt it is substituted for tin. Figures 37 to 44 show the structures of Babbitt alloys of different compositions and prepared under varying cooling conditions.

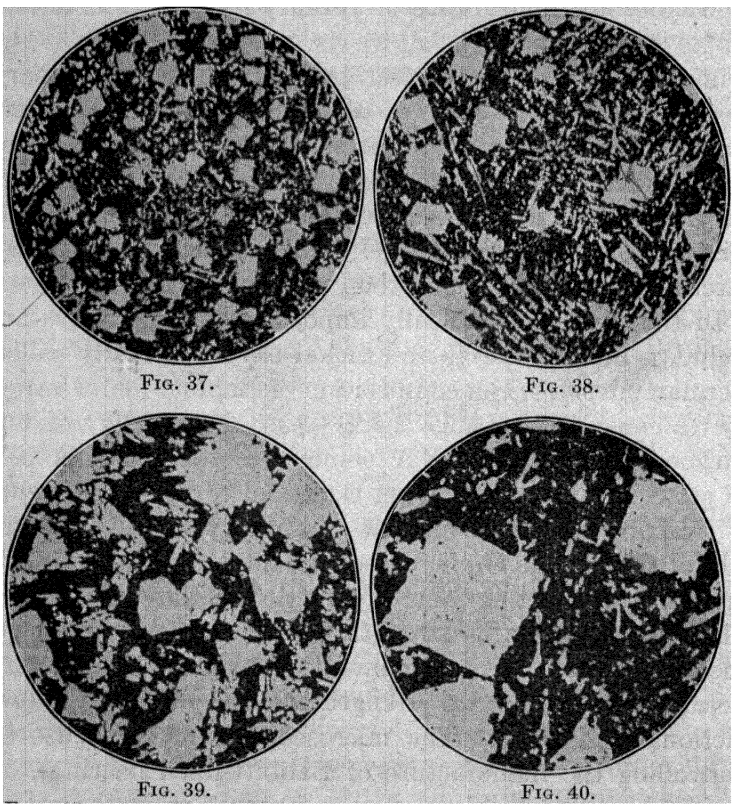


FIG. 37. FIG. 38.

FIG. 39. FIG. 40.

FIGS. 37 to 40.—The white, square, or angular masses are SbSn. The small white particles, often star shaped, are Cu_6Sn_5. The dark matrix is chiefly tin in a fine ternary eutectic.

Nickel silver is composed of copper, nickel, and zinc. It has a wide use in the production of noncorrodible articles, table ware (with or without silver plating), and the like.

Alloys with four or more components are not uncommon. Some of them find important application in the manu-

facture of easily melted fuse plugs for automatic sprinkler systems. **Wood's metal** corresponds to the ternary eutectic of Bi, Pb, and Sn to which a small amount of Cd is added. It melts at 70°C.

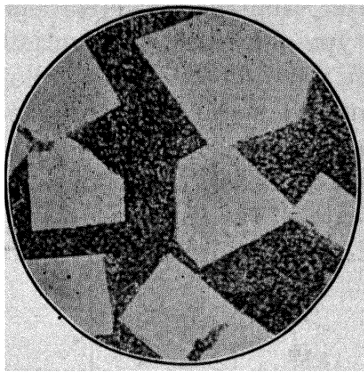


FIG. 41.—Tin 50 per cent, antimony 15 per cent, lead 33.5 per cent, copper 1.5 per cent. Large crystals are SbSn. Matrix is eutectic.

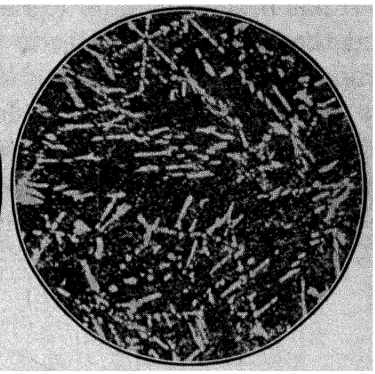


FIG. 42.—Tin 90 per cent, antimony 5 per cent, copper 5 per cent. White particles are CuSn. Matrix is eutectic.

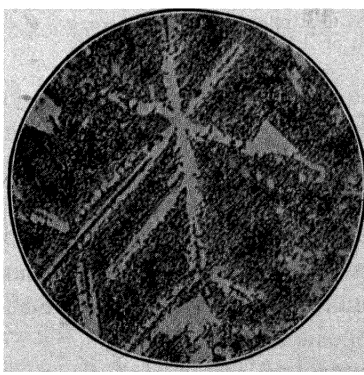


FIG. 43.—Tin 83⅓ per cent, antimony 8⅓ per cent, copper 8⅓ per cent. A few angular, white crystals of SbSn and a large star crystal of CuSn. Matrix is eutectic.

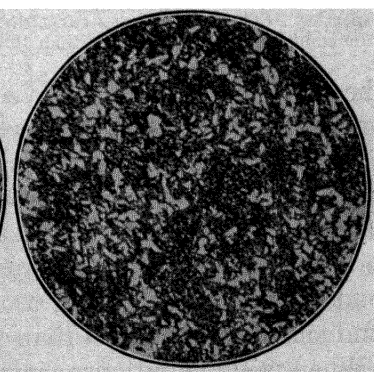


FIG. 44.—Tin 5 per cent, antimony 15 per cent, lead 80 per cent. White particles are antimony and SbSn. Matrix is eutectic.

The various types of diagrams just considered are of more than theoretical interest as a definite relationship exists between the physical properties of alloys and their internal structure. While not enough information is available to

make it possible to calculate the physical properties of all alloys with accuracy, the general effects of structural changes have been so well established that much useful information is given by a simple inspection of any diagram.

It has been shown, for example, that the tensile strength and the hardness of eutectic-type alloys are substantially proportional to the percentage composition of the alloy. In other words, a straight line connecting the hardness value of one metal with that of the other, as the composition of the alloy changes, gives a sufficiently exact indication of changes in hardness or strength of the composite alloys.

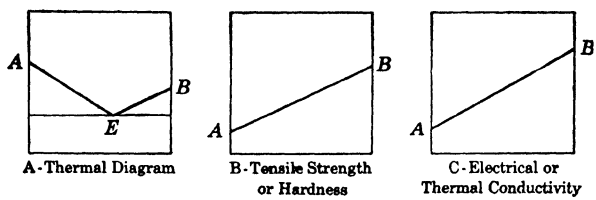


FIG. 45.—Relations between thermal diagram and mechanical or electrical properties. (The conductivity curve does not follow the tensile strength curve if the conductivity of *B* is lower than that of *A*.)

The electrical conductivity of the eutectic alloy will be found almost directly proportional to the *volume* of each of the two metals in the system. These relations are suggested in the three sketches of Fig. 45. These curves suggest that in general the eutectic-type alloy would not be selected if greatly increased hardness or electrical conductivity were desired, as neither the hardness nor the conductivity can exceed that of the metal.

When solid solutions occur in an alloy system, very characteristic changes in the mechanical and electrical properties of the resulting alloys are found.

While the relations between the properties of solid-solution alloys and the corresponding thermal diagrams cannot be calculated with the approximate accuracy that is possible with the eutectic-type alloys, it is nevertheless true that the effects on one metal of the solution in it of another are of much greater magnitude and, from a practical

viewpoint, of far greater importance. The hardness and tensile strength of any metal are markedly increased by the addition to it of any other metal that it will hold in solid solution. Since the solution of the harder and stronger metal, copper, in soft, weak tin might logically be expected to harden and strengthen the tin, it would at first sight seem illogical that the same effect should be obtained by reversing the process. It is true, however, that the addition of even a small amount of soft tin to the much harder copper greatly strengthens and hardens the latter. It is certain that any metal dissolved in another hardens and strengthens the solvent metal, whether

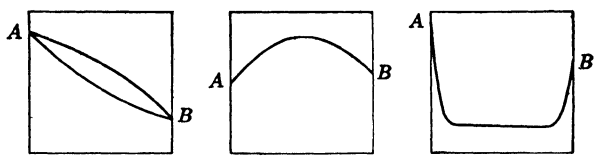


FIG. 46.—Relations between thermal diagram and mechanical or electrical properties.

the dissolved metal is harder or softer than the solvent metal. The effects of the formation of solid solutions on electrical conductivity are even more striking, as the solution of an exceedingly small amount of one metal in another often causes a considerable decrease both in electrical and in heat conductivity. The general relations are shown in Fig. 46.

The steepness of the sides of the U-shaped curve in *C*, Fig. 46, is especially significant as it indicates the marked effect on the electrical conductivity produced by a small amount of the dissolved metal. This fact is of great importance in the production of copper for electrical purposes (p. 94).

Figure 46 shows clearly that if strong, hard alloys are desired, or alloys having high electrical or heat resistance, those showing partial or complete solid solubility in the thermal diagram should be selected.

The curves relating the properties of alloys in which intermetallic compounds occur to the thermal diagram depend on the relation between the compound and its constituent metals. Almost without exception, the compounds are much harder than their components, but they may or may not dissolve their constituents or be dissolved by them. The solubility relations in this case determine

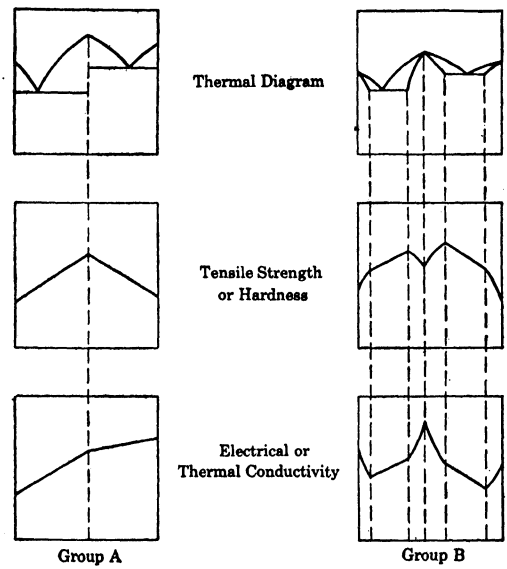


FIG. 47.—Relations between thermal diagrams and properties.

the mechanical and electrical (or thermal) properties (see Fig. 47).

In the practical use of the relations described, it must be remembered that they are for the most part of a general character and in many instances are based on incomplete experimental data. They are, however, sufficiently well established to make them of very real value in the selection of alloys for particular purposes. As a single illustration, it is evident that for the manufacture of an electrically resistant material a solid-solution-type alloy would always be selected rather than one of the eutectic type.

CHAPTER III

THE PLASTIC DEFORMATION AND ANNEALING OF METALS[1]

One of the most characteristic properties of metals and alloys is the high degree of plasticity which they combine with their high strength. Metals and alloys are generally capable of undergoing considerable deformation without rupturing, even under suddenly applied loads. This combination of strength and plasticity is found in no other class of materials and is of great industrial importance. It permits the shaping of metals into many forms, such as beams and rails by rolling, crank shafts and axles by forging, car wheels by pressing, rivets by upsetting, automobile parts by stamping, bowls and shells by spinning, and thin-walled containers by deep drawing. After being formed, the various metal shapes may be used for countless applications where ductility and resistance to shock as well as high strength are essential. In service, metals can deform without breaking to accommodate the inevitable misalignments and changing stress conditions which occur in structures and machines. In fact, this deformation actually increases the hardness and the strength of metals under stress.

Plastic deformation of metals is also utilized to improve some of their physical properties. The cold rolling of metal strip to increase the hardness and the cold drawing of wire to increase the strength are common metallurgical operations. This phenomenon of *work hardening,* as it is called, is another fascinating characteristic of metals closely associated with plasticity, and will be considered in some detail later in this chapter.

[1] This chapter was written by Dr. Morris Cohen, Assistant Professor of Physical Metallurgy, Massachusetts Institute of Technology.

Crystalline Structure of Metals.—In order to understand the mechanism by which metals deform, it is necessary to refer to the crystalline nature of metals. As mentioned on page 3, metals consist of aggregates of grains, each grain being a crystal with a more or less irregular outline where contact is made with the adjacent grains. Within each grain, the metal atoms are arranged in a very definite geometric pattern which repeats itself in three dimensions to build up the solid grain. This pattern of atoms is called the *unit cell* of the structure and these are combined to form

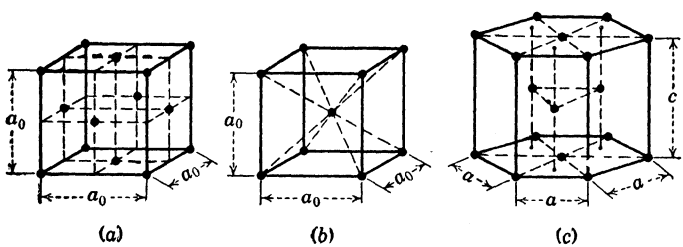


FIG. 48.—Arrangements of atoms commonly found in metals. (*a*) Face-centered cubic unit cell. (*b*) Body-centered cubic unit cell. (*c*) Hexagonal close-packed unit cell.

a *space lattice.* The dimensions of the unit cell are known as *lattice parameters.* Each metal has its characteristic space lattice and lattice parameters. The three arrangements of atoms which are most commonly found in metals are shown in Fig. 48. Copper, lead, nickel, aluminum, silver, gold, and γ-iron have face-centered cubic structures. α-, β-, and δ-iron, chromium, molybdenum, tungsten, and vanadium belong to the body-centered cubic class. Zinc, cadmium, magnesium, and titanium have the hexagonal close-packed arrangement of atoms.[1] The lattice parameters vary from metal to metal, but are all of the order of magnitude of one-hundred-millionth of an inch.

[1] Metallic solid solutions have the same crystal structure as the solvent metal, while intermetallic compounds usually have very complicated structures quite different from those of the component metals.

Because of the regular array of metal atoms in a space lattice, the atoms in each grain can be considered to lie in various families of parallel planes. This is illustrated in Fig. 49 for the simplified case of a two-dimensional lattice. It is quite evident that the interplanar spacing d depends upon the particular set of planes under consideration, and there are one or more sets of planes (in this case, there are two) which have the greatest interplanar spacing. These planes of maximum spacing represent planes of weakness

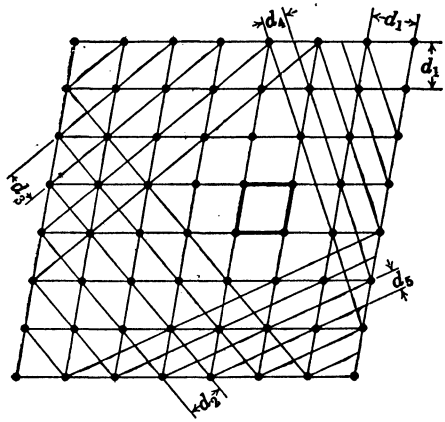


FIG. 49.—A two-dimensional space lattice showing various families of parallel planes. The unit cell is drawn in heavy lines.

within each grain, and hence play an all-important part in the deformation of metals.

Deformation of Single Crystals.—The mechanism of deformation in metals is most conveniently studied by working with large single crystals rather than with the usual polycrystalline specimens. If a single crystal is subjected to very small external stresses, the space lattice of which the crystal is composed deforms by a slight displacement of the atoms from their normal stable positions. This is called *elastic deformation* because when the external stresses are removed, the atoms return to their stable positions, and the crystal recovers its original shape. On the other hand,

if the applied loading on the crystal is increased, the atoms are forced so far from their normal positions that they cannot return when the external stresses are removed. This produces a permanent set in the crystal, and we say that the crystal has undergone *plastic deformation.* The difference between elastic and plastic deformation is illustrated in Fig. 50.

In general, metal crystals deform plastically by a process of slip along the atomic planes of greatest interplanar spacing, as is shown in Fig. 50, because the applied stresses cause the space lattice to yield by shearing the atomic

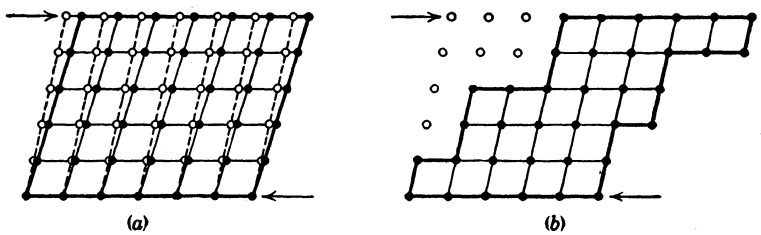


FIG. 50.—Deformation of a simple space lattice. (*a*) Elastic deformation. (*b*) Plastic deformation.

bonds along the crystallographic planes of weakness. In other words, whole blocks of atoms glide past each other along the active slip planes in a manner analogous to the deformation of a pack of cards in which various groups of cards slide with respect to adjacent groups along the parallel "planes of weakness." In crystals, however, the direction of the movement on the parallel slip planes is not random, but is restricted to one of the crystallographic directions of greatest linear density of atomic packing. As the magnitude of the stresses acting on the crystal is progressively increased, the number of active (parallel) slip planes and the distance of slip along these planes also increase. It is important to emphasize that metal crystals deform plastically by this shearing process even though the crystals may be stressed in tension or in compression. This is demon-

strated in Fig. 51. The crystals become elongated in the direction of flow, not because they are pulled or squeezed out like particles of pitch or wax, but because the crystal blocks which are moving with respect to one another actually rotate and tend to become parallel to the axis of tension or perpendicular to the axis of compression.

In metal crystals, there is usually more than one direction in which slip can take place with equal ease. For example, in a hexagonal close-packed crystal, the family of planes

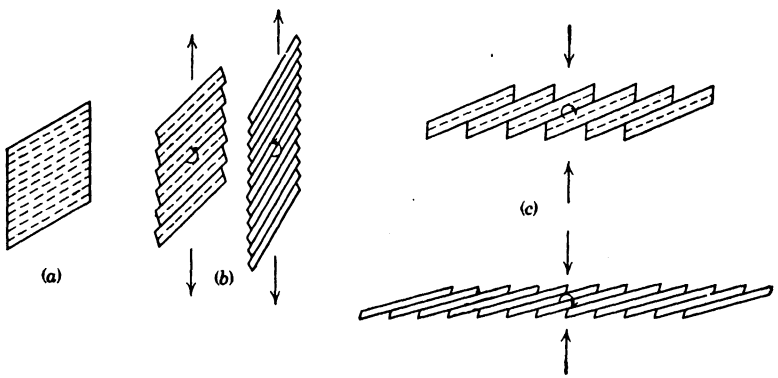


FIG. 51.—Deformation of a single crystal by slipping. (*a*) Before deformation. (*b*) Deformed in tension. (*c*) Deformed in compression. Note the rotation of the crystal blocks and the subsequent elongation of the crystal in the direction of flow. The dotted lines represent potential planes of slip.

parallel to the basal plane (see Fig. 48) has the largest interplanar spacing, but there are three directions in these planes which have maximum linear density of atomic packing. These directions lie parallel to the sides of the basal hexagon. Hence, there are three possible directions for slip in a hexagonal crystal. In a face-centered cubic crystal, there are twelve possible slip directions in view of the fact that there are four families of parallel planes of maximum interplanar spacing with three directions of densest atomic population in each plane. This explains the high degree of plasticity shown by the face-centered cubic metals as compared to the hexagonal metals. It has been found that of all the equally possible modes of slip in a single

crystal, slip actually takes place along that particular set of weak planes and in that principal direction which happen to lie closest to the position and direction of the maximum resolved shear stress acting within the crystal. In the face-centered crystals, *double slip* sometimes occurs because the rotation of the active slip planes toward the axis of tension or away from the axis of compression causes one of the other three families of possible slip planes to rotate into a position lying closer to the maximum resolved shear stress than the active set of planes. In this case, the slipping process is transferred to the new set of planes.

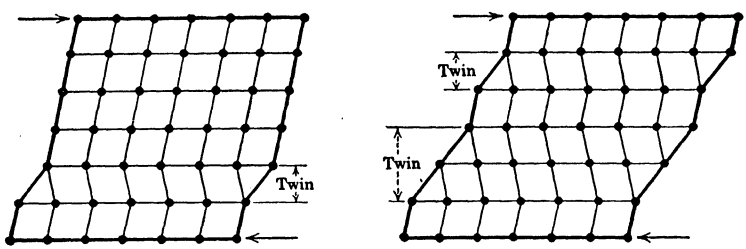


FIG. 52.—Progressive deformation of a space lattice by mechanical twinning.

Brief mention must be made of another mechanism of plastic deformation called *mechanical twinning* which frequently occurs in hexagonal close-packed and face-centered cubic crystals, but only occasionally in body-centered cubic crystals. The process of simple slip just described involves the movement of relatively large blocks of atoms with respect to neighboring blocks. In each block, all the atoms move the same distance. The various blocks may move by different amounts, but the extent of the movement is always an integral number of atomic spacings. In other words, after the slip stops, the orientation of all the unit cells is the same throughout the crystal (see Fig. 50). In mechanical twinning, however, each plane of atoms shifts with respect to the adjacent planes by a small but definite fraction of an atomic spacing. This is illustrated in Fig. 52. It will be noted that mechanical

twinning results in a reorientation of the unit cells in such a way that they become mirror images of the unit cells in the unaffected part of the crystal. The plane on which this type of deformation occurs is called the twinning plane and represents a plane of symmetry between the twinned and untwinned portions of the crystal. As in the case of slip, twinning takes place preferentially along certain crystallographic planes. The change in orientation caused by twinning may provide favorable opportunities for slip to occur, and hence both deformation processes often take place in the same crystal.

Deformation of Polycrystalline Metals.—In a piece of metal which consists of an aggregate of crystals or grains, the orientation of the space lattice varies from grain to grain. Obviously, then, the plastic deformation of polycrystalline metals is far more complicated than that of single crystals. Yet, the process is basically the same. When a piece of metal is subjected to external loading, the stresses are transmitted to the individual grains through the surrounding grains. The stress in any grain can be resolved into a shear component parallel to each possible direction of slip or twinning and a normal stress component perpendicular to each shear component. If the elastic limit in shear in one of these possible directions is exceeded by the resolved shear stress in this direction, then plastic deformation will begin. The grains do not all start to deform at the same time because some are more favorably oriented than others for slipping or twinning. As the deformation proceeds under the action of increased external forces, slip or twinning occurs along more and more parallel planes in the active grains. Other grains begin to deform just as soon as the resolved shear stresses for less favorable orientations become sufficiently large. During the deformation process, each grain rotates so that the active planes move toward the axis of tension or away from the axis of compression. In this way, the grains become elongated

in the direction of flow. The deformation of polycrystalline metal is the integrated result of the combined deformation of the individual grains. This is illustrated diagramatically by the cold-rolling process shown in Fig. 53.

The mechanism of plastic deformation in polycrystalline metals is complicated by the fact that the stresses exerted on any grain are exceedingly complex and cannot be determined even from a thorough knowledge of the external loading. In a specimen stretched in simple tension, some of the grains may be stressed in compression, bending, or shear, as well as in tension. The stresses may not only

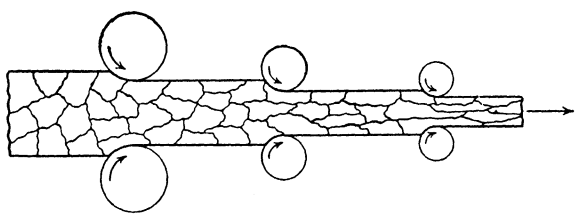


FIG. 53.—Schematic illustration of the deformation of grains during the cold rolling of a polycrystalline metal.

vary from one grain to the next, but also from point to point within the same grain. Furthermore, as the grains change their shape and orientation, the stress distribution must change continuously in an unpredictable fashion with increasing amounts of plastic deformation. Accordingly, it is not surprising to find that in some grains the slip or twinning planes become bent, and the movement is not confined to one family of planes, but occurs on two or three (possibly more) sets of planes according to the dictates of the changing orientation and stress conditions.[1]

[1] As a matter of fact, because of the variations in stress within some grains, the grains may divide themselves into irregularly shaped regions or bands each of which deforms as a single crystal in a direction that differs from those of the adjacent bands within the same grain. These bands rotate separately as the deformation continues with the result that a single grain may give rise to a number of elongated (deformation) bands with different crystallographic orientations.

The situation existing along the grain boundaries during the plastic deformation of polycrystalline metals is not clearly understood. The deformation of each individual grain is restricted by the grains on all sides which have different orientations and hence different directions for slip or twinning. Furthermore, each grain undergoing deformation rotates with respect to the adjacent grains which also rotate. As a result, the deformation of metals involves appreciable movement along the grain boundaries as well

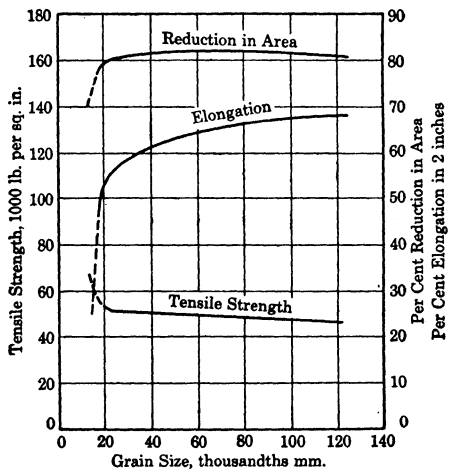


FIG. 54.—Relationship between physical properties and grain size of 66-34 brass. (*After Pratt, A. S. M. Metals Handbook*, 1936 *ed.*)

as along the planes of weakness within the grains. Unfortunately, there is no satisfactory method available at the present time for studying the conditions along the grain boundaries. However, since the slipping or twinning process must change direction at a grain boundary, it follows that a given metal with many grain boundaries (small grain size) is less plastic, and hence harder and stronger, than the same metal with fewer grain boundaries (large grain size). The effect of grain size on physical properties is shown in Fig. 54 for a solid-solution alloy containing 66 per cent copper and 34 per cent zinc (high brass).

Metallographic Aspects of Plastic Deformation.—If a sample of polished metal is plastically deformed, a microscopic examination reveals many dark bands on the polished surface, as in Fig. 55. These bands are approximately parallel within each grain, but change direction from one grain to the next. They are due to the fact that the polished surface of the metal becomes covered with many microscopic steps formed by the projecting ends of the crystal layers which have been displaced with respect to

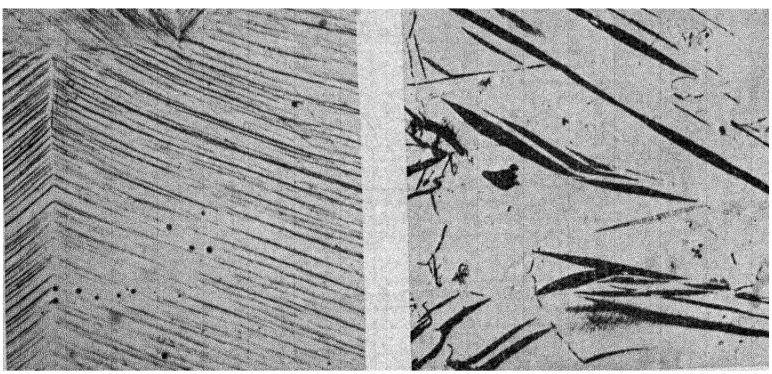


FIG. 55.—(*a*) Slip bands in deformed 70-30 brass (mag. 100 ×). (*b*) Twin bands in deformed cadmium (mag. 100 ×). Both polished before deformation. Note that the slip bands appear as fine black lines while the twin bands are considerably wider.

one another by the slipping or mechanical twinning process. The dark markings are called *slip bands* or *twin bands*, according to the type of deformation which takes place. The diagram in Fig. 56 indicates the optical reason for the appearance of these bands. Rays *A* strike the horizontal surfaces and are reflected back through the microscope to the eye to produce light regions within the grains. Rays *B* strike the oblique surfaces and are reflected out of the field of vision to form dark bands. The number of these surface markings increases with the degree of plastic deformation. With large amounts of deformation, other sets of

bands appear within each grain (corresponding to double and triple slip), and the bands become bent and distorted.

When the surface of a cold-worked metal is repolished, the dark bands disappear because the projecting ridges are removed. The etching characteristics of this repolished surface are of particular interest to the metallographer. If the preceding deformation happened to take place by mechanical twinning, the traces of the twins with the polished surface are readily revealed by etching because of the difference in orientation between the twinned regions and the parent grain, as illustrated in Fig. 57-a. These

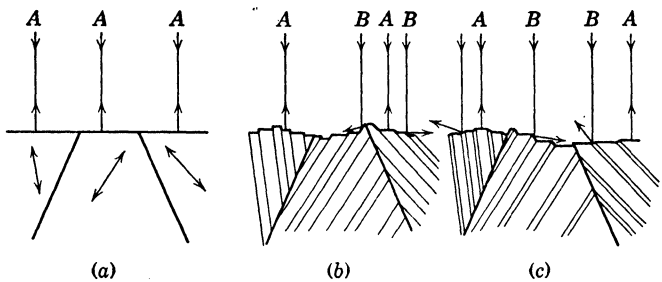


FIG. 56.—Schematic explanation of the formation of slip bands and twin bands on a polished surface. (*a*) Before deformation. (*b*) After deformation by slipping. (*c*) After deformation by twinning.

twins, as brought out by etching a specimen of deformed cadmium, are shown in Fig. 57-b. The deformation bands mentioned in the footnote on page 58 can also be disclosed by etching because of their differing orientations. On the other hand, if the deformation is due to slipping, there is no difference in orientation on either side of the slip planes. Hence, in general, etching cannot reveal the traces of slip planes unless the etching reagent is sufficiently sensitive to attack preferentially the disturbed metal along the slip planes. For example, the slip bands in deformed α-brass (polished after the deformation) can be brought out quite readily by suitable etching (Fig. 59), but this has not yet been done with α-iron. In Fig. 58-a, the etching of a sample of deformed iron discloses the elongated

grains, but the slip bands do not appear. However, if the iron is deformed by a sudden shock, mechanical twins may

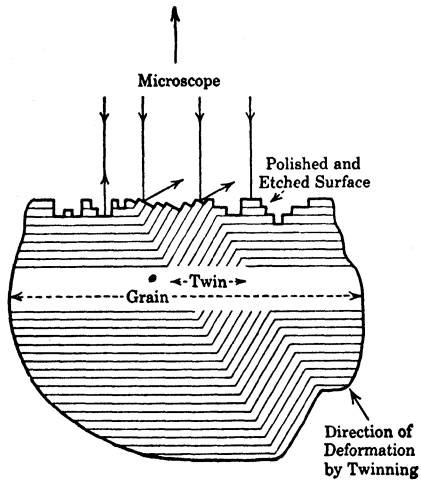


FIG. 57-a.—Schematic explanation of the appearance of twins after polishing and etching. The orientation of the etch pits (which governs the amount of light reflected back through the microscope to the eye) is dependent upon the orientation of the space lattice.



FIG. 57-b.—Etch bands in deformed cadmium. Polished and etched after the deformation. Etched with HNO_3. Mag. 100 ×.

be formed,[1] and these can be revealed by etching without

[1] Mechanical twins in α-iron are known as *Neumann bands.*

any difficulty as shown in Fig. 58-b. The bands which are developed by etching are generally called *etch bands*, regardless of the mechanism of the deformation.

Figure 59 shows the effect of increasing amounts of plastic deformation on the microstructure of α-brass as revealed

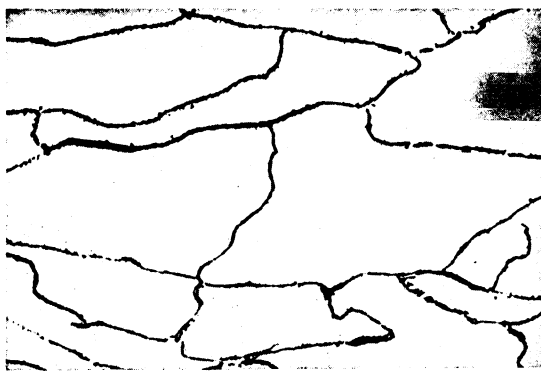


FIG. 58-a.—Compressed iron, after polishing and etching. Etched with nital. Mag. 500 ×.



FIG. 58-b.—Neumann bands (mechanical twins) in iron deformed by impact. Etched with nital. Mag. 500 ×.

by polishing and etching *after* the deformation. Note the progressive increase in the number and distortion of the etch bands and the marked elongation of the grains.

Effects of Plastic Deformation.—The plastic deformation of metals at ordinary temperatures has a very striking

effect on the mechanical properties. Plastic deformation lowers the ability of a metal to undergo further deformation, and by the same token increases the ability of the metal to resist further deformation. This can be demon-

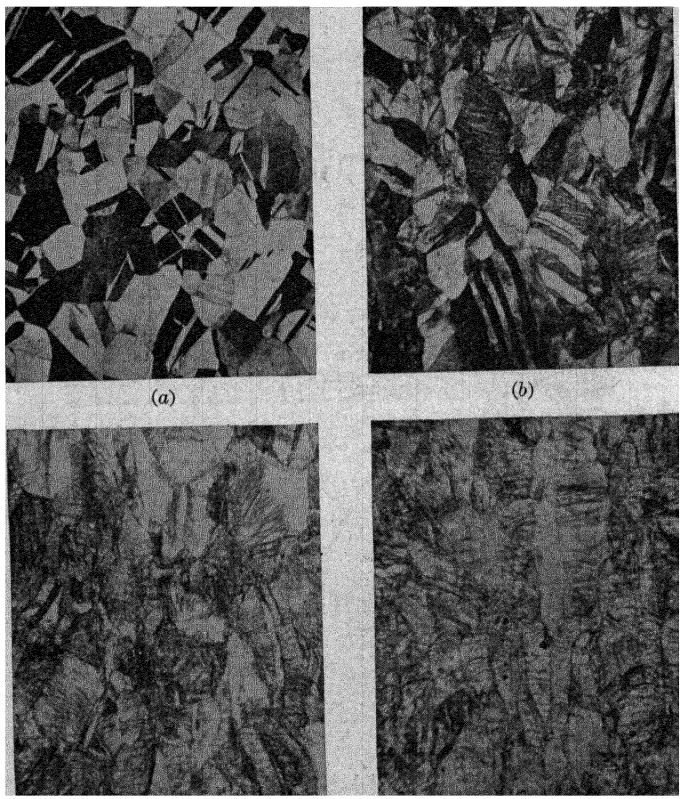


FIG. 59.—Effect of cold rolling on the microstructure of 70-30 brass. (*a*) Unworked. (*b*) Rolled to 38.6 per cent reduction. (*c*) Rolled to 60.0 per cent reduction. (*d*) Rolled to 69.0 per cent reduction. Etched with $NH_4OH + H_2O_2$ Mag. 50 ×. (*Courtesy American Brass Company.*)

strated very simply by bending a piece of soft copper wire back and forth with the fingers. At first, the wire bends quite easily, indicating a relatively low strength combined with high plasticity. As the bending is continued, it

becomes progressively more difficult to bend the wire further. In short, the wire becomes stronger. Finally, however, the wire will break suddenly during a bend even though the strength is now relatively high. This is due to the fact that the cold work caused the metal to lose its plasticity. In general, the strength properties of metals, such as the tensile strength, yield strength, proportional limit, elastic limit, proof stress, and hardness, are increased by cold working. On the other hand, the plastic properties

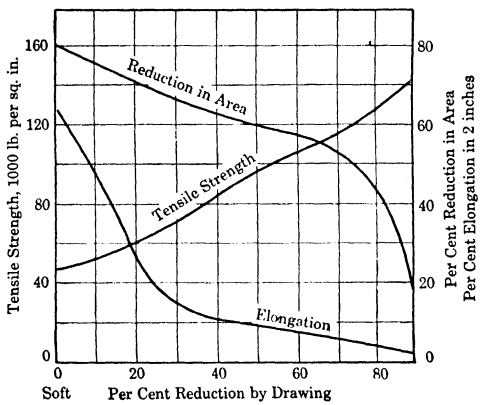


FIG. 60.—Effect of cold drawing on the physical properties 66-34 brass. (*Pratt, A. S. M. Handbook*, 1936 *ed.*)

such as ductility (measured by the reduction in area and elongation in a tensile test) formability, malleability and toughness are decreased. These general effects of cold working are referred to as *work hardening* or *strain hardening*. Some of the changes produced by the cold drawing of brass are shown in Fig. 60.

An appreciable part of the energy expended in the deformation of a metal is absorbed by the metal; the rest is converted into heat. This increase in internal energy is evidenced by the fact that a cold-worked metal dissolves more rapidly in acid solutions (and therefore has lower corrosion resistance) than the same metal in the unworked condition. In addition, metals become more electronega-

tive in their electrochemical behavior as the degree of cold working is increased. This often leads to localized corrosion at bends in pipes and in tanks since the bending of the metal causes it to become anodic (and hence to dissolve preferentially) with respect to the remainder of the (unworked) metal.

At least a part of the increased internal energy due to cold working is in the form of residual elastic strains which result from the inability of many of the atoms along the slip and twinning planes and along the grain boundaries to find stable positions in the space lattices of the grains after the deformation has ceased. The stresses produced by these residual elastic strains are called *internal stresses.*[1] The presence of internal stresses may be undesirable from at least three points of view. (1) Some cold-working operations, such as rolling and drawing, leave the surface layers of the metal in tension and the inner layers in compression. The tensile stresses in the surface tend to pull the grains apart and make the metal particularly sensitive to intergranular corrosion in the presence of certain reagents. The season cracking of cold-worked brass in the presence of mercury or ammonia (p. 113) and the caustic embrittlement of boiler plate around punched rivet holes are both manifestations of internal tensile stresses at the metal surface in contact with the corrosive medium. In general, intergranular corrosion is not stimulated by compressive stresses. (2) Surface tensile stresses act to open up, and exaggerate the deleterious effect of, surface imperfections. Such internal stresses increase the notch sensitivity and decrease the toughness and fatigue resistance of cold-worked metals. (3) Internal stresses cause dimensional changes after machining, and thereby prevent metals from maintaining close tolerances. The algebraic sum

[1] Internal stresses may also be produced by phase transformations where appreciable volume changes occur; by rapid cooling, such as in casting, quenching, and welding; and by electrodeposition of metals.

of the internal stresses in a cold-worked specimen must be zero when no external forces are acting. Hence, the various internal stresses must nicely counterbalance one another. When the outer layers of the metal are removed by machining, the delicate balance of internal stresses is upset and a certain amount of plastic deformation will take place in the metal. This may go on for a considerable length of time at ordinary temperatures until the balance of stresses is readjusted. In the meantime, the external dimensions also change. The result is that metal parts containing internal stresses cannot be accurately machined to permanent dimensions. The method for removing internal stresses is discussed on page 73.

Two other general effects of plastic deformation are worthy of mention. The electrical resistance increases and the density decreases[1] during cold working. For most metals, the maximum increase in electrical resistance is less than 3 per cent. Tungsten and molybdenum are the outstanding exceptions in that their resistance is increased 50 and 18 per cent, respectively, by severe drawing. The decrease in density as a result of deformation is small, being less than 0.5 per cent for most metals.

Theories of Work Hardening.—Many attempts have been made to explain the cause of work hardening in metals, but none has been entirely successful. The so-called theories of work hardening are simply hypotheses which have been put forth to provide at least a qualitative picture of the work-hardening mechanism.

We have seen that the cold working of a metal causes the metal to resist further deformation more effectively. Since the deformation takes place by a slipping[2] action

[1] Some investigators have found an increase in density during the early stages of working. This is probably due to the closing up of voids or discontinuities in the metal.

[2] For the sake of simplicity, the theories of work hardening will be discussed in terms of slip, but it must be understood that similar arguments may be applied to mechanical twinning.

along certain crystallographic planes within the grains, it immediately follows that cold working is accompanied by an increase in the resistance to additional amounts of slip. At first thought, we might assume that the increased resistance to slip is due to the obstruction of the neighboring grains which are simultaneously slipping in other directions. This end-resistance increases progressively with slip as more and more crystal blocks are edged out into the abutting grains. However, while this grain boundary effect may account for a part of the work hardening of polycrystalline metals, the fundamental cause of work hardening must be more profound since single crystals also undergo work hardening during plastic deformation.

On the basis of the simple picture of the deformation of single crystals as discussed on page 53, it might be expected that when slip between two crystal blocks starts along some particular plane, the slip would continue on this plane until the crystal is sheared in two. Actually, this never happens. The increased resistance to slip actually strengthens the slip plane to the point where it becomes stronger in shear than other (parallel) planes in the same family. Consequently, the slip stops on the active plane, and is continued between two other crystal blocks along some other parallel plane. This increases the resistance to slip along the second plane until a third plane "gives way," and so on. Soon many thousands of parallel planes will have participated in the deformation process, and since the stress necessary to cause further slip steadily increases as the deformation proceeds, it follows that the crystal becomes harder and stronger and less plastic. Thus, the major question which must be answered by any theory of work hardening is "what actually happens along a slip plane during plastic deformation to increase the resistance to further slip and thereby cause the slip to become self-stopping?"

Three of these theories will be considered here. The *amorphous metal theory* was advanced by Beilby, who

polished a number of metal crystals and found that the surfaces became harder to scratch and lost the directional properties characteristic of crystalline substances. Beilby visualized that during the polishing operation, the surface atoms were torn loose from their positions in the space lattice to form a superficial film of amorphous (non-crystalline) metal. Since amorphous materials do not have a regular arrangement of atoms, and therefore have no planes of weakness such as occur in crystalline materials, amorphous metal would be expected to be stronger and harder than crystalline metal. Beilby further pictured that during plastic deformation there is sufficient disturbance along the slip planes and grain boundaries to produce thin layers of amorphous metal between the mutually rubbing crystal blocks. According to this theory, the strong amorphous metal thus formed acts as a cement which increases the resistance to further slip. This causes the slip to stop on the operating planes and compels the crystal to slip along new planes as the deformation proceeds. The greater the deformation, the more planes participate, and the greater the amount of amorphous metal formed. Therefore, the theory accounts for the progressive increase in strength and the decrease in plasticity during the deformation of metals. The generation of amorphous metal also explains the increase in electrical resistance, the decrease in density,[1] and the increase in internal energy[2] found in cold-worked metals.

The Beilby hypothesis was later extended by Rosenhain to the concept that the metal along the grain boundaries (even in unworked metals) is amorphous because the boundary atoms are equally attracted by two grains and therefore cannot crystallize out on either lattice. This assumption serves to account for several interesting

[1] Because of the lack of a regular atomic arrangement in amorphous metal, the atoms are not as densely packed as they are in crystalline metal.

[2] Amorphous metal is an unstable phase and therefore has higher internal energy than the corresponding crystalline metal.

properties of metals. We have seen that other things being equal, a fine-grained metal is harder and stronger than the same metal with coarse grains. But this is not true when the metals are tested at elevated temperatures. As the testing temperature is raised above room temperature, the fine-grained metals soften more rapidly than the coarse-grained metals, and at high temperatures actually become weaker than the coarse-grained metals. Furthermore, when metals are broken at ordinary temperatures, the fracture takes place through the grains (transcrystalline), while at higher temperatures the fracture follows along the grain boundaries (intercrystalline). These effects signify that the grain boundaries in a metal are regions of strength at low temperatures, but are regions of weakness at high temperatures. Since amorphous substances, which are stronger than the corresponding crystalline substances at ordinary temperatures, are believed to soften more rapidly than the crystalline substances on heating, the above phenomena can readily be explained on the assumption that amorphous metal exists at the grain boundaries. The intermediate temperature at which the amorphous metal and crystalline metal are equally strong is called the "equicohesive temperature." At this temperature, the strength of a metal is independent of the grain size, and the fracture passes through the grains and along the grain boundaries indiscriminately.

In spite of the clear picture offered by the amorphous metal theory, it has not been accepted wholeheartedly by most metallurgists because x-ray investigations have failed to reveal the presence of amorphous metal even after severe deformation. While recent electron diffraction studies have indicated that amorphous metal may actually be produced on the surface of a metal by polishing, there is still no positive evidence that amorphous metal is generated along slip planes or that it exists at grain boundaries. All that can be said at the present time is that if amorphous

metal plays a role in the work hardening of metals, the amounts involved must be exceedingly small.

According to the *fragmentation theory*[1] of work hardening, the plastic deformation causes tiny crystal fragments to break loose along the active slip planes and grain boundaries and to rotate into orientations which differ slightly from the parent orientation. These fragments are visualized to interfere mechanically with further slip just as sand or grit would increase the sliding friction between two highly polished steel plates. The strengthening effect of grain boundaries at ordinary temperatures is simply explained on the basis of the end-resistance to slip which is exerted by the abutting grains. Obviously, this obstruction to slip increases as the grain size becomes smaller. While the concept of fragmentation has the advantage over the amorphous-metal theory in that the former does not require the formation of a new phase and that there is some x-ray evidence to verify the occurrence of fragmentation as a result of plastic deformation, this theory does not account for the intergranular fracture and the rapid weakening of the grain boundaries at high temperatures.[2] Furthermore, even though the formation of many new interfaces by fragmentation during cold working may account for the increase in electrical resistance and internal energy and the decrease in density, the explanations are not as convincing as those offered by the amorphous metal hypothesis.

The more recent theory of *lattice distortion* pictures that during plastic deformation, the planes do not remain plane, but become bent and twisted because many of the atoms

[1] This theory is essentially the same as the *slip interference* theory proposed by Jeffries and Archer.

[2] It is conceivable, however, that the rapid weakening of the grain boundaries at high temperatures is simply due to the presence of minute amounts of impurities which lower the melting point of the grain boundary regions. This would eliminate the necessity for the assumption that amorphous metal exists at the grain boundaries.

along the active slip planes do not find stable positions in the lattice. As shown by means of x-rays, this causes a roughening of the lattice planes which would be expected to increase the resistance to further slip along these planes. These submicroscopic lattice strains nicely account for the energy absorbed by the metal during cold working, and also explain the higher electrical resistance and lower density of cold-worked metals as compared to the unworked metals. It is further assumed that there is lattice distortion at the grain boundaries where the atoms are displaced from their normal positions because of the attraction by the atoms in the adjacent grains. This accounts for the strengthening effect of the grain boundaries at ordinary temperatures. On the other hand, the lattice distortion theory does not explain the weakness of the grain boundaries at high temperatures. (However, see footnote on p. 71.) Another shortcoming of this theory is that a cold-worked metal can be heat-treated to relieve most of the lattice distortion without softening the metal.

In reviewing these three theories, it should be noted that there is no conflict among them. It is quite possible that all three phenomena of amorphism, fragmentation, and lattice distortion occur during plastic deformation and contribute jointly to the work-hardening effects. As a matter of fact, these theories are very similar in the ultimate analysis. As the crystalline fragments in an aggregate become progressively smaller, a size is reached beyond which there are not enough atoms in each particle to form a space lattice. The regular arrangement of atoms is lost, and the aggregate approaches the amorphous state. Similarly, if the degree of lattice distortion is increased, the regular pattern of atomic arrangement which characterizes the lattice gradually disappears, and again amorphism is obtained. The essence of the three theories as far as work hardening is concerned is the formation of a highly disorganized condition along the slip (or twinning) planes and

grain boundaries in such a way that the resistance to further slip is increased and the capacity for further slip is decreased.

Annealing of Metals

Recovery or Stress Relief.—Since work-hardened metals are in a state of high internal energy, they will revert to the stable state if the dislocated atoms in the distorted lattice are given sufficient mobility to find stable positions. This happens when cold-worked metals are heated. The internal stresses are relieved as the lattice recovers its normal shape, and hence, such an annealing process is called *stress relieving* or *recovery*. Although complete recovery cannot be attained in polycrystalline metals, it is nevertheless true that the rate at which internal stresses are relieved and the extent to which they are relieved increase with the time and temperature of heating. Recovery begins before any observable change in microstructure but is accompanied by a decrease in electrical resistance. During this recovery process, the physical properties remain substantially unchanged, although there is a tendency for the strength properties to fall off somewhat in lightly worked metals, and to increase somewhat if the previous cold working is severe (see Figs. 61 and 64). Cold-drawn cartridge cases and condenser tubes can be stress-relieved to prevent season cracking without losing the high strength and hardness produced by the cold working. The internal stresses in castings, forgings and welds may be similarly relieved.

Recrystallization.—If the annealing temperature is gradually raised, a point is reached at which work-hardened metals begin to soften and weaken rapidly. At the same time, the metals begin to regain their plasticity. These effects are shown in Fig. 61. The microstructure also changes markedly during this stage of annealing. The distorted elongated grains produced by the previous cold

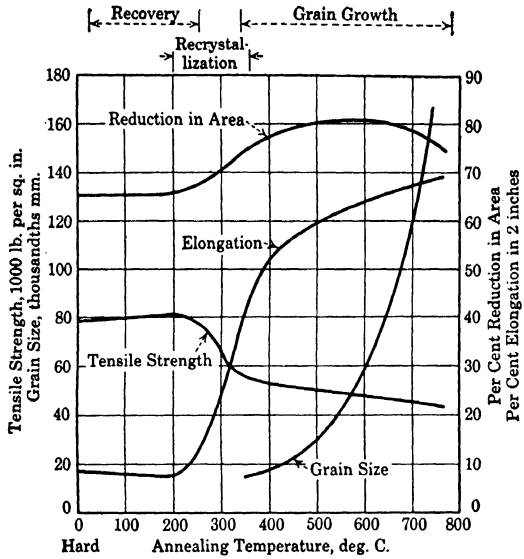


FIG. 61.—Effect of annealing on the properties of cold worked 66-34 brass. (*Pratt, A. S. M. Handbook*, 1936 *ed.*)

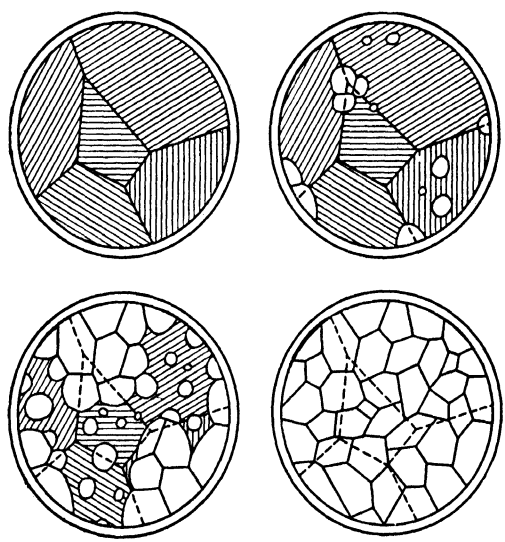


FIG. 62.—Schematic illustration of the recrystallization process.

working are gradually replaced by a number of tiny well-formed grains which continue to grow at the expense of the strained grains until the latter disappear and the structure consists entirely of the newly formed grains. This phenomenon is called *recrystallization*, and is illustrated schematically in Fig. 62. The new grains are equiaxed, relatively strain-free, contain no etch bands, and are generally much smaller than the previous grains in the cold-worked metal. To summarize, recrystallization is accompanied by

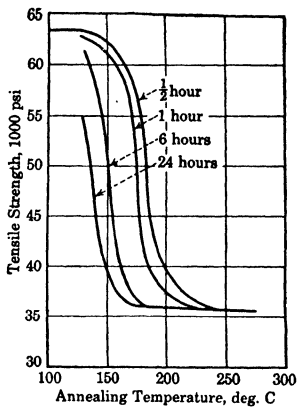


FIG. 63.—Effect of annealing time on the recrystallization temperature of copper wire. (*Alkins and Cartwright.*)

1. A rapid change in physical properties in the direction of the unworked state;
2. Disappearance of elongated, distorted grains;
3. Disappearance of etch bands;
4. Further relief of internal stresses;
5. Grain refinement (except in special cases).

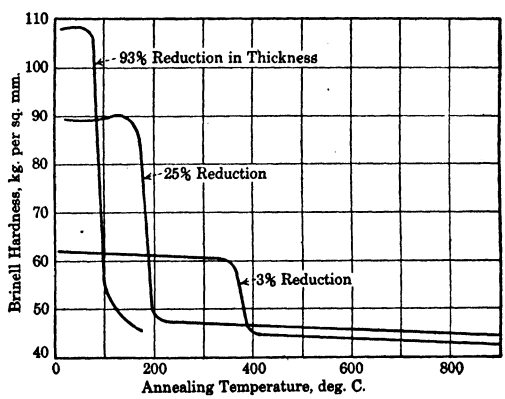


FIG. 64.—Effect of degree of cold rolling on the recrystallization temperature of copper. (*Köster.*)

Within limits, the temperature at which a cold-worked metal begins to recrystallize is lowered by increasing the

time of annealing, as shown in Fig. 63. Increasing the amount of cold work also lowers the recrystallization temperature (see Fig. 64) because of the higher internal energy and greater degree of instability. Recrystallization starts in the most severely deformed regions, and as the newly formed crystallites grow, other recrystallization centers spring up in the less distorted regions. Thus, with a given time of annealing, recrystallization normally takes place over a range of temperatures; and at any given temperature in this range, recrystallization takes place over a period of time. The order of magnitude of the recrystallization temperatures of the common metals after drastic deformation is given in Table I in which the metals are arranged according to their melting points. Impurities generally raise the recrystallization temperatures of metals.

The grain size at the completion of recrystallization depends principally on the degree of deformation prior to the annealing. The higher the degree of cold work, the lower will be the temperature necessary to produce complete recrystallization in a given annealing period, and the smaller will be the grain size. This is readily understood from the fact that severe deformation gives rise to many recrystallization centers and hence, the final grain size must be very small. In the commercial fabrication of metal parts, such as wire drawing, cupping, and rolling, the degree of deformation is usually sufficient to result in a very fine grain size after recrystallization. Therefore, it is customary to speak of recrystallization as a grain refining operation. However, with very slight amounts of deformation, only very few recrystallization centers are formed, and the grain size after recrystallization may be exceedingly large. This is called *exaggerated grain growth* or *germination*. In fact, a rod of polycrystalline metal can be recrystallized into a single crystal by straining the rod by a small critical amount and then heating it to the proper temperature. It follows as a corollary that if a metal is not deformed or strained in

TABLE I.—APPROXIMATE RECRYSTALLIZATION TEMPERATURES FOR SEVERELY WORKED METALS

Metal	Melting point, °C.	Approximate recrystallization temperature, °C.
Tin	232	Below room temp.
Cadmium	321	Room temp.
Lead	327	Below room temp.
Zinc	419	Room temp.
Magnesium	651	150
Aluminum	660	150
Silver	961	200
Gold	1063	200
Copper	1083	200
Nickel	1452	600
Iron	1535	450
Platinum	1755	450
Molybdenum	2620	900
Tungsten	3400	1200

any way, recrystallization cannot take place at any temperature (unless a phase change happens to occur). The effect of degree of deformation on the recrystallized grain size can be demonstrated by heating a tapered test specimen which has been pulled in tension in order to produce a strain-gradient. No recrystallization will take place in the heavy end of the specimen because of the lack of sufficient deformation. Just beyond the unrecrystallized zone in the direction of the small end, there will be a region with very large grains because of the limited number of recrystallization centers. From here the grain size will decrease gradually toward the small end of the bar where the strain is greatest, and the recrystallization centers are most numerous. If a higher annealing temperature is used, the region of exaggerated grain growth will occur closer to the heavy end of the bar. In general, there is a critical combination of strain and annealing temperature which will cause exaggerated grain growth. This is demonstrated in Fig. 65 for an iron-silicon alloy.

Recrystallization can also be brought about by the plastic deformation of a metal above its recrystallization temperature. Such deformation is called *hot working.* In the same sense, the term *cold working* can now be defined more broadly as plastic deformation at any temperature below the recrystallization temperature. Since hot working is the equivalent of cold working followed by annealing above the recrystallization temperature, it is obvious that hot working does not produce work hardening. The high plasticity of such metals as lead and tin is principally due to the fact that these metals recrystallize below room temperature. Therefore, the deformation of these metals at room temperature is *hot working and not cold working.*

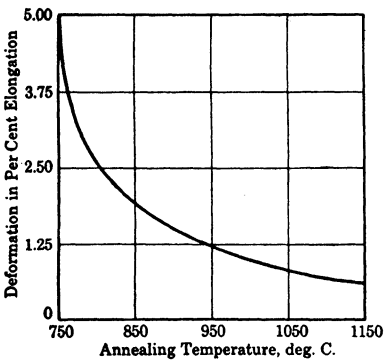


FIG. 65.—Relationship between degree of deformation and annealing temperature necessary to produce exaggerated grain growth in a 4 per cent silicon steel. (*After Ruder.*)

When face-centered cubic and hexagonal close-packed metals recrystallize, the newly formed grains are usually twinned. These twins are called *annealing twins* to differentiate them from the mechanical twins which are formed during deformation. While both types of twins show the same lattice relationship with respect to the mother orientation, the distorted grains with mechanical twins disappear while the new grains with the annealing twins appear during recrystallization. Under the microscope, the annealing twins are revealed as broad bands which etch out differently from the rest of the grain. This is due to the differences in orientation as illustrated in Fig. 57*a*.

Grain Growth.—The recrystallization of a cold-worked metal is said to be complete when the distorted grains are

entirely replaced by the newly formed grains. However, the curves in Fig. 61 indicate that metals continue to become softer and more ductile as the annealing temperature is raised beyond that necessary to complete the recrystallization. This is due to *grain growth* which always occurs after recrystallization provided that the recrystallized-grain size is reasonably small. In slightly deformed metals where abnormally large grains may be formed as a result of recrystallization, very little (if any) subsequent grain growth occurs at higher annealing temperatures.

When grain growth occurs above the recrystallization temperature, the grain size attained depends principally upon the temperature and secondarily upon the time of annealing. At any given annealing temperature above recrystallization, the grains grow to a size which is characteristic of the temperature, and no perceptible growth occurs thereafter. The rate at which the grains grow to attain this characteristic size increases rapidly with increasing temperature, as indicated in Fig. 66. If the time of annealing is too short for the grains to stop growing at any given temperature, then the grain size attained is a function of the time as well as the temperature of heating. Figures 61 and 67 show the increasing grain size which is produced in recrystallized brass by raising the annealing temperature (the annealing time being constant).

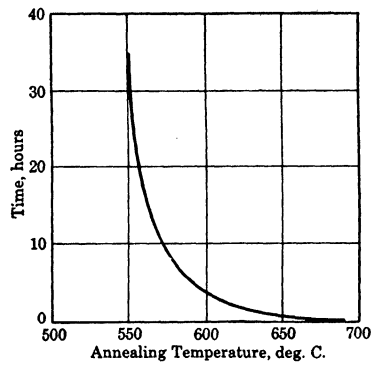


FIG. 66.—Effect of annealing temperature on the time required for deformed iron to reach constant grain size. (*After White and Wood.*)

Grain growth occurs because metals strive toward still lower energy states than attained by recrystallization. Most of the internal stresses are removed by the time recrystallization is complete, but since the newly formed

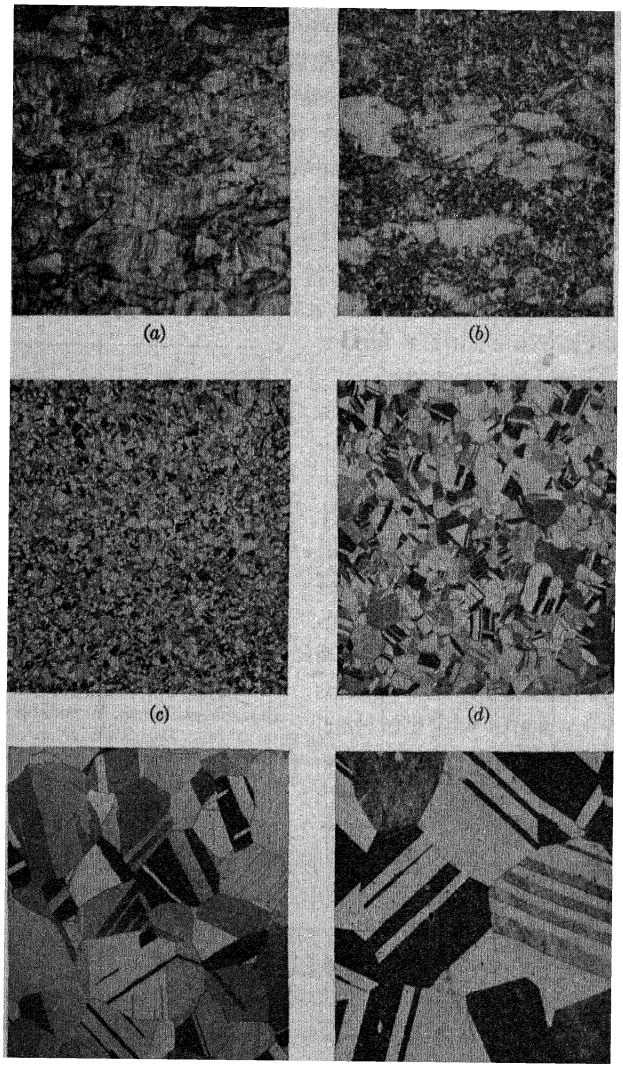


FIG. 67.—Recrystallization and grain growth in 70-30 brass, cold rolled 50 per cent. (*a*) As rolled. (*b*) Annealed at 350°C. (*c*) Annealed at 400°C. (*d*) Annealed at 550°C. (*e*) Annealed at 750°C. (*f*) Annealed at 850°C. Etched with $NH_4OH + H_2O_2$. Mag. 50 ×. (*Courtesy American Brass Company.*)

grains are small, the grain boundary area (representing regions of disturbance) is large and the total internal surface energy is still considerable. The growth of the grains effects a decrease in the internal energy by decreasing the grain-boundary area. In general, the process of grain growth involves an expansion of the boundaries of the larger grains at the expense of the smaller ones which have higher surface energies and which are therefore less stable than the larger grains. In this way, the large grains become larger and the small ones disappear.

The recrystallization and grain growth processes are of great industrial importance. Most metals work harden so readily that they lose the major part of their plasticity before they can be shaped to their final form. An attempt to carry the fabrication to completion would result in rupture. However, annealing above the recrystallization temperature practically removes the work-hardening effects so that the metals recover their formability and can be put through additional shaping operations. For example, the cold rolling and drawing of brass tubing is made possible by several intermediate annealings during the fabrication. At the same time, the softening of the metal decreases the wear on the shaping dies and reduces the power necessary to continue the deformation. The annealing may be carried out appreciably above the recrystallization temperature in order to take advantage of the increased ductility due to the larger grain size. However, if the grains are very large because of too high an annealing temperature or exaggerated grain growth, subsequent working causes an undesirable roughening of the surface into an "orange peel" pattern. This is due to the unequal deformation of the individual grains. Coarse grains can be refined by cold working and reheating just above the recrystallization temperature.

CHAPTER IV

THE NONFERROUS ALLOYS OF TECHNICAL IMPORTANCE

No attempt will be made to describe or even to name more than a few of the large and constantly increasing number of nonferrous alloys used in practice. Certain of them are of such great technical interest and importance, however, that their properties must be considered. Many have been referred to in connection with the equilibrium diagrams, and others are of such special character that their consideration is out of place here. The majority of the important nonferrous alloys not yet discussed fall into one of two groups: (1) the smaller, containing aluminum and its alloys; (2) the larger, the alloys of copper, particularly the brasses and bronzes.

Aluminum and Its Alloys.[1,2]—Aluminum is one of the newest of the industrial metals, as its production by a process that was commercially economical was not accomplished until 1886. Commercial aluminum is from 98 to 99.8 per cent pure, the impurities being usually iron, silicon, and copper. A process for still further refining aluminum has been developed, giving a metal of a purity of 99.99 per cent. The chief uses of aluminum in the unalloyed conditions are (1) as plate, sheet, foil, rod, tubing, and extruded shapes for general manufacturing purposes; (2) for the manufacture of cooking utensils and chemical apparatus; (3) in the electrical industry; (4) as a pigment; and (5) for the deoxidation of steel.

[1] EDWARDS, FRARY, JEFFRIES, "The Aluminum Industry," McGraw-Hill Book Company, Inc., New York, 1930.

[2] This section on aluminum has been revised by Mr. J. D. Edwards, Aluminum Company of America.

The electrical uses of aluminum depend on the fact that its conductivity in wire form is about 61 per cent of that of annealed copper. Because of the relatively low tensile strength (25,000 lb. per square inch in wire form), the wire is usually stranded in cable form around a galvanized steel core; the standard type of steel-cored cable has a core with a tensile strength of about 190,000 lb. per square inch. More than 730,000 miles of aluminum cable have been installed, largely for the transmission of electricity at high potentials.

The alloys are numerous and constantly increasing in number and complexity. These may be divided into the following two classes: (1) the casting alloys and (2) the wrought alloys. A few typical examples of each class will be considered.

The most commonly used casting alloys in American practice contain copper, silicon, and magnesium as the important alloying elements. The most important member of this group is that containing about 8 per cent copper. It is known as No. 12 alloy and is used for many automobile parts, as for example, crankcases, oil pans, transmission housings, step plates, handles, brackets, streetcar fare boxes, parts of gas meters, and a large number of other uses. The mechanical properties of this alloy vary with its method of casting (Figs. 68, 69) but are approximately as follows: tensile strength 19,000 to 23,000 lb. per square inch; elongation from 1 to 3 per cent in 2 inches.

Another important group of casting alloys is that of the aluminum-silicon alloys in which the silicon is either about 5 or 12 per cent. The alloy with 12 per cent silicon is remarkable in that its properties depend to a great extent on the method of preparation. When it is made by melting the aluminum and silicon together the alloy is known as *normal*. If the normal alloy is treated either with an alkali metal fluoride or with metallic sodium or potassium before casting, the modified alloy is made. The tensile

strength of the normal alloy with 5 per cent silicon is about 18,000 lb. per square inch, with an elongation of about

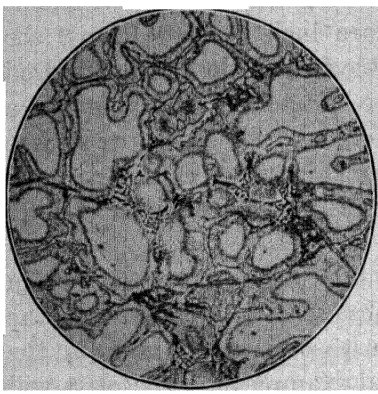


FIG. 68.—Round bar of No. 12 (aluminum 92 per cent, copper 8 per cent) sand cast at 700°C. Large dendrites formed by slow cooling. Vilella's etch. Mag. 100 ×. (*Corson.*)

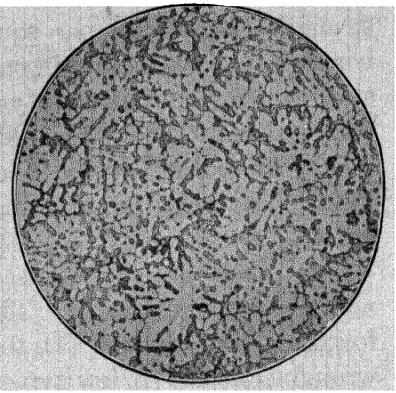


FIG. 69.—Round bar of No. 12 (aluminum 92 per cent, copper 8 per cent) chill cast at 670°. Small dendrites formed by chilling. Vilella's etch. Mag. 100 ×. (*Corson.*)

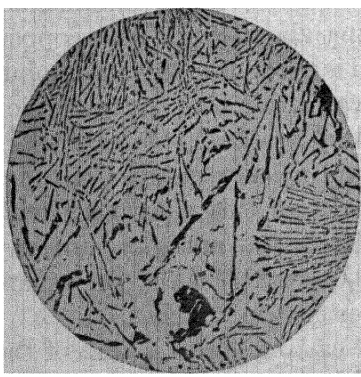


FIG. 70.—Aluminum-silicon alloy (silicon 13 per cent), unmodified sand-cast alloy. The dark constituent is silicon. Etched with ½ per cent hydrofluoric acid. Mag. 100 ×. (*Aluminum Research Laboratories.*)

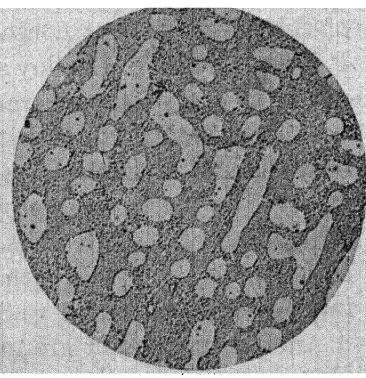


FIG. 71.—Aluminum-silicon alloy (silicon 13 per cent). Sodium-treated sand-cast alloy. Shows the modified structure. Etched with ½ per cent hydrofluoric acid. Mag. 100 ×. (*Aluminum Research Laboratories.*)

5 per cent. The modified form with 12 per cent silicon is much finer-grained and will have a tensile strength of about 26,000 lb. per square inch with an elongation of 8 per cent.

These alloys have an unusually low contraction on solidification and can therefore be cast in complicated form more simply than No. 12 alloy (Figs. 70, 71). The binary alloys with 4 to 10 per cent magnesium are finding important uses; the alloy with 10 per cent magnesium is used in the heat-treated form.

In addition to these three types of binary alloys, a number of alloys with three or more components are in use. One such group of alloys contains copper, silicon, and magnesium, and the castings have their properties improved by heat treatment.

An important use for casting alloys is in the manufacture of pistons for automobile and aircraft engines. The advantages of aluminum-alloy pistons over the cast-iron type lie both in the reduced weight and in the greater heat conductivity. This last mentioned property makes the cooling of the motor less difficult. An aluminum-alloy piston is the only type used in airplane motors, as well as in many modern automobiles.

One of the objections to the use of aluminum alloys for pistons has been the marked decrease in the tensile properties of most of them at high temperatures, thereby limiting the temperature at which the engine can be operated. The demands for an alloy that would stand higher operating temperatures led to the development of a number of suitable alloys. Among these may be mentioned *Y*-alloy, which was developed at the British National Physical Laboratory during the World War. Its composition is approximately aluminum 92.5 per cent, copper 4 per cent, nickel 2 per cent, and magnesium 1.5 per cent. This alloy may also be worked and heat-treated so that its properties will be considered again in the class of wrought alloys (Fig. 72). Most pistons made in America are permanent-mold castings containing 10 per cent copper, 1.25 per cent iron, and 0.25 per cent magnesium. These are most commonly used in the heat-treated condition (p. 89), and will

have a tensile strength of about 38,000 lb. per square inch and 125 to 140 Brinell (1000 kilogram load). (A still more recent development is an alloy with silicon 12 per cent, copper 1 per cent, magnesium 1 per cent, and nickel 2.5 per cent. This alloy has a low coefficient of expansion, is 4 to 5 per cent lighter than *Y*-alloy, is hard, and has good bearing properties.)

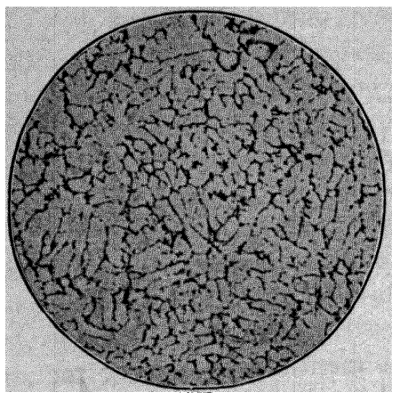


FIG. 72.—*Y*-alloy (copper 4 per cent, nickel 2 per cent, magnesium 1.5 per cent) chill cast at 750°C. Dark masses probably $CuNiAl_5$. Mag. 100 ×. (*Corson.*)

Wrought Alloys.—The development of cast aluminum alloys following the cheap production of aluminum by the Hall-Heroult process was a major contribution to the metallurigcal industry, especially in the application of light alloys to automobile construction. (For wrought products such as plate, sheet, rod, tubing, and extrusions, commercially pure aluminum, 99.0 to 99.3 per cent, is extensively used. When somewhat higher strength is required, the alloy 3*S*, which contains about 1.25 per cent manganese, is employed. It was not, however, until the discovery of the heat-treated wrought alloys that aluminum took its place as one of the most important metals in use today.) (The publication by Wilm[1] in 1911 of a paper on duralumin is one of the most outstanding metallurgical contributions of this century. The composition of duralumin has the following limits:

Element	Per cent
Copper	3.5 to 4.5
Magnesium	0.3 to 1.0
Manganese	0.4 to 1.0
Silicon	0.3 to 1.0
Aluminum	Remainder

[1] WILM, A., "Light Aluminum Alloys," *J. Inst. Metals*, **6** (1911), 334.

The properties that have given it a preëminent position in the alloy field are acquired as a result of a novel heat treatment. A typical series of production steps is the following:

1. Cast an ingot.
2. Mechanically work (roll, forge, stamp) hot and then cold.
3. Heat at 495 to 515°C.
4. Quench in cold water.
5. Age (at room temperature or higher).

The size and shape of the casting depend on the form to be produced from it and may vary from a small one to one weighing 3000 lb. or more. The alloy softens to a workable condition at temperatures of 300°C. or slightly higher and the metal may then be worked hot and finally cold after it has cooled to room temperature. An essential part of the cycle is mechanical work which may take any of the usual forms of rolling, drawing, hammer forging, or the like. The tensile strength as a result of this deformation will be from 35,000 to 43,000 lb. per square inch with an elongation of from 2 to 4 per cent. The next operation consists in heating the worked alloy for a time at a temperature between 495 and 515°C. The metal is thereafter quenched in cold water. Immediately after quenching the tensile strength is about 44,000 lb. per square inch and the elongation 19 per cent. The physical properties stay unchanged at room temperature for a short time (from 30 minutes to an hour), and then the remarkable phenomenon known as aging begins to be evident. This is shown by a gradual increase in tensile strength over a period of 4 or 5 days, at the end of which time the alloy has reached its maximum tensile strength of 60,000 lb. per square inch, or slightly more, with no decrease in ductility, which is still 19 per cent, as it was before the strengthening and hardening occurred. The effect of this cycle of operations is to produce an alloy that is about as strong and

ductile as a low-carbon steel, but which has approximately one-third the weight (Figs. 73, 74). While the composition and heat treatment just described still remain a standard, various other high-strength alloys susceptible to heat treatment are now available. In this group may be included 24*S* of the Aluminum Company of America with 4.4 per cent copper, 0.5 per cent manganese, 1.5 per cent magnesium; 53*S* of the same company containing about 1.3 per

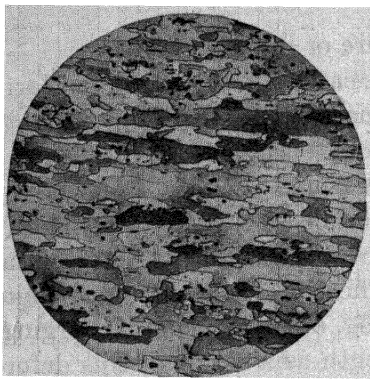


FIG. 73.—Duralumin sheet (4 per cent copper, 0.5 per cent magnesium, 0.5 per cent manganese). Heat treated at 510°C. and quenched. Shows characteristic grain structure of sheet. Keller's etch. Mag. 100 ×. (*Aluminum Research Laboratories.*)

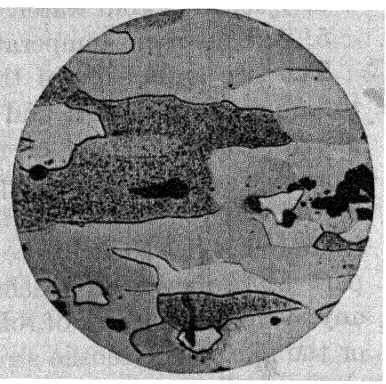


FIG. 74.—Microstructure at higher magnification. Essentially a solid solution with some particles of $CuAl_2$ and Al-Cu-FeMn. Kellers' etch. Mag. 500 ×. (*Aluminum Research Laboratories.*)

cent magnesium, about 0.7 per cent silicon, and 0.25 per cent chromium.

Of the other alloys, quite similar in composition and general properties, the best known example is the British *Y*-alloy, previously mentioned on page 85. In the worked and heat-treated condition, this alloy has a tensile strength varying from 40,000 to 62,000 lb. per square inch, depending on its mechanical and heat treatment. It also has appreciable ductility; its elongation is from 17 to 26 per cent in 2 inches.

Much experimental work has been done and a number of theories have been advanced to account for the remarkable

increase in strength of the duralumin-type alloys when heat treated. The phenomenon is unquestionably associated with the existence of the compounds $CuAl_2$ and Mg_2Si and the fact of their much greater solubility at the high solution temperature (about 500°C.) than at the low precipitation temperature which is used during aging. The theory will be considered in greater detail under the topic Age Hardening (p. 117).

Heat Treatment of Aluminum Castings.—It was not until some years after the discovery of the improved strength of wrought alloys effected by heat treatment that a practical method of heat-treating castings was discovered. The time of heating at the high (solution) temperature is much longer with cast than with worked alloys and is from a few hours to several days, depending on the size of the casting and its composition. A marked increase in tensile properties follows the reheating at temperatures from 120 to 160°C. after quenching. This form of heat treatment is called *artificial aging* or *precipitation heat treatment.* The time at the lower (precipitation) temperature also varies from 1 to 18 hours. The resulting strength of the cast alloys depends, of course, on their composition and the particular heat-treating cycle used; a tensile strength of 40,000 lb. per square inch is not unusual while, in special cases, a tensile strength of 49,000 lb. per square inch has been obtained.

Corrosion of Aluminum Alloys.—The general subject of corrosion is considered on page 195, but the selection of aluminum alloys for special purposes so often involves their corrosion resistance that a brief discussion of these special problems is included here. The metal aluminum would be of little industrial importance if it were not for the fact that it is instantly covered by a thin film of highly protective aluminum oxide whenever it is exposed to the air. This film is self-renewing so that the metal and its alloys under normal conditions are always protected to a marked

degree. The alloys will stay bright for long periods of time when exposed to conditions that would cause the rapid rusting of iron or steel. An example of this is found in the cap of the Washington monument, a small pyramid of aluminum which, in spite of its exposure to the weather for 50 years, still reflects sunlight. Certain of the alloys as, for example, those containing manganese or silicon, are more resistant to corrosion than the aluminum-copper alloys. Pure aluminum and some of its alloys are almost unaffected by sea water, while others are less resistant to attack. The selection of suitable compositions for use on shipboard or near salt water is then of much importance.

Wrought alloys of the duralumin type, when improperly heat treated, are sometimes injured by intergranular corrosion, which leads to a dangerous embrittling of the material. This trouble is met less frequently than formerly because of improved methods of manufacture and heat treatment. A curious fact is that duralumin artificially aged (heated for hardening at temperatures higher than room temperature) is much more susceptible to corrosion than the normally aged metal. The alloys may be protected against corrosion by grease, paint, varnish, enamel, or similar coating. An effective method called *anodic oxidation* consists in making the part to be protected the anode in chromic acid or other suitable electrolyte and artificially increasing the thickness of the oxide film. Metal treated in this way is much more resistant to corrosion than the untreated metal, but its chief advantage is that the treated metal is in the best possible condition for protection by paints or other coatings.

Effective protection against corrosion is obtained also with Alclad products which are made by bonding thin surface layers of 99.75 per cent aluminum to a heat-treatable duralumin-type alloy. With these products, a combination of high strength and excellent resistance to corrosion is obtained. The coating is anodic to the core; hence, it electrolytically protects the edges and scratched or abraded

areas where the core may be exposed.) A cross section of Alclad 24S-T sheet is shown in Fig. 75. This type of material is employed chiefly for aircraft construction.



FIG. 75.—Alclad 24S-T sheet. Shows full cross section of composite product with 99.75 per cent aluminum surface layers and heat-treated layers and heat-treated 24S alloy core. Keller's etch. Mag. 100 ×. (*Aluminum Research Laboratories.*)

Jointing of Aluminum.—The jointing of aluminum may be accomplished by welding or riveting. Aluminum alloys can be welded satisfactorily by electrical resistance and pressure methods such as spot, butt, and seam welding, or by the usual fusion methods with oxyhydrogen or oxy-acetylene gas. The welding metals generally employed are 99.2 per cent aluminum and 5 per cent silicon alloy. The chief requirement for satisfactory welding is the removal of the oxide film by mechanical means or by the use of a suitable welding flux. For large structures and for aircraft construction where members are highly stressed, jointing is generally done by riveting.

Uses of Aluminum and Its Alloys.—Aluminum is available in all commercial forms, and the many applications of this metal and its alloys are in substantial measure due to its availability in so many fabricated forms. There are

in commercial use in the United States approximately 20 wrought alloys and 27 casting alloys. The primary products of the aluminum industry are bar, cable, die castings, foil, forgings, hydraulic-extruded shapes, ingot, impact extrusions, permanent-mold castings, plate, powder, rivets, rod, sand castings, screw-machine products, sheet, structural shapes, tubing, and wire. The following tabulation gives an approximate idea of the relative amounts of aluminum used in different fields of application:

	Per cent		Per cent
Transportation (land, air and water)	33	Chemical	6
Cooking utensils	16	Miscellaneous foundry and metal working	5
Electrical conductors	12	Iron and steel foundry	4
Machinery and electrical appliances	11	Food and beverage	4
Building construction	6	General miscellaneous	3

Some of the articles made of aluminum have been mentioned in discussing various aluminum alloys. It would take an almost endless list, however, to include all of them. Of great importance is the extensive and growing application of aluminum for structural purposes. The strong alloys of aluminum have a combination of strength and lightness which admirably adapts them for use in the building of lightweight structures. This field of application has now become so extensive that it leads all others in the amount of aluminum employed. The modern airplane and streamline train are but two striking examples of the use of aluminum in the transportation industry. Of especial significance, however, in the elimination of dead weight and the saving of transportation costs is the use of aluminum in the fabrication of truck bodies, tanks, booms, and the like.

Magnesium.—Next to aluminum in importance in the light-metal class is magnesium. It was discovered only a

few years later than aluminum and was produced commercially on a small scale in 1863. For many years its use was confined to the manufacture of flashlight powder, flares, and similar purposes, and it was not until 1910 that the production of structural alloys was announced in Germany, to be followed by commercial production in the United States in 1915. The elements commonly alloyed with magnesium are aluminum, manganese and zinc. The German alloys are known under the general name *Elektron*, with distinguishing letters and numbers. The sole producer of magnesium in the United States is the Dow Chemical Company. Magnesium and its alloys in fabricated forms are also supplied by the American Magnesium Corporation. In this country, the important alloys contain from 2 to 10 per cent aluminum, from 0.2 to 1.5 per cent manganese, and for special purposes, small percentages of cadmium and copper. The alloys are about two-thirds as heavy as the aluminum alloys with tensile strengths in the cast condition from 18,000 to 35,000 lb. per square inch, depending on the composition and heat treatment, and with elongations of from 3 to 12 per cent. In the wrought condition, the tensile strengths are from 38,000 to 48,000 lb. per square inch, with elongations of from 5 to 16 per cent. Magnesium and its alloys are outstanding in their ease of machining, a distinct advantage for many uses. The resistance of these alloys to corrosion is less than with the aluminum alloys and their protection more difficult. Under most circumstances, however, especially with alloys of higher manganese content, the corrosion resistance is excellent. Because of the very light weight of the magnesium alloys, together with good mechanical properties, they are being used to a rapidly increasing extent in the manufacture of various aircraft and automobile parts, as for example, furniture, fuel tanks, wheels, and propellers; in one foreign plane, sheet magnesium alloy is used throughout in covering the wings and body.

Copper and Its Alloys.—Enormous quantities of pure copper are used in the electrical industry because of its very high conductivity. Copper forms solid solutions with many of the common elements, including practically all of those with which it is associated in its production from the ore; thus its conductivity is greatly affected by its method of production and purification. The rapid decrease in conduction due to slight addition of the dissolving element makes evident the harmful effects of even small percentages of dissolved impurities on the conductivity of the copper and the necessity of accurate analysis if the metal is to be used for electrical work. Oxygen dissolves in copper to an appreciable extent and also unites with it to form cuprous oxide, Cu_2O. As indicated in the diagram (Fig. 8, p. 11), the compound then forms with the copper a eutectic series of alloys with a eutectic at 3.5 per cent Cu_2O (0.39 per cent oxygen). Since the presence of this eutectic has a harmful effect, on both the electrical and mechanical properties of the metal, all high-grade copper is deoxidized in the process of manufacture. This may be done by the use of phosphorus, silicon, boron, magnesium, and, probably, other readily oxidizable elements. Deoxidation by means of silicon in the form of copper silicide gives copper with high conductivity. Boron is highly effective as a deoxidizer, and boronized copper is not infrequently specified for electrical work.

For general industrial purposes, copper is used in the form of rolled sheets, tubes, bars, and drawn wires. These mechanical operations[1] have such marked effects, not only on the physical, but also on the metallographic properties of copper, that they will be considered in some detail. Copper as cast has a tensile strength of from 17,000 to 20,000 lb. per square inch, and its ductility is indicated by an elongation of from 40 to 50 per cent in 2 inches.

[1] For a description of the mechanical testing of alloys and of the effects of work see ROSENHAIN, "Physical Metallurgy," Chap. XI, 1917.

It is possible by simple mechanical work, such as rolling or drawing, to increase the tensile strength to 50,000 or more lb. per square inch. This increase in tensile strength is accompanied by a great increase in hardness and a marked decrease in elongation.

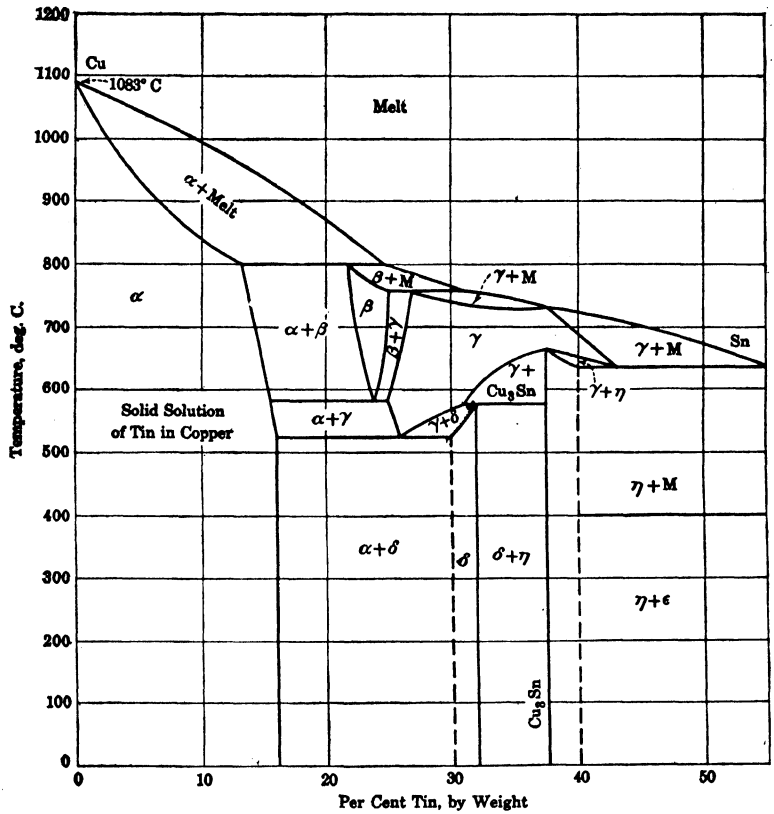


FIG. 76.—Copper-tin equilibrium diagram.

Bronze. Copper-tin.—The equilibrium diagram of the copper-tin alloys is very complex as Fig. 76 shows; it consists of one definitely established compound, CuSn, and five solid solutions in which it is possible that the compounds Cu_3Sn, Cu_5Sn_2, Cu_4Sn, and Cu_5Sn exist, although this fact has not been fully established.

The important tin bronzes are practically all included in that section of the diagram in which the percentage of tin is less than 12 per cent or, in other words, the desirable properties are associated with the α-crystals. Four classes of bronzes are of importance.

1. Coinage bronze containing 96 to 92 per cent copper is used largely in the production of "copper" coins and medals, the small amount of tin present increasing the hardness and wearing qualities of the copper.

2. Gun metal and **gear bronze** vary in composition from 92 to 88 per cent copper. Gun metal is no longer used in the manufacture of ordnance but is often used where strong, heavy castings are to be made. In order to increase the fluidity of the metal and to make the casting operation simpler, a small amount of zinc is frequently added. A standard alloy of this class has the composition 88 per cent copper, 10 per cent tin, and 2 per cent zinc. This is usually known as **Government bronze,** *G metal,* or simply 88, 10, and 2. It has a fairly high tensile strength, 32,000 to 45,000 lb. per square inch, and is often used where pressures, steam or hydraulic, are to be met, or for bearings subject to heavy loads. A bronze known as **85 and 3 fives** with 85 per cent copper and 5 per cent each of tin, zinc, and lead is also very widely used.

Another bronze of the same class consists of 89 per cent copper and 11 per cent tin and is very generally used, under the name of **English gear bronze,** in the manufacture of heavy gears. A brilliant mirror surface is developed at the contact between the teeth of the gear and the driving mechanism, and an excellent bearing and wearing surface results.

3. Bearing Bronzes.—These alloys vary from 81 to 87 per cent copper and usually contain one or more elements in addition to the tin. The best example of this class is the bearing bronze to which phosphorus (in the form of phosphor copper) and lead have been added.

These alloys, called **phosphor bronzes,** are of two classes, those to which phosphorus is added only as a deoxidizer and those in which an excess is present to act as a hardener. In the first class, the function of the phosphorus is simply to increase the strength and ductility of the alloy by reducing the Cu_2O and other oxides. In many cases, in spite of the marked improvement in physical properties, the actual amount of phosphorus is negligible. The low phosphorus



FIG. 77.—Low phosphorus bronze. Copper-rich dendrites (dark) in a copper-tin solid solution matrix. Several black areas indicate gas pockets. Etched with $NH_4OH + H_2O_2$. Mag. 100 ×.

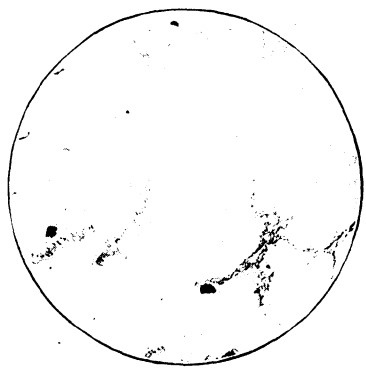


FIG. 78.—High tin-bronze showing the eutectoid of α and δ (blue) in a matrix of copper-tin solid solution. Etched with $NH_4OH + H_2O_2$. Mag. 250 ×.

bronzes have a tensile strength of about 29,000 lb. per square inch as cast and of 40,000 to 60,000 lb. per square inch in the wrought condition. The elongation varies from 5 to 15 per cent in 2 inches, depending upon the conditions. In the second class, the phosphorus, even though present in small quantities, usually less than 1 per cent, forms extremely hard particles of Cu_3P, too brittle in themselves to be used as a bearing but forming an excellent nonabrasive skeleton in the strong, tough bronze matrix. Lead is frequently added to bronze in small amounts and, as it is an almost insoluble constituent, it is found fairly uniformly distributed throughout the metal in the form of drops. Lead gives

to the metal two valuable characteristics. It makes it more easily machinable and, to a certain extent, self-

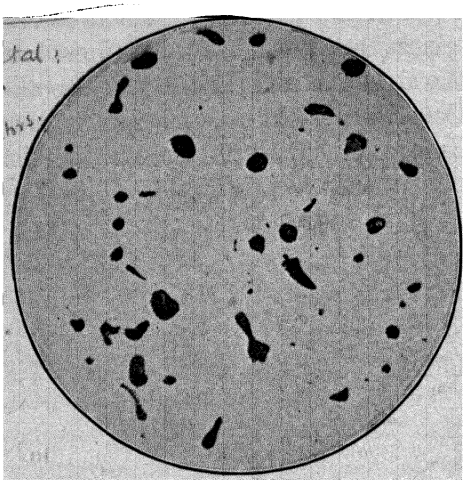


FIG. 79*a*.—Plastic bronze. Dark masses of lead fairly uniformly distributed in bronze (light) matrix. Mag. 100 ×. Not etched.

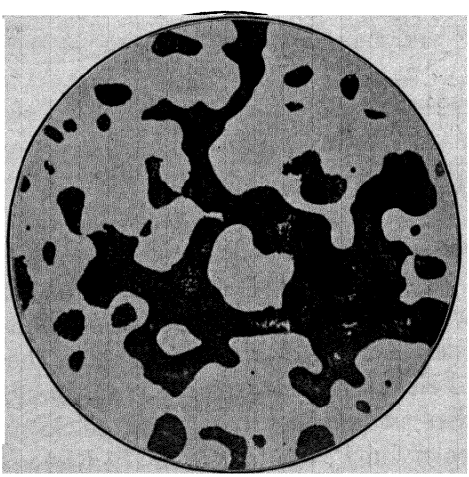


FIG. 79*b*.—Plastic bronze showing badly segregated lead (dark) in the bronze matrix (light). Mag. 100 ×. Not etched.

lubricating because of the soft, greasy character of the suspended lead. The lead drops are sources of weakness in an otherwise strong metal, so that the amount of lead must

be carefully adjusted to fit the conditions under which the bearing is to be used. For most purposes, the lead content is less than 2 per cent, although in the plastic bronzes it may reach 50 per cent. If in the making of high-lead **plastic bronze** for bearings the bronze-lead emulsion is cooled rapidly enough, the lead will be found uniformly distributed throughout the bronze in the form of spherical drops (Fig. 79*a*). The segregation of the lead, which is the frequent cause of failure in service, is shown in Fig. 79*b*. This trouble is often overcome by the addition of small amounts of nickel, iron sulphide, or other material with a high melting point. The usual bearings of this type contain from 10 to 30 per cent lead. The bronze gives the necessary strength while the lead increases the plasticity and acts as a lubricant. Bearings of this type are commonly used for heavy loads, as, for example, in locomotive journals or for carrying the rolls in a rolling mill. Copper-lead emulsions solidify in the same way as do the plastic bronzes and under the name **plastic copper** are used in airplane engine bearings.

4. Bell Metals.—These alloys contain from 75 to 80 per cent copper. The former is of especial interest because it must either be worked at a temperature above dull redness or the hot metal must be suddenly chilled (quenched) and then worked cold. Reference to the diagram (Fig. 76) will show that work is done in either case on the β-solid solution. In the first case, the work is done while the alloy is in the β-temperature range; and, in the second case, the sudden chill retains the bronze in the condition in which it existed at the higher temperature (see p. 39). With the increase in tin to more than 25 per cent, the brittleness becomes so great that the alloys are handled only with difficulty and are used exclusively for decorative purposes where the material is not subjected to stress or shock.

Aluminum Bronze.—Another technical copper alloy of great importance is the alloy with aluminum known as

aluminum bronze. The diagram (Fig. 80) is not unlike the tin-bronze and brass diagrams in its general character and complexity. The only alloys of technical importance, however, lie in the α-field (copper solid solution varying from 0 to about 10 per cent aluminum) and, at the opposite

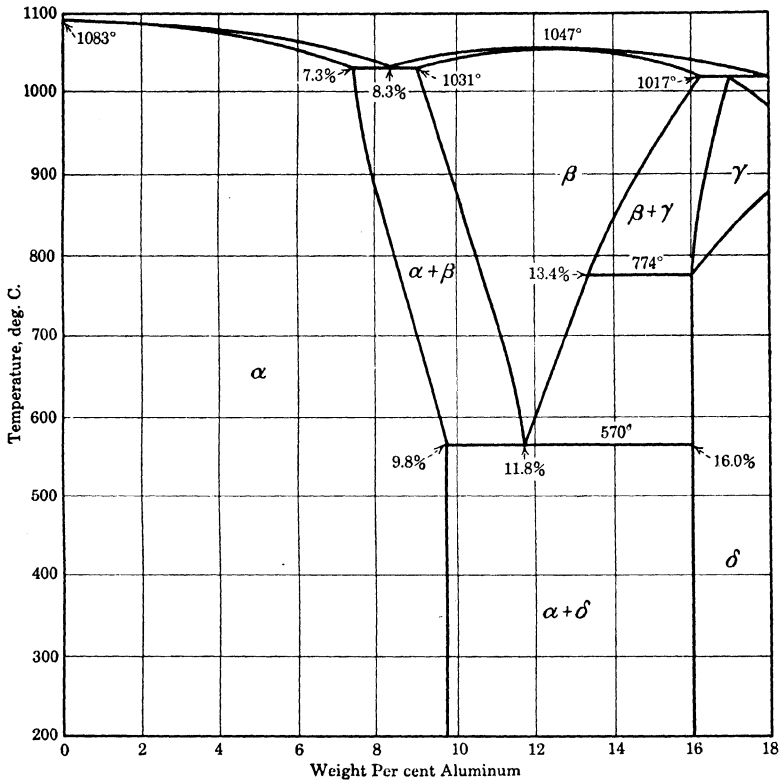
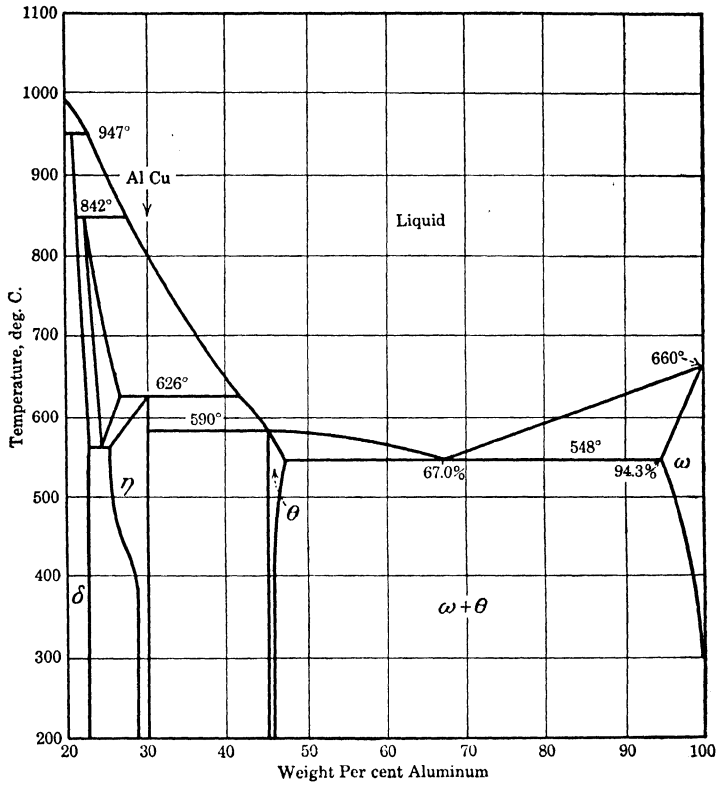


FIG. 80.—Copper-

side, in the η-field, which is a series of solid solutions of copper in aluminum, saturated at about 10 per cent copper. The light alloys of aluminum with copper have already been mentioned on page 83. The alloys in the α-field have remarkable physical properties, the addition of aluminum causing a striking increase in tensile strength. In castings, for example, while 30 per cent zinc gives a

brass with a tensile strength of about 30,000 lb. per square inch and 10 per cent tin will give a bronze with about 40,000 lb. tensile strength, the addition of 10 per cent aluminum to copper gives an **aluminum bronze** with a strength of about 65,000 lb. per square inch. Its elongation is about



aluminum diagram.

20 per cent, nearly as great as that of brass and twice as great as that of tin bronze, and the alloy is considerably harder than either. Aluminum bronze is used in the manufacture of castings requiring strength and toughness, and is especially resistant to shock or to alternating stresses. It has the added advantage that it is from 10 to 15 per cent lighter than the corresponding brasses and tin bronzes.

This alloy would be more extensively used if it were not for certain difficulties in its manufacture that sometimes cause lack of uniformity in the finished product. Properly made aluminum bronze is a very valuable alloy.

Beryllium-copper.—The newest addition to the group of copper-base alloys is beryllium-copper. The range of composition is at present from 1 to 2.25 per cent beryllium with pure copper, and the higher percentage gives the best properties. The tensile strength of the annealed alloy is about 60,000 pounds per square inch with an elongation of approximately 65 per cent. By cold rolling the tensile strength may be increased to 100,000 lb. or more with a corresponding decrease in elongation to 4 per cent. An outstanding characteristic of these alloys is that they may be greatly improved by *precipitation heat treatment.* This consists in working, quenching from 800°C., and then reheating at a temperature between 250 and 350°C. The temperature of reheating and the time at the reheating temperature determine the final properties. The tensile strength may be increased to 200,000 lb. per square inch with a corresponding decrease in elongation to 3 per cent. By varying the temperature and time many combinations of tensile strength and ductility may be obtained.

In addition to the ordinary uses for which an alloy with these properties is suitable, the beryllium-copper alloys have a very high fatigue resistance and are being used successfully in spring manufacture. Another distinct advantage of these alloys is that they may be fabricated into nonmagnetic and nonsparking tools for use in lacquering plants, oil refineries, and similar industries in which a fire or explosion hazard exists. The hardness may be varied from 215 to 400 Brinell according to the heat treatment. The electrical conductivity is much higher than that of steel, phosphor bronze, or other high-strength materials but is considerably lower than that of copper. The corrosion resistance is excellent. The main objection

to these alloys at present is the high cost. With increased production the cost should be materially decreased in the future.

Silicon bronze, which is sold under various trade names, contains in addition to copper from 1.50 to 4.00 per cent silicon and from a trace up to 1.00 per cent manganese. Its excellent corrosion resistance coupled with high tensile properties (from 40,000 up to 100,000 lb. per square inch)

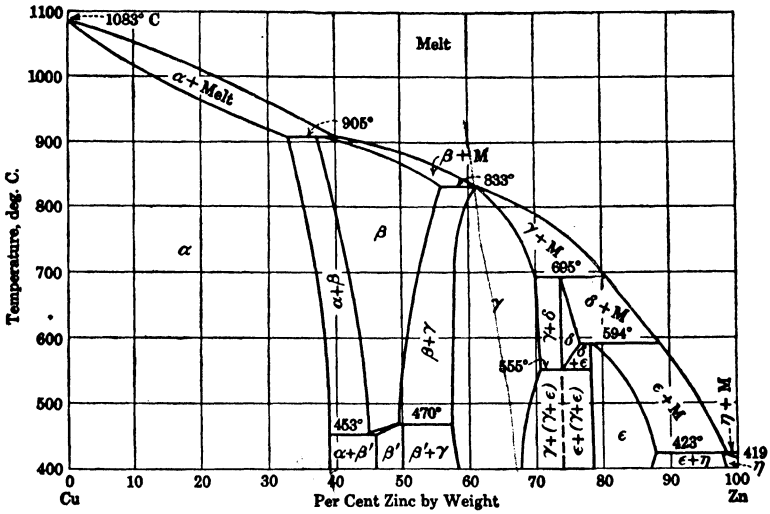


FIG. 81.—Copper-zinc equilibrium diagram.

makes it useful for many purposes, as, for example, in the production of screws, bolts, range boilers, ventilators, sewage disposal equipment and the like. **Silicon-tin bronze** is a similar alloy containing in addition to the silicon about 0.5 per cent tin. Its properties are similar to those of silicon bronze, but it is capable of withstanding unusually severe cold work which may bring its tensile strength up to 160,000 lb. per square inch, although this is accompanied by a marked decrease in ductility.

Brass.—The copper-zinc alloys are the most important of the copper alloys because they are relatively inexpensive

as compared with tin bronze. The diagram for the brasses is, like that of the bronzes, very complex, consisting of six series of solid solutions that probably contain, as in the other case, definite compounds (Fig. 81).

The γ-solid solution, which begins to be formed when the percentage of zinc is increased above 50 per cent, probably contains the compound Cu_2Zn_3 and is so brittle that alloys in which it occurs are practically valueless except for decorative purposes where strength and ductility are not

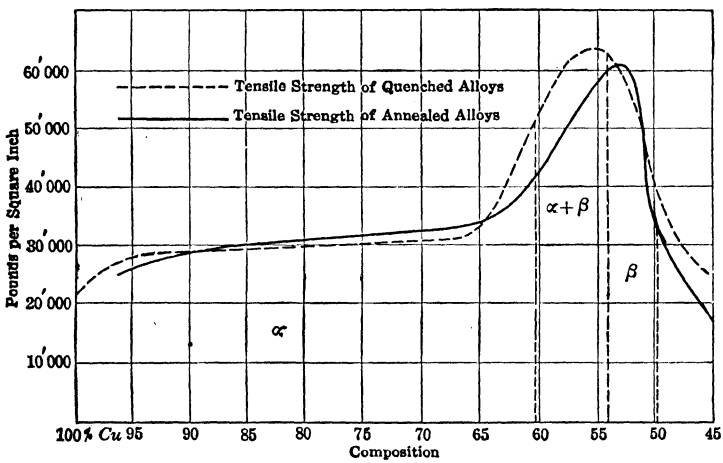


FIG. 82.—Relation between chemical composition of copper-zinc alloys and tensile strength. (*After Johnson, J. Inst. Metal*, **20**, 233.)

required. This limits the technically important brasses to three classes; α-brass, from 0 to 39 per cent zinc; $\alpha + \beta$-brass, from 39 to about 45.5 per cent zinc; and β-brass, from 45.5 to about 50 per cent zinc, at which point ductility drops to nearly zero. The curves above show the relationships between the tensile-strength properties and the metallographic constitution of cast copper-zinc alloys (Fig. 82).

It will be seen that the strength of cast brass increases from about 28,000 lb. per square inch with 1 per cent zinc to more than 60,000 lb. per square inch with 45 per cent zinc (pure β), so that, by choosing the composition,

any desired strength within these limits may be obtained. It must be clearly understood at this point that the figures just given are not absolute but relative, as the physical properties vary within fairly wide limits, even with cast material, depending on various factors such as the shape of the cast piece, the material of which the mold is made, and the rate at which the metal cools.

The actual number of commercial brasses is very great, but, for convenience, they may be grouped into a few classes. The cost decreases with the increase in the percentage of zinc, so that very high copper alloys are less widely used.

1. Gilding Metal or Jewelry Brass.—This contains from 1 to 20 per cent zinc and is used under various trade names in the manufacture of cheap jewelry. The color of some of the alloys in the group is not unlike that of standard gold.

2. Dutch Metal.—These alloys contain between 20 and 25 per cent zinc, are very malleable, and are used largely in the hammered form as substitutes for gold leaf. Recently, a brass containing 20 per cent zinc has been used in making condenser tubes.

3. Brass for Cold Working.—The group in which the zinc varies from 27 to 35 per cent includes by far the largest number of the technically important brasses. This range of compositions lies at the zinc-rich end of the α-brass field and, therefore, includes the alloys of high tensile strength coupled with maximum ductility. In this class are found the alloys used for sheet metal, tubes, wire, cartridge cases, and other articles that are to be subjected to severe mechanical work.

4. Muntz Metal and Similar Alloys.—These contain from 39 to 49 per cent zinc and include the α- and β- and the pure β-brasses. The shape of the curves in the Cu-Zn diagram, Fig. 81 (p. 103), indicates clearly the fact that alloys of this class are subject to marked modification in their properties by heat treatment. Drastic quenching

from 800°C. or above retains the metal in the form of undecomposed β-brass, although it is practically impossible to prevent at least a slight reformation of α-crystals (Fig. 83). Reheating the quenched metal causes the gradual

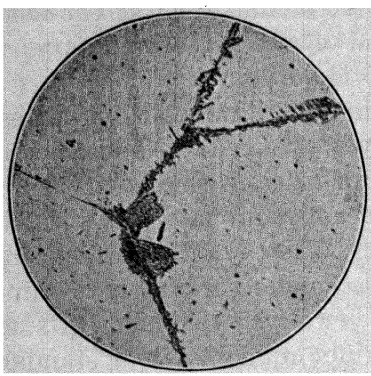


FIG. 83.—Quenched from 825°C. Large grains of β-brass (light). Small reeds of α at grain boundaries. Dark spots are lead.

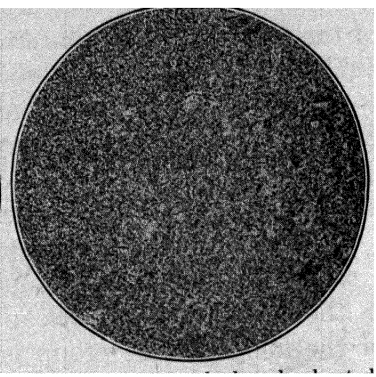


FIG. 84.—Quenched and reheated at 400°C. Shows very fine α and β mixture.

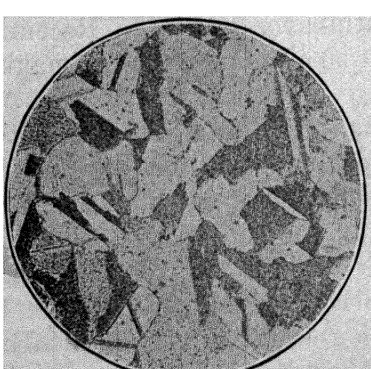


FIG. 85.—Quenched and reheated at 450°C. Shows large α-twinned crystals.

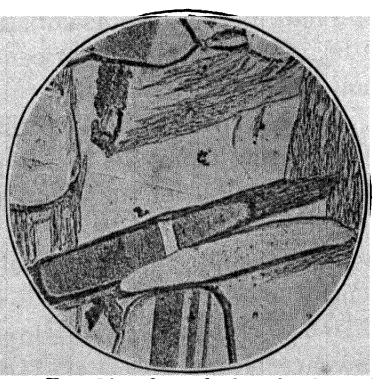


FIG. 86.—Quenched and reheated at 750°C. Shows gradual solution of the banded α structure and the production of structureless β.

formation of α-crystals. With a reheating temperature of 250 to 300°C., these are in a very finely divided condition, but, as the reheating temperature increases, the size of the α-crystals also increases with a corresponding decrease

in the tensile strength of the metal. The changes produced by various forms of thermal and mechanical treatment are shown in Figs. 83 to 90. Figure 91 shows the relations between mechanical properties and reheating

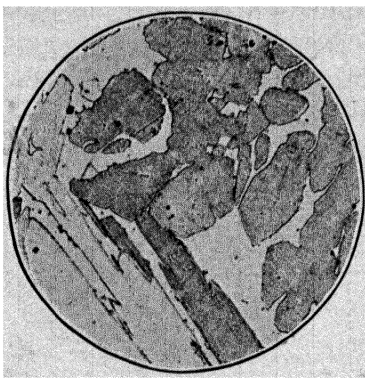


FIG. 87.—Furnace cooled from 825°C. Irregular masses of α in light structureless β.

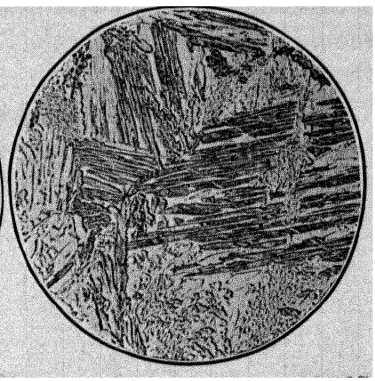


FIG. 88.—Air-cooled from 825°C. Needless of α in light matrix of β.

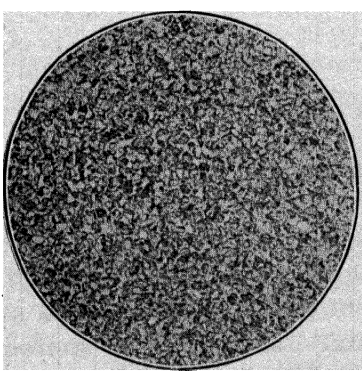


FIG. 89.—Hot-worked material, rapidly cooled. Fine, uniform mixture of α and β.

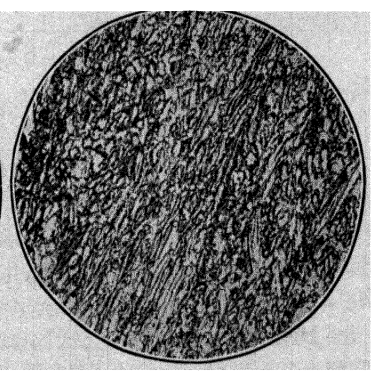


FIG. 90.—As in Fig. 89 but followed by cold work. Marked elongation of the grains.

temperatures. Owing to the fact that normally cooled alloys of the Muntz-metal type are composed of two components, α and β, they are usually worked hot so that the metal may be in a homogeneous condition. Pure β-brass shows no tendency to form twin crystals even after

it has been worked and annealed. It is colored yellow by $NH_4OH + H_2O_2$ and may be distinguished in this way from α-brass. A mixture of NH_4OH and ammonium persulphate or a dilute acid solution of $FeCl_3$ is often successfully used in the examination of Muntz metal as the β is darkened, while the α is practically unaffected by a short treatment with these reagents.

Alloys of the Muntz-metal type are fairly resistant to corrosion by salt water if the α- and β-crystals are small and intimately mixed. They are used to a considerable extent in the sheathing of wooden ships, for condenser tubes,

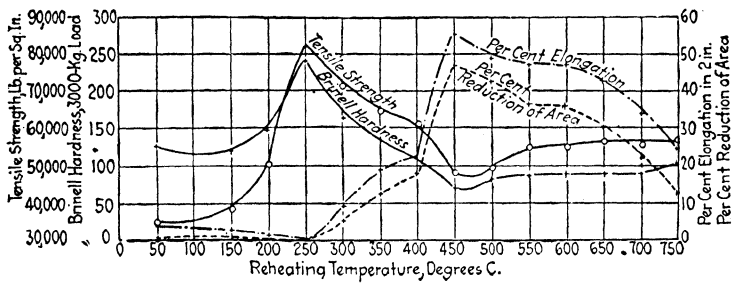


FIG. 91.—Physical properties of test specimens quenched from 825°C. and reheated as indicated.

and for other purposes where the lesser ductility is not a serious objection. Because of the cheapness of zinc, the Muntz-metal alloys are sometimes substituted for the more expensive α-brass. Corrosion may be reduced by the addition of about 1 per cent tin, as in **naval brass.**

5. Brass Solder.—For brazing iron, the solder contains 35 per cent of zinc, while, for soldering brass, the alloy of 50 per cent is most commonly used.

6. White Brass.—When the percentage of zinc is more than 50, the resulting alloys become increasingly lighter in color and are very brittle. These alloys are known as the *white brasses* and are used only for ornamental castings.

α-Brass.—The most important single alloy is that whose composition is very near to 70 per cent copper and 30 per

cent zinc. It possesses great ductility, about 56 per cent elongation, and a tensile strength when cast of 30,000 to 35,000 lb. per square inch, a strength that is greatly increased by mechanical work. In the form of annealed sheet, α-brass will have a tensile strength of 40,000 to 50,000 lb. per square inch with an elongation of more than 60 per cent in 2 inches. By cold rolling the tensile strength may be increased to 140,000 lb. per square inch but the elongation in this case is almost zero.

One of the most important uses of this 70-30 brass is in the production of shell or cartridge cases, which in the process of manufacture are subjected to severe mechanical work. (See Chap. III.) Practically all brass shell cases, from those used for the small revolver to the large cases used in naval guns, are made by a series of punching and drawing operations. As was stated on page 65, this working produces an elongation of the crystal grains and a marked hardening and increase in brittleness of the metal. The micrograph, Fig. 92, is of interest in demonstrating the value of metallographic as well as chemical control in studying cold-worked brass. The chemical analysis is excellent, but the stress has been enough to produce great distortion of the crystal grains. This strained condition can be almost wholly relieved by suitable annealing. This operation would also markedly soften the brass. The striking feature of cold-worked α-brass that has been annealed is the production of twin crystals characterized by alternate dark and light bands. These twins may be so small as to be scarcely visible at a magnification of 75 diameters, or



FIG. 92.—Severely cold-worked metal showing distorted grains and etch bands.

they may be so large that with the same magnification a single crystal may cover the entire field of vision of the microscope. These differences in crystal size are shown in Figs. 92 to 98, all of which show α-brass of the same

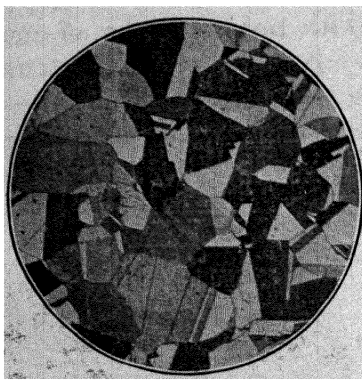


FIG. 93.—Medium twin crystals due to annealing at 650°C.

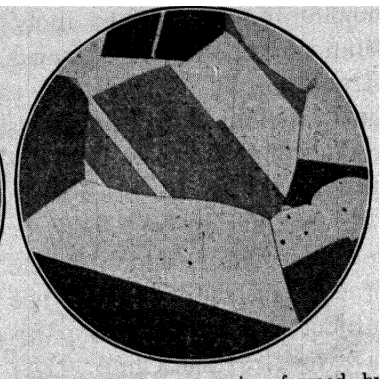


FIG. 94.—Large grains formed by annealing at 800°C.

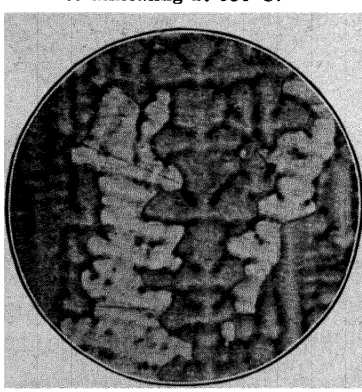


FIG. 95.—As cast. The dendritic structure is characteristic of quickly cooled metal.

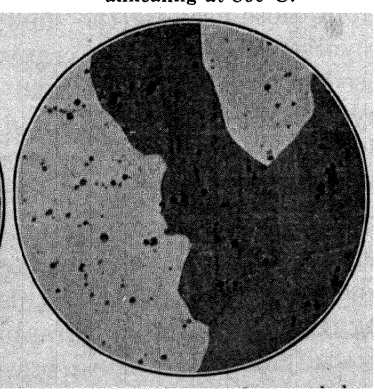


FIG. 96.—Cast and annealed at 800°C. The large masses are homogeneous grains. The differences in shade are due to differences in orientation of the grains. The small black spots are lead.

chemical composition (70 per cent copper and 30 per cent zinc) but differing in amount of mechanical work and in heat treatment. Although it may be said, in general, that the higher the annealing temperature, the larger the crystal

grains, other conditions being equal, it is also true that the crystal size depends on the amount of cold work to which the brass has been subjected.[1] This means that for each sample of cold-worked brass there is an annealing temperature that will produce crystals of the desired size, this temperature depending on the extent to which the brass has been deformed by mechanical work. Fine crystal grains indicate increased tensile strength and hardness with decreased ductility, while large crystals are usually accompanied by softness and lower tensile strength.

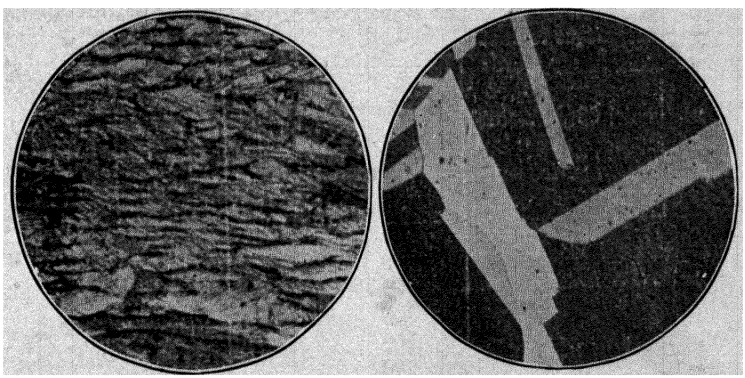


FIG. 97.—Cast and compressed 50 per cent. Elongation of the grains is marked.

FIG. 98.—Same as Fig. 97 but annealed at 800°C.

This connection between crystal size and physical properties has led to the introduction of definite grain-size requirements in many specifications, not only for brass and bronze but also for steel. A convenient means of studying grain size has been proposed by Jeffries[2] and is recommended by the American Society for Testing Materials.

The method consists in projecting the magnified image of the specimen onto a ground-glass plate[3] on which

[1] MATHEWSON and PHILLIPS, *A.I.M.E.*, February, 1916.

[2] ZAY JEFFRIES, "Grain Size Measurements," *Met. Chem. Eng.*, **18**, 185, 1918.

[3] It is often convenient to substitute a sheet of translucent paper (Japanese vellum) for the ground glass, so that a permanent record may be retained.

has been inscribed a circle 79.8 millimeters in diameter (area = 5000 square millimeters). The ground glass is placed with its ground surface toward the specimen, and on the outer, smooth surface the number of whole crystals included in the circle is counted. This may be done conveniently by checking each crystal with a soft pencil. The number of grains intersecting the circumference of the circle is then counted, and 0.5 of this number, added to the number completely included in the circle, gives a close approximation of the total number of grains present. To obtain the number of grains per square millimeter, the

Diameter of circle in millimeters	Magnification used	Multiplying factor to obtain grains per square millimeter
79.8	10	0.020
79.8	25	0.125
79.8	50	0.500
79.8	75	1.125
79.8	100	2.000
79.8	150	4.500
79.8	250	12.500
79.8	500	50.000

grain count is multiplied by a factor that depends on the magnification used. The standard magnifications, as recommended by the American Society for Testing Materials, are, for steels, 50, 100, 200, and 500 diameters, and for nonferrous alloys, 25, 75, 150, and 250 diameters. The multiplying factors are given in the table.

If the grain size is to be expressed as the average diameter of the crystal in millimeters, or its area in square millimeters, the following formulas from Jeffries' paper will be found useful:

z = completely included grains.

w = boundary grains.

x = equivalent number of whole grains in 5000 square millimeters (circle 79.8 millimeters in diameter or rectangle with area of 5000 square millimeters); $x = \frac{1}{2}w + z$.

m = magnification.

f = multiplying factor used to obtain grains per square millimeter (see table); $f = \frac{m^2}{5000}$.

n = number of grains per square millimeter; $n = fx$.

d = diameter of average grain in millimeters; $d = \frac{1}{\sqrt{n}}$.

a = area of average grain in square millimeters; $a = \frac{1{,}000{,}000}{n}$.

Instead of making an actual count of the grains in a given area, the information as to grain size may be obtained more quickly, though less accurately, by a comparison of the projected image with a series of photomicrographs taken at the same magnification and in which the grain size of each member of the series is known.

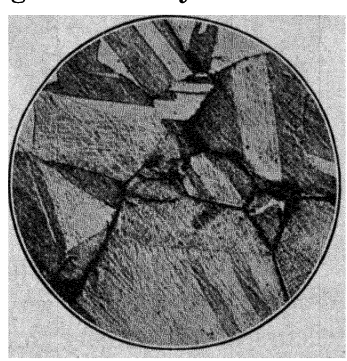


FIG. 99.—"Season cracks" in α-brass. The black lines are intercrystalline cracks. Etched with $NH_4OH + H_2O_2$. Mag. 100 ×.

One of the most serious defects in worked brasses and bronzes is the strained condition leading to the formation of what are known as *season cracks*. Various articles of cold-worked brass may be so badly strained and so imperfectly annealed that storage for a period of from several weeks to a number of months, particularly in a moist climate, leads to a spontaneous breakdown of the strained metal and the production of large or small season cracks (Fig. 99). It has been shown that while season cracking may possibly occur in the absence of corroding agents, it is

markedly accelerated by two specific reagents, ammonia and salts of mercury. The cracks differ from normal cracks in that they are always *intercrystalline*, *i.e.*, they follow the grain boundaries.

It happens frequently that this dangerous condition is not at all apparent, even on careful inspection, so it has become the custom in many instances to insist on a test for season cracking, with a specified number of samples from an entire lot. This can be done effectively by the immersion of the cleaned samples in a 1 per cent solution of mercurous nitrate containing 1 per cent of concentrated nitric acid. Satisfactory material should show no cracks in a 4-hour period. The season-cracking phenomenon is greatly accelerated by this treatment and the tendency to crack is disclosed. The danger of season cracking is practically removed by annealing the material for 1 hour at a temperature of about 300°C. No appreciable softening results.

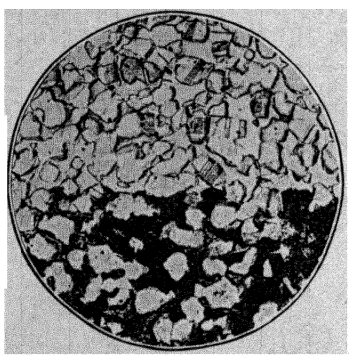


FIG. 100.—"Dezincified" Muntz metal. Etched with $NH_4OH + H_2O_2$. Mag. 100 ×.

Another type of failure, shown in Fig. 100, is called *dezincification*. The way in which this kind of corrosion occurs is still subject to question, but the net effect is the partial or complete removal of the zinc from the brass, leaving the copper either in a spongy or massive condition, depending on the conditions which cause it. Extensive dezincification may leave a condenser tube in so fragile a form that it can readily be crushed between the fingers.

It is essential that α-brass that is to be exposed to severe mechanical treatment should be free from bismuth, antimony, iron, and lead, as all are sources of weakness. For brass that receives only a moderate treatment, small percentages of iron or lead will not be dangerous. Iron

gives to the alloy increased strength coupled with increased hardness and decreased ductility, while lead acts, as it does with bronze, to reduce the tensile strength but to make the brass far more readily machined. Bismuth and antimony tend to form brittle envelopes around the α-crystals and to destroy the ductility that makes cold work possible.

For special purposes, small percentages of other elements are added to the brass alloys. The use of *lead* has been

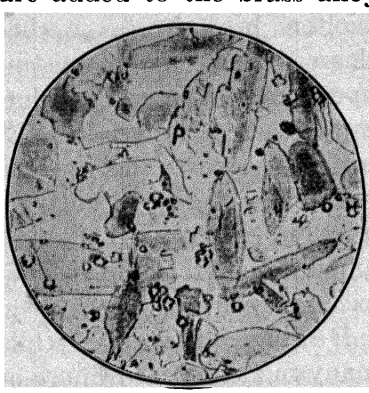


FIG. 101.—Manganese bronze showing the α-reeds in a β-matrix and the small particles of the iron-zinc compound. Mag. 100 ×.

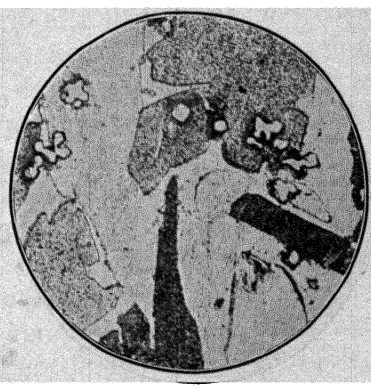


FIG. 102.—Same as Fig. 101 but at 250 ×. This shows the iron-zinc compound embedded in the brass matrix.

mentioned as improving the machining qualities although reducing the tensile strength, but only when the percentage of lead is very low (less than 0.5 per cent) can the brasses be worked hot. *Tin*, when added in small quantities, increases the hardness of brass but causes a marked decrease in ductility. When it is added to 70-30 brass in amounts from 1 to 1.5 per cent, an alloy that is very resistant to sea water, **Admiralty metal,** is formed. This alloy is now used almost exclusively in the manufacture of high-grade condenser tubes. The addition of *manganese* in amounts less than 4 per cent gives to the brasses very desirable properties. It is usually added to brasses of the Muntz-metal type, together with small amounts of

tin, iron, and aluminum. An alloy of this general type, called, unfortunately, **manganese bronze** (Figs. 101, 102, and 103), when it should be **manganese brass,** is much used in making propeller blades, rudders, and ship fittings exposed to sea water, and for other engineering purposes requiring a strong, noncorrodible alloy. Its tensile strength is about 50,000 to 60,000 lb. per square inch with an elongation of more than 45 per cent. *Aluminum*, when added in very small amounts, increases the fluidity of molten brass to a marked degree, rendering the casting operation easier and producing cleaner castings. It materially increases the strength of the brass but rapidly reduces its ductility so that the amount added should never exceed 3 per cent.

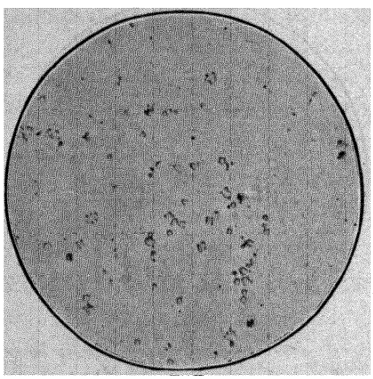


FIG. 103.—Manganese bronze unetched showing the iron-zinc compound. Mag. 100 ×.

Bearing Metals.—While many modern bearings are of the ball or roller type, there is still an extensive use of antifriction metals of various compositions. Several of the alloys have been discussed (phosphor bronze, p. 96, plastic bronze, p. 99, plastic copper, p. 99, Babbitt metal, p. 45), but a few others should be considered briefly. **Frary metal** is an alloy with approximately 97 per cent lead, 2 per cent barium and 1 per cent calcium with or without sodium in very small amounts. This unusual alloy has, in general, as good antifrictional properties as Babbitt metal and is less affected by temperature increases. Silver and some of its alloys are being used to an increasing extent in automobile bearings. The addition of from 1 to 3 per cent cadmium to Babbitt seems to make a marked improvement and other bearing alloys in which cadmium is the chief constituent also have promise. **Oil-**

less bearings, in which graphite is mixed with copper either mechanically or by a metallurgical process, are used as bearings of parts not easily reached for lubrication.

Zinc is a much more widely used metal than is commonly recognized because so large a proportion of its total consumption is found in connection with other metals, notably in its use in galvanizing, sherardizing, or other applications in steel protection. During the last decade the volume of zinc consumed was about 95 per cent that of copper. In addition, zinc is used in the form of rolled sheets, as a constituent of brass, and in recent years to an ever increasing extent in the production of die castings. For this use it is alloyed with from 3.5 to 4.5 per cent aluminum with or without 2.5 to 3.5 per cent copper.

Age Hardening.—The increased hardness and tensile strength produced by the heat treatment of the copper-beryllium alloys (p. 102) and the marked changes associated with duralumin (p. 87) and other heat-treatable aluminum alloys (p. 89) illustrate the general phenomenon of age hardening, a metallurgical operation that is of rapidly increasing importance.

Certain types of alloys, when heated to an elevated temperature, quenched, and then held for a time at some predetermined lower temperature, show definite changes in properties with time. This constant-temperature process is referred to as *aging*, or more commonly, as *age hardening*, since the increase in hardness is the most striking change that occurs. Age hardening may take place at room temperature or at some higher temperature, depending on the composition of the alloy. In general, the tensile strength, yield point, and elastic limit increase during aging, while the ductility and malleability decrease. The magnitude of these changes is shown below.

Aging will occur only with those alloys of the solid-solution type in which the solubility of the dissolved constituent decreases with falling temperature. This condition is

shown in Fig. 104 in which Z represents a typical age-hardenable alloy. At room temperature this alloy consists of two phases in equilibrium: a saturated solid solution A and another constituent of composition H. The second phase may be a pure metal, an intermetallic compound,

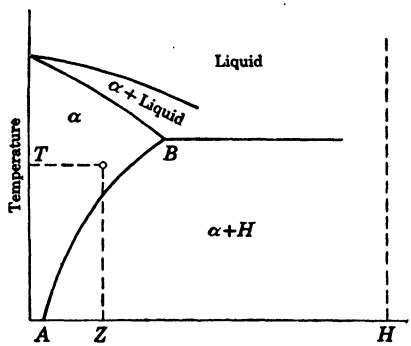


FIG. 104.—Type of equilibrium diagram of an alloy susceptible to age-hardening

or another solid solution. If the alloy Z is heated above the solubility curve AB to a temperature T, all of the con-

PHYSICAL PROPERTIES OF AGE-HARDENABLE ALLOYS[1]

Alloy	As quenched			As aged		
	Brinell hardness	Tensile strength, lb. per sq. in.	Elongation, per cent	Brinell hardness	Tensile strength, lb. per sq. in.	Elongation, per cent
Aluminum + 4% copper	65	38,800	6	100	50,000	1
Copper + 2.75% beryllium	116	88,000	29	365	161,000	5
Copper + 6% nickel silicide	68	47,000	55	205	115,000	16
Lead + .085% calcium	...	3,800	..	...	7,400	
Iron + 12% molybdenum	155	58,200	6	230	147,000	1
Nickel + 2.50% beryllium	175	80,000	17	500	150,000	2
Copper-nickel (67% nickel) + 4% aluminum	140	90,000	50	300	175,000	20

[1] MERICA, *Trans. A.I.M.E.*, 99, 18.

stituent H goes into solution. If the alloy is now suddenly cooled to some low temperature, perhaps room temperature, it will consist of a supersaturated solution of composition Z

which is unstable with respect to H. This operation is called a *solution heat treatment* and is an essential part of the age-hardening process. Such an alloy will tend to reach equilibrium by precipitating H until the composition of the solid solution has again become A. At the low temperature, however, it is possible that the mobility of the atoms is so limited that this precipitation process is either entirely prevented or takes place slowly over a definite period of time. This latter possibility has led to the adoption of the *precipitation theory* to explain age hardening. When a solid phase, such as H, Fig. 104, precipitates from a solid matrix, the crystallites of H form keys along the potential slip planes of the matrix, thus increasing the resistance to slip. This results in an increase in hardness with a corresponding change in other properties. In the initial stages of precipitation the crystallites are too small and too few in number to cause a marked increase in hardness. However, as they increase in size and number, the hardness rises continuously until a critical particle size is reached. This causes a maximum resistance to slip and, therefore, maximum hardness. Further coalescence of the crystallites above this critical size reduces the resistance to slip and the hardness decreases.

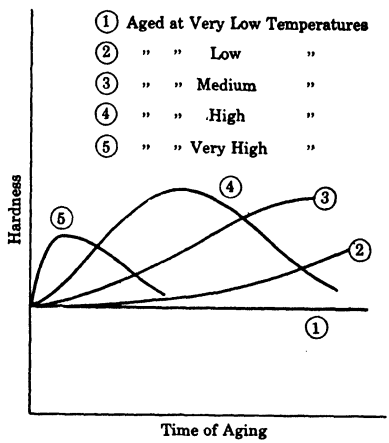


FIG. 105.—Age-hardening curves for a hypothetical alloy.

A typical set of aging curves is shown in Fig. 105. These may be readily explained on the basis of the precipitation theory.

Curve 1. At very low temperatures the atomic mobility of the quenched alloy is so low that precipitation of the

hardening constituent cannot take place and hardness does not change with time.

Curve 2. If the aging temperature is raised, the atomic mobility is increased and a temperature is reached at which the precipitation of the hardening constituent begins after a period of time. The time interval before precipitation starts is called the incubation period. When precipitation starts the hardness increases, and as the particles grow, the hardness continues to rise.

Curve 3. At a somewhat higher aging temperature, the incubation period is shorter and the increase in hardness is more rapid. The maximum hardness is also greater because at the higher temperature the precipitated particles attain the critical size for maximum hardening.

Curve 4. At a still higher temperature the precipitated particles not only reach the critical size as indicated by the hardness peak, but even coalesce beyond the critical size to cause a decrease in hardness. This softening is called *over-aging.*

Curve 5. At very high aging temperatures, the precipitation is very rapid, and the maximum hardness is actually lower than that attained at the lower temperatures.

While the precipitation theory accounts for the changes in hardness and allied properties, the measurement of these changes alone does not prove that precipitation actually takes place. Other evidence is needed. If precipitation does take place during aging, a volume change would be expected and could be shown by density or dilatometric measurements. Since the precipitation of the constituent is caused by the decomposition of a solid solution, the electrical conductivity of the alloys should increase and the lattice parameter should also change as the hardening progresses. These indications of precipitation have been found during the age hardening of many alloys such as copper-beryllium, aluminum-silicon, silver-copper, iron-molybdenum, and iron-tungsten.

There is, however, an important group of age-hardenable alloys including aluminum-copper (duralumin), iron-carbon, and iron-nitrogen, which are abnormal in the sense that during the aging at ordinary temperatures a marked increase in hardness occurs while the volume remains constant, the electrical conductivity decreases instead of increases, and the lattice parameter of the solid solution remains constant. Apparently, then, these alloys age-harden without precipitation and the precipitation theory cannot explain the hardening. The hardening must be due to changes taking place within the supersaturated solid solution. The *knot theory* has been advanced to account for this apparently anomalous situation. Reference to the aluminum-copper system shows that when duralumin with about 4 per cent copper is heated to 510°C. before quenching, the alloy consists principally of an aluminum-rich solid solution. After quenching, the solid solution becomes supersaturated with respect to the $CuAl_2$ and there is a tendency for this compound to precipitate. According to the knot theory, the $CuAl_2$ particles cannot form if the copper atoms remain widely scattered throughout the aluminum lattice. The theory therefore suggests that immediately after quenching the copper atoms begin to diffuse from point to point on the aluminum lattice into those positions that will be favorable for the formation of $CuAl_2$ crystallites, but that the atomic mobility is not great enough to allow the actual precipitation. This means that after complete aging at room temperature the copper is still in solid solution; but instead of being distributed at random, the copper atoms are now segregated in groups or knots, thus causing severe distortions in the aluminum lattice. These distortions roughen the potential slip planes and so increase the hardness. The lattice distortion also decreases the electrical conductivity, and since there is no actual precipitation, no volume or lattice-parameter changes occur.

When duralumin is aged at elevated temperatures (perhaps 300°C.), the atomic mobility increases to such an extent that the knots actually precipitate to form $CuAl_2$ particles. This precipitation can be shown by density, conductivity, and x-ray measurements. At 300°C., then, the age hardening of duralumin is explained by the precipitation theory. On aging between 150 and 200°C., hardening begins before precipitation. Precipitation finally takes place, however, with a further increase in hardness. In this temperature range, therefore, both the precipitation theory and the knot theory are needed.

More recent work has shown that even an alloy which normally age hardens by precipitation can be made to harden prior to precipitation if a low aging temperature is used. Hence, it is quite possible that knot formation and precipitation should not be regarded as two separate phenomena but rather as two consecutive processes in the general mechanism of age hardening.

CHAPTER V

IRON AND STEEL

The most important applications of metallography, as well as the most difficult, involve a study of the uses, defects, and methods of heat treatment of iron and steel. The difficulties in the study of this series of iron-carbon alloys may be traced to various causes, among them the fact that in this field, even in what are known as the plain carbon steels, we are dealing, not with a simple alloy of iron and carbon, but with an exceedingly complex alloy of iron, carbon, phosphorus, manganese, sulphur, and silicon. While the effects of the last four elements, when they are present in small quantities, as is usually the case, are not comparable with the effects produced by comparatively slight changes in carbon content, no single constituent can be wholly neglected. An increase in any one of them, above a certain maximum, causes far-reaching changes in the physical and metallographic properties of the metal. When elements like chromium, nickel, vanadium, or tungsten are added in making the alloy steels the situation becomes so complex that little is known from an equilibrium standpoint.

A second factor that complicates the exact study of the iron-carbon diagram is that the iron exists in several allotropic forms, each one of which has different physical properties, notably magnetic properties, and each one varies in its ability to dissolve carbon.

Critical Points in Pure Iron.—When molten iron is cooled under conditions that make it possible to determine the temperature changes taking place as it cools to room temperature, breaks in the cooling curve will be found at

about 1537°C. (the freezing point of iron), 1403°C., 906°C., and 768°C. The slight effect at 1403°C. is due to an allotropic change in the iron. This is confirmed by x-ray analysis (see p. 299) and magnetic examination. The form of iron existing above 1403°C. is called δ-iron and has been studied independently by several investigators. From 1403°C. to 906°C. the crystal form of the iron is that of the face-centered cube (p. 52) and is known as γ-iron. The heat evolution at 906°C. is marked, there is a sharp change in the crystal form, and the iron loses most of its power for dissolving carbon.

The causes of the slight heat evolution at about 768°C. are not so clear. The x-ray shows the space lattice of the iron to be the same above 768°C. (up to 906°C.) as it is below it, indicating the absence of change in crystal form at this temperature. There is a marked magnetic effect in the neighborhood of this point, but the change is not a sharp one. Some investigators find a slight dilation at 768°C., but this has been questioned by others. If allotropy is defined as a change in crystal form, then β-iron, which would occur in the range from 906°C. to 768°C., does not exist as an allotropic form. Many metallographers doubt its existence. It is certain, however, that discontinuities in several properties of iron occur at 768°C., so that the existence or nonexistence of β-iron is largely a question of definition. Fortunately, the changes taking place at this temperature are not involved in any of the ordinary processes of heat treatment, so that the occurrence of iron in the β-form may be left, for the present, as an academic question.

If the iron is reheated, the temperature changes just considered take place in the reverse direction corresponding to absorptions of heat. The first of these occurs at 768°C., the temperature found in cooling. The second absorption of heat, however, corresponding to the formation of γ-iron, is always found at a temperature higher than the change

on cooling. Temperatures corresponding to these heat effects, occurring both when iron is cooled from a high temperature and when it is heated from a low one, together with other heat changes to be considered later, are commonly known as *critical points*, though sometimes as *retardations*, or *transformation points*.

These points were first investigated by the French metallurgist, Osmond, and the symbols proposed for them by him have been universally adopted. All are indicated by the letter *A* (*arrêt* meaning "arrest"). Points found on cooling are called *Ar points* (*r* from the French *refroidissement*, meaning "cooling"), while the reverse changes are known as *Ac points* (*c* from *chauffage*, meaning "heating"). The *Ac* points are in general from 10 to 30°C. higher than the *Ar* points. Complete identification of a critical point is made by giving it a number, the higher number corresponding to a higher temperature effect. Ar_4 would then indicate that point at about 1403°C. where the first evolution of heat on cooling is noticed. Ar_3 would correspond to the heat evolution at about 906°C., and Ac_3 to the point at which heat is absorbed on heating. The Ac_3 point would be found at 915 to 935°C. depending on the purity of the material. Ar_2 and Ac_2 occur at the same temperature (about 768°C.). The A_1 point is not found in pure iron but is associated with the carbon in steel and will be considered later.

Many attempts have been made to prepare chemically pure iron, but, while solid impurities can be excluded, it is practically impossible to remove all the gases that have been dissolved. The purest forms commercially available are *electrolytic iron* (Figs. 106, 107), often containing more than 99.95 per cent iron, and *American ingot iron*, a form of open-hearth iron, containing 99.90 per cent or more of iron (Fig. 108).

An extensively used form of iron known as *wrought iron* is commonly made by the *puddling process*. Pig iron is

quickly melted in a furnace, the temperature of which is somewhat lower than the melting point of pure iron. This rapid melting is for the purpose of removing most

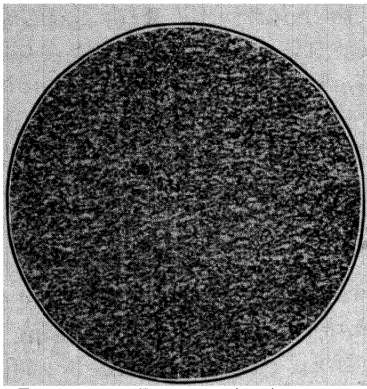


FIG. 106.—Electrolytic iron as deposited. Etched with nital. (See appendix.) Mag. 250 ×.

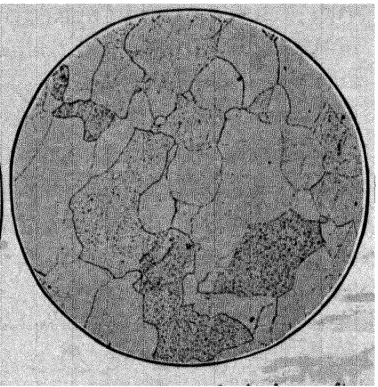


FIG. 107.—Electrolytic iron after annealing at 900°C. Shows grains of pure iron. Etched with nital. Mag. 150 ×.

of the manganese, silicon, and phosphorus. Carbon is then removed therefrom by the addition of iron oxide; as the carbon content decreases, the melting point of the mass increases, so that, when the carbon is almost gone and comparatively pure iron appears in the bath, the product becomes pasty. The pasty mass is rolled into balls and these are removed to the *squeezer*, a form of roll that squeezes from them most of the slag originally present in the mass. The still plastic mass is then rolled into bars; as a result, the slag remaining in the iron is greatly elongated and is visible under the microscope, usually as stringers or fibers, though sometimes as slag masses of considerable size

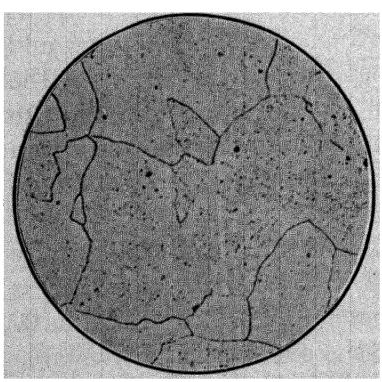


FIG. 108.—"Armco" iron (American ingot iron). Shows ferrite grains. Etched with nital. Mag. 100 ×.

(Figs. 109, 110). The transverse section of wrought iron shows irregular, rounded masses, representing cross sections of the slag fibers (Fig. 111). It should be noticed that the iron itself shows the regular polyhedral structure of all pure metals. The fibrous structure is due to the slag. The outstanding characteristic of wrought iron is its ease of welding and its resistance to shock. It is frequently said to possess better resistance to corrosion than steel.

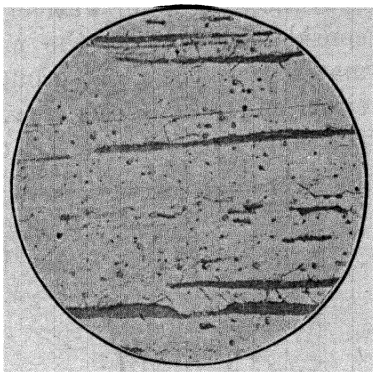


FIG. 109.—Dark slag fibers in ferrite. Longitudinal section.

The *Aston Process* is a so-called synthetic one for making wrought iron. The constituents in pig iron are removed to a great extent in a Bessemer converter, after which the molten metal is poured into a suitable liquid slag that has been made

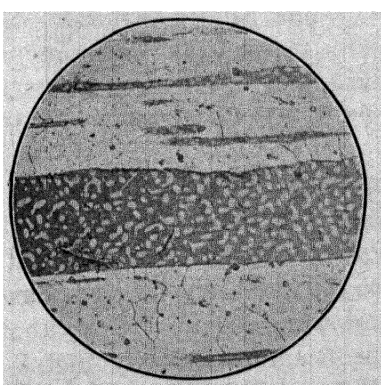


FIG. 110.—Large slag mass showing a duplex structure. Matrix is ferrite. Longitudinal section.

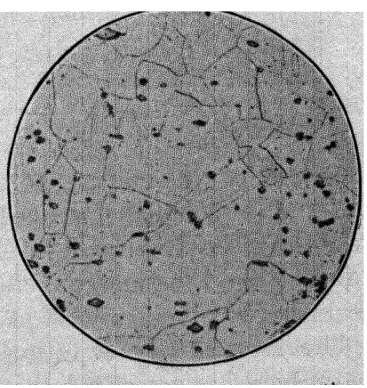


FIG. 111.—Transverse section showing cross sections (dark) of slag fibers.

in an open-hearth furnace. The liberation of gases produced at this stage breaks up the metal into fine particles. These particles become mixed with slag and

settle to the bottom of the container in a form similar to the puddled balls produced in the regular process. The operations that follow are the same as those for the puddled iron.

While these comparatively pure iron alloys are used to a considerable extent, the most important of all metallic materials is the great group of iron-carbon alloys known either as (1) *steel* or as (2) *cast iron*, depending on the composition, especially on the carbon content. It is beyond

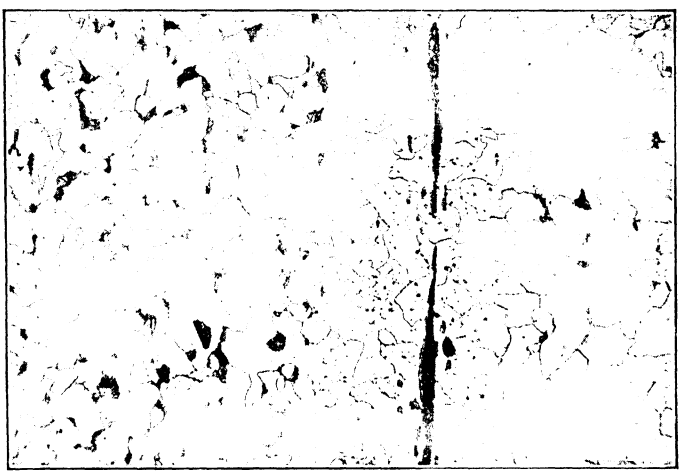


FIG. 112.—Supposedly genuine wrought iron but actually wrought iron (center section with slag) mixed with mild steel. Nital etch. Mag. 100 ×.

the scope of this book to consider, except in a general way, the many problems connected with the metallography and the heat treatment of iron and steel. For detailed information, the reader is referred to one of the larger books dealing exclusively with iron and steel.[1]

The Iron-carbon Equilibrium Diagram.—Many metallographers have studied the alloys of iron and carbon in great detail and have proposed equilibrium diagrams or have suggested modifications of the earlier ones. The

[1] SAUVEUR, "The Metallography and Heat Treatment of Iron and Steel." Carnegie Handbook, "The Making, Shaping, and Treating of Steel," BULLENS-BATTELLE, "Steel and Its Heat Treatment."

diagram shown in Fig. 113 represents one that has been constructed from the data of a number of investigators. The liquidus is represented by *ADIF* and the solidus by *ABCHIJ*. The δ-iron region is shown on a larger scale in Fig. 114.

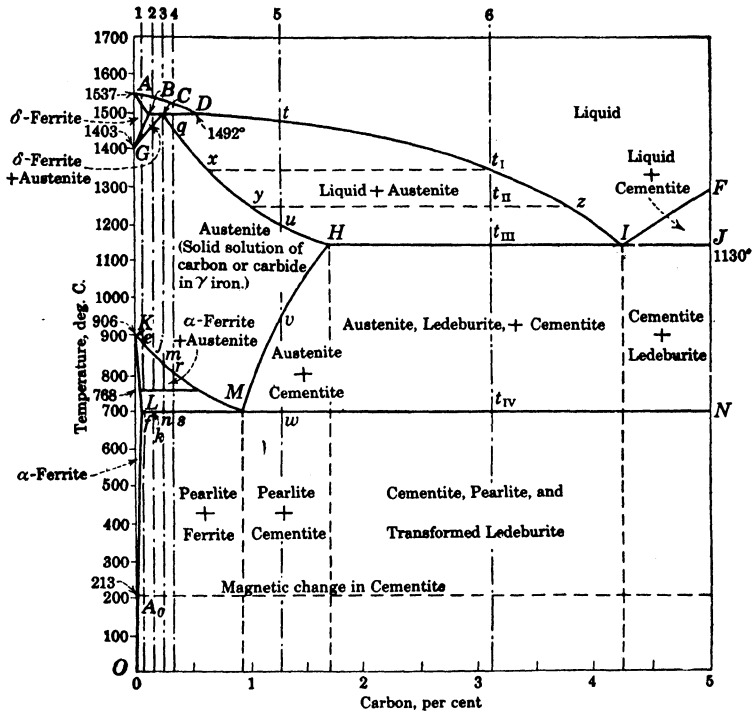


FIG. 113.—The iron-carbon equilibrium diagram.

The iron-carbon diagram shows the presence of a eutectic *I*, which is known as *ledeburite*. It consists of an intimate mixture of the solid solution of composition *H* and iron carbide, Fe_3C, known as *cementite*, corresponding to *J*. It also shows the presence of a eutectoid *M*. The composition *M* consists of an intimate mixture of the solid solution *L* and iron carbide *N*. The eutectoid, when highly polished, etched, and viewed by light reflected from its surface at

certain angles, has the iridescence of mother-of-pearl and is known metallographically as *pearlite*.

Ferrite is the term that is applied to solid solutions in which body-centered iron (either δ or α) is the solvent. The solid solution in which δ-iron is the solvent is designated δ-ferrite while that in which α-iron is the solvent is termed α-ferrite. According to this nomenclature, the area bounded by *ABG* is δ-ferrite and the area *KLO* is α-ferrite. The area *GCHMK* represents a solid solution

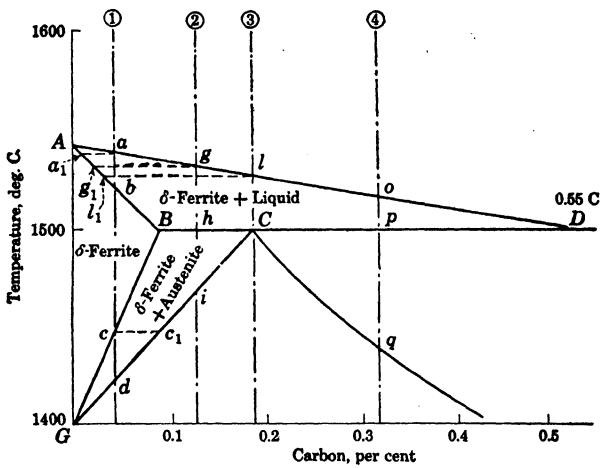


FIG. 114.—δ-iron region of iron-carbon equilibrium diagram.

in which γ-iron is the solvent. This solid solution is termed *austenite*.

A discussion of a number of alloys of iron and carbon with varying amounts of the latter will clarify the interpretation of the diagram.

Alloy 1 (Figs. 113 and 114) on cooling to *a* begins to solidify with the separation of δ-ferrite of composition a_1. On further cooling the carbon content of the δ-ferrite crystals increases until the solidification is completed at *b*; unsaturated δ-ferrite exists from *b* to *c*. Further cooling from *c* to *d* causes a gradual transformation of δ-ferrite into

austenite. This transformation is completed at *d*. Austenite is present as such until the temperature *e* is reached, when α-ferrite begins to form. Between *e* and *f*, α-ferrite continues to form while the remaining austenite becomes enriched in carbon as it shifts in composition along the line *KM*. At *f* the excess α-ferrite has the composition *L* and the remaining austenite the composition *M*. At this temperature (eutectoid temperature), the austenite is transformed into pearlite. The final structure is α-ferrite and pearlite.

Alloy 2 behaves in a manner similar to alloy 1 except that at *h* a peritectic change takes place. At this temperature, solid of composition *B* reacts with liquid of composition *D* to form austenite of the composition *C*. More solid of composition *B* is present than is necessary to react with *D* to form *C*. On further cooling, δ-ferrite shifts in composition along *BG* and the austenite along *CG* until at *i* the change into austenite is complete. On further cooling the changes are similar to those taking place in alloy 1, the α-ferrite beginning to form at *j*.

Alloy 3 behaves exactly like alloy 2 except that the amount of δ-ferrite of composition *B* is just sufficient to react with all of the liquid of composition *D* to form austenite of composition *C*. Alloy 4 has liquid left over after dissolving all of *B* so that, on further cooling, the composition of the liquid shifts along *DI* and the austenite along *CH* until *q* is reached. α-ferrite begins to form when the alloy reaches the temperature designated by *r*. At *s* the remaining austenite is transformed into pearlite.

Alloy 5 begins to solidify at *t*, final solidification takes place at *u*, and at *v* carbon comes out of solution as iron carbide, Fe_3C. This point is known as an *Acm point*. The solubility of carbon in γ-iron decreases with decrease in temperature and the austenite therefore shifts in composition along *HM*. At *w* the remaining austenite has reached the eutectoid composition and is transformed

into pearlite. This alloy will show cementite together with pearlite.

The formation of the eutectoid on cooling is always accompanied by a marked evolution of heat. If the percentage of carbon is high (0.75 per cent or more) and if the cooling from a high temperature takes place in a darkened room, the heat evolution is great enough to produce a visible reddening of the metal. Because of this reheating phenomenon this point is often called the

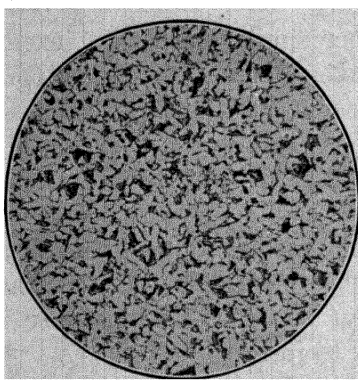


FIG. 115.—Carbon 0.12 per cent. Dark areas are pearlite. White matrix is ferrite. Mag. 100 ×.

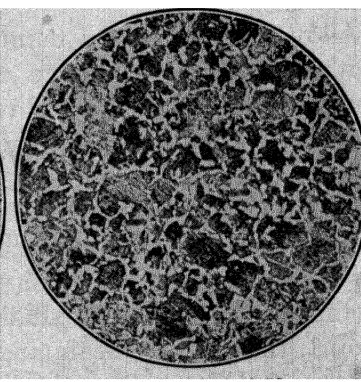


FIG. 116.—Carbon 0.50 per cent. Dark areas are pearlite. White matrix is ferrite. Mag. 100 ×.

recalescence point. It represents the Ar_1 point. The reverse of this change takes place at a somewhat higher temperature than that corresponding to Ar_1 and represents the Ac_1 point. The temperature range including the critical points is often called the *critical range*.

Steels containing less carbon than that corresponding to the *eutectoid* (0.85 per cent carbon) are known as *hypo-eutectoid* steels while those with more than 0.85 per cent carbon are known as *hyper-eutectoid* steels.

Alpha iron has a tensile strength of from 40,000 to 45,000 lb. per square inch and a eutectoid steel has a tensile strength of from 115,000 to 125,000 lb. per square inch. The tensile strength decreases with increase in carbon beyond the

eutectoid composition in the case of slowly cooled steels. In the same manner, the ductility, as measured by the elongation in the tensile test, decreases with increase in the carbon content.

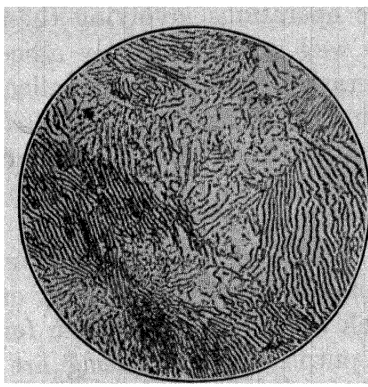


FIG. 117.—Carbon 0.85 per cent. Pearlite. Mag. 250 ×.

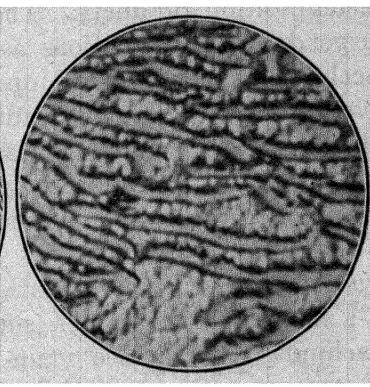


FIG. 118.—Carbon 0.85 per cent. Pearlite showing Fe_3C lamellae. Mag. 3,000 ×.

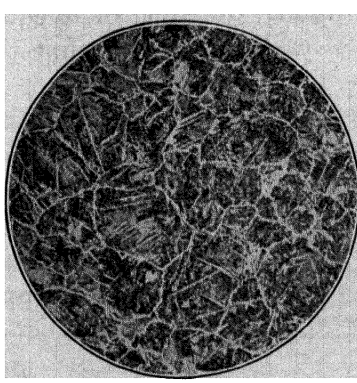


FIG. 119.—Carbon 1.3 per cent showing dark pearlite and white network of cementite. Etched with nital. Mag. 100 ×.

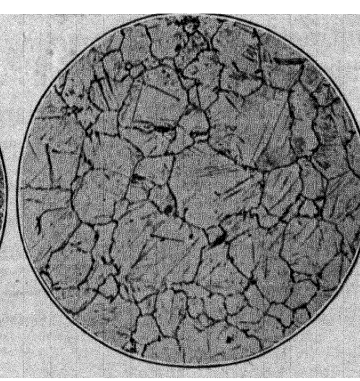


FIG. 120.—Carbon 1.3 per cent. Etched with alkaline sodium picrate to distinguish cementite from ferrite. Cementite is etched black and ferrite (in pearlite) is unattacked.

The microstructures of steels with increasing carbon content are shown in Figs. 115 to 120 inclusive.

Incomplete Transformations.—While the steels in complete equilibrium (pearlitic steels) are much used for

special purposes in which ductility is essential, by far the greater part of the steel used in industry is that in which the transformation of austenite to pearlite has been more or less suppressed with the formation of intermediate decomposition products. The operations involving these suspended transformations as well as other closely allied mechanical and chemical operations are grouped collectively under the general heading *the heat treatment of steel.* The operations commonly classified under heat treatment are annealing, normalizing, quenching or hardening, tempering or drawing, and case hardening.

Annealing.—The first of these processes, annealing, precedes almost every operation, either of heat treating or of a mechanical character, such as in the preparation for machining. The three main purposes of annealing are: (1) to soften the steel to make it more easily machined or to meet definite mechanical specifications; (2) to relieve stresses produced by forging, rolling, drawing, or unequal contraction, as in the cooling of castings; (3) to refine the grain structure of the steel.

Annealing involves three steps; (1) heating to a suitable temperature, (2) holding for a definite time at the high temperature, and (3) slow cooling.

1. Heating.—The steel should be heated slowly and uniformly to a temperature that is determined by its carbon content. The following ranges of temperature are recommended by the American Society for Testing Materials:

Carbon Content, Per Cent	Annealing Temperature, °C.
Less than 0.12	875 to 925
0.12 to 0.25	840 to 870
0.30 to 0.49	815 to 840
0.50 to 1.00	790 to 815

It will be noted that the temperature is slightly above the upper critical point (Ac_3) in each case. A heating temperature 20 to 30°C. above the critical range is satis-

factory for the annealing of hypo-eutectoid steels (less than 0.85 per cent carbon).

The mechanism of grain refinement in a hypo-eutectoid steel can be illustrated by selecting an annealed medium-

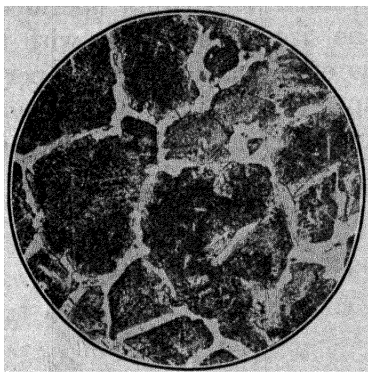


FIG. 121.—Overheated medium-carbon steel. Large dark masses are pearlite with white ferrite network.

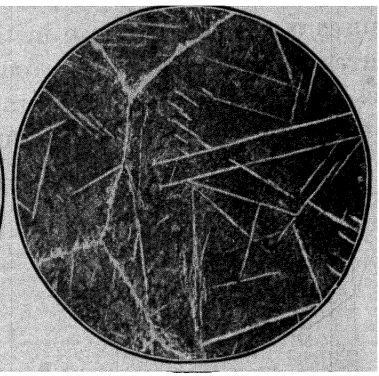


FIG. 122.—Overheated high-carbon steel. Large dark masses are pearlite. Light network and needles are cementite.

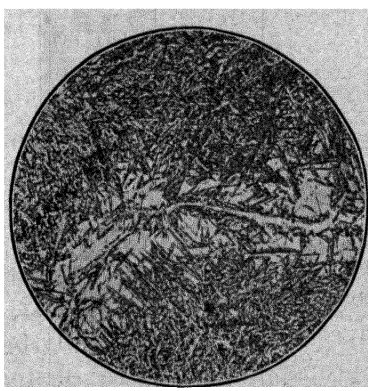


FIG. 123.—Burned high-carbon steel showing fusion at the grain boundaries and martensite (p. 124).

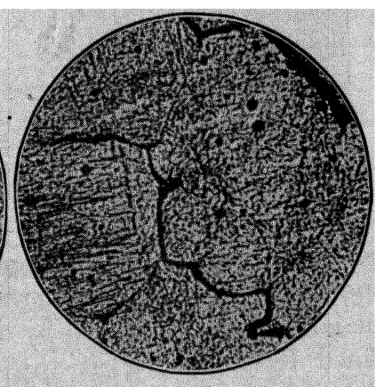


FIG. 124.—Burned high-carbon steel showing separation of the grains and martensite.

carbon steel with a large grain size. On heating, the pearlite will be transformed into austenite at Ac_1. This transformation gives birth to a number of austenite grains within the area formerly occupied by the pearlite. In

heating from Ac_1 to Ac_3, a gradual absorption of the ferrite by the austenite grains takes place until at Ac_3 these austenite grains occupy completely the area of the original grain.

An increase in temperature much above that specified causes a marked increase in the size of the grains with a corresponding decrease in some of the mechanical properties, notably the shock resistance of the steel. Excessive temperatures either in the annealing or in the hardening

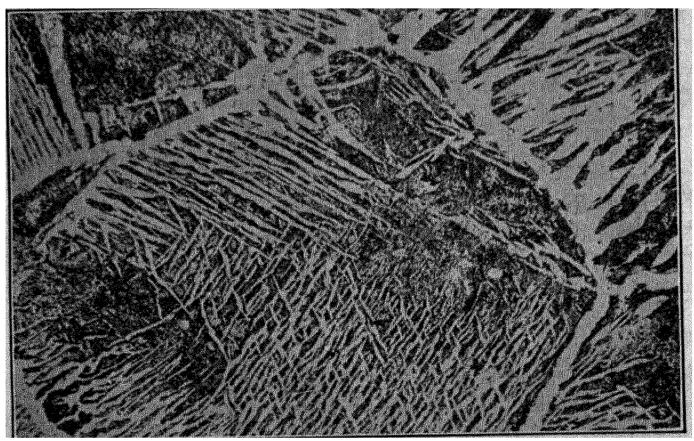


FIG. 125.—Overheated hypo-eutectoid steel. The white interlaced masses of ferrite form what is called the Widmanstätten structure. Etched with nital. Mag. 100 ×.

operation lead to marked grain growth. Steel in this condition is said to be overheated (Figs. 121 and 122). The large grains produced by overheating can generally be refined by annealing at the proper temperature or by normalizing. Burned steel cannot be restored by heat treatment and must be remelted.

2. Heating Period.—The time during which the steel should be kept at the annealing temperature depends on the original condition of the material and the purpose of the annealing. Under normal circumstances, the time is about 1 hour per inch for a piece 12 inches thick or smaller.

Alloy steels require a longer heating period than plain carbon steels.

3. Cooling.—Rapid cooling from a temperature above the critical range results in varying degrees of hardness, as will be shown later (p. 142). Since the usual purpose of annealing is to produce soft (pearlitic) steel, the cooling is retarded (*a*) by cooling in the furnace; (*b*) by insulated cooling in which the steel is packed in lime, clay, sand, ashes, or other heat-insulating material; (*c*) by air cooling

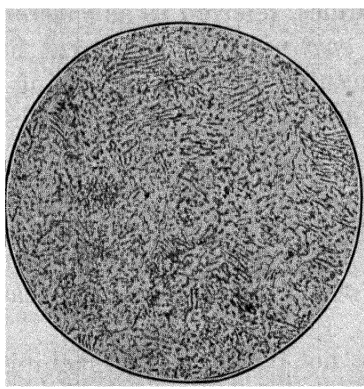


FIG. 126.—Annealed 0.85 per cent carbon steel showing the beginning of the spheroidization of iron carbide (cementite) in the pearlite. Etched with nital. Mag. 250 ×.

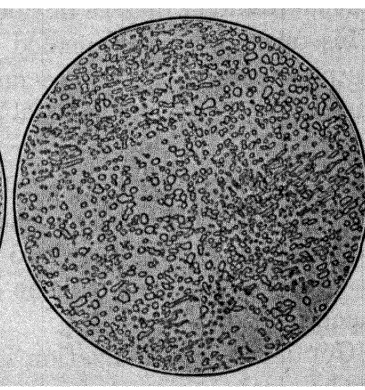


FIG. 127.—High-carbon steel (1.2 per cent carbon) showing complete spheroidization of the iron carbide. Spheroids are iron carbide and matrix is ferrite. Etched with nital. Mag. 500 ×. (*Zavarine.*)

under special conditions and with a carbon content of less than 0.50 per cent without danger of serious hardening. In the case of hypo-eutectoid steels, normalizing involves air cooling from above the critical range.

In dealing with very high carbon steels (hyper-eutectoid), the pearlite is greatly in excess of the cementite. If the cementite is fairly finely divided, the purposes of annealing can best be accomplished by heating above the Ac_1 point rather than above the Ac_m temperature.

In case the cementite occurs in the form of needles or spines or as a network of hard, brittle material, normalizing

by heating above the Acm temperature is often used in order to dissolve the cementite; the metal is then cooled rapidly. Unless the piece to be normalized is large, air cooling is rapid enough to prevent the re-forming of the cementite. The high temperature necessary for normalizing causes a grain growth that can be overcome by a second annealing slightly above Ac_1. Long-continued heating slightly below Ac_1 causes the separation of the cementite, not in the usual form of needles or spines, but as rounded masses or nodules, referred to as *spheroids*. This operation, often called *spheroidizing*, is a great help in producing a structure suitable for the machining of high-carbon steels (Figs. 126 and 127). Tool steel with its cementite in the network or mesh form is difficult to cut, but may be machined fairly readily if the needle-like or network cementite is changed to the spheroidal form. In high-carbon steels, about 75 per cent of the iron carbide is spheroidized to give the requisite softness for ready machinability.

Complete spheriodization is not desirable for machining as the steel then becomes too soft for the purpose.

Mechanical Work.—While much steel is used as cast, more of it is subjected to some form of mechanical work, as rolling, forging, wire drawing, or other operations. It is necessary in this connection to consider the temperature at which mechanical work is performed. A distinction is to be made between hot and cold work.

Hot Work.—No precise statement as to the boundary between hot and cold work can be given, but, in general, hot work is done in that temperature range in which the grains of the metal are not permanently deformed by mechanical action. The temperature division between hot and cold work is commonly considered to be the critical range, at least in the case of hypo-eutectoid steels. Hot work is carried out above Ar_3 and cold work below Ar_1. In the range between Ar_3 and Ar_1, a deformation of the

ferrite takes place, but, if work stops at a temperature high enough above Ar_1, re-formation will take place with a restoration of the equiaxed grains. The danger of passing into the true cold-working range, however, is great enough so that it is probably safer to take Ar_3 as the lower limit of hot working. An exception is found in very low carbon steels which, after severe deformation, may recrystallize at temperatures as low as 450°C. and always below 700°C. Hot work, then, with steels of this class and with wrought iron may be carried out at much lower temperatures than can be used with ordinary steels.

The purposes of hot work are mainly three: (1) to change the shape of the part; (2) to close small holes or cavities in the metal; and (3) to refine the grains.

The first of these is the obvious one of making a tool, a rail, or other fabricated part from the plastic metal. The second purpose takes account of the fact that steel is sometimes unsound, owing to the presence of small cavities (gas pockets) in the metal. Hot work on material in this condition closes the blowholes, increases the density, and improves the mechanical properties of the metal. The third, and a very important function of hot work, is to refine the grains of the steel and thus to improve its mechanical properties. This is one of the best methods of restoring overheated steel to a useful condition.

After the steel has been heated to the necessary temperature above the critical range, it may be formed by (1) hammering and drop forging, (2) pressing, or (3) rolling. With parts that are to be greatly reduced in thickness or that are originally thin, forging puts the steel in excellent condition. With larger pieces and with less reduction, the drop hammer has more nearly local effects, so that improvement in quality and refinement of the grains take place largely at or near the surface. To insure a more uniform condition of heavy steel parts, the forging press is often used. The use of this method results in a kneading

action extending to a much greater depth than is the case with drop forging. Rolling is the cheapest and most rapid method of shaping steel, and, while the quality of

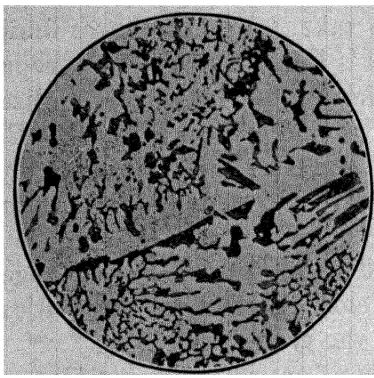


FIG. 128.—Steel as cast. Dark is pearlite. White is ferrite. Nital etch. Mag. 100 ×.

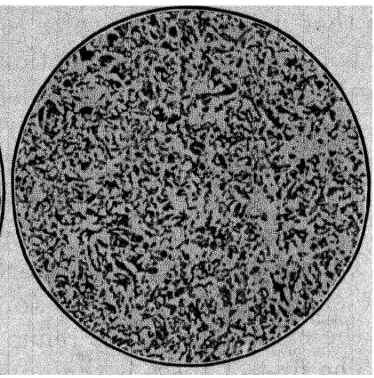


FIG. 129.—Cast steel refined by reheating slightly above Ac_3. Dark particles are pearlite. White matrix is ferrite. Nital etch. Mag. 100 ×.

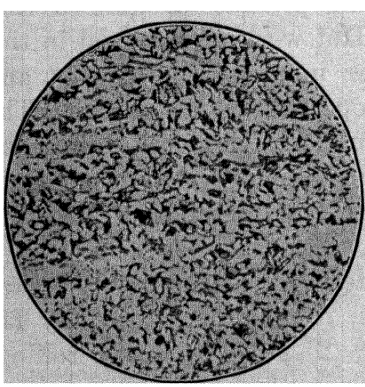


FIG. 130.—Cast steel refined by hot working to Ar_3. Dark particles are pearlite and white field is ferrite. Nital etch. Mag. 100 ×.

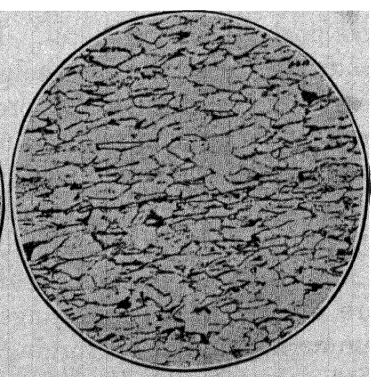


FIG. 131.—Cold-worked low-carbon steel showing elongated grains of ferrite containing dark pearlite. Nital etch. Mag. 100 ×.

the steel produced is not quite equal to that made by forging or pressing, it is excellent material and widely used in the form of rails, bars, and structural shapes, and for similar purposes.

Finishing Temperature.—An important term used in connection with hot working is *finishing temperature.* This refers to the temperature at which the mechanical operation stops. Owing to the growth of the grains after

MEDIUM CARBON STEEL. NITAL ETCH. MAG. 100 ×.

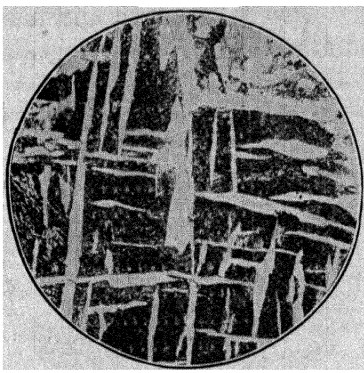


FIG. 132.—Very coarse structure resulting from slight work at a high temperature. Dark is pearlite. White is ferrite.

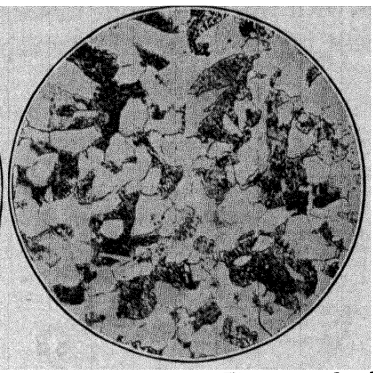


FIG. 133.—Same as Fig. 132, refined by reheating slightly above Ac_3.

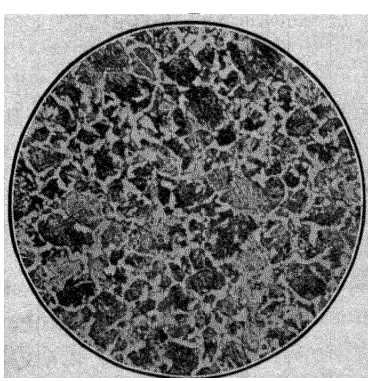


FIG. 134.—Hot-rolled steel finished above Ar_3. Dark is pearlite and white is ferrite.

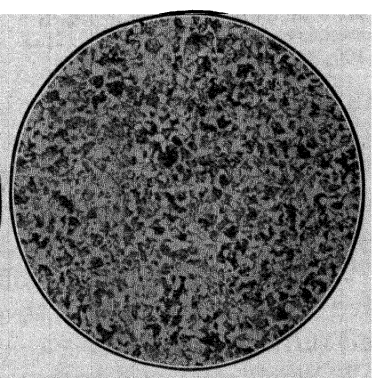


FIG. 135.—Same as in Fig. 134 but refined by reheating at Ac_3.

the work stops, it follows that the higher the finishing temperature the larger will be the grains and the less satisfactory the material. So close a relation exists between grain size and finishing temperature that a skilled

observer can usually determine the approximate temperature by a study of the grain size. Some of the effects of work and annealing are shown in Figs. 128 to 137.

Cold Work.—Cold work is carried out at temperatures below the critical range. The effects are exactly the same as with the nonferrous metals. Tensile strength and hardness increase, with a corresponding decrease in ductility.

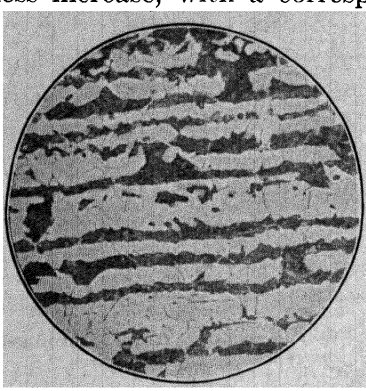


FIG. 136.—Banded structure often found in hot-rolled low-carbon steel. Etched with nital. Mag. 100 ×.

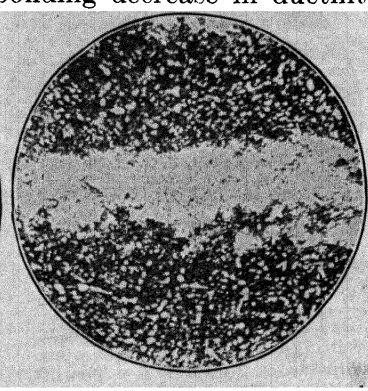


FIG. 137.—White ferrite streaks in hot-worked high-carbon steel. Nital etch. Mag. 250 ×.

An elongation of the grains is often noted. Cold working is often done for one or more of the following reasons:

1. It is always possible to finish more exactly to a required size and with a better surface than is possible by hot working.

2. Wire and sheets are often drawn or rolled cold to give the desired tensile strength, hardness, springiness, and surface condition.

3. Small axles and shafts are often cold-rolled to increase stiffness and to increase the surface hardness.

Hardening.—The diagram, Fig. 113, page 129, shows that in the irregular area *GCHMK* a solid solution of carbon in γ-iron exists. It is not known positively whether in this solution the carbon occurs in atomic dispersion or is combined as the carbide. The former condition is more proba-

ble. Hardening of steel, then, in the usual meaning of the word, is caused by suddenly cooling, or quenching, from the proper temperature.

Hardening involves two operations: (1) heating and (2) rapid cooling, or quenching. As the sudden cooling for the purpose of hardening subjects the steel to a shock of great severity because of the sharp temperature drop, it follows that the preparatory heating must be carried out with great care. Assuming that the piece to be hardened has been carefully annealed or normalized, the temperature is raised gradually enough to allow it to increase as uniformly as practicable throughout the mass of metal. Too rapid heating often means nonuniform heating with the great danger of cracking due to the stresses set up on quenching. The temperatures needed are substantially the same as in the annealing operation, *i.e.*, above Ac_3 for the hypo-eutectoid steels and above Ac_1 when the carbon content is 0.85 per cent carbon or greater. Overheating and burning are even more dangerous with steel that is to be hardened than with annealed steel. Heating in lead or a fused salt is often done in heating for hardening in order to insure uniformity of heating. As a result of the heating, a complete solution of the carbon in γ-iron is effected in the case of hypo-eutectoid and eutectoid steels, and most of the carbon is dissolved in the hyper-eutectoid steels.

The quenching operation may be carried out under exceptional conditions in such a way that the complete solid solution, austenite, is retained at room temperature. This is generally not possible in the case of a plain carbon steel, even after the very rapid cooling of a high-carbon steel. The slow cooling following the annealing operation leads to a complete decomposition of the solid solution into a mixture of ferrite and pearlite, cementite and pearlite, or pearlite alone, depending on the original carbon content.

The transformation products of austenite are determined by the rate of cooling. As previously stated, the product

obtained on slow cooling is pearlite, generally associated with ferrite or cementite. More rapid cooling produces primary *sorbite*, named after Sorby. As the cooling rate is increased, the products become primary *troostite*, named after the French metallurgist, Troost, and martensite, after Martens.

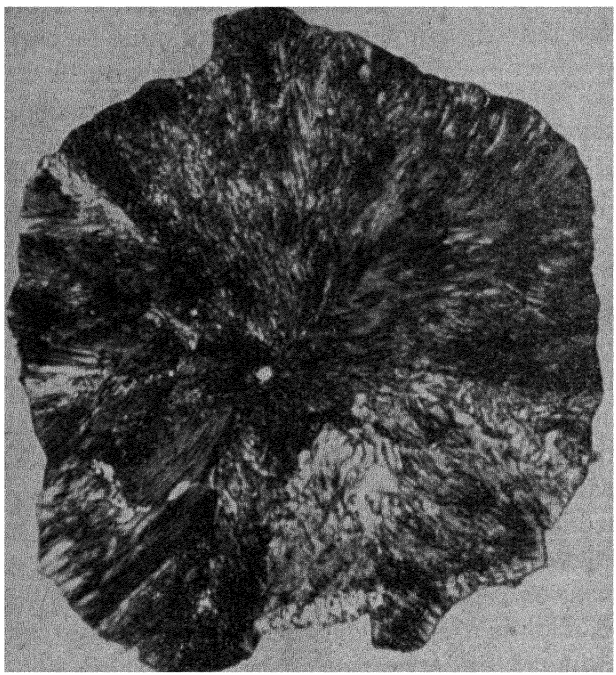


FIG. 138.—Showing lamellar structure of nodular or primary troostite. Mag. 2000 (Wells.)

In recent years, it has been shown by a number of investigators that troostite and sorbite when obtained from austenite by regulating the cooling rate and after careful polishing and etching show evidence of a lamellar structure when examined at high magnifications. The structure of troostite is shown in Fig. 138. Because of this resemblance to pearlite, the terms *very fine* and *fine* pearlite have been recommended to identify troostite and sorbite as trans-

formation products of austenite. It has also been recommended that the terms troostite and sorbite should be restricted to the products obtained by tempering martensite. The tempering of steel will be discussed later. In order to avoid confusion the authors will use the prefix *primary* before these two terms to identify the troostite and sorbite when obtained from austenite by regulating the cooling rate and these terms without any prefix to identify them when produced by tempering martensite.

The toughness of austenite is exemplified by the high-manganese and high-nickel steels, as well as by a certain type of rustless alloy such as the one containing approximately 18 per cent chromium and 8 per cent nickel. They are discussed in the section dealing with alloy steels.

The investigations of Bain[1] and Davenport have resulted in clarifying to a great extent the behavior of steels when rapidly cooled from the austenitic condition. These studies were conducted by determining the rate of transformation of austenite when specimens were rapidly cooled to subcritical temperatures. The procedure was to quench small specimens that were in the austenitic state into molten lead which was kept at the subcritical temperature under consideration. These specimens were then removed from the bath at definite intervals and quenched in water. By this procedure any untransformed austenite was converted into martensite. A microscopic examination disclosed the extent of the austenite transformation after each time period. Finally, the time required to complete the austenite transformation was determined for each subcritical temperature.

A molten alloy of lead and bismuth was used at temperatures below which lead was unsuitable. The progress

[1] DAVENPORT, E. S., and BAIN, E. C., "Transformation of Austenite at Constant Subcritical Temperatures," Trans. *A.I.M.E.*, **90** (1930), pp. 117–154.

BAIN, E. C., "On the Rates of Reactions in Solid Steel," Trans. *A.I.M.E.*, **100** (1932), pp. 13–46.

of the transformation below 300°C. was determined dilatometrically.

The results obtained were plotted as shown in Fig. 139. It is to be noted that the time is plotted on a logarithmic scale. A study of this diagram shows that the transformation of austenite at Ar_1 and slightly below is comparatively slow while the austenite transformation in the

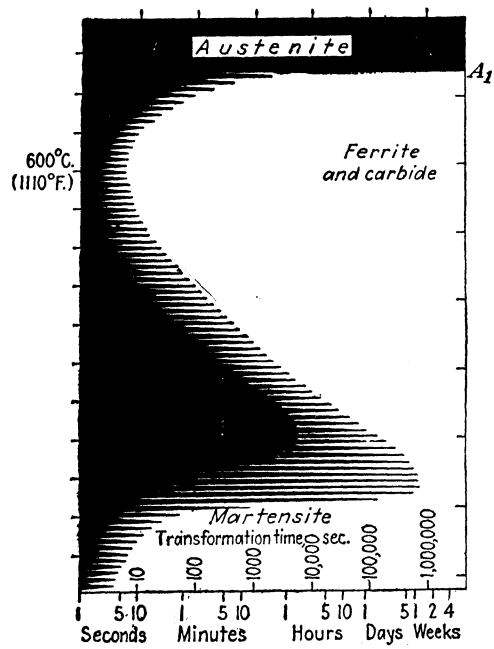


FIG. 139.—Relation of austenite transformation at subcritical temperature to time and temperature.

neighborhood of 600°C. is very rapid. At the temperature at which the transformation takes place very rapidly the product of transformation is primary troostite. Actually this transformation takes place over a temperature range and not at a definite temperature. Above the temperature range at which primary troostite forms, the products of transformation are primary sorbite and pearlite, the latter being formed at the higher temperature.

Below the temperature range at which primary troostite forms, the time for the completion of the austenite transformation increases rapidly and then decreases, reaching a minimum at about 100°C. The temperature range at which the austenite transforms into primary troostite is Ar' and that at which martensite forms is Ar''. Between these two, the product of transformation is known as *bainite.*

Since the diagram indicates that the rate at which austenite is transformed into primary troostite is very rapid and the same for the transformation into martensite, it is obvious that if a martensitic structure is desired, the steel must be cooled very rapidly through Ar' in order to prevent the formation of primary troostite. It can be cooled slowly, however, from there on since very little austenite will be transformed before the Ar'' temperature (100°C.) is reached.

It has been stated previously that the transformation of austenite into primary troostite takes place over a temperature range rather than at a constant temperature. The critical cooling velocity represents the rate of cooling through Ar' necessary to completely transform austenite into martensite.

Since the critical cooling rate varies with different steels, it is obvious that its determination supplies a criterion as to the hardenability of the steel under consideration.

A Bain *S*-curve for a steel containing 0.78 per cent carbon is shown in Fig. 140. Since the publication of this paper by Davenport and Bain, the term *bainite* has been accepted as the name of the structure obtained between Ar' and Ar''.

Figure 141 shows the relation between the time and temperature of the initial transformation of a eutectoid steel and the critical cooling velocity. The curves originating at *E* represent time-temperature curves for different rates of cooling. *FG* represents the temperature and time interval

after passing 750°C., for all natural cooling rates, at which the austenite transformation begins. Air cooling was used in this case.

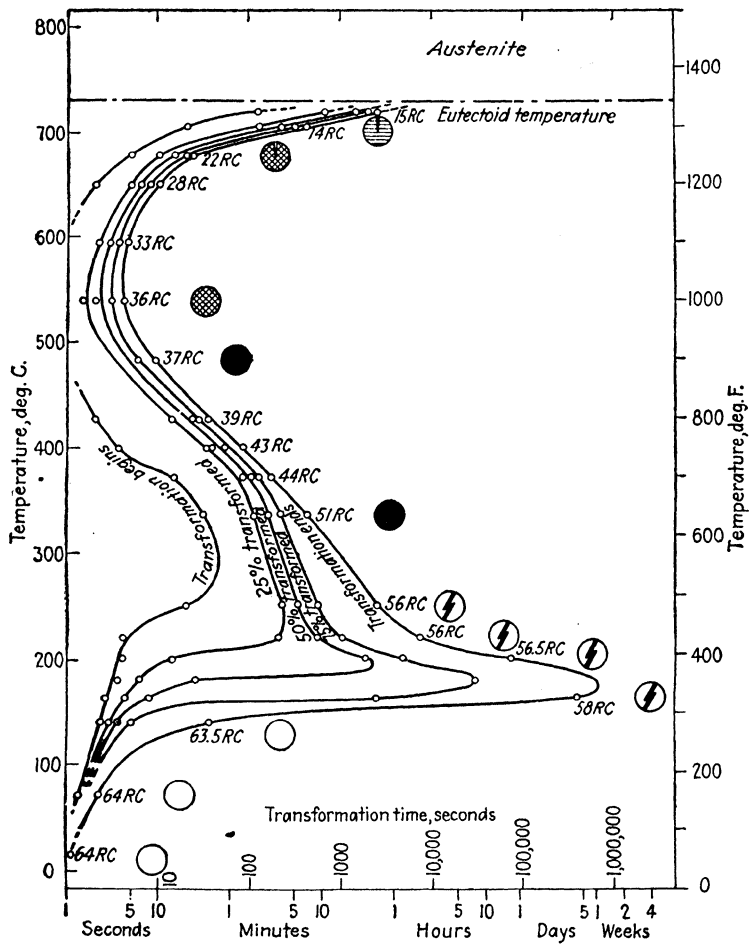


FIG. 140.—Bain *S*-curve for steel with 0.78 per cent carbon.

In Fig. 139 it is noted that the transformation of austenite into bainite takes place very slowly at about 150°C. Since austenite is tough and ductile whereas martensite is hard and brittle, articles which have to be fully hardened and

comparatively free from distortion can be removed from the quenching medium when cooled to approximately 150°C., straightened and then air-cooled to produce the desired results.

The process of quenching thin sections from a temperature above the critical range into a bath at a predetermined

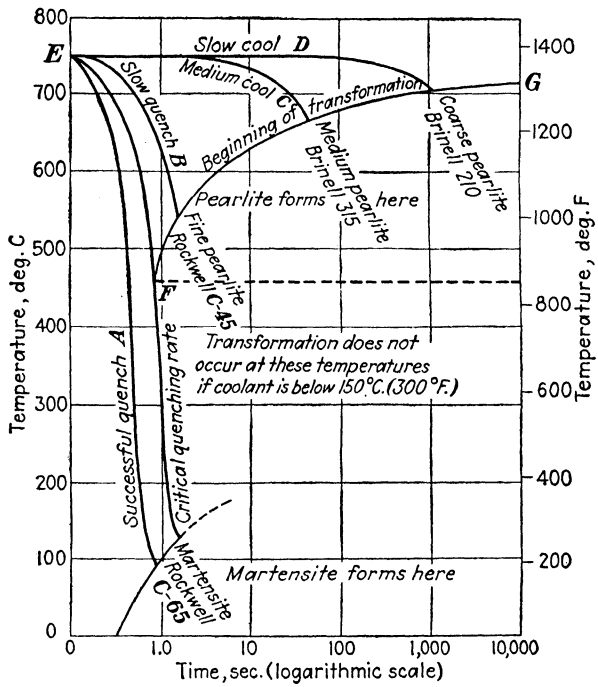


FIG. 141.—Relation between time and temperature of the initial transformation of eutectoid steel and critical cooling velocity.

temperature, but above that at which martensite is produced, and holding for a period of time to completely transform the austenite is being used commercially under the name of *Austempering*. An improvement in toughness and ductility is obtained by this method over that obtainable by ordinary quenching followed by the tempering of the martensite to the same hardness.

Austenite exhibits the polygonal grain structure characteristic of pure metals and solid solutions. It is nonmagnetic. When subjected to cold work followed by a reheating to a suitable temperature, there is produced a

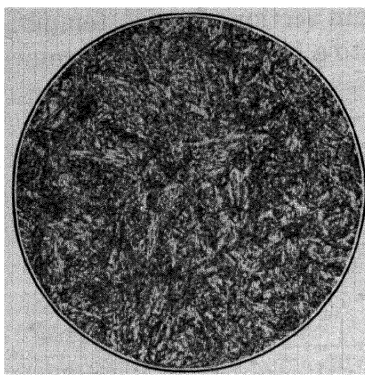


FIG. 142.—Martensite showing acicular structure. Mag. 500 ×.

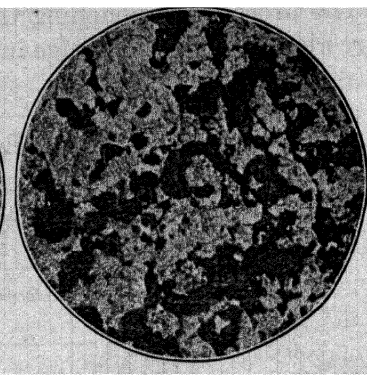


FIG. 143.—Martensite and primary troostite (black). Mag. 250 ×.

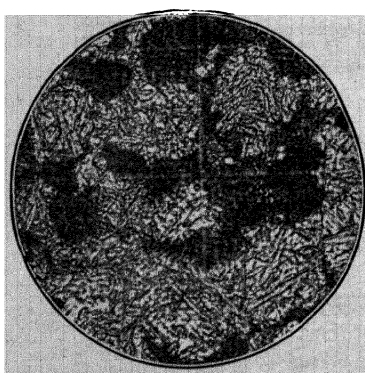


FIG. 144.—Same as Fig. 143 but at Mag. 500 ×. Needle-like structure of martensite is shown. Primary troostite is dark.



FIG. 145.—Austenite (white matrix), martensite (dark zigzagged masses), and primary troostite (dark rounded patches). Nital etch. Mag. 250 ×.

twinned structure similar to that exhibited by α-brass after a similar treatment. Such a structure is shown on p. 176.

Martensite is the usual product of a drastic quenching operation (Fig. 142). It is generally considered to be a

super-saturated solid solution of carbon in α-iron and is so hard as to be practically nonmachinable. Associated with the hardness is a brittleness that makes it undesirable except in a few special cases. It has been used, because of its great hardness, in the making of burglar-proof safes, in special files, and in the surfaces of some die blocks.

In practice the martensite is allowed to change partly to troostite, giving the metal increased toughness and ductility with a corresponding decrease in hardness and tensile strength. Troostite consists of finely divided carbide particles in α-iron. Whether martensite or primary troostite is formed as the result of the transformation of austenite on quenching depends on the cooling rate, which is in turn determined by the size of the piece that is being hardened, the composition, and the hardening medium. In the great majority of cases, the speed of cooling may be controlled by the use of brine, caustic soda solutions, water, or some one of a small list of animal, vegetable, or mineral oils. Brine or sprayed water will provide a high cooling rate and therefore produces a high hardness, while a viscous oil cuts down the cooling rate considerably. Between these extremes there are a few oils of varying degrees of viscosity which are suitable for intermediate quenching rates.

A few fundamental principles are followed in the hardening of steel: (1) heat slowly and uniformly; (2) quench from as low a temperature as will be effective—hypo-eutectoid steel is quenched from above Ac_3; eutectoid and hyper-eutectoid steels should be quenched from slightly above Ac_1; (3) cool evenly to minimize distortion; (4) avoid sharp or réentrant angles in the part to be quenched whenever possible; (5) temper immediately after hardening.

Austenitic Grain Size in Steel.—The heat treatment of steel is closely related to the austenitic grain size. It has been previously stated that in the case of a hypo-eutectoid steel, the minimum grain size in general is obtained at Ac_3

or the temperature at which the ferrite is completely absorbed so that only austenite grains are present. Heating beyond this temperature generally leads to an increase in the grain size. Since the austenite grain size at any temperature persists in the final product regardless of the rate of cooling, it is obvious that a knowledge of the austenitic grain size at the particular temperature in question is desirable in order to obtain information regarding the properties to be expected in the final product.

The austenitic grain size that is existent at any temperature can be determined by the microscopic examination of the treated specimens. Any treatment that can be given to a steel after it has been heated to the temperature in question that makes it possible to ascertain the grain size is suitable for the determination of the austenitic grain size.

In the case of hypo-eutectoid steels, the heat treatment involves heating to Ac_3 or above followed by a rate of cooling to give the desired structure. A convenient method for determining the austenite grain size in these steels is to cool slowly from the heating temperature of Ac_3 or above to a temperature below Ar_3, holding at this temperature for a period of time in order to develop a ferrite network, followed by slow or rapid cooling. Oil quenching generally develops primary troostite, which etches dark in contrast to light ferrite.

Eutectoid steels may be quenched from the heating temperature by partially immersing the specimen in water. The cooling gradient present in the steel will develop at some point a martensitic matrix with primary troostite at the grain boundaries. The latter structure etches very rapidly and provides desirable contrast to make it possible to determine the grain size. The grain size of a hardened eutectoid steel can be determined also by means of Vilella's *martensite reagent* (1 gram picric acid and 5 cubic centimeters of hydrochloric acid in 95 cubic centimeters of ethyl alcohol). This reagent develops contrast between the

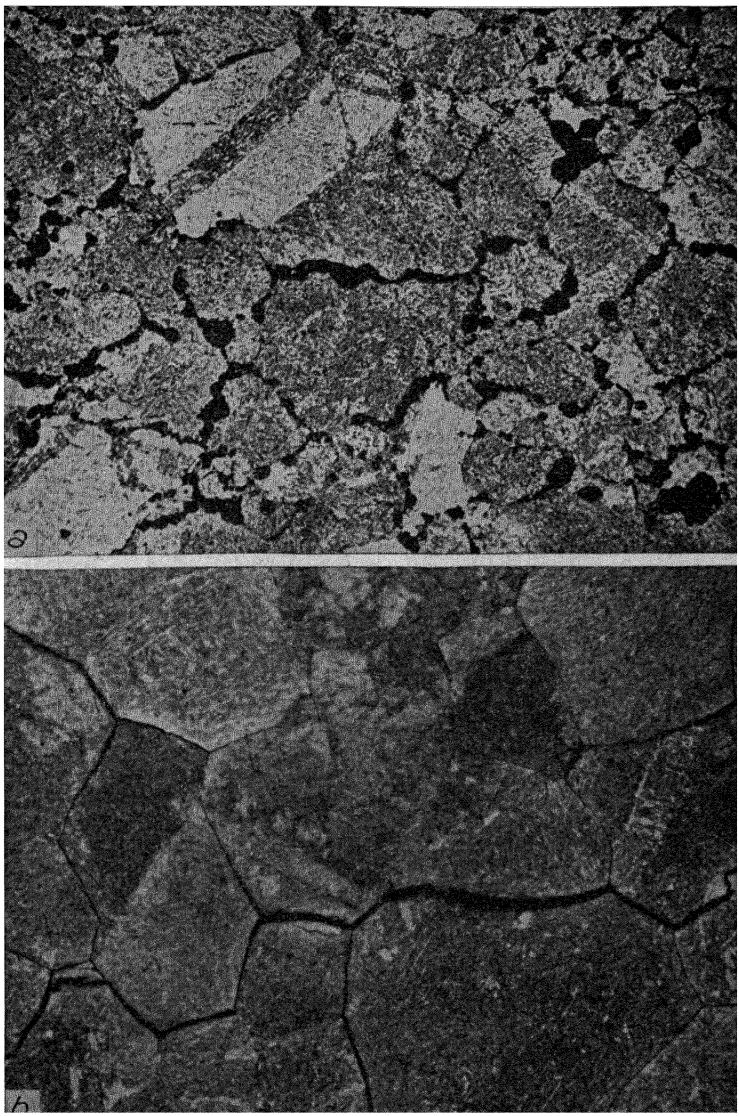


FIG. 146.—Illustration of how the reagent 1 per cent picric acid and 5 per cent hydrochloric acid brings out the actual prior austenite grains. Mag. 100 ×.

a. Martensitic structure showing typical turn grains of prior austenite.

b. Fracture of hardened steel, slightly tempered; note path of fracture follows boundaries of prior austenite grains. (*Vilella*.)

martensite of individual austenite grains Several light repolishings and etches may be necessary to produce satisfactory results. (Fig. 146.)

In the case of hyper-eutectoid steels, cooling so as to form a carbide network from the heating temperature will serve to delineate the austenite grains. If the formation of a carbide network is not feasible, the treatment should be the same as that recommended for a eutectoid steel.

Tempering and Toughening.—When steel is heated above the critical range and cooled quickly or slowly, one

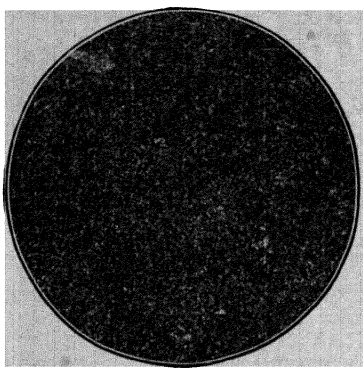


FIG. 147.—Troostite in 0.85 carbon steel, quenched from 775°C. and tempered at 300°C. Mag. 250 ×.

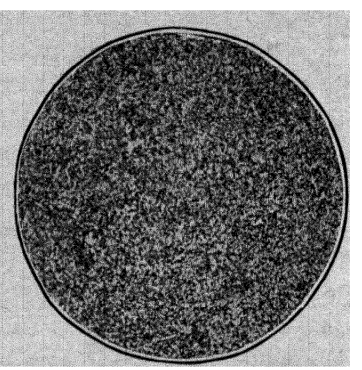


FIG. 148.—Sorbite in 0.85 carbon steel, quenched from 775°C. and tempered at 600°C. Nital etch. Mag. 250 ×.

or more of the several intermediate forms will be produced. Most of the changes will take place when a quenched steel is reheated to suitable temperatures. For example, martensite passes, as the reheating temperature increases, into troostite, sorbite, or spheroidized cementite, depending on the selected temperature. These changes, involving always a decrease in hardness but an increase in ductility, are referred to as *tempering* or *toughening*, depending on the temperature involved. When hardened steel (martensite) is reheated, a measurable softening is found at a temperature slightly above 100°C. The microscope shows that this softening is due to the formation of a small amount

of troostite. As the tempering temperature increases, the amount of troostite also increases and reaches its maximum at about 400°C. In the range, then, from 100 to 400°C. the steel consists of mixtures of martensite and troostite in proportions depending on the reheating temperature. This range is commonly called the tempering range. The higher the tempering range, the softer and more ductile will be the steel.

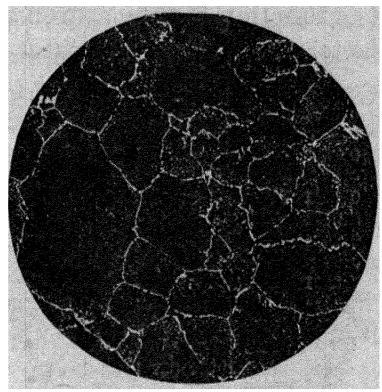


FIG. 149.—1.20 per cent carbon steel. Possessed coarse grain and carbide network before hardening. Quenched in water from 775°C. Tempered at 250°C. Carbide network and troosto-martensite (dark). Nital etch. Mag. 100 ×.

It has been explained that a hyper-eutectoid steel when slowly cooled consists of a carbide network and pearlite. If such a steel is quenched from just above Ac_1, the carbide network will be retained since only about 0.90 per cent carbon can go into solution at this temperature. The network persists even after tempering so that the final structure will be unsatisfactory, owing to the presence of this brittle network. Figure 149 shows the microstructure of a steel containing 1.20 per cent carbon that possessed a coarse grain with a carbide network before quenching. After tempering at 250°C., the structure is mainly troosto-martensite together with the brittle network. This steel, after it has been spheroidized (Fig. 150), then quenched from slightly above Ac_1, and finally tempered at 250°C., will show small carbides distributed throughout a troosto-martensitic matrix as indicated in Fig. 151.

The network structure can also be eliminated by quenching the steel from Acm, at which temperature the carbon (or carbide) is all in solution. Cooling at a rate sufficient to prevent its separation as a network can be accomplished by

quenching in oil or, in many instances, by cooling in air. A steel treated in this manner will be coarse grained. This condition can be corrected by quenching from Ac_1 followed by tempering. The structure produced will be similar to Fig. 149 except that there will be an absence of excess carbide particles.

It should be noted that the softening due to tempering is a function of time as well as of temperature, although the latter has much the greater effect. It is nevertheless true

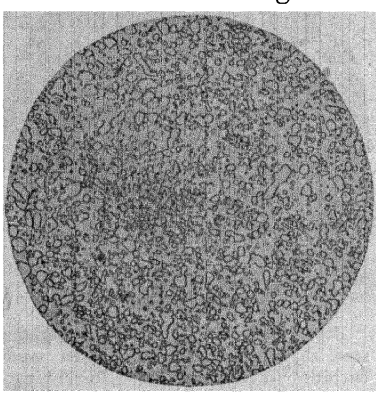


FIG. 150.—1.20 per cent carbon steel, oil quenched from 900°C., then subjected to prolonged heating at 715 to 720°C. Spheroidized cementite in ferrite matrix. Nital etch. Mag. 500 ×.

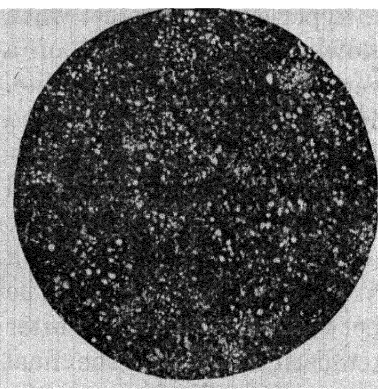


FIG. 151.—Spheroidized 1.20 per cent carbon steel, water quenched from 775°C. and tempered at 250°C. White carbide particles in troosto-martensite. Nital etch. Mag. 500 ×.

that long-continued heating (several hours) at one temperature will give the temper color and softness characteristic of a higher temperature.

At 400°C., the maximum amount of troostite is present (Fig. 147) in the reheated steel, and, as the temperature increases above this value, a gradual decrease in troostite and a corresponding increase in sorbite takes place. Sorbite is the toughest of the steel structures, so that the range in which it is produced is often, though by no means universally, referred to as the *toughening range*, and the operation of heating above 400°C. is therefore often called

toughening. Between 500 and 600°C. the hardened steel becomes almost wholly sorbitic. This structure has been found associated with the most desirable combination of strength and ductility. Figure 148 shows such a structure in an 0.85 per cent carbon steel after quenching at 775°C. followed by reheating to 600°C. It consists of finely divided carbide particles in an α-iron matrix. Toughening also increases the elastic ratio. Since it is the elastic limit on which the working properties of steel depend, an increase in this respect is of fundamental importance. Sorbitic, or toughened, steel is also more resistant to alternating or fatigue stresses than any other structure in steel, and for this reason this type is desired in material used for bridge members, crankshafts, axles, and similar parts subjected to serious alternations of stresses. A higher reheating temperature just below Ac_1 causes the agglomeration of the carbide particles to form cementite spheroids embedded in ferrite.

The actual operations of tempering and toughening are carried out by various methods, depending on the exactness of temperature control needed in the operation. Open furnaces, sand plates, and other simple forms of heating are often used, but for the exact reproduction of a desired hardness much more definite temperature regulation can be realized in a bath of fused salt or metal, in oil, or by means of a suitable furnace. The uniform excellence of modern tools depends, in a large measure, on exact and automatic temperature control in the tempering furnace.

Case Hardening.—One of the earliest known methods of steel making consisted in heating a low-carbon ferrous material, such as wrought iron, with carbon or other carbonaceous material. The iron absorbed an appreciable amount of carbon from the surrounding material and after remelting to get rid of the slag and to produce an homogeneous material, it became steel. This product was known as *cement steel,* and the process as the *cementation process.* A more carefully controlled method of introducing

carbon, but based on the same principles, is found in the modern case-hardening operation, the purpose of which is to produce a hard wear-resistant surface (case) on a softer shock-resisting center (core). This is done by increasing the carbon content at the surface, producing in this manner a high-carbon steel in contact with low-carbon material. The combination of surface hardness and interior toughness is often desired in the production of certain tools, gears, ball and roller bearings, and similar parts. The operation involves four steps: (1) a selection of suitable material; (2) a selection of a carburizing substance; (3) heating for carburizing; and (4) heat treatment of the carburized piece.

(1.) Various steels are used for case hardening. If it is a simple steel, it should have the lowest carbon content that will allow satisfactory machining, unless special core properties are desirable. This is usually considered to be from 0.15 to 0.25 per cent.

Several alloy steels are commonly used for case carburizing. Nickel slows down the rate of penetration of the carbon into the steel, but it adds so much to the toughness and shock resistance of the material that the increased difficulty of carburizing is justified. Chromium, to the amount of about 0.5 per cent, is a satisfactory addition to steel to be case hardened as it increases the rate of penetration of the carbon, reduces the grain size of the core, and adds specifically to the hardness. For high-quality parts the core is sometimes made of a steel containing 2.5 per cent nickel and 0.5 per cent chromium, a combination that adds the hardness produced by chromium to the toughness produced by nickel. Nickel-molybdenum steels containing 1.50 to 3.50 per cent nickel and 0.15 to 0.30 per cent molybdenum are also widely used for case hardening and are excellent for the purpose.

(2.) The best evidence now available indicates that the introduction of carbon does not take place directly but indirectly through the formation of a gas, probably carbon

monoxide. Many investigators believe that the following reaction takes place at the surface, followed by the diffusion of the iron carbide into the steel: $2CO + 3Fe \rightarrow Fe_3C + CO_2$. This mechanism is questionable. Since the iron carbide molecule is much larger than the carbon atom, it is more likely a diffusion of the carbon as such and not as iron carbide for the latter cannot pass through the iron lattice. If this is true, then it is more likely that the carbon monoxide or other gas decomposes at the surface to produce carbon in the atomic state or approaching it, whereby it can enter and readily diffuse into the steel.

It is possible to use solid, liquid, or gaseous carburizing materials. Solid carburizing materials are still used on a large scale although carburization by means of gases is rapidly gaining prominence. There are many solid carburizers such as coke, wood charcoal, charred bones, charred leather, or various mixtures such as barium or sodium carbonate with charcoal. Carburizing gases include illuminating gas under certain conditions, methane, butane, and propane. The products of the decomposition of certain oils are being used for introducing carbon.

(3.) If a solid carburizing agent is used, the articles to be case hardened are packed in metal boxes containing the carburizing compound and are then heated gradually in a furnace to a temperature above the critical range so that the iron may be in the γ-form. The exact temperature depends on the nature of the steel, the carbon content of the case desired, and the composition of the carburizing agent. These governing factors are commonly determined by experiment. In general, it may be said that the higher the carburizing temperature and the longer the time of heating, the deeper will be the case. It is further true that with most solid carburizers the carbon content of the case also increases with the carburizing temperature.

(4.) The heat treatment of the carburized material necessarily involves those steps necessary for the treatment of

two distinct kinds of steel, the low-carbon core and the eutectoid or hyper-eutectoid case. Bearing this in mind, the duplex treatment is readily understood. The carburized part, coarsened in grain by the carburizing temperature, is first reheated to slightly above its Ac_3 point and quenched, preferably in oil. This leaves the core in as fine-grained a condition as possible. This treatment of the low-carbon steel core is wholly unsuitable for the high-carbon steel case, so that the quenching is repeated, this time from the temperature Ac_1. In this case, water quenching is generally preferred for plain carbon steels. After the second quenching, the part is reheated below the critical range to remove quenching stresses and to toughen the case.

If a hyper-eutectoid case is produced, cementite will appear at the grain boundaries on slow cooling. In order to eliminate this undesirable network, heating to Acm is necessary, followed by cooling at a rate such that it will not reappear. Quenching in oil is recommended. In order to prevent the appearance of this network structure quenching from the carburizing pot is practiced.

The simplification of the case hardening of many steels so as to avoid the double heat treatment has resulted from the work of McQuaid and Ehn.

McQuaid-Ehn Test.—In 1922, McQuaid and Ehn noted that certain heats of steel, when carburized, exhibited soft spots after hardening. These areas contained primary troostite. Other heats, when given the same treatment, were entirely martensitic. To the first class, the term *abnormal* was given while the second class was termed *normal.* The main reason for this difference in behavior was traced to the melting practice.

Fig. 152*a* shows a carburized abnormal steel in which the cementite is very broad at the grain boundaries and is surrounded by ferrite whereas a carburized normal steel (Fig. 152*b*) shows a fine carbide network without ferrite.

Although it was noted that abnormal steels were in general finer grained than normal steels, it is possible for an abnormal structure to exist in a coarse-grained steel.

It is now known that the addition of aluminum at a certain stage in the manufacture of a steel has a decided effect on its grain-size characteristics. It is generally believed that alumina (aluminum oxide) particles are produced which are in a fine state of dispersion and have a marked effect in inhibiting grain growth. As a result, steels which

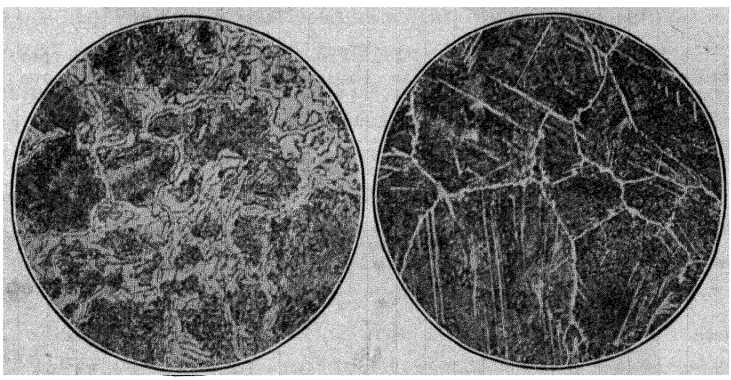


FIG. 152*a*.—Carburized "abnormal" steel. Material was carburized at 955°C. (1750°F.) for 6 hours and furnace cooled. Dark masses are pearlite and the white ribbon-like material is iron carbide surrounded by ferrite areas. Nital etch. Mag. 250 ×.

FIG. 152*b*.—Carburized normal steel. Dark masses are pearlite and the white network and needles are cementite. No free ferrite is present. Nital etch. Mag. 250 ×.

will normally coarsen in structure when heated above the critical range will remain fine-grained at fairly high temperatures when manufactured so as to have aluminum oxide particles in a fine state of dispersion.

Since carburizing is conducted at temperatures generally from 900 to 950°C., the structure of the steel after carburizing at about 930°C. followed by slow cooling serves to indicate the austenitic grain size of the steel at this particular temperature. The McQuaid-Ehn test has been generally recognized as a means to determine the austenite grain



FIG. 153.—"Abnormal" steel case hardened but not tempered. Large black area is primary troostite and indicates a soft spot. It is surrounded by martensite with small troostite spots. Nital etch. Mag. 150 ×.

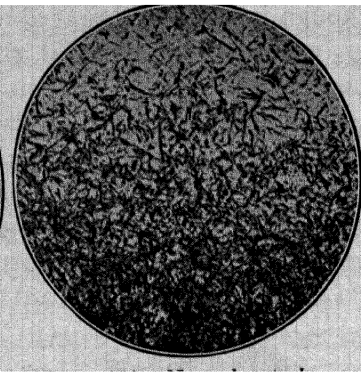


FIG. 154.—Normal steel case hardened. Shows martensite above and troosto-martensite below. Nital etch. Mag. 150 ×.

Hyper-eutectoid zone. Pearlite and cementite.

Eutectoid zone. Pearlite.

Hypo-eutectoid zone. Pearlite and ferrite.

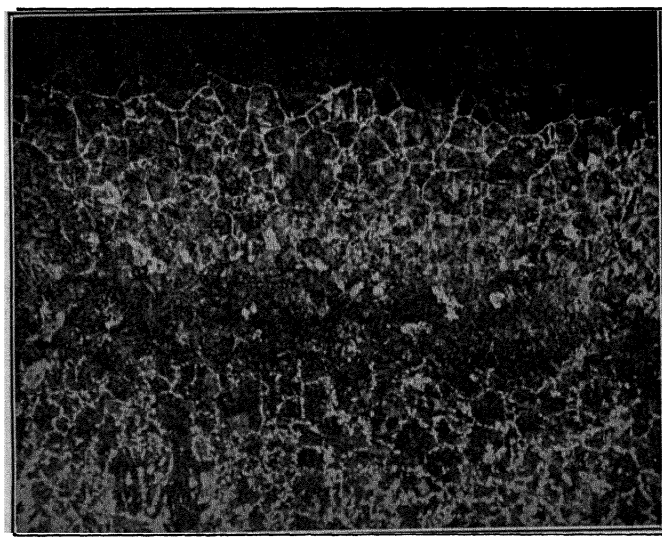


FIG. 155.—Carburized steel showing excess cementite in the outer layer. Nital etch. Mag. 75 ×.

size of a steel. This test consists in carburizing the steel for a period of 8 hours at 930°C. followed by slow cooling. A hyper-eutectoid zone is produced in the carburized layer. The presence of the carbide network serves to delineate the grains, making it possible to count them.

At the carburizing temperature, the grains are austenitic. Those in the carburized zone which are delineated by the carbide network indicate the size of the austenite grains at the temperature in question, in this instance, 930°C.

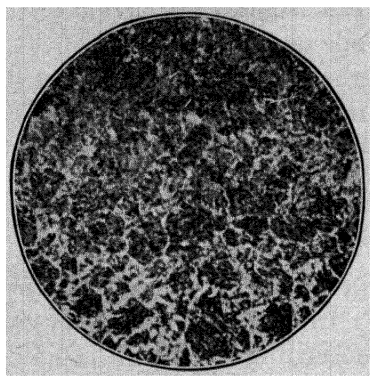


FIG. 156.—Carburized steel showing no excess cementite in outer layer. Nital etch. Mag. 75 ×.

The steels after this treatment are classified as coarse-grained or fine-grained. The former represents those which exhibit large grains after the McQuaid-Ehn test, while the latter represents those which show small grains after this treatment. The McQuaid-Ehn test serves as a means to determine the classification of the steels under consideration. Although it was first employed to study the characteristics of carburizing steels, its use has been broadened to include steels, both carbon and alloy steels, that are not used in the case-hardened state.

The American Society for Testing Materials has adopted a grain-size classification by giving a number designation to each steel. These numbers range from 1 to 10. A series of standard photomicrographs at 100 × is provided so that the grain size of an unknown steel can be readily determined by applying the McQuaid-Ehn test and then comparing its grain size with the standard micrographs. The average grain size of a steel at 100 × is determined by the expression 2^{n-1} in which n represents the grain-size number. The result is equal to the average number of

grains per square inch at 100 ×. A grain size from 2 to 4, for example, will be coarse-grained. A No. 4 grain-size will contain an average number of grains equal to 2^{4-1}, or 8 grains per square inch at 100 ×. A steel with a classification of 6 to 8 is typical of a fine-grained steel.

Figs. 157, 158, 159 show photomicrographs representing coarse-, medium-, and fine-grained steels.

A steel which may be fine-grained by the McQuaid-Ehn test is generally fine-grained at any temperature below the one used in the test (930°C.). More complete information about the behavior of a steel can be obtained by determining the temperature at which the grain size begins to coarsen. Such a determination will provide valuable information which can be used as a guide in its heat treatment.

A fine-grained steel such as one with a 6-8 grain size possesses certain advantages over a coarse-grained one.

In case hardening, the fact that the steel is fine-grained according to the McQuaid-Ehn test signifies in general, that the carburized zone that is produced at the carburizing temperature will be fine-grained and therefore eliminates the necessity for a double quench as described on page 159. Many steels are now being case-hardened by resorting to a single quench directly from the carburizing pot, followed in general by tempering at a low temperature. A coarse-grained steel cannot be quenched from the carburizing temperature without further treatment, since the grain size of the case will be large and the case will therefore tend to be brittle. The refinement of the case requires reheating to a temperature slightly above Ac_1 followed by quenching and tempering.

If the steel is fine-grained and shows nonuniformity in surface hardness, proper hardening can be achieved by raising the quenching temperature, or by using a more drastic quenching medium.

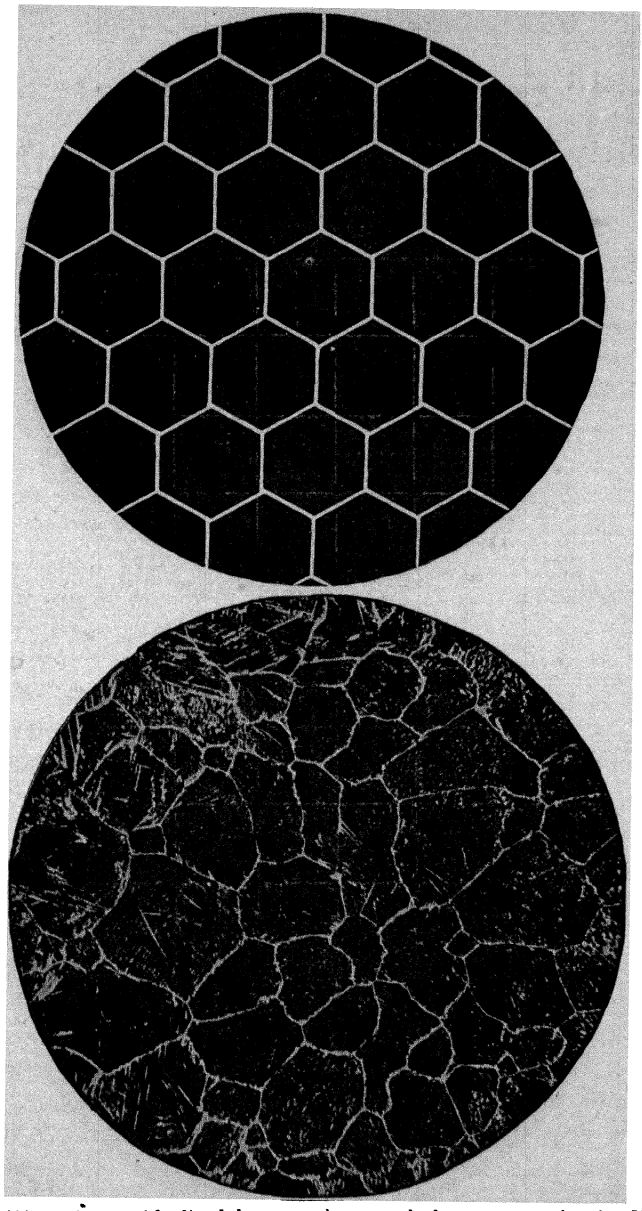


FIG. 157.—Upper, idealized hexagonal network for mean grain size No. 3, A.S.T.M. scale, 4 grains per square inch at 100 ×. Lower, A.S.T.M. standard grain size No. 3, 3 to 6 grains per square inch at 100 ×. (This and the two figures following are taken from Kehl's book. See page 250.)

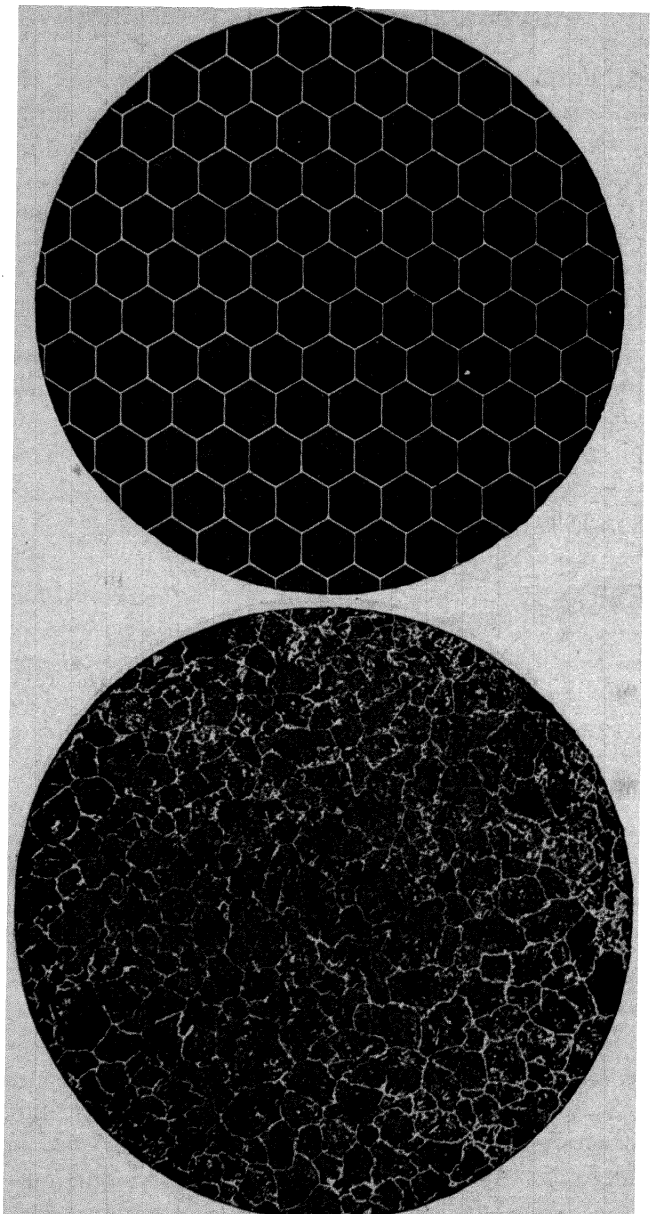


FIG. 158.—Upper, idealized hexagonal network for mean grain size No. 5, A.S.T.M. scale, 16 grains per square inch at 100 ×. Lower, A.S.T.M. standard grain size No. 5, 12 to 24 grains per square inch at 100 ×.

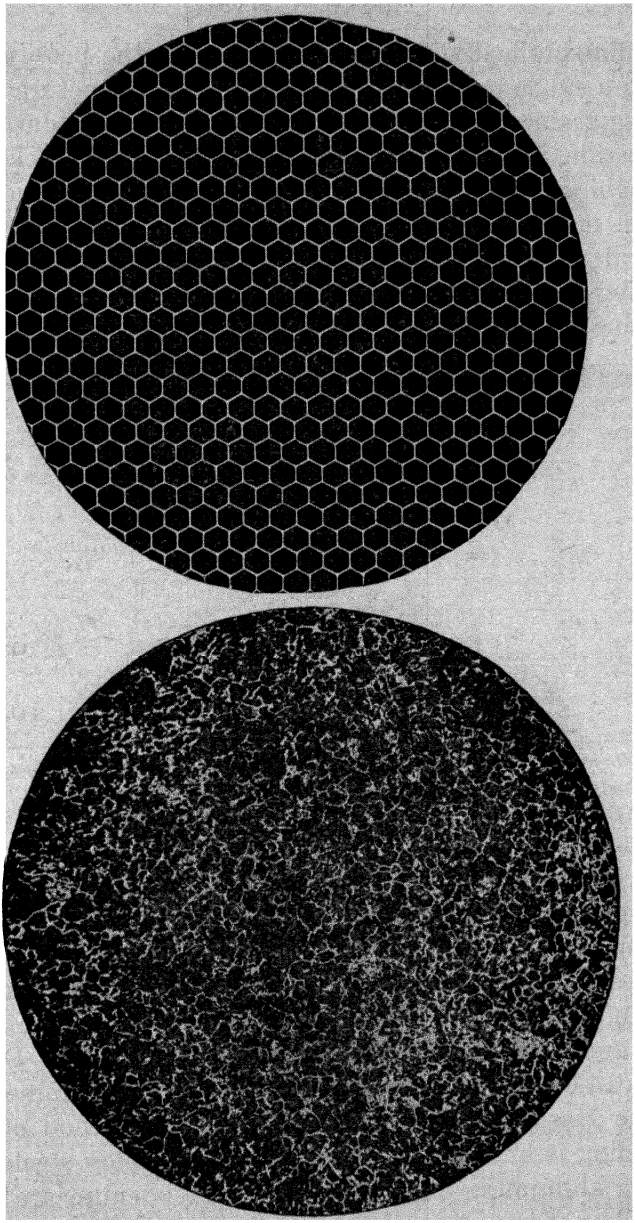


FIG. 159.—Upper, idealized hexagonal network for mean grain size No. 7, A.S.T.M. scale, 64 grains per square inch at 100 ×. Lower, A.S.T.M. standard grain size No. 7, 48 to 96 grains per square inch at 100 ×.

A fine-grained steel, besides providing the possibility of using a single quench, produces a tougher structure than a coarse-grained steel when given the same treatment. Less distortion is encountered and less danger of cracking on quenching is experienced. It also hardens less deeply, which may be an advantage in some cases, but is more difficult to machine than a coarse-grained steel. By heating above its coarsening temperature, the machinability of a fine grained steel can be improved, after which it can be

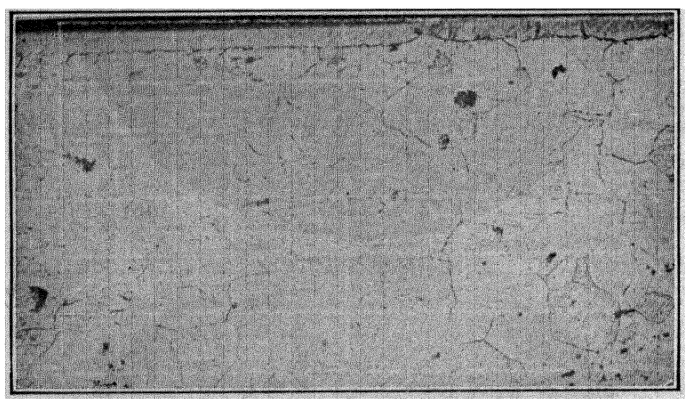


FIG. 160.—Cyanide case, showing superficial layer. Nital etch. Mag. 200 ×.

subsequently heat-treated to produce the desired grain refinement.

Various conditions found in case-hardened steel are shown in Figs. 152 to 156.

Sometimes when a superficial case is desired, the steel may be cyanide (surface) hardened by holding it in molten sodium or potassium cyanide at about 825°C. for a short time and then quenching in water (Fig. 160). Deeper cases can be produced by increasing the time of immersion.

Case Hardening with Ammonia.—This method of case hardening is known as *nitriding*. Special alloy steels containing aluminum, chromium, and molybdenum are heat-treated so as to possess a sorbitic structure. The machined parts are then exposed to the action of ammonia gas at a

temperature of 500 to 540°C. for the required length of time and then cooled in the container. The flow of the ammonia is regulated to produce approximately 30 per cent dissociation of the gas.

The ammonia dissociates partially into nitrogen and hydrogen according to the following reaction:

$$2NH_3 \leftrightarrows 2N + 3H_2$$

The nitrogen at the moment of dissociation is in the active state and combines with aluminum and chromium to form nitrides, which are precipitated in the form of very fine

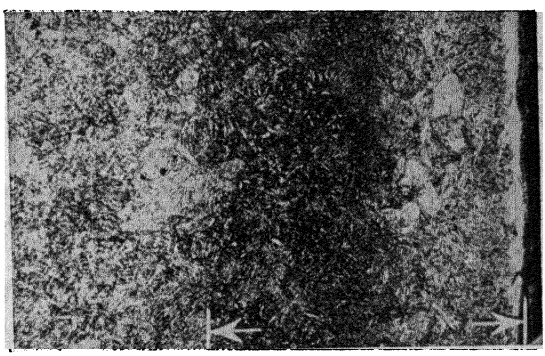


FIG. 161.—Nitrided nitralloy. Carbon 0.37, aluminum 1.06, chromium 1.28 molybdenum 0.22. Nitrided at 515°C. (960°F.) for 48 hours.

particles to produce a keying effect similar to that exhibited in the hardening of duralumin. When these nitrides are critically dispersed, the case exhibits the maximum hardness.

Extreme hardness of the surface is produced by this method. This hardness is retained at quite high temperatures (at least 450°C.) and provides great resistance to wear. Since the nitriding temperature is very low and no additional heat treatment is required after the exposure to the ammonia gas, the parts can be nitrided with a minimum of distortion.

Alloy Steels.—A plain carbon steel is essentially an alloy of iron and carbon together with comparatively small amounts of manganese, silicon, sulphur, and phosphorus.

In spite of the great range of properties that can be imparted to plain carbon steels by heat treatment, it is not sufficiently great to meet all the requirements of many of our present industries, notably the automotive and aircraft industries. In many of these cases high values for tensile properties together with great toughness and shock resistance are demanded and therefore necessitate the use of steels that are not classified as carbon steels but as *alloy steels.*

H. D. Hibbard[1] defines an alloy steel as one that contains one or more elements other than carbon in sufficient proportion to modify or improve substantially and positively some of its useful properties.

Certain of the alloy steels, besides providing the user with more desirable physical properties than can be obtained with a plain carbon steel, provide a greater temperature range for heat treatment. In order to harden a plain carbon steel properly a drastic quench from within a narrow range of temperature may be required, whereas an alloy steel may be chosen which can be given a far less drastic quench from within a wider range of temperature to impart similar or better physical properties to the product.

Steels containing one alloying element are called *ternary* steels, while those containing two alloying elements are called *quaternary* steels. Carbon and manganese are the other two important elements in this classification.

Most of the alloying elements combine with carbon to form carbides. Chromium, manganese, molybdenum, tungsten, and vanadium belong to this group. The carbides are partly or wholly soluble in γ-iron but come out of solution on slow cooling to room temperature. Aluminum, nickel, silicon and copper do not form carbides. They are soluble in γ-iron and are retained in solid solution in ferrite at room temperature. Alloy-steel compositions

[1] HIBBARD, H. D., "Manufacture and Uses of Alloy Steels," *Bur. Mines Bull.*, p. 100.

may be chosen which will show a martensitic structure when quenched in oil, air or even in some instances, after furnace cooling. A few will retain an austenitic structure even after slow cooling.

A number of alloying elements form a γ-loop with iron. A typical example is that of iron and molybdenum as shown in Fig. 162. As the molybdenum content is increased

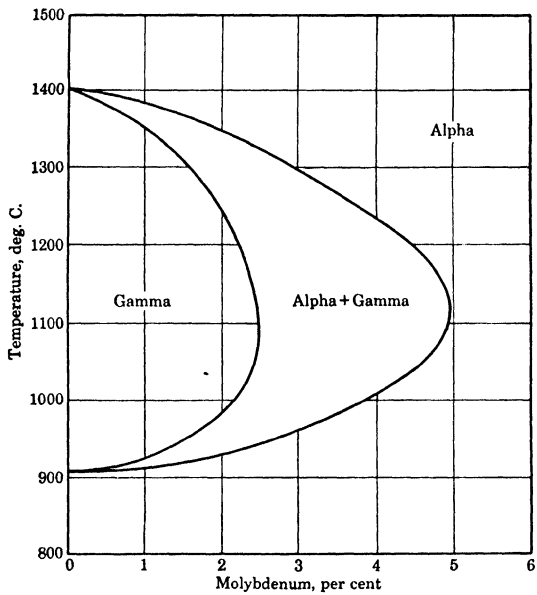


FIG. 162.—The γ-loop in the iron-molybdenum system.

the γ-phase changes to $\alpha + \gamma$, and finally to α. Other elements which form the γ-loop with iron are chromium, tungsten, vanadium, phosphorus, silicon, and aluminum.

A reference to Fig. 162 shows that a composition may be chosen so that the alloy will be entirely ferritic at all temperatures. In the presence of carbon, the steel becomes amenable to heat treatment. It may be hardened by quenching from a temperature within the γ-loop, whereas it will be soft if the composition is within the ferritic area. If quenched when within the $\gamma + \alpha$ area, the steel will be

partially hardened, since ferrite will be present with martensite.

The alloying elements in general have a profound effect on the change of austenite into its transformation products. The tendency to form intermediate products or to retain the original structure after heating to a suitable temperature followed by slow cooling increases with the carbon content and with the percentage of alloying element.

Owing to the effect of the alloying elements in retarding the structural transformations, it is possible to obtain certain structures in alloy steels on slow cooling that can be obtained in carbon steels only by very rapid cooling.

This effect can be shown by the Bain *S*-curve for the particular steel in question. The longer the time for the austenite to transform into primary troostite, the lower will be the critical cooling velocity of the steel.

The various alloying elements are effective in either raising or lowering the critical points. Chromium, tungsten, silicon, and molybdenum are among those that raise the critical points, while nickel and manganese are two that lower these points.

In the following pages a brief discussion will be given of the effects of the various elements in steel, including those that are present in all steels as well as those that are present strictly as alloying elements.

Sulphur.—Provided a sufficient amount of manganese is present in a steel, the sulphur will be present as manganese sulphide, MnS. Any excess sulphur will be present as iron sulphide, FeS, the presence of which imparts *red shortness* to the steel; it is present at the grain boundaries and fuses at the forging temperature, thereby destroying the continuity of the grains.

Most of the specifications of the Society of Automotive Engineers give 0.05 to 0.055 per cent as the maximum sulphur content. This content is lower in the case of tool steels and considerably higher in screw stock.

Many steels now being used contain sulphur from 0.075 to 0.15 per cent together with manganese as high as 1.65 per cent. This high sulphur content is for promoting machinability. Selenium is being added to certain alloy steels for the same purpose.

Phosphorus.—The phosphorus content is generally kept low in steels in order to prevent *cold shortness* or brittleness under impact. This element shows a marked tendency to segregate. A high-carbon tool steel contains approxi-

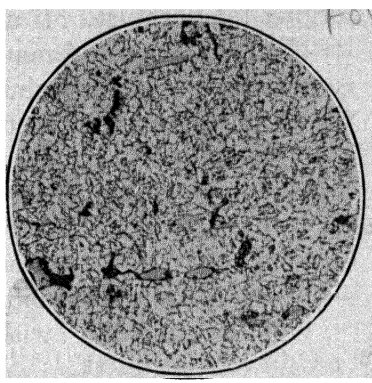


FIG. 163.—Manganese sulphide islands (gray) in mild steel. Nital etch. Mag. 100 ×.

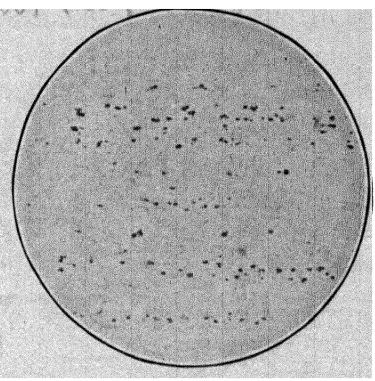


FIG. 164.—Inclusions in low-carbon steel. Unetched. Mag. 100 ×.

mately 0.02 per cent, while a Bessemer screw stock contains about 0.10 per cent phosphorus.

Silicon.—Silicon is present in small amounts in all steels. Its function is that of a deoxidizer. It forms a silicide, FeSi, with iron and is present in solid solution in both γ- and α-iron.

A low-carbon steel (generally under 0.05) with 3.5 to 4.5 per cent silicon finds wide application in transformer manufacture as it possesses a low hysteresis loss and high permeability.

A steel containing approximately 0.5 per cent carbon, 0.7 per cent manganese, and 2 per cent silicon after quenching in oil from 900°C. and tempering at 455°C. gives

excellent strength and toughness and is widely used for leaf and coil springs.

Chromium-manganese-silicon, silicon-chromium, and silicon-vanadium steels are also used.

Manganese.—Manganese is a constituent of all steels. It is primarily a deoxidizer. It also combines with sulphur in steel to form manganese sulphide. As such it appears as elongated masses in rolled or forged parts in the direction of working (Fig. 163). This is due to its plasticity at the forging temperature. If an insufficient amount of manganese is present, the sulphur will combine with iron to form iron sulphide.



FIG. 165.—Nonmetallic inclusions in "ghost line" in low-carbon steel. Nital etch. Mag. 100 ×.

An excess of manganese over that necessary to form MnS combines with carbon to form Mn_3C. This carbide is found associated with Fe_3C in cementite.

Manganese lowers the critical point and shifts the eutectoid carbon content to the left. The eutectoid contains about 0.75 per cent carbon when the manganese content is 2 per cent.

The relationship between the carbon and the manganese determines whether the steel should be hardened by quenching in water or oil or by air cooling. A steel containing 0.85 per cent carbon and little sulphur should contain not over 0.40 per cent manganese if it is to be water quenched because of the danger of cracking. Steels containing 0.25 to 0.50 per cent carbon, together with 1 to 2 per cent manganese, are important alloy steels, especially for general structural purposes.

A tool steel containing about 0.90 per cent carbon and 1 to 1.25 per cent manganese, together with 0.50 per cent

each of chromium and tungsten, possesses nondeforming or nonshrinking properties after oil quenching. The presence of chromium imparts a greater depth of hardness while the tungsten gives greater density and better cutting properties. These so-called nondeforming, nonshrinking, oil-hardening steels are used for taps, reamers, and various types of dies, as well as for master tools and gages.

A high-manganese steel containing 11 to 13 per cent of manganese and about 1 to 1.20 per cent carbon is of great industrial importance. Hadfield's manganese steel, so-called from the name of the inventor, is water quenched from 1000°C. and has an austenitic structure. In this condition the steel is tough, is very difficult to machine, and possesses marked resistance to abrasion. Excess carbide present at the austenitic grain boundaries in the "as-cast" condition is shown in Fig. 166. The carbide is dissolved by the γ-iron on heating to the temperature given above. The microstructure of the quenched steel is shown in Fig. 167. The surface of this austenitic manganese steel becomes markedly hardened under the effects of severe cold work, owing, possibly, to the production of martensite. This surface is continuously produced in service. Slip bands or deformation lines produced by the plastic deformation of this steel are shown in Fig. 168. The annealing of the cold-worked material results in the production of twinned crystals as indicated in Fig. 169.

Hadfield's manganese steel is used extensively in mining machinery such as rock crushers, dredging shovels, and other parts subjected to abrasion or unusual wear. Special rails, railroad frogs, and switches are also made of this steel. Since it is nonmagnetic and offers great resistance to abrasion, it is almost universally used in faceplates for lifting magnets.

Nickel.—Nickel is purely an alloying element since it lacks the properties of a deoxidizer and a scavenger. It is soluble in both γ- and α-iron. It has the property of

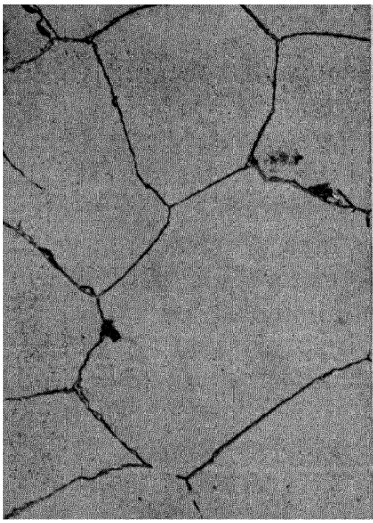


FIG. 166.—Cast manganese steel, carbon 1.14 per cent, manganese 13.19 per cent. Austenite and carbide. Nital followed by 10 per cent HCl. Mag. 250 ×. (*Avery.*)

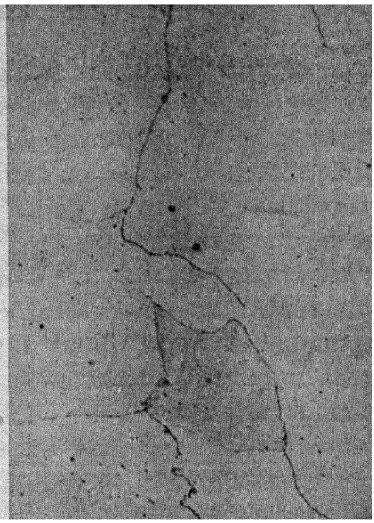


FIG. 167.—Cast manganese steel, quenched in brine from 1000°C. Austenite. Mag. 250 ×. (*Avery.*)

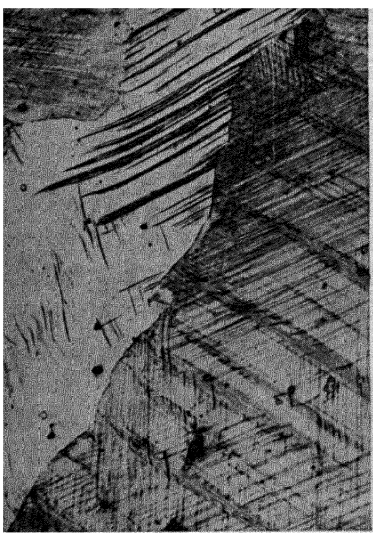


FIG. 168.—Cast manganese steel, cold worked. Slip bands and deformation lines. Mag. 100 ×. (*Avery.*)

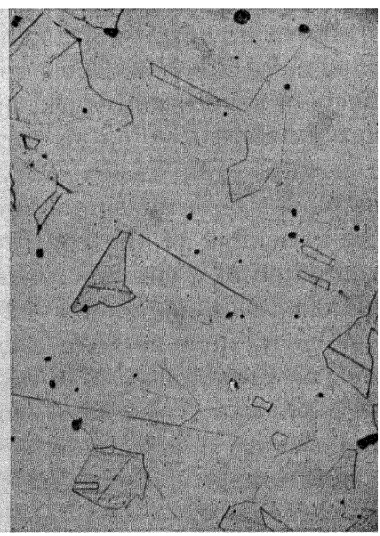


FIG. 169.—Cast manganese steel, cold worked, then heated to 1000°C. Twinned austenite. Mag. 100 ×. (*Avery.*)

increasing the tensile strength and the elastic limit without producing a corresponding loss in ductility. It has a marked effect on the toughness which it greatly increases. This toughness is retained at very low temperatures.

Nickel lowers the critical temperatures. A 25 per cent nickel steel is austenitic at room temperature. Most of the nickel steels have a nickel content of 1.5 to 5 per cent. Although these steels may be used in the untreated condition, in which state they show physical properties superior to those of plain carbon steels with the same carbon content, their properties are not fully developed unless the metal is properly heat treated. The standard nickel structural steels contain from 3 to 4 per cent nickel and from 0.10 to 0.60 per cent carbon.

Nickel steels are frequently used for case hardening. Better physical properties are obtained for the core than with a plain carbon steel. Nickel also hinders grain growth and gives desirable properties to the case, especially in the prevention of a sharp line of demarcation between the case and the core. Nickel is widely used in steels in combination with other elements, such as chromium and molybdenum.

Nickel steels containing a higher nickel content than those mentioned are used for special purposes. A 22 per cent nickel steel shows marked resistance to salt-water corrosion and has been used in valve stems and other parts of pumps operating with salt water. When the nickel content is increased to 24 to 32 per cent, the alloy shows increased resistance and is used in making heating coils for flatirons, toasters, and other heating apparatus. **Invar** contains 36 per cent nickel and is characterized by its low coefficient of expansion at ordinary temperatures. Because of this property, it is used in making balance wheels for watches, clock pendulums, and parts of surveyors' instruments to avoid compensating devices. A 46 per cent nickel steel containing 0.15 per cent carbon, known as **platinite,**

has about the same coefficient of expansion as platinum or glass. **Permalloy** contains about 80 per cent nickel and after a special heat treatment possesses high magnetic permeability.

Chromium.—Chromium differs from nickel in that it is essentially a hardening rather than a toughening element. It forms a γ-loop with iron. With carbon, it forms a carbide that is essentially Cr_4C. The amounts of chromium that are used are from 0.5 to about 5.0 per cent, with carbon usually from 0.5 to 1.20 per cent. Those used for case hardening contain from 0.15 to 0.25 per cent carbon with chromium from 0.60 to 0.90 per cent.

Chromium steels are used where high hardness and wear resistance are essential. Steels containing chromium are used for a great variety of purposes, among which are ball and roller bearings, races, rolls for cold rolling, and permanent magnets.

Chromium-nickel Steels.—The ratio of the nickel to the chromium in most of the commercial chromium-nickel steels is about 2½ parts of nickel to about 1 part of chromium. The steels most commonly used contain 1.5, 2.5, and 3.5 per cent nickel, respectively, with a corresponding chromium content of 0.6, 1.10, and 1.5 per cent. A combination of high ductility and toughness, together with great strength, surface hardness, and depth of hardening, is obtainable with this combination. Chromium-nickel steels are extensively used for case hardening as well as for structural purposes.

In general, the cooling rate after tempering has no effect on the properties of most steels. This is not always true in the case of the higher chromium-nickel steels. These steels may lose considerable of their toughness if slowly cooled from a tempering temperature of approximately 425 to 650°C. This *temper brittleness* can be prevented by quenching from the tempering temperature.

Vanadium.—Vanadium is a powerful deoxidizer and scavenger. It also possesses alloying properties since the major portion is present as complex carbides in the steel.

Vanadium has a marked tendency to reduce grain growth and to cause refinement of structure. Steels containing this element show a high tensile strength and a high elastic limit, together with high ductility and marked resistance to alternating stresses. The amounts of vanadium in steels are generally low, usually from 0.15 to 0.25 per cent, and seldom exceed 1 per cent. The vanadium content may be higher in certain alloy steels, for example, in certain types of high-speed steel in which 0.5 to 2 per cent may be present.

A steel containing vanadium can be hardened, without injurious effects, from a higher temperature than a plain carbon steel of similar composition. Vanadium gives a wider hardening range to the steel.

Chromium-vanadium Steels.—Vanadium intensifies the effects of chromium in steel. The steel most commonly used contains 0.15 to 0.25 per cent vanadium and 0.80 to 1.10 per cent chromium. These steels are used interchangeably with the nickel and the chromium-nickel steels of similar carbon content for heat-treated automotive forgings requiring greater strength, toughness, and resistance to fatigue than it is possible to obtain with plain carbon steels.

Molybdenum. Chromium-molybdenum and Nickel-molybdenum Steels.—Molybdenum is used solely as an alloying element. Although used to a limited extent alone, it is generally associated with other alloying elements, usually chromium or nickel. The molybdenum content is generally from 0.15 to 0.25 or 0.25 to 0.50 per cent.

Molybdenum has the property of increasing the tensile strength and elastic limit without causing a corresponding decrease in ductility. Molybdenum steels, after heat

treatment, are more ductile than many of the other alloy steels having the same tensile strength and they are remarkably resistant to impact. They are easily worked and machined and form a loosely adherent scale when heated for forging.

A low-carbon steel containing 1.5 to 2 per cent nickel and 0.20 to 0.30 per cent molybdenum is widely used for case hardening. This steel, with a grain-size specification of 5–7, and therefore fine-grained, is commonly hardened by the single-quench method. If carburized at 900 to 925°C., the parts should be cooled to about 820°C. before quenching in oil. If quenched from the carburizing temperature, considerable retained austenite may be present and the tendency will be for the surface to flow under load when placed in service. When quenched at the lower temperature, the parts will be both hard and tough, since the combination of martensite and a small quantity of retained austenite is ideal for many applications. Tempering at about 180°C. will relieve quenching strains.

Chromium-nickel-molybdenum steels offer excellent resistance to severe stresses.

Tungsten.—Tungsten is a valuable alloying element. Along with iron it combines with carbon to form a double carbide. It is used alone or in various combinations with other elements. Many tools contain from 1 to 2 per cent tungsten with about 0.5 per cent chromium or with 0.5 per cent chromium and 0.2 per cent vanadium.

Tungsten produces a dense and fine structure. In large amounts, as in high-speed steel, it imparts the property of *red hardness*, the ability of the tool to maintain a cutting edge when heated to a red heat by the friction of the cutting.

Tungsten magnet steel usually contains from 0.65 to 0.75 per cent carbon and from 5 to 6 per cent tungsten.

Many combinations of tungsten with other alloying elements are to be found in such steels as drawing-die steels,

pneumatic steels, battering and hot-work steels, and high-speed steels.

Aluminum.—The use of aluminum as an alloying element in steel is a comparatively recent introduction. Its presence is highly desirable in steels that are to be surface hardened with ammonia (see p. 168) as the nitride that is formed imparts maximum hardness to the case when critically dispersed. It is generally combined with molybdenum or with chromium and molybdenum. About 1 per cent aluminum is generally present in these steels. It is also used to control the grain size in steel.

Copper.—Copper is being widely used as an alloying element. It is a ferrite-strengthening element. It is present in steels in an amount varying from 0.15 to 0.25 per cent to resist atmospheric corrosion. It has been gaining increased importance in low-alloy steels in combination with nickel or chromium and other elements to produce steels with a high-yield strength in the non-heat-treated state. When present above 0.75 per cent in low- and medium-carbon steels, the steels can be precipitation-hardened. A steel with 1 to 1.5 per cent copper will show, after quenching and tempering at 400 to 600°C., this precipitation-hardening effect.

Lead.—The presence of 0.15 to 0.25 per cent of lead greatly increases the machinability of steels. It occurs in a highly emulsified state, the lead particles being visible only at a high magnification. This effect is accomplished without a decrease in the physical properties.

High-speed Steels.—This effect of the modern high-speed steels was Mushet's steel, which was developed about 1870 and contained from 7 to 12 per cent tungsten with high carbon and manganese contents.

Mushet's discovery of the effects of tungsten was not followed up and its possibilities were not recognized for nearly thirty years. About 1898, Taylor and White commenced the study of tool steels with the hope of

developing a tool that could be operated at high speeds and at correspondingly high temperatures without losing its cutting edge. Such a steel was evolved by them. Modifications of this steel have been made, both as to composition and as to heat treatment, but credit for this outstanding contribution to steel metallurgy must be given to these two investigators.

Many types of high-speed tool steels are now available, but only two compositions will be discussed as showing the general nature of these highly important steels without which the development of the modern machine shop would have been impossible. In general, they are combinations of tungsten, chromium, and vanadium. The first type, known as the *tungsten-high-vanadium steel*, has a composition range as given below:

C	Cr	W	V
0.65 to 0.75 per cent	3.25 to 4.25 per cent	13 to 14.50 per cent	1.5 to 2 per cent

The class known as the *high-tungsten low-vanadium group* (18W, 4Cr, 1V) varies in composition as follows:

0.65 to 0.75 per cent	3.50 to 4.50 per cent	17.50 to 18.50 per cent	0.90 to 1.25 per cent

High-speed steel having this composition is the one most generally used. A steel of the same composition, but with 2 per cent vanadium or with about 4 per cent cobalt, is often used for special cases, such as in the machining of hard castings.

The manufacture and the heat treatment of high-speed steels are of vital importance in developing its remarkable properties. The original ingot structure very often shows a marked eutectic segregation at the grain boundaries as indicated in Fig. 170. Since this structure can be eliminated only by mechanical work, it is highly desirable to forge the material in order to break down the segregated carbides. The ingots of high-speed steel are comparatively

small and therefore large tools commonly show streaks of these segregates.

The heat treatment of the 18-4-1 high-speed steel consists in preheating the steel to about 850°C., then heating to a temperature varying from 1230°C. to 1315°C. and quench-

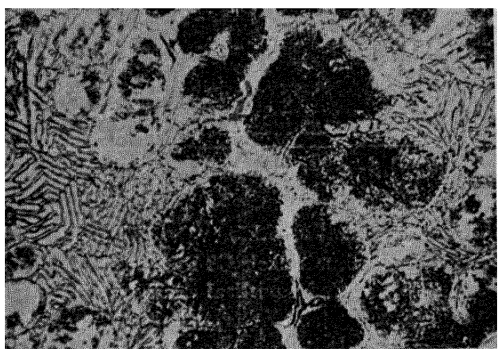


FIG. 170.—Cast high-speed steel showing presence of eutectic. Nital etch. 500 ×.

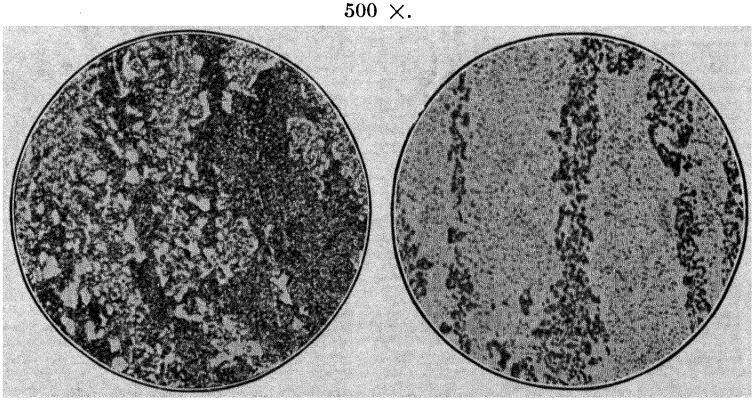


FIG. 171.—Rolled material showing light tungsten carbide segregates (often called carbide envelopes). Nital etch. Mag. 250 ×.

FIG. 172.—Tungsten carbide segregates and small carbides etched dark with Murakami's reagent. Mag. 250 ×.

ing, usually in oil, although quenching in an air blast is sometimes done. The hardened steel is generally tempered in the range of 565 to 625°C.

Quenched high-speed steel shows martensite with retained austenite and undissolved carbides. A polyhedral grain

structure is readily revealed, but prolonged etching and an examination at a high magnification are generally necessary to detect the martensitic structure (Fig. 173). Properly

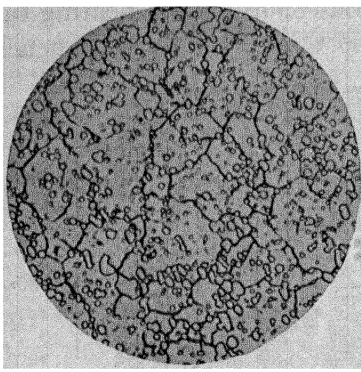


FIG. 173.—High-speed steel quenched in oil from 1260°C. Austenite, martensite, and undissolved carbides. Nital etch. Mag. 500 ×.

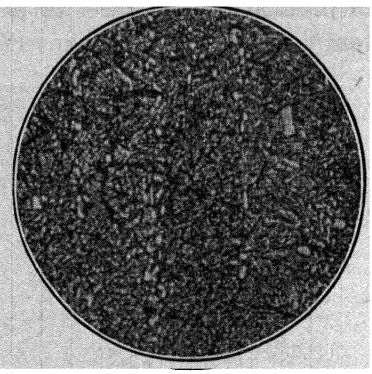


FIG. 174.—Material quenched in oil from 1260°C. and tempered at 580°C. Undissolved carbides (light) in troosto-martensitic matrix (dark). Nital etch. Mag. 500 ×.

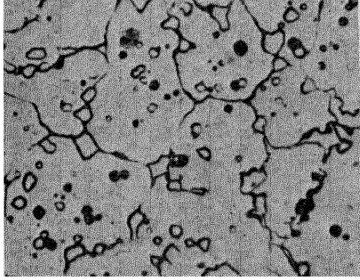


FIG. 175*a*.—Overheated high-speed steel. Large grain size. Mag. 500 ×.

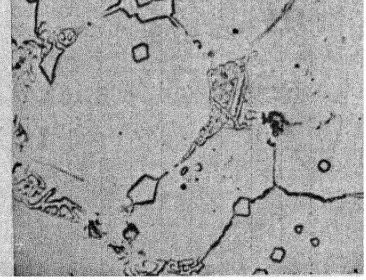


FIG. 175*b*.—Burned high-speed steel. Eutectic in austenite-martensite matrix. Nital etch. Mag. 500 ×.

quenched and tempered high-speed steel shows an absence of grain boundaries. Such a structure is shown in Fig. 174.

In tempering high-speed steel little if any effect is noted below 200°C. Beyond this point, especially near 400°C., a decrease in hardness takes place. With further increase

in temperature the hardness increases and reaches a maximum at from 565 to 600°C. The decrease in hardness is due to the tempering of the martensite, while the increase is due to the transformation of the retained austenite to martensite. The increase in hardness produced by reheating beyond the temperature exhibiting minimum hardness is called *secondary hardening*. Figure 176 illustrates these effects.

Since large deposits of molybdenum ore are present in this country, the use of molybdenum as a substitute for

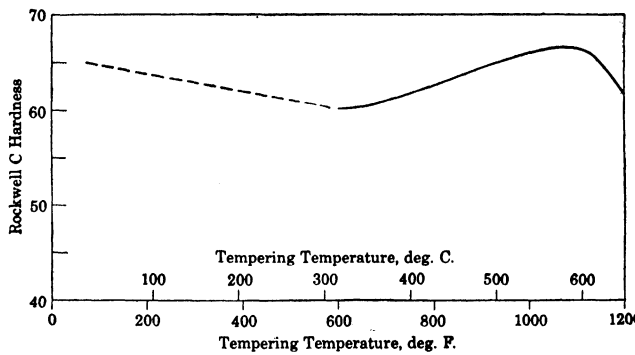


FIG. 176.—The hardness developed in high-speed steel after quenching and tempering.

tungsten in high-speed steel has been given a great deal of attention. In case of war, the supply of tungsten might be cut off, since the principal source is China. A typical composition of a molybdenum high-speed steel is as follows: Carbon 0.80 per cent, chromium 4, molybdenum 9, tungsten 1.5, vanadium 1.25. This steel is heated to a temperature of approximately 1225°C. before quenching and tempered at 560°C. Molybdenum high-speed steel is somewhat susceptible to decarburization. The use of special means, such as a controlled atmosphere in the heating furnace, to prevent decarburization has greatly enhanced its use as a substitute for the 18-4-1 (18W, 4Cr, 1V) steel.

Corrosion-resistant Iron Alloys.—*Stainless steels and irons* or *rustless steels and irons* are terms that are generally

applied to the corrosion-resistant alloys of varying carbon content, the properties of which are mainly dependent on the presence of a high chromium content. A certain amount of chromium, either elemental or as carbide, must be present in solid solution in order to impart corrosion resistance to the alloys.

Pure iron is slightly soluble in water. The presence of approximately 8 per cent chromium prevents this solution.

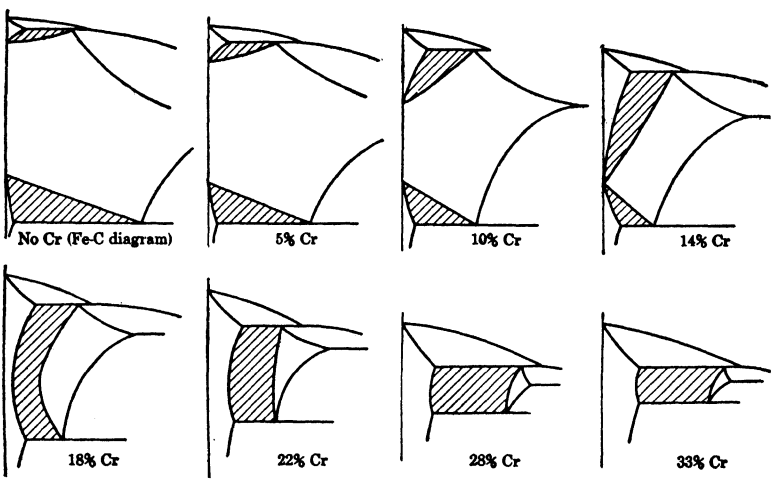


FIG. 177.—Diagrams showing the effect of the presence of chromium on the iron-carbon constitutional diagram. (*Krivobok and Grossmann.*)

If carbon is present to form chromium carbide, the possibility of electrolytic action will exist between the undissolved carbide and the matrix. The presence of an additional 2 per cent chromium is necessary to counteract this effect. In the presence of carbon, the amount of chromium that must be present in solution in the iron is 10 to 11 per cent in order to provide adequate corrosion-resisting properties. Since each part of carbon is combined with about 17 parts of chromium, every part of carbon that is present as undissolved carbide will affect 17 parts of chromium.

Figure 177 shows the effect of an increasing chromium content on the iron-carbon diagram. It will be noted that the eutectoid carbon content is progressively shifted to the left up to 18 per cent chromium, the δ- and the α-ferrite areas increase until they ultimately merge when the chromium content reaches 13 per cent, and the austenite region decreases in area.

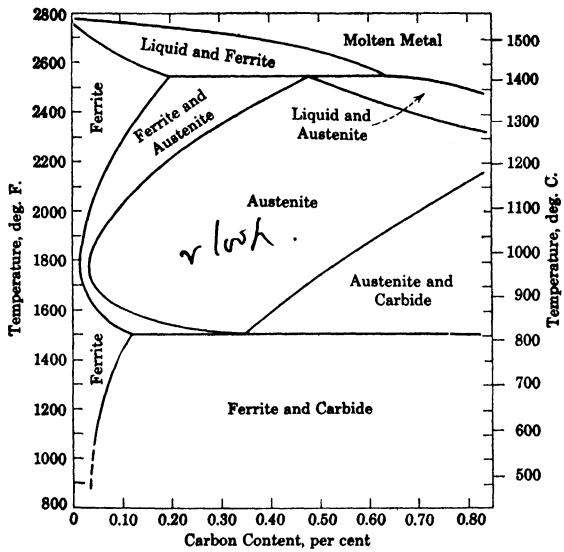


FIG. 178.—The approximate constitution of 14 per cent chromium alloys with varying carbon content. (*Bain.*)

The corrosion-resistant iron alloys may be divided into three groups, *i.e.*, ferritic, martensitic, and austenitic.

Figure 178 shows the approximate constitution of 14 per cent chromium alloys with varying carbon content. If the amount of carbon is negligible, the alloy will be ferritic under all conditions and will not respond to heat treatment except as it may affect the grain size. With an increase in carbon content, the alloys may become partly or wholly austenitic on heating to the proper temperature and will show, in general, a mixture of ferrite and martensite,

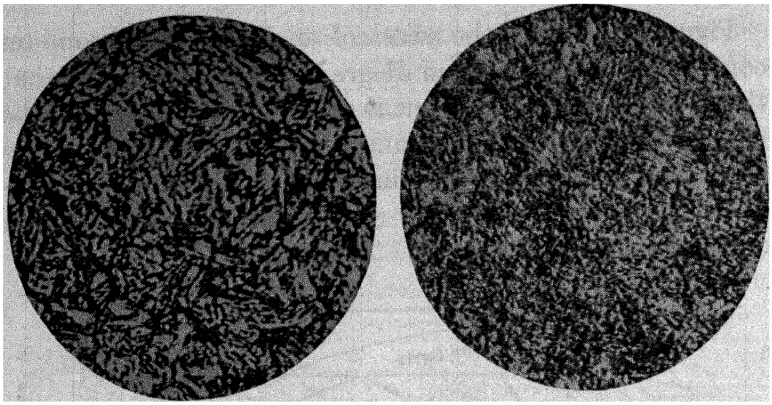


FIG. 179.—Stainless iron with 0.10 per cent carbon and 13 per cent chromium, quenched in oil from 953°C. (1750°F.). Martensitic structure. Glyceregia etch. Mag. 500 ×.

FIG. 180.—Stainless steel with 0.30 per cent carbon, 13 per cent chromium, quenched in oil from 981°C. (1800°F.) and tempered at 500°C. Martensitic structure. Glyceregia etch. Mag. 500 ×.

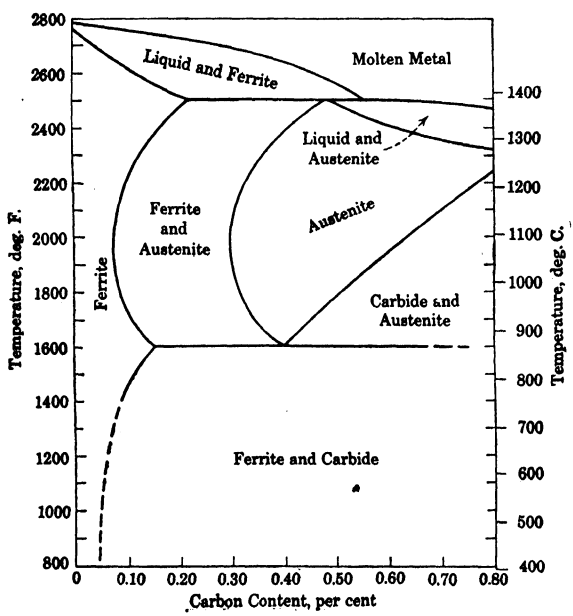


FIG. 181.—The approximate constitution of the 18 per cent chromium alloys with varying carbon content. (*Bain.*)

martensite, or martensite together with undissolved carbides after quenching.

Figure 179 shows the microstructure of a low-carbon, 13 per cent chromium alloy after hardening by quenching.

The cutlery type of stainless steel contains approximately 0.30 to 0.35 per cent carbon or that corresponding to the eutectoid in the presence of 13 to 14 per cent chromium.

A martensitic structure is readily obtainable by heating the alloy into the austenitic region and quenching. Quenching in oil from about 1000°C. produces such a structure. This structure is retained even after tempering at approximately 475°C. Figure 180 shows the presence of martensite in the quenched and tempered steel.

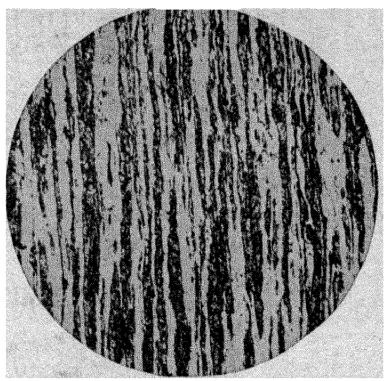


FIG. 182.—Stainless iron containing 0.09 per cent carbon and 18 per cent chromium, quenched in oil from 953°C. (1750°F.) shows ferrite (clear areas) and martensite (dark). This temperature is within the ferrite and austenite area. See Fig. 181.

The approximate constitution of the 18 per cent chromium alloys with varying carbon content is shown in Fig. 181. The alloy is wholly ferritic, provided that the carbon content is sufficiently low. With increase in the carbon content, the material becomes amenable to heat treatment and will show progressively ferrite and martensite, martensite, and martensite with undissolved carbides after quenching from the proper temperatures. With the high-carbon alloys, some austenite may be retained on quenching, owing to the sluggishness that is imparted to the transformation into martensite by the chromium. Figure 182 shows the microstructure of a low-carbon 18 per cent chromium alloy.

The austenitic alloys are most readily obtained in the presence of nickel. The effect of nickel on the iron-carbon

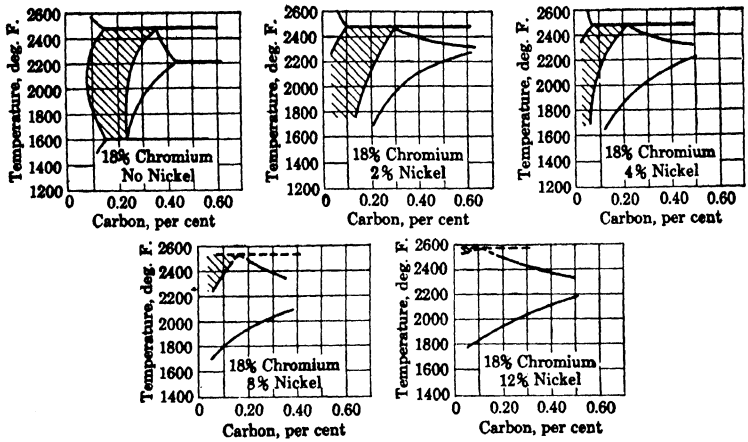


FIG. 183.—Diagrams illustrating the influence of nickel in modifying 18 per cent chromium-iron-carbon constitutional diagram. (*Krivobok and Grossmann.*)

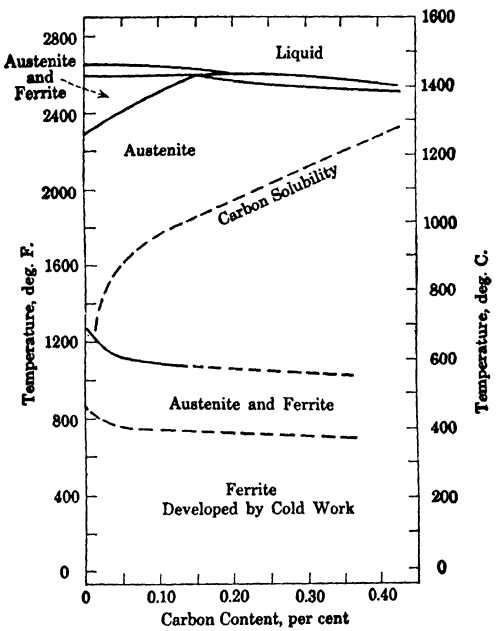


FIG. 184.—The approximate composition of the 18-chromium-8-nickel alloys with varying carbon content. The dotted line indicates carbon solubility. The ferrite and austenite boundary lines assume carbide in solution. (*Bain.*)

diagram containing 18 per cent chromium is shown in Fig. 183.

A well-known alloy of this type is the so-called "18-8," containing approximately 18 per cent chromium with 8 per cent nickel. The approximate constitution of this alloy with varying carbon content is shown in Fig. 184. Under equilibrium conditions the stable structure is ferrite. Austenite, however, can be retained on quenching and ferrite is produced only after cold working. The precipita-



FIG. 185.—Slip bands in cold-worked "18-8" alloy and general carbide precipitation upon slip planes within the grain. Mag. 2000 ×. (*Bain, Aborn and Rutherford.*)

tion of this ferrite takes place at the slip planes in the austenite and undoubtedly retains carbon in supersaturated solution to produce a condition similar to martensite (Fig. 185). The marked increase in hardness over that produced by cold working a low-carbon steel to the same extent is undoubtedly due to the difference in the condition of the ferrite.

The reheating of the cold-worked austenite alloy beyond its recrystallization temperature produces a progressive increase in grain size with increase in temperature, the effect being the same as that which is produced on reheating

many of the nonferrous alloys under similar conditions. The structure consists of twin crystals as indicated in Figs. 186 to 190 inclusive.

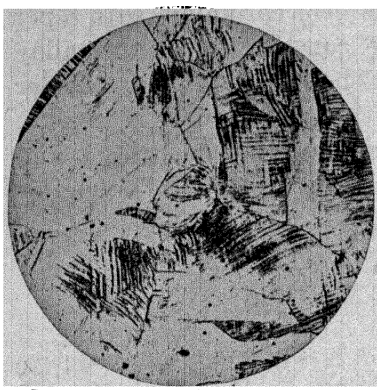


FIG. 186.—"18-8" cold-worked after quenching in oil from 1149°C. (2100° F.). HF + HNO_3 etch.

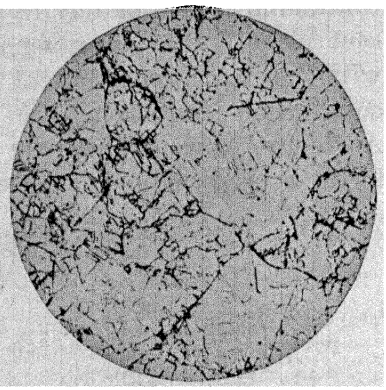


FIG. 187.—Cold-worked "18-8" annealed at 871°C. (1600°F.).

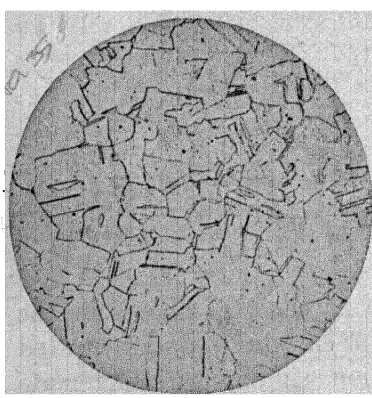


FIG. 188.—Cold-worked "18-8" annealed at 981°C. (1800°F.). Mag. 100 ×.

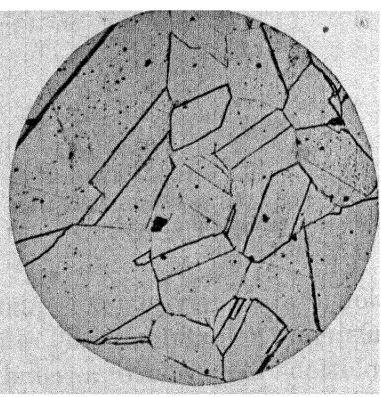


FIG. 189.—Cold-worked "18-8" annealed at 1093°C. (2000°F.). Mag. 100 ×.

It is possible to retain the delta (δ) constituent or the high-temperature ferrite provided that the carbon content is low. It is more readily obtainable if the ratio of the chromium to the nickel content is greater than "18-8." Delta areas are shown in Figs. 191*a* and 191*b*.

It has been previously stated that, in order that the high-chromium alloys may possess maximum corrosion resistance, the chromium should be present in solid solution. If a sufficient amount of the chromium precipitates as chromium carbide, the particular regions where this takes place will be depleted of their chromium content and will no longer possess proper corrosion resistance.

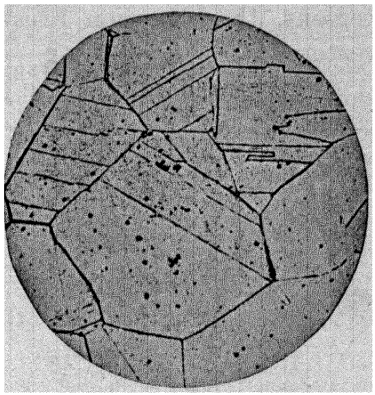


FIG. 190.—Cold-worked "18-8" annealed at 1204°C. (2200°F.). Mag. 100 ×.

Alloys of the "18-8" type are susceptible to intergranular corrosion owing to the precipitation of the chromium as carbide at the grain boundaries when the material is reheated within the temperature range of approximately 538 to 760°C. (1000 to

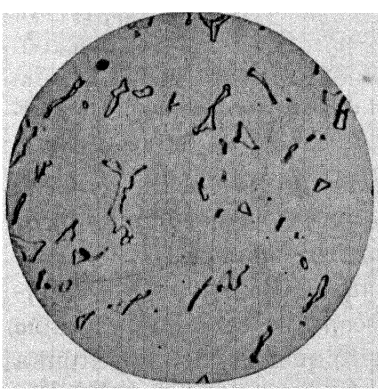


FIG. 191*a*.—Ferrite in "18-8." Etched with 10 per cent hydrochloric acid. Mag. 500 ×.

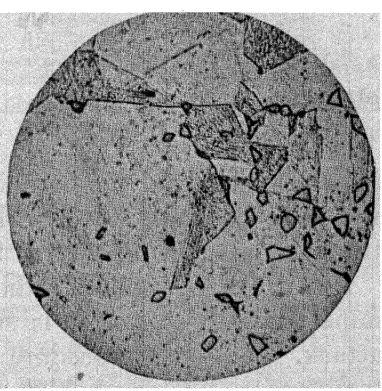


FIG. 191*b*.—Ferrite in "18-8." Glyceregia etch. Mag. 300 ×.

1400°F.). If the metal has been previously cold worked, the chromium carbide will also precipitate at the slip planes. The presence of the precipitated carbides at the grain

boundaries is shown in Fig. 192. If conditions are produced whereby the chromium can diffuse into the depleted regions, the corrosion resistance of the material will be restored.

As previously stated, the chromium carbide precipitates essentially as Cr_4C. The addition of some element that will cause the precipitation of carbon as its carbide instead of as chromium carbide will permit the chromium to

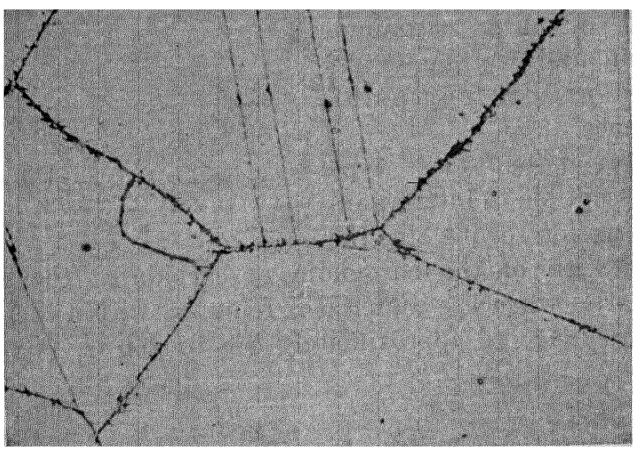


FIG. 192.—**Carbide particles** precipitated at grain boundaries in "18-8" alloy. Mag. 3000 ×. (*Bain, Aborn and Rutherford.*)

remain in solution; the corrosion resistance of the material will thus be maintained. The addition of columbium or titanium is generally used for this purpose.

A test can be applied to the austenitic material to determine whether or not it is susceptible to intercrystalline attack. A typical procedure is to quench the alloy from a temperature sufficiently high to produce complete solubility of the carbide and then to reheat to about 650°C., after which it is subjected to the action of a boiling acid copper sulphate solution (Strauss solution).[1] The effect of the

[1] A solution of 111 grams of copper sulphate and 98 grams of concentrated sulphuric acid in 1 liter of water. Bain and his associates recommend a

modified solution on susceptible material is shown in Fig. 193.

Corrosion.—While a detailed discussion of the problems of corrosion would be out of place in a consideration of the principles of metallography, the question is one of such vital importance to industry that a brief summary seems justified. The losses due to corrosion cannot be estimated with any accuracy as they include not merely the direct costs of replacing the corroded material but indirect losses such as the closing of a factory for repairs with the consequent decrease in production. Many figures have been suggested as indicating the cost of corrosion to the world and it is probably of the order of two billion dollars annually. Ferrous alloys are, of course, more likely to fail by corrosion but the nonferrous metals are by no means immune and contribute to a considerable extent to the total corrosion losses. Several special types of corrosion have been considered earlier in discussing dezincification (p. 114), season cracking (p. 113), and stainless steel (p. 193).

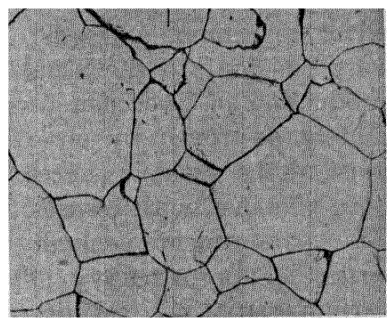


FIG. 193.—Microstructure of disintegrated metal after sensitization and corrosion. Mag. 100 ×. (*Bain, Aborn and Rutherford.*)

Many general theories of corrosion have been advanced during the last hundred years, each of which has some adherents even today, but most investigators have agreed that the *electrolytic theory* in some form is the true answer to the problem. Four factors of primary importance are concerned in any discussion of the electrolytic theory, but, in addition, many secondary conditions may profoundly

modified solution containing 13 grams $CuSO_4.5H_2O$ and 47 cubic centimeters H_2SO_4 (sp. gr. 1.84) in a liter of solution. See THUM, "The Book of Stainless Steels," 1935.

affect not only the corrosion rate but, in some cases, may actually determine whether or not corrosion will occur.

The first of these primary factors is the *normal potential* of the metal, often spoken of as *solution pressure.* All metals have a tendency to go into solution in the form of ions. With some metals, as, for example, sodium and potassium, this tendency is great, and such metals corrode readily. At the other end of the series will be found silver, platinum, and gold, which will be recognized as very resistant to the usual corroding agents. Since the production of hydrogen (even though it may be immediately destroyed by an oxidizing agent) is essential in most of the usual instances of corrosion, the metals have been classified with respect to their relation to hydrogen. This arrangement, generally known as the *electrochemical series,* is approximately as follows: potassium, sodium, barium, strontium, calcium, magnesium, aluminum, manganese, zinc, iron, cobalt, cadmium, nickel, lead, tin, *hydrogen,* bismuth, copper, antimony, arsenic, mercury, silver, palladium, platinum, gold, silicon, tantalum, tungsten, molybdenum, vanadium, and chromium. It must always be remembered that this list merely indicates the general relation of the pure metals to each other and to hydrogen, but that many other factors must be considered in using the list as a measure of corrosion resistance, especially with those metals that are not far removed from hydrogen in their solution pressure.

The second factor is the *concentration of the metal ions in the solution.* The tendency of a metal to go into solution as a result of its solution pressure is opposed by the presence in the solution of its ions. The higher the concentration of the ions of the metal in the solution, the less will be the effective solution pressure and, therefore, if other factors are excluded, the slower will be the corrosion rate. In the case of iron, for example, a tenfold increase in the concentration of ferrous ions in the solution changes the solution

potential from about −0.43 to −0.40 volt, in this way considerably decreasing the tendency of the iron to corrode.

The third factor is the *hydrogen-ion concentration* of the solution in contact with the metal. Since the acidity of the solution is often of fundamental importance in determining whether or not a metal will corrode, it was felt desirable to find a simple method of indicating the acidity or alkalinity of a solution. This has led to the use of what is called *the pH value,* which is based on the dissociation of water into its hydrogen and hydroxide ions. The product of the concentrations of the hydrogen and hydroxide ions is 10^{-14} so that, when the two ions are present in equal amounts, the concentration of each is 10^{-7}. This is the case in pure water, and the solution is neutral. Acid solutions have a greater hydrogen-ion concentration and alkaline solutions a greater hydroxide-ion than 10^{-7}.

As numbers with negative exponents are not easy to remember, the pH value has been adopted as indicating the log of 1 hydrogen-ion concentration.

Results calculated from this expression consist of a series of small whole numbers from which the acidity or alkalinity of a solution may be seen at once. The pH value of neutral water is 7. Acids have pH values below 7 and alkalies have pH values greater than 7. As an example, calculation will show that a solution with a pH of 3 is distinctly acid and that its acidity is $\frac{1}{10}$ that of another solution with a pH of 2. Most natural waters have pH values between 6 and 8 but in exceptional cases they may be found as low as pH 5. With respect to the corrosion of iron and steel, it may be said, in general, that if the pH value is greater than 10 the corrosion is slow; in the range from pH 5 to pH 10 corrosion is moderate; if the pH is less than about 4.5 the attack is rapid, and with very low values it may be violent.

The fourth major factor is the *solution pressure* of hydrogen, which, when in contact with a solution, behaves

like a true metal. When hydrogen is present as a gas, a condition that exists when hydrogen bubbles are evolved during corrosion, the solution pressure may be taken as zero with respect to that of the metals. If, however, the atomic hydrogen formed is at once oxidized by oxygen (depolarized), its solution pressure becomes much less than zero and the corrosion of the metal on which it would otherwise form is greatly increased.

While the behavior of metals in general can be predicted in an approximate way by a consideration of these four factors, it must be remembered that many other conditions have to be considered in any complete discussion of the problem. In this list are included the method of manufacture of the metal or alloy, the temperature of the corroding solution, the velocity of the corroding solution, the contact of the metal with a dissimilar metal, the possible effects of electric currents (stray currents), and probably thirty or forty other factors of lesser importance. This great number of variables makes a detailed study of the corrosion problem extremely complex.

While the effect of oxygen has been indicated under factor four (p. 197), its importance cannot be overemphasized. It is universally agreed *that oxygen is the prime factor in almost all ordinary corrosion problems* and that if its complete absence could be assumed the corrosion problem would practically cease to exist. This fact has been beautifully shown by Evans,[1] by means of a simple experiment. Two strips of iron are partially immersed in a dilute solution of potassium chloride and are separated from each other by a parchment membrane. Outside the solution the strips are connected together through a milliammeter which indicates any flow of electricity from one plate to the other. Under ordinary conditions nothing happens and there is no deflection of the ammeter needle. If, now, air is bubbled into one of the two compartments, the

[1] EVANS, "Corrosion of Metals," 1926, p. 80.

needle at once moves, indicating the production of an electric current in spite of the fact that the solutions in each part of the cell are the same, and that the two pieces of iron have identical compositions. A study of the system shows that the *unaerated* plate has become the anode and is dissolving rapidly while the *aerated* strip has become the cathode and is dissolving slowly if at all. This experiment shows clearly why the corrosion of a boiler is likely to occur in seams, around rivet holes, and at other points to which oxygen does not easily come. The corrosion of iron and steel is usually due, then, to *differences* in the oxygen concentration at different points. This is called *differential aeration.*

A somewhat complex situation exists in the case of copper and its alloys. There is little doubt but that copper obeys the same laws as iron and other more reactive metals in respect to aeration, but its solution pressure is so low and is so markedly affected by the presence of copper ions in the solution that the removal of copper ions by *stirring* becomes the determining factor in its corrosion. Normally, then, the corrosion of copper is most active where the motion of the corroding medium is greatest. Failure of copper tubes often occurs at sharp bends where the scouring action is unusually severe. This condition makes it very difficult in many circumstances to determine whether failure is due to corrosion in the restricted use of the term (electrolytic action), or to erosion (mechanical action). In many instances both effects are involved.

Protection against Corrosion.—It was stated previously that in most cases of corrosion (those not due to direct solvent action of active chemical reagents) oxygen is the determining factor. It is also clearly recognized that the formation of films on metals may be of vital importance in eliminating or at least markedly reducing corrosion. The production and character, both chemical and physical, of these films have so marked an influence on corrosion that it

is often stated that corrosion effects are nothing but manifestations of film formation. These films are commonly of the oxide type but may be sulphides as in the manufacture of "oxidized" silver, in which the silver is protected to some extent by a sulphide skin, or with lead, in which the surface becomes covered with a thin layer of insoluble lead sulphate.

An interesting generalization concerning the physical characteristics of these films was made by Pilling and Bedworth,[1] who correlated the protective effect of an oxide film with the relative densities of the metal and its oxide. If the formation of the oxide is accompanied by a decrease in volume, the oxide film will shrink and crack, permitting further easy access of oxygen. If, on the other hand, the formation of the oxide occurs with an increase in volume, provided this increase is not too great, the underlying metal will be covered at all times by a more or less continuous film which, if it is chemically nonreactive, serves to protect the metal from further attack. This conception explains the rapid corrosion of sodium, lithium, barium, and similar metals which form light, nonadherent oxides and the resistance to many types of corrosion of aluminum which, while it is normally quite reactive, becomes covered the instant it is in contact with air with a thin, continuous nonreactive film of aluminum oxide.

These protective films are in general so thin as to be transparent. Evans has succeeded, however, in isolating many of them so that their existence is not a matter of speculation but is an experimentally determined fact. Practical examples of the protective effect of these films are numerous. The passive form of iron is due to the formation of a thin, closely adherent film of ferric oxide; the Parker process for protecting steel against rust depends on the production of an insoluble phosphate film; and the resistance to atmospheric corrosion of copper-bearing steel

[1] *J. Inst. Metals*, **29** (1923), 529.

is without question due to the character of the surface film resulting from oxidation. These considerations with regard to the formation of protective or nonprotective films indicate clearly that the most effective method of protecting a metal against corrosion is to keep it from contact with the corroding agent. Seven general methods of more or less completely separating the metal from the corroding medium are the following:

1. A thin film of oxide, phosphate, sulphate or other insoluble material produced either artificially or as a natural result of the corrosion.

2. A layer of paint, enamel, or varnish. Certain types of paints or varnishes are more resistant to attack than others, but the literature of paint protection is so extensive that a detailed discussion is not possible. In general, it may be said that oxidizing pigments like red lead or the chromates of lead or zinc are most effective. These pigments tend toward the formation of a thin protective oxide film.

3. A layer of more protective metal. The metals most commonly used for this purpose are zinc, tin, nickel, copper, chromium, aluminum, cadmium, cobalt, and in special cases silver, gold, or the platinum-group metals. Alloys are also used occasionally, especially brass and the copper-nickel alloys. These layers of metal may be applied in various ways, for instance: (*a*) by electrodeposition; (*b*) by dipping in the molten protective metal as in galvanizing or tinning; (*c*) by heating in metallic dust. If zinc dust is used, the process is called *sherardizing*, while, with aluminum powder, it is known as *calorizing*. *Chromizing* consists in heating the metal to be coated in a mixture of powdered chromium and aluminum oxide. (*d*) Coatings may be applied by spraying following the original suggestions of Schoop. The wire to be used for the protective coat is fed from a reel through an oxyhydrogen or oxygas flame coming from the barrel of a spray *pistol*. The pistol grip makes it possible to direct the stream of metal vapor

against the surface to be protected. Almost all of the pure metals and many alloys can be applied in this way. (*e*) Metallic coatings are being applied mechanically to an increasing extent. Copper-clad steel plates are commonly made by casting a copper shell around a steel billet. The composite billet is rolled into a sheet which then consists of a steel central section protected by a firmly adherent copper layer of the desired thickness. While details of manufacture are not available, it is probable that Alclad sheet (p. 90), Nickel Clad, and other duplex metals are made in a somewhat similar manner.

4. Many tarry or bituminous mixtures are used in the covering of buried water, oil, or gas mains and for the protection of structural ironwork under bad atmospheric conditions as, for example, in chemical plants.

5. Cement or concrete is frequently used as a protective coat or liner for large steel water mains, or in aqueducts when the water is corrosive in character.

6. Protection by glass or enamels is very common, as is shown by the extensive use of enameled kitchenware and bathroom equipment.

7. Finally the use of oil or grease to protect machine parts from rusting is too familiar to need comment.

In many instances the protection of the metal against corrosion is impracticable because of the excessive cost of material, difficulty in the fabrication of coated metal, or for other reasons. Under these conditions, an effort is made to reduce the corrosive character of the liquid (generally water) in contact with the metal. Purification of the water involves one of two operations or often both:

1. Removal of oxygen.
2. Removal of chemical impurities.

1. Since oxygen is one of the main factors in corrosion, its removal or at least its reduction in amount greatly lessens the corrosiveness of the water and in this way

extends the service life of the pipe, boiler, or other part to be used. Oxygen may be removed by: (*a*) *deactivation*, or (*b*) *deaeration*. In deactivation, the water to be treated is passed over cheap scrap iron or steel. This reacts with the oxygen in the water, reducing the concentration to such an extent that no serious corrosion takes place in the system that is being protected. The scrap metal in the deactivator is replaced at intervals at a relatively slight expense.

Deaeration consists in the mechanical rather than the chemical removal of air. The water is preheated before it goes into the system, preferably under slightly reduced pressure, and in this way most of the oxygen is mechanically eliminated.

2. In special cases the corrosiveness of a water may be due to chemical substances dissolved in it. Sodium carbonate (soda ash) is often used to reduce acidity and occasionally dilute sulphuric acid is used to correct excessive alkalinity. In both instances, the concentrations must be most carefully controlled or the corrosion inhibitors will do more harm than good. Sodium silicate (water glass) has been used to an increasing extent in recent years and also certain of the phosphates of sodium, especially in connection with the feed water for boilers and large heating systems.[1]

Cast Iron.—Reference to the iron-carbon diagram (p. 129) shows that the cast-iron field begins at 1.7 per cent carbon although the carbon content of commercial alloys is seldom below 2.2 per cent. The liquidus to be considered for these alloys consists of two branches, *DI* and *IF*. Primary austenite separates from the liquid along *DI* while cementite separates along *IF*. The eutectic consists of an intimate mixture of austenite having the

[1] For a detailed discussion of the corrosion problem, the reader is referred to SPELLER, "Corrosion: Causes and Prevention," McGraw-Hill Book Company, Inc., New York, 1935, and HEDGES, "Protective Films on Metals," D. Van Nostrand Company, Inc., New York, 1932.

composition H and cementite. This eutectic is known as *ledeburite.*

An alloy of composition 6 on reaching the temperature t_{I} begins to solidify with the separation of primary austenite of composition x. At t_{II} the composition of the solid solution is y, which is in equilibrium with liquid of composition z. At t_{III} the primary austenite will be of composition H and the liquid of composition I. At this temperature the liquid solidifies to form the eutectic, ledeburite. On

WHITE CAST IRON

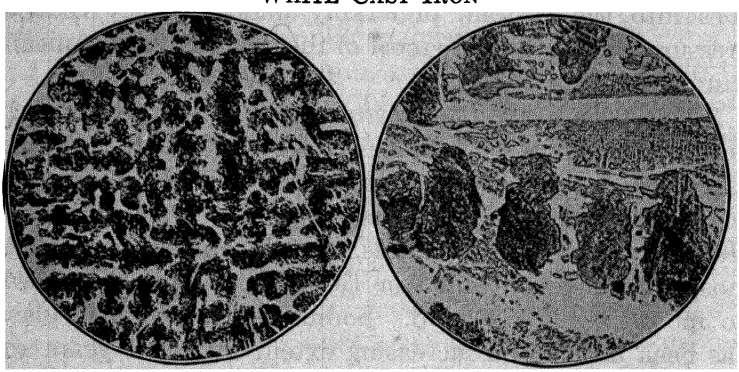


FIG. 194.—Typical structure. Dark is pearlite and white is cementite. Nital etch. Mag. 100 ×.

FIG. 195.—High phorphosus white iron. Dark is pearlite, white is cementite, and fine feathery structure is the phosphorus-rich eutectic. Nital etch. Mag. 250 ×.

cooling from the eutectic to the eutectoid temperature, the austenite changes in composition along HM with a decrease in solubility of the carbon in γ-iron from 1.7 to 0.85 per cent. Pearlite is formed at the eutectoid temperature, the final product consisting of excess cementite and pearlite. This product is *white cast iron.* It has a white fracture and is hard and brittle owing to the large amount of cementite that is present. Its formation is favored by rapid cooling, low silicon, and moderately high manganese and sulphur.

White-iron castings are difficult to machine and are so brittle that they have only a limited application. It is often necessary to produce soft and fairly strong cores

with very hard surfaces, as, for example, in car-wheel treads or on the surfaces of rolls. In such instances, the mold is made with a sand core and a metal rim. The slow

WHITE CAST IRON

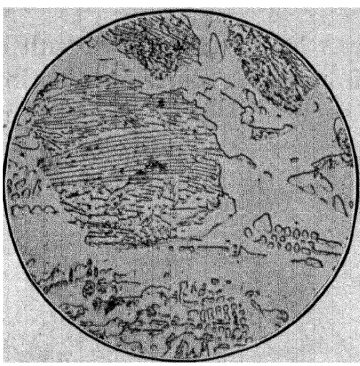


FIG. 196.—Same as Fig. 195 at 500 ×.

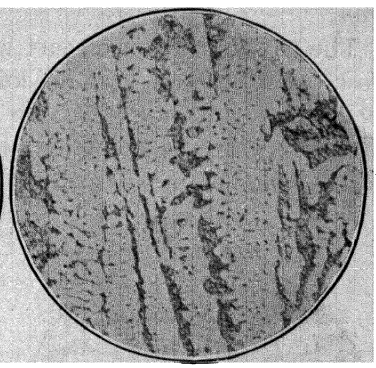


FIG. 197.—Outermost rim of chill casting. Pearlite is dark and cementite white. Mag. 150 ×.

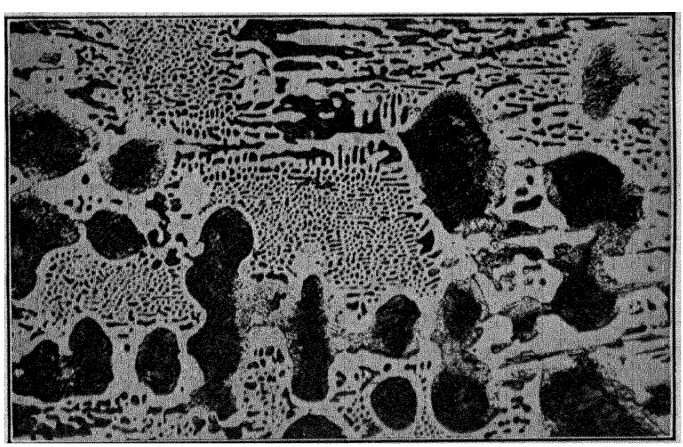


FIG. 198.—Low-phosphorus white iron. Large black masses are pearlite. White is cementite. Fine structure is the eutectic, originally *ledeburite* (the eutectic of austenite and cementite, point *E*, Fig. 134). The austenite has changed into pearlite at Ar_1. Nital etch. Mag. 100 ×.

cooling of the center produces soft or gray iron, while the rapid cooling by the metal chill forms hard or white iron. The most important use of white iron is in the manufacture

of malleable castings. Between the outer white-iron layer of a chilled casting and the center with a gray-iron core, there is an intermediate structure showing the characteristics of both white and gray iron. This structure is called *mottled iron.*

The common form of cast iron is obtained as a result of slow cooling and a high silicon content, together with low manganese and sulphur. In such an alloy, the primary austenite forms in the same manner as in white iron. The excess cementite, as well as that which separates from

GRAY CAST IRON

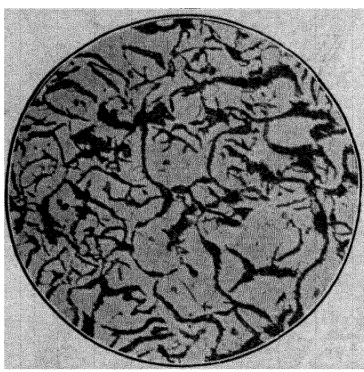


FIG. 199.—Unetched. Shows intersecting graphite flakes. Mag. 100 ×.

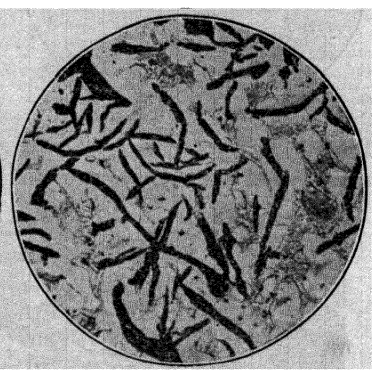


FIG. 200.—Low in combined carbon. Black graphite flakes embedded mainly in ferrite. Nital etch. Mag. 100 ×.

the austenite in cooling from the eutectic to the eutectoid temperature, decomposes into ferrite and free carbon as graphite in the form of flakes. The austenite is transformed into pearlite at the eutectoid temperature, thereby producing a product that consists of pearlite, ferrite, and graphite. The cementite in the pearlite resulting from the eutectoid inversion may decompose under certain conditions into ferrite and graphite. In this case the final product will contain only ferrite and graphite. It is obvious, therefore, that gray cast iron may vary widely in its microstructure and corresponding mechanical properties, depending on its composition, method of casting, and rate of cooling. In all

cases it contains excess carbon in the form of graphite flakes, which give to the material the dark colored fracture to which the term *gray iron* is due.

GRAY CAST IRON

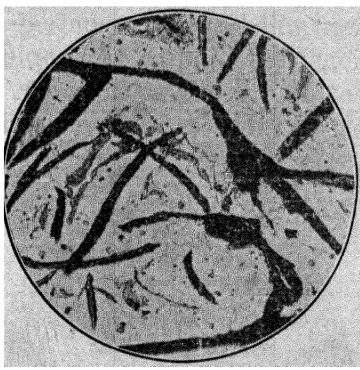


FIG. 201.—Similar to Fig. 200 but with larger graphite flakes. Low in tensile strength. Nital etch. Mag. 100 ×.

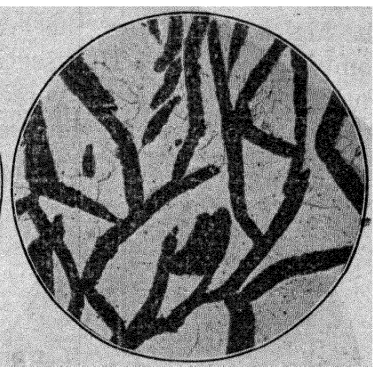


FIG. 202.—Large intersecting graphite flakes in ferrite. Very weak material. Nital etch. Mag. 100 ×.

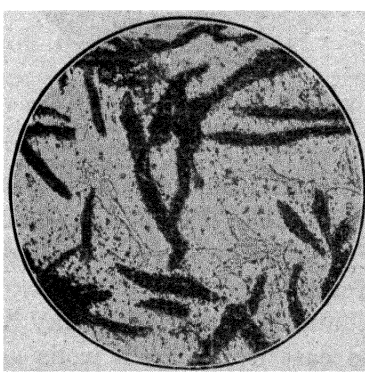


FIG. 203.—Graphite in ferrite with phosphorus-rich eutectic. Nital etch. Mag. 100 ×.

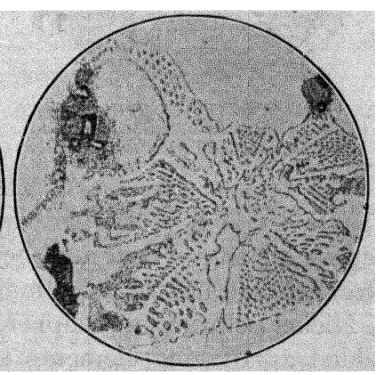


FIG. 204.—Same as Fig. 199 but at 250 × showing phosphorus-rich eutectic. Nital etch.

A structure that is frequently present in cast iron is the ternary eutectic of iron phosphide, iron carbide, and the solid solution. The eutectic of iron phosphide and the solid solution of the phosphide in γ-iron is known as *steadite*.

For general purposes, gray cast iron containing small graphite flakes uniformly distributed throughout a matrix of pearlite represents the best material. The relative amounts of free and combined carbon (graphite and cementite) are largely determined by the silicon content; the higher the silicon, the lower will be the percentage of combined carbon. Thin sections that tend to cool rapidly must contain a higher percentage of silicon in order to become gray cast iron than sections that cool more slowly.

GRAY CAST IRON

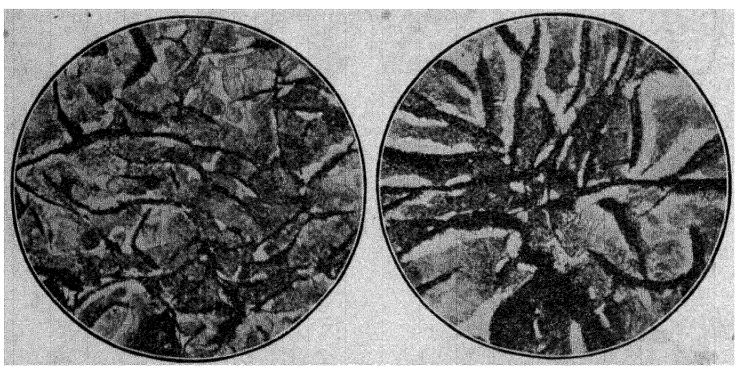


FIG. 205.—Medium graphite flakes in a field of pearlite. Good material. Nital etch. Mag. 100 ×.

FIG. 206.—Large graphite flakes in pearlite. Nital etch. Mag. 100 ×.

The tensile strength of gray cast iron may vary from 15,000 to 70,000 lb. per square inch. The high value represents that which may be obtained in the case of high-strength and heat-treated material.

Nickel, chromium, copper, and molybdenum may be added as alloying elements to cast iron. Such irons are frequently used to withstand more severe service than the ordinary material. Nickel is usually added in amounts from 0.25 to 5 per cent for general purposes. This element is a graphitizer and promotes machinability by eliminating the tendency to form free carbide. It improves the wearing qualities, decreases grain size, and increases the strength and density of gray cast iron. It also decreases the depth of chill in those castings in which a chill is undesirable.

The addition of a sufficient amount of nickel (10 to 18 per cent) produces an austenitic structure with corresponding changes in physical properties. Changes in the coefficient of expansion also take place with increase in nickel content.

The microstructure of an austenitic gray iron is shown in Fig. 207. Such an iron is used for heat-resisting purposes

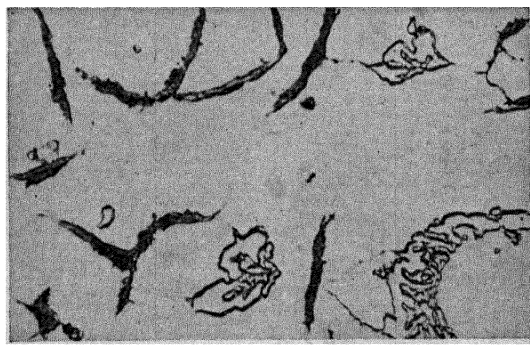


FIG. 207.—"Ni-resist." Total carbon 2.84, silicon 1.55, manganese 1.03, nickel 14.5, chromium 2.34, copper 6.0 per cent. Graphite and carbide-austenite eutectic in austenite matrix. Nital etch. Mag. 500 ×.

for temperatures up to 815°C. (1500°F.). It is non-magnetic and has high corrosion and scale resistance.

Chromium increases the amount of combined carbon and increases the tendency to chill or to form white iron. It is added to produce increased hardness and wear resistance.

The approximate effect of chromium on soft iron is given as follows by Bornstein[1] and Bolton: Improved heat and corrosion resistance can be obtained by the addition of large amounts of chromium.

Chromium, Per Cent	Structure
0.0	Ferrite and coarse graphite
0.3	Less ferrite and finer graphite with pearlite
0.6	Fine graphite and pearlite
1.0	Fine graphite and pearlite and small carbides
3.0	Graphite disappears
5.0	Much massive cementite
10.0 to 30.0	Fine cementite

[1] BORNSTEIN, H., and J. W. BOLTON, "Cast Iron," Metals Handbook 1939 ed., p. 628.

Nickel-chromium cast iron is produced in various combinations, generally containing below 3 per cent nickel and 1 per cent chromium. Nickel and chromium in combination refine the structure and increase the strength and hardness without impairing the machinability.

A very hard, tough, and strong product can be obtained by adding 4.5 per cent nickel and 1.5 per cent chromium to white cast iron.

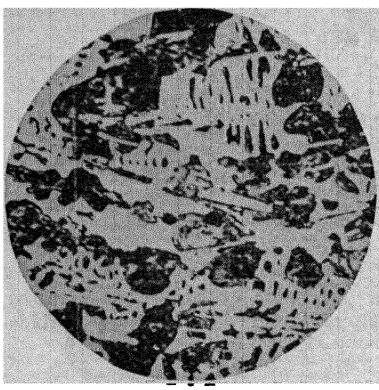


FIG. 208.—"Ni-hard." Total carbon 3.30, silicon 0.90, nickel 4.50, chromium 2.50 per cent. Pearlite is dark, cementite light. Nital etch. Mag. 250 ×.

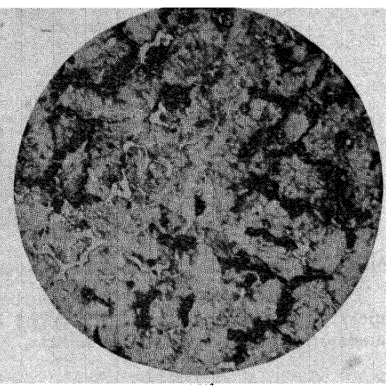


FIG. 209.—"Nitricastiron" as cast. Total carbon 2.90, silicon 1.60, manganese 0.60, aluminum 1.00, molybdenum 0.75, chromium 0.40 per cent. Pearlite, carbide and graphite. Nital etch. Mag. 100 ×.

Molybdenum is widely used as an alloying element in gray cast iron. It increases the tensile strength, transverse strength and deflection, hardness, and impact resistance. It is usually added in quantities of from 0.25 to 1.25 per cent.

Other elements that are used for alloying cast iron include titanium, vanadium, aluminum, and zirconium.

Pearlitic cast iron is a term that is commercially applied to a gray iron of low-silicon content that is prevented from forming a white or mottled iron by being cast in heated molds.

Aluminum is a graphitizing element. It is added to cast iron principally for the purpose of producing a material

that will be susceptible to nitriding. The structure of a nitridable cast iron is shown in Fig. 209. In the "as-cast" condition it shows pearlite, graphite, and free cementite. After air cooling from 950°C. and reheating to 725°C., the structure is changed to graphite, ferrite, and finely

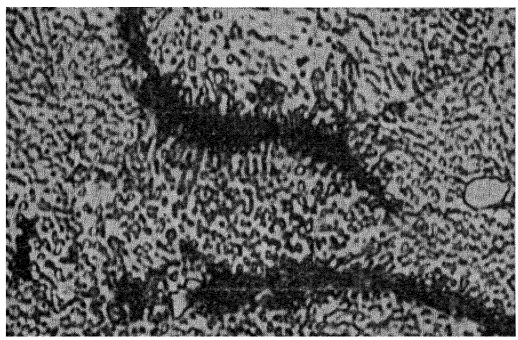


FIG. 210.—"Nitricastiron" air-cooled from 935°C. (1750°F.) and reheated at 760°C. (1400°F.) for 4 hours. Excess carbide, graphite, and spheroidal carbides in ferrite. Nital etch. Mag. 1000 ×.

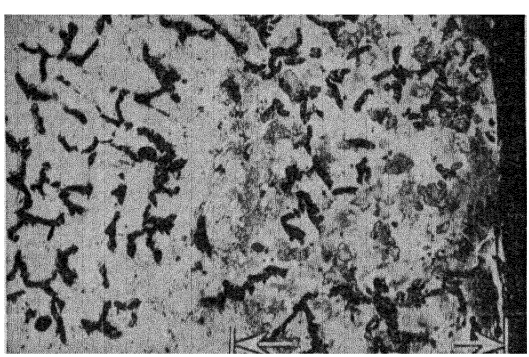


FIG. 211.—Nitrided "nitricastiron." Nitrided at 538°C. (1000°F.) for 60 hours. Nital etch. Mat. 100 ×.

spheroidized cementite as shown in Fig. 210. Figure 211 shows the nitride case produced after subjecting this material to the action of ammonia gas for 60 hours at 525°C.

Semi-steel is an indefinite term that is applied to any cast iron in which steel scrap is used as a part of the charge to be melted.

Malleable cast iron is made by the annealing of white cast iron within a certain range of composition and depends primarily on the reaction $Fe_3C \rightleftarrows 3\ Fe + C$. The free carbon formed under these conditions is crystallographically

MALLEABLE CAST IRON

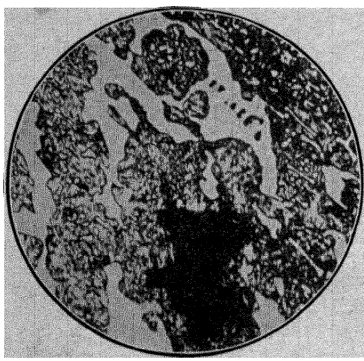


FIG. 212.—Beginning of malleabilizing. Black area is temper carbon, dark masses are pearlite, and white is cementite. Nital etch. Mag. 250 ×. (*Zavarine.*)

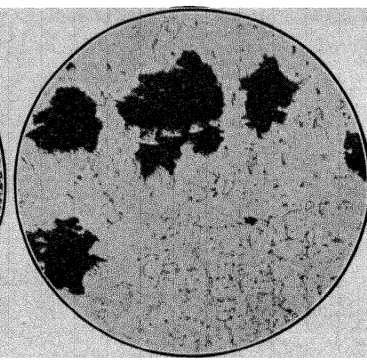


FIG. 213.—Temper carbon in ferrite. Small light areas are undecomposed cementite. Nital etch. Mag. 100 ×.

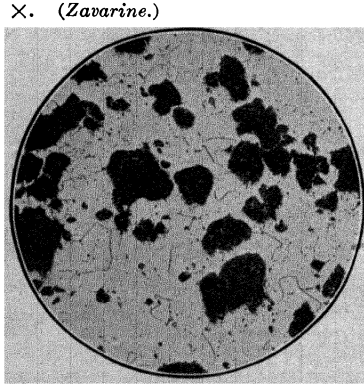


FIG. 214.—Average-sized particles of temper carbon. Nital etch. Mag. 100 ×.

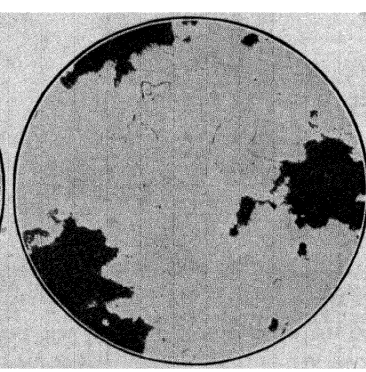


FIG. 215.—Large masses of temper carbon in ferrite. Nital etch. Mag. 100 ×.

the same as the graphite in gray cast iron but different in form. It does not occur in flakes but in nodules and is known as *temper* carbon.

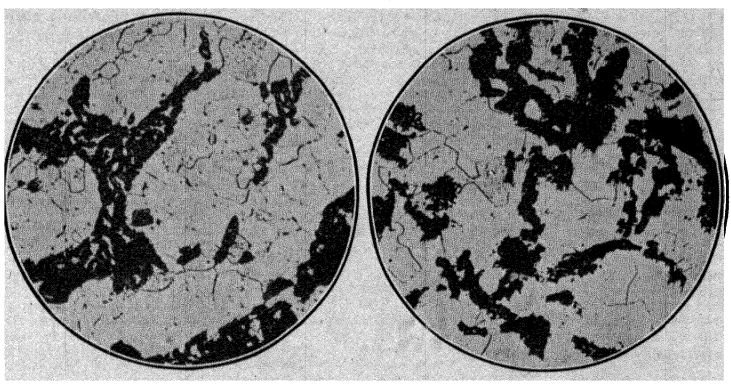
Malleable cast iron is ductile and consists almost entirely of ferrite and temper carbon.

The massive cementite in white cast iron is decomposed above the A_1 temperature, while that which exists as pearlite must be decomposed below A_1.

Two distinct forms of malleable cast iron are recognized, *black-heart*, the usual American type, and *white-heart*, the form commonly made abroad.

Black-heart malleable iron depends for its formation on the decomposition of iron carbide, but without the removal of the carbon by oxidation, except at the outer rim. The

MALLEABLE CAST IRON



a *b*

FIGS. 216*a* and *b*.—Unsatisfactory structure shows that original material was mottled instead of white iron. Black masses are graphite flakes and temper carbon in ferrite. Mag. 100 ×.

packing material is generally some material such as sand, cinders, or mill scale to support the castings. In certain furnaces the use of packing material is unnecessary. The annealing temperature may be as high as 980°C. and the total annealing cycle may require 6 or 7 days.

The presence of the finely divided carbon in the form of temper carbon imparts a black fracture to the material. Surface decarburization during annealing is difficult to avoid. This decarburization produces a ferrite rim of considerable thickness.

The tensile strength of a high grade black-heart malleable iron may reach 54,000 lb. per square inch, with an elongation

of approximately 18 per cent. Malleable cast iron is used for castings that must withstand shock where gray cast iron would probably fail because of low ductility. They are used for automobile parts, in railway equipment, and in large quantities in the production of agricultural machinery.

White-heart malleable cast iron is made by annealing white cast iron packed in iron oxide (mill scale or hematite

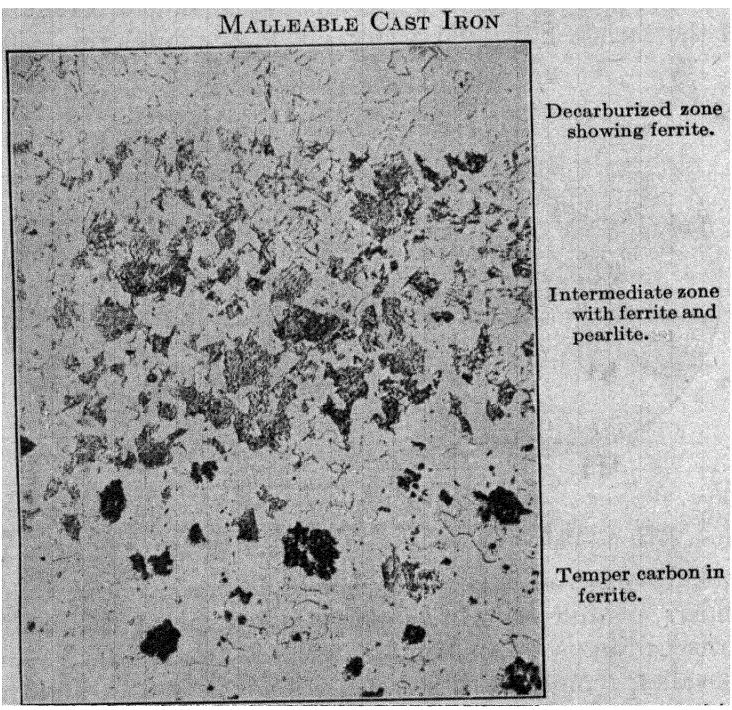


FIG. 217.—Typical "picture frame" effect due probably to improper composition. Mag. 100 ×.

ore) for several days at a temperature of 900 to 950°C. or higher. The decomposition of the cementite is followed by the removal of all or most of the resulting carbon by oxidation.

Modifications of malleable iron have come into extensive use. In one instance, the malleabilizing process is conducted so that part of the combined carbon is converted

into temper carbon and the remainder is spheroidized. Such a structure is obtained by first heating at a high temperature, cooling by air, and then reheating below Ac_1.

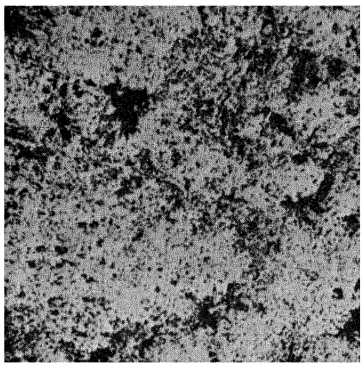


FIG. 218.—Pearlitic malleable iron. Temper carbon and spheroidal cementite in ferrite. Nital etch. Mag. 100 ×.

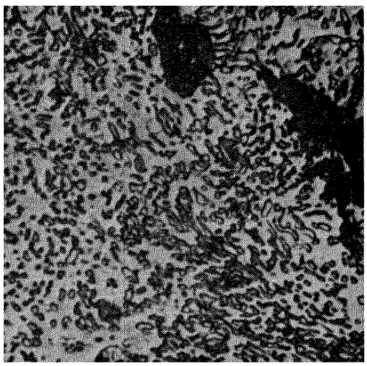


FIG. 219.—Same material as in Fig. 218 but at Mag. 1000 ×.

The structure of such a material is shown in Figs. 218 and 219 at 100× and 1000×, respectively. This material shows a much higher tensile strength than ordinary malleable iron.

CHAPTER VI

THE MACROSCOPIC EXAMINATION OF STEEL

The results of the chemical analysis of a piece of steel are based on the assumption that the elements present are uniformly distributed to form a homogeneous material. The same restrictions hold for a mechanical investigation. The method used to determine whether or not this uniformity exists is based on the examination of the material at a low magnification, *i.e.*, either with the unaided eye or with a simple magnifier after polishing and etching. This so-called *macroscopic* examination has several advantages over a microscopic one, which it should precede in a great many cases, in that the preparation of the specimens for examination is much simpler, much larger areas may be examined, and the interpretation of the results is easier. Although polishing with No. 00 or No. 000 emery paper is preferred, it is often possible to obtain the desired information by etching specimens that have been carefully machined or ground. This is especially true when macro-etching with a 50 per cent solution of hydrochloric acid in water. A macroscopic examination tells what has taken place in the ingot mold, discloses segregated areas, various defects, and reveals the flow lines in material that has been forged.

Mechanism of Segregation.—In order to understand the manner in which segregation may take place in steel, it is necessary to consider the mechanism of selective solidification. In the case of a pure metal, the temperature at which the material solidifies remains constant. If, however, a material such as steel is chosen, the effects of other elements, especially carbon and phosphorus, will have to be taken

into consideration. Carbon exists in solution as such or as iron carbide, phosphorus as iron phosphide. The sulphur exists as manganese sulphide provided that sufficient manganese is present.

When an ingot mold is filled with liquid steel, the metal immediately in contact with the mold will solidify first, since the heat loss at this point is the greatest. The crust thus formed fixes the external dimensions of the ingot. As solidification proceeds inwardly, successive layers freeze progressively, and a shrinkage cavity forms in the upper central part of a normally cooled ingot. This is due to the decrease in volume of the metal in passing from the liquid to the solid state. Such a shrinkage cavity is known as a *pipe*.

Impurities in a substance lower its melting or freezing point, provided that these impurities are soluble when the substance is in the liquid state. This lowering of the temperature at which solid material separates from the liquid proceeds as the concentration of the impurities in the solution increases.

Figure 220 shows the simplified equilibrium diagram of the iron-carbon alloys and illustrates this principle.

AC is a line drawn through the temperatures at which solid material begins to separate from the liquid, the temperature varying with the carbon content. AB is a line drawn through the temperatures below which the material is in the solid state. The compositions of the solid separating from the liquid and of the remaining liquid can be determined at any given temperature within the solidification range by drawing a horizontal line through this temperature so as to intersect the lines AC and AB. For example, at the temperature t, the composition of the solid is represented by the point f and is approximately 0.60 per cent carbon, while the composition of the residual liquid is represented by the point g or approximately 1.60 per cent carbon, although the carbon content of the original

liquid was 0.85 per cent. These compositions of solid and liquid at temperature t are determined by noting the points of intersection with DE of the vertical lines drawn from points c and d.

The important points to be noted in the study of this diagram are that the solid material that separates with the gradual decrease in temperature becomes enriched in carbon and that the liquid from which it separates also

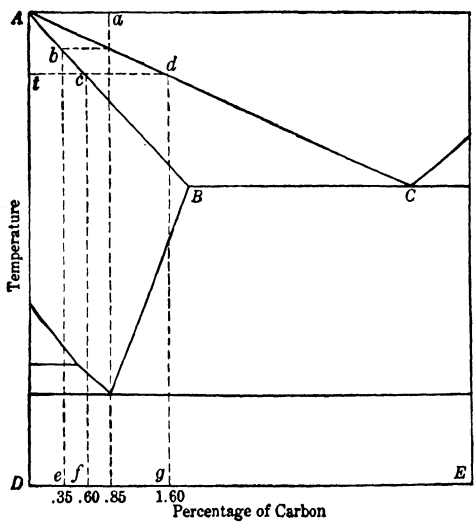


FIG. 220.—Iron-carbon diagram.

becomes enriched in carbon and is at all times higher in carbon content than the solid that separates from it. The same procedure is followed in considering phosphorus. Therefore, the material immediately in contact with the ingot mold contains the least amount of carbon, phosphorus, and sulphur.

Figures 221 and 222 show the manner of solidification and the steel ingots resulting from the use of two types of molds. The shrinkage cavity in each case is clearly visible. The concentration of carbon, phosphorus, and sulphur

increases and reaches a maximum in the region of the "pipe."

It is obvious that the "pipe" should occupy such a position that it can be discarded, leaving only sound metal. Where the product warrants the cost, it is necessary to cast the ingot with its large end up and to have the top of the ingot formed in a material of poor heat conductivity, called a *hot-top*.

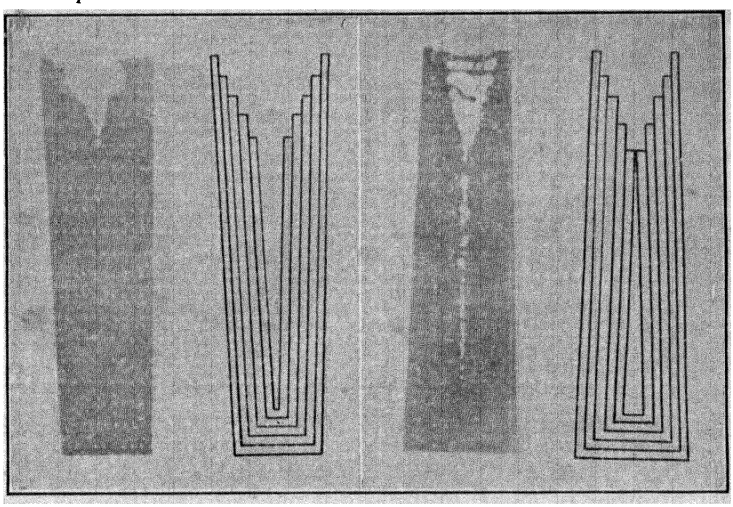


FIG. 221. FIG. 222.

FIGS. 221 and 222.—Location of pipe in ingot as affected by the type of mold. (*Brearly.*)

Dendrites.—The manner in which crystallization takes place is shown in Fig. 223. The crystals form at right angles to the walls of the ingot mold. The solid material with the least amount of carbon and phosphorus is at the point *e*, with increasing amounts toward the tip *f* and to the tips of the branches. Such a development is known as a *dendrite*, a conglomeration of which gives rise to what is known as a *dendritic* or a *pine-tree* structure. The interdendritic filling contains a higher percentage of carbon, phosphorus, and sulphur than the dendrites themselves. Later, carbon diffuses back into the dendrites, leaving

the interdendritic filling higher in phosphorus than the dendrites but lower in carbon content. Also, the quantities of these elements increase toward the upper central part of the ingot so that the last liquid to solidify will contain the largest amount of these elements. Actual dendrites in ferrosilicon are shown in Fig. 224. They were present in a large gas cavity or *blowhole.*

In this dendritic solidification, the impurities are very often entrapped by the dendrites. The formation of a

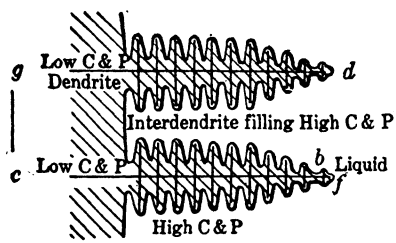


FIG. 223.—Characteristic dendrite formation. (*After H. M. Howe.*)

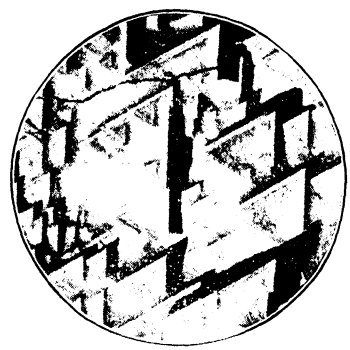


FIG. 224.—Dendrites formed in a blowhole in ferrosilicon.

vast number of small and closely packed dendrites creates small local segregates, thereby favoring their removal by diffusion and by mechanical work. A low pouring temperature followed by rapid solidification creates this condition.

The carbon begins to diffuse immediately after solidification. Two of the characteristics of phosphorus are its tendency to segregate and the persistency of its segregation. Therefore, the phosphorus content between any two dendrites or in the interdendritic filling remains practically the same after passing through the transformation range as after solidification. The sulphur is present as manganese sulphide, provided that sufficient manganese is present. This compound is insoluble in the solid material and, therefore, does not possess the property of diffusion. It is

entrapped by the dendritic branches or is mechanically pushed ahead into the last portions of the solidifying liquid.

The dendrites form at practically right angles to the walls of the ingot mold. The crystals immediately in contact with the mold or the surface crystals that have formed from rapid cooling are termed *chill crystals.* The *columnar crystals* are the long dendrites which may fill up the whole of the ingot if the supply of fluid metal does not fail or if the crystals do not meet any solid obstruction. To form columnar crystals the metal in the ingot must remain liquid for a comparatively long time. In practice, it may happen in relatively small ingots, but in large ingots the center is cooled down to the freezing point before the columnar crystals have grown across the ingot. The solidification of the remaining metal takes place from a large number of independent centers, the result being that the center of the ingot is filled with numerous small crystals of no special shape, the axes of which do not lie in any definite direction in relation to the walls of the ingot mold. These crystals may be termed *free,* or *equiaxed, crystals.*

The structure of a tool that fractured in hardening is shown in Fig. 225. The hardening operation was performed correctly and the chemical analysis was satisfactory. The macrostructure shows clearly the presence of the original ingot structure, which had not been broken down by mechanical work. The presence of such a structure, however, does not necessarily indicate unsatisfactory material, as the failure in this instance was due mainly to the presence of an excessive amount of nonmetallic inclusions. Their presence was revealed on microscopic examination. Figure 226 shows the dendritic structure in a die that failed in service. These two specimens were etched with the Le Chatelier and Dupuy reagent (see p. 247).

It will be noted that dendritic segregation accompanies the formation of dendrites. If complete diffusion of the segregating elements takes place, the dendritic structure

cannot be detected by macro-etching since the dendrites will be chemically homogeneous. If these dendrites are chemically heterogeneous owing to lack of diffusion, especially when it is due to phosphorus, which produces persistent segregation, the resulting structure can be revealed by etching with suitable reagents.

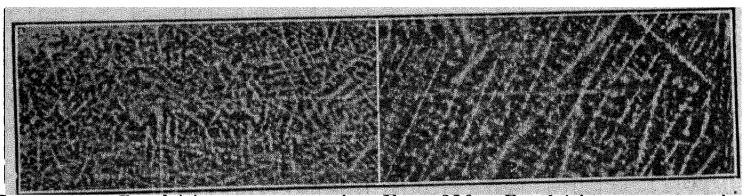


FIG. 225.—Dendritic structure in defective tool. Mag. 2½ ×.

FIG. 226.—Dendritic structure in defective die. Mag. 2½ ×.

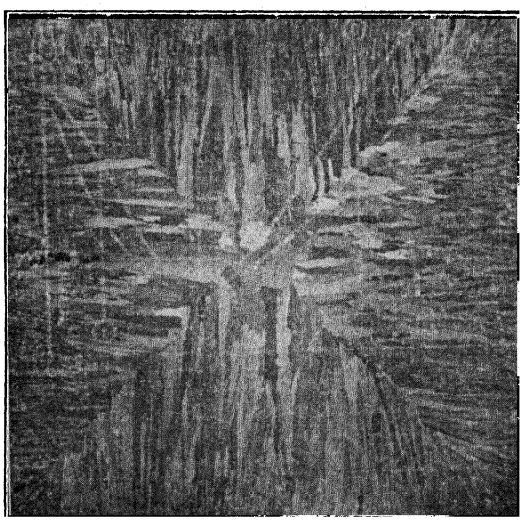


FIG. 227.—Crystallization of hot steel in a square mold. (*Brearly.*)

Careful distinction should be made between the term *dendrites* and *dendritic segregation*. The dendrites are an integral part of the large grains which form on solidification of the liquid material. These macro-grains break down into micro-grains on cooling from the solidus to the thermal critical range. The result is that the dendrites may

disappear but not the dendritic segregation unless the segregating elements have diffused to produce complete homogeneity. Etching with suitable reagents reveals the presence of dendritic segregation and not the original dendrites.

Figure 227 represents the structure obtained when a square mold is filled with very hot liquid steel. Crystals

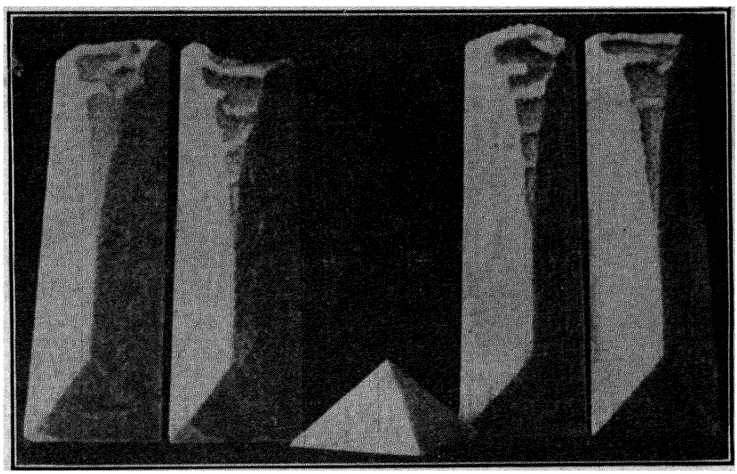


FIG. 228.—Breakdown of a hot-cast wax ingot showing the effects of directional growth. (*Brearly.*)

form which lengthen toward the center because they are free to grow in that direction. Since the only solids interfering with their growth lengthwise are similar crystals growing from adjacent sides of the mold, the cold ingot will consist of four triangular prisms composed of long, needle-like crystals, one face of each prism corresponding to the interior face of the mold against which it formed. The growth of crystals, or dendrites, from the bottom of the mold has proceeded in the same manner so that the four triangular prisms rest each on one face of a four-sided pyramid. If these geometrical components of an ingot cast from very hot steel could be pulled apart, they would appear separately as shown in Fig. 228, which represents

the geometrical components obtained by dissecting a hot-cast wax ingot.

It is evident that in the solidified ingot there are certain definite zones in which there is only moderate cohesion among the crystals of the steel and consequently these positions in the ingot are zones of weakness. The zones in particular are: (1) the junction of each columnar crystal with its neighbors; (2) the junction of each set of columnar crystals; (3) the junctions of the columnar and the free crystals. Cracks may occur between the faces of the geometrical components. The end appearance of a billet in which the cracks have occurred along the planes of intersecting crystals in a hot-cast ingot is shown in Fig. 229. An ingot or casting made from steel that has been poured from a high temperature may crack from the cooling stresses. Also, any tendency to pull while in the mold may produce deep-seated cracks when the metal is heavily rolled or forged.

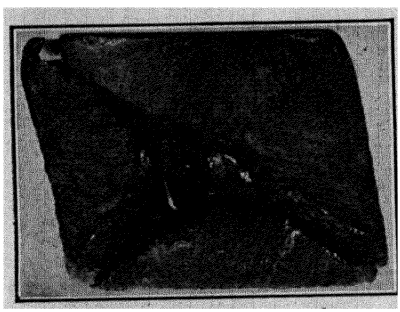


FIG. 229.—Actual failure in a hot-cast ingot. (*Brearly.*)

It is evident from the discussion given above that the depth to which the chill and the columnar crystals extend depends greatly on the casting temperature. If very deep, the ingot or casting will be mechanically weak, and more likely than not the ingot will crack before it becomes a billet or a bar. If these crystals are of barely visible depth, the ingot, if otherwise sound, will be strong and exceptionally resistant to either careless heating or rapid forging. An ingot or casting composed mainly of free crystals has no geometrical components. An important quality precaution, therefore, in the production of good ingots is an efficient control of the casting temperature. Neglect of this leads to fragile ingots that crack on cooling or on

reheating and rolling. Corrugated ingot molds are often used to prevent the formation of weak zones.

It is obvious that a sufficient amount of the ingot to include the shrinkage cavity or pipe must be discarded. Gases are evolved when the steel passes from the liquid to the solid state. These gases bubble through the liquid and escape. If a crust is allowed to form on the top, these gases cannot escape except into the pipe, thereby enlarging it and causing it to extend farther into the ingot.

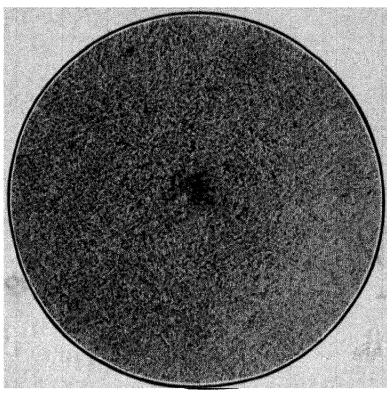


FIG. 230.—Irregular black area is a "pipe" in the center of the bar.

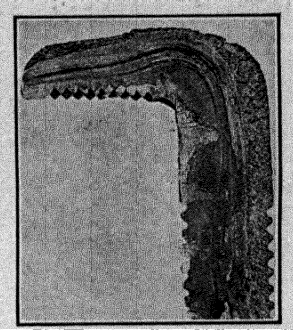


FIG. 231.—Failure of wrench jaw due to a "pipe."

Sometimes it happens that the pipe is not completely removed and gives evidence of its presence in bars or in the fabricated articles. This pipe, upon being exposed to the air while hot, becomes coated with iron oxide, which prevents it from being welded together when mechanically worked. The macrograph in Fig. 230 shows the presence of a pipe in a bar that failed in forging. A wrench jaw that was forged from this bar subsequently broke into two parts. The two parts held together only along the outer edge. The fracture of this article is shown in Fig. 231.

Very often the gases that are formed in the process of solidification become entrapped to form blowholes. Sometimes the formation of blowholes is purposely resorted to

in order to decrease the size and the depth of the pipe. It is claimed by many metallurgists that such a procedure does no harm in cases where the ingots are to receive a great deal of mechanical work. These blowholes contain mainly the reducing gases, carbon monoxide and hydrogen, and become welded when the ingot is rolled or forged.

The use of rusty molds may produce a regular honeycomb effect in an ingot or casting due to the formation of carbon

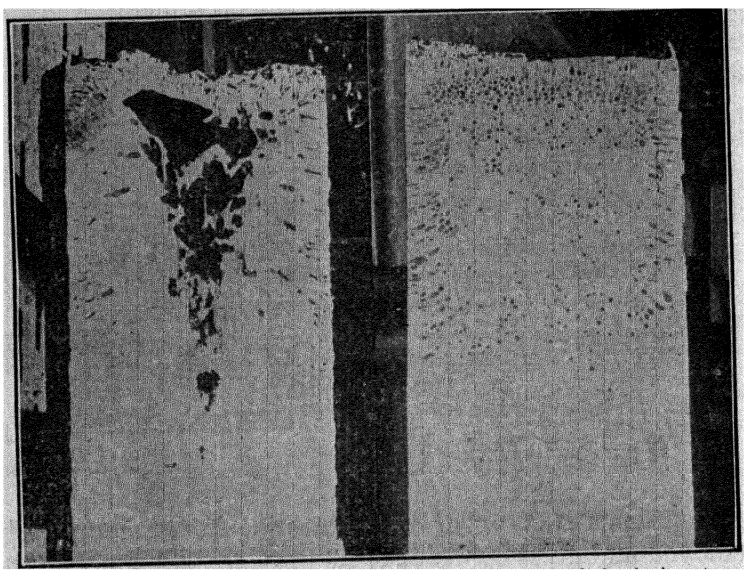


FIG. 232.—Pipe in ingot.

FIG. 233.—Blowholes in ingot.

monoxide and carbon dioxide as the result of the reaction of the carbon in the steel with the iron oxide constituting the rust.

The positions of the pipe and the blowholes in a number of ingots are shown in Figs. 232 to 234. Figure 234 shows an unusually bad structure since the blowholes are externally seated. Scaling of the surface of this ingot may readily expose the blowholes to the air. Subsequent rolling of the hot ingot will not weld these cavities since they have become coated with iron oxide as the result of exposure to air while

hot. These cavities become elongated in the direction of rolling and give rise to *seams*. Figure 235 shows a seam in a steel bar.

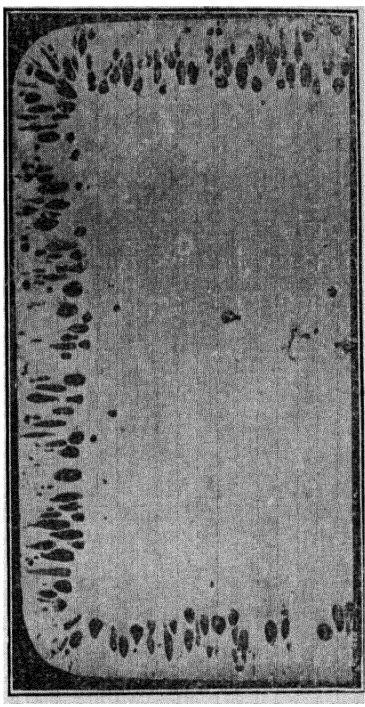


FIG. 234.—External blowholes in ingot. Transverse section.

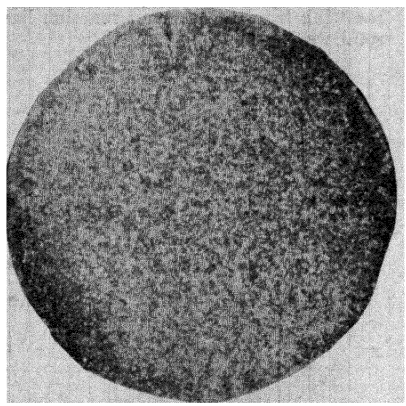


FIG. 235.—Seam (irregular shaped area) in a steel bar.

Tests for Steel Defects.—It has been mentioned previously that the elements in steel that are most likely to segregate are carbon, phosphorus, and sulphur. The reagents commonly used to detect segregation may be classified as follows:

Carbon segregation	Heyn's reagent
	Iodine reagent
	Ammonium persulphate
	Humfrey's reagent
	Rosenhain and Haughton reagent
	Acids
Phosphorus segregation	Same as for carbon
	Stead's reagent
	Canfield's reagent
	Le Chatelier and Dupuy reagent
Sulphur segregation	Same as for carbon
	Sulphur-print method

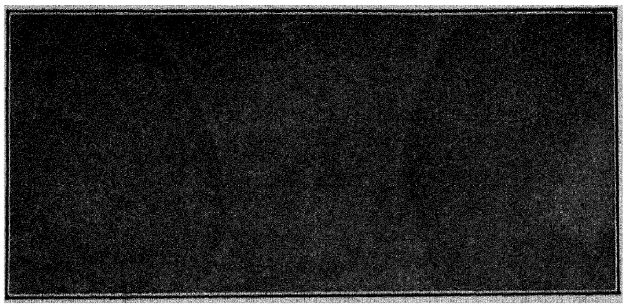


FIG. 236.—Thermit weld (longitudinal section) etched with Heyn's reagent. Center section shows slightly lower carbon content in the weld and that the iron resulting from the thermit reaction has melted the ends of the bars to form a solid weld.

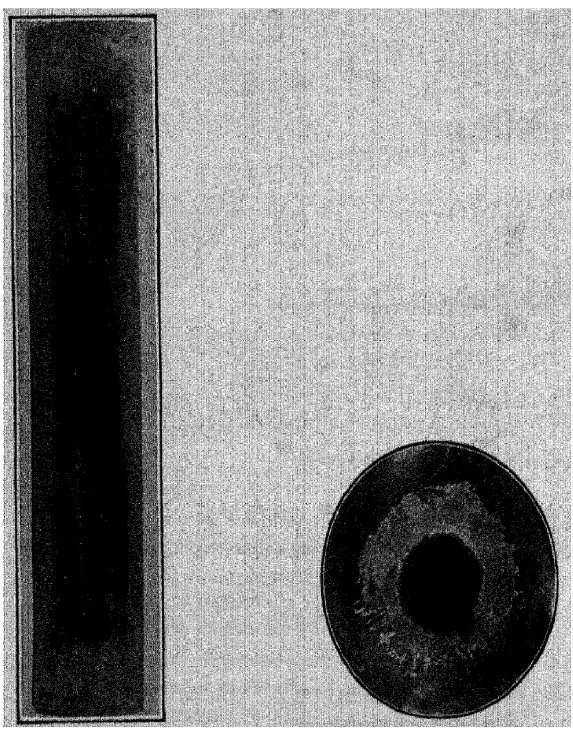


FIG. 237.—Mild steel etched with ammonium persulphate to show segregation. One-fourth size.

FIG. 238.—Phosphorus segregation in a defective shaft. Lighter area is phosphorus rich.

Figure 236 is a photograph of a thermit weld, etched with Heyn's reagent. The contrast in etch between the low-carbon and the higher carbon areas is shown. This macrograph shows, furthermore, that the molten iron that was produced as the result of the thermit reaction has melted

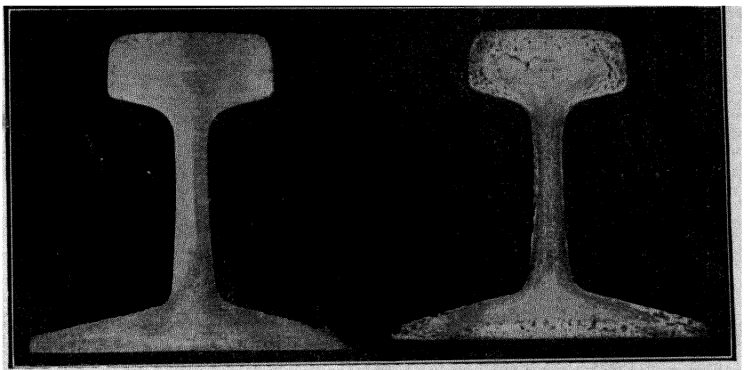


FIG. 239.—Macrograph of good rail.

FIG. 240.—Segregations in rail.

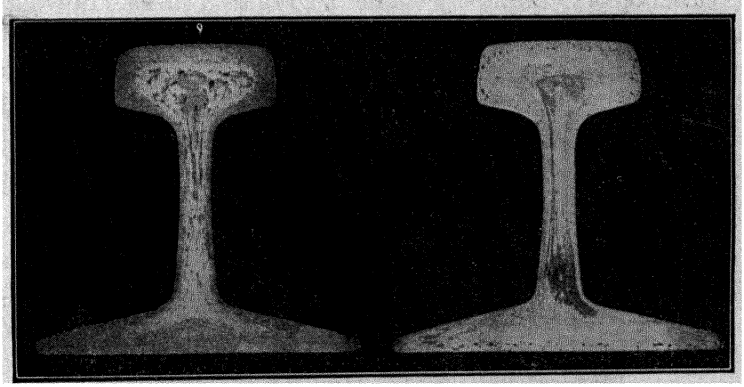


FIG. 241.—Phosphorus-rich areas light in head and web.

FIG. 242.—Carbon segregation in head and web.

the ends of the two bars being welded to form the indicated junction.

Ammonium persulphate has been highly recommended by Rawdon of the Bureau of Standards. This recommendation is well deserved, as the solution is easy to prepare and to apply and gives excellent results (see Fig. 237).

The macrograph in Fig. 238 is that of a section of a steel shaft that failed in service. The specimen was etched with the iodine reagent. A spiral crack, which developed at the segregated ring, extended the entire length of the shafting. Drillings from the center and from the outside edge showed

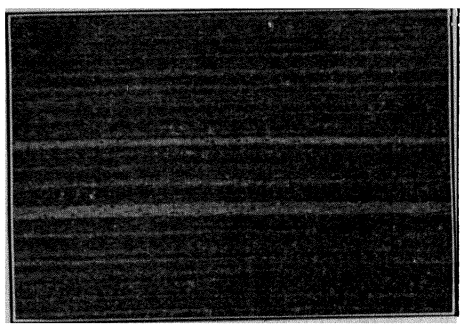


FIG. 243.—Phosphorus-rich streaks (ghost lines) in rolled steel.

a satisfactory analysis. The segregated area, however, analyzed 0.23 per cent phosphorus. Sections of steel rails serve as excellent specimens for macroscopic study (Figs. 239 to 242). The macrograph of the first rail section indicates satisfactory material. Phosphorus-segregated areas are denoted by the light etching, while carbon and sulphur segregations are denoted by the dark areas.

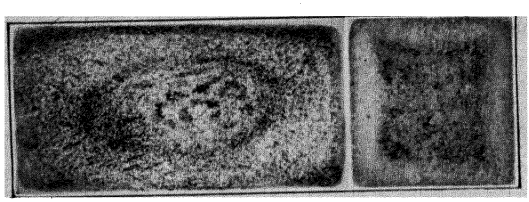


FIG. 244. FIG. 245.

FIGS. 244 and 245.—Reproduced from direct-contact "sulphur prints," showing sulphide segregates (dark).

Stead's reagent gives excellent results when used for the detection of phosphorus segregation. It has, however, the disadvantage that the specimen must be well polished. The macrograph in Fig. 243 shows streaks or *ghost lines*,

indicative of phosphorus segregation, in a longitudinal section.

The detection of sulphur segregation is best determined by the sulphur-print method (p. 244). Figures 244 and 245 show clearly the dark sulphide areas.

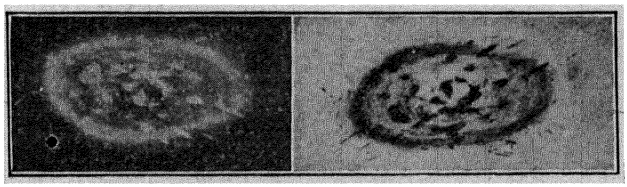


FIG. 246. FIG. 247.

FIG. 246.—Phosphorus segregation shown by Canfield's reagent. Light areas are phosphorus rich.

FIG. 247.—Phosphorus segregation shown by Humfrey's reagent. Dark areas are phosphorus rich.

Canfield has proposed a reagent for detecting phosphorus segregation (p. 248). Figure 246 shows the results obtained with this reagent. Figure 247 is the same specimen (phosphorus segregation) etched with Humfrey's reagent.

The reagent developed by Le Chatelier and Dupuy is supposed to indicate the segregation of oxygen as oxide. This reagent has been found to indicate phosphorus segregation in the same manner as Stead's reagent. Figure 248 shows streaks that supposedly indicate oxide but probably indicate phosphorus segregation instead. This reagent is excellent to show dendritic segregation but will not give satisfactory results when the specimen is in the hardened condition. Both Stead's reagent and that of Le Chatelier and Dupuy require the presence of free ferrite to give results. The iodine reagent, however, will indicate the dendritic segregation when it is present in a hardened piece of steel.

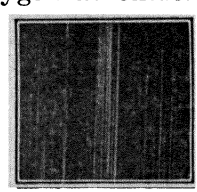


FIG. 248.—Possible oxide streaks.

Directional Properties of Steel.—It has previously been mentioned that the dendrites produced when steel solidifies are formed at right angles to the walls of the mold. These

dendrites or the resulting micro-grains, together with the dendritic segregation, become elongated and are made parallel in the rolling and forging operations to produce the so-called *fiber* in steel. The appearance of this fiber may be shown by the etching of the longitudinal sections of steel

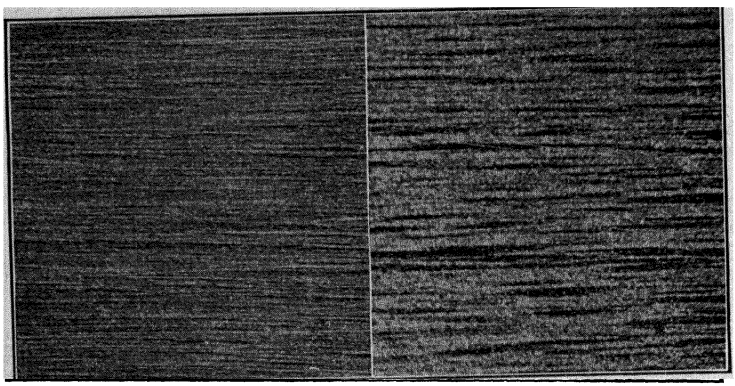


FIG. 249.—Macrograph of steel bar showing fine fibers.

FIG. 250.—Macrograph of steel bar showing coarse fibers.

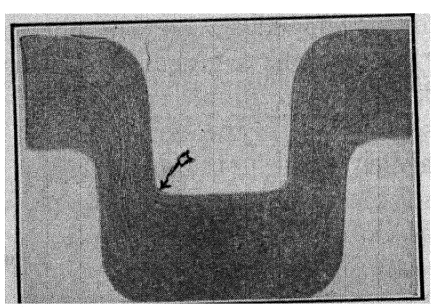


FIG. 251.—Forged crankshaft showing "snaky" fiber.

bars. Macrographs 249 and 250 show this fibrous character in steel bars that have been etched with the Le Chatelier and Dupuy reagent. Note the much finer structure in Fig. 249 than in Fig. 250.

A study of fiber in steel is of great importance, particularly in the manufacture of such articles as crankshafts, gears, and other forgings. A crankshaft, for example, may

be fabricated so as to cause the fiber to produce a snaky grain, *i.e.*, the fiber follows the direction of forging, or it

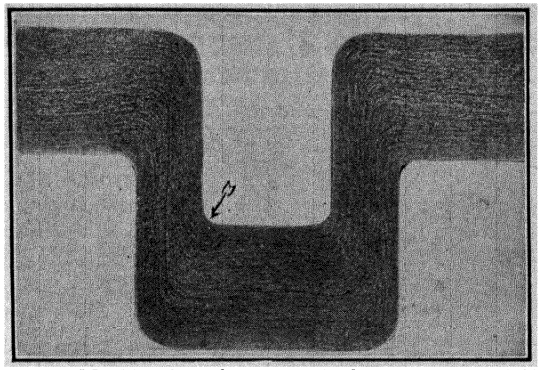


FIG. 252.—Machine-forged crankshaft showing "snaky" fiber.

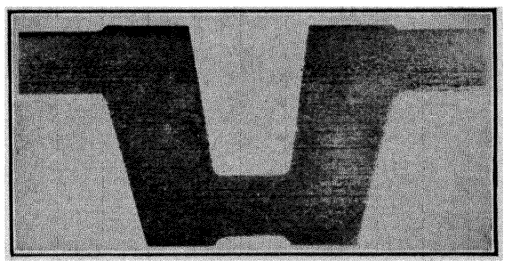


FIG. 253.—Bad condition of fiber in a shaft machined from bar stock.

may be roughly cut out and then machined to the desired shape, in which case the fiber will produce a straight-grained structure. Figure 251 shows a crankshaft that has been properly made in which the snaky grain is present.

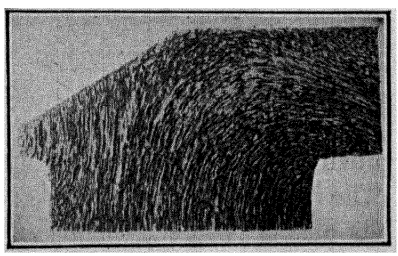


FIG. 254.—Section of crankshaft etched with H_2SO_4 to show fiber.

Figure 252 shows a machine-forged crankshaft, which also has this structure. Figure 253 shows a crankshaft that has been improperly made. A crankshaft that has been made in such a manner that the applied stress will be

perpendicular to the direction of the fiber will have far greater shock-resisting properties than one that has been made so that the applied stress will be parallel to the direction of the fiber. A normal fracture in a crankshaft takes place at the point indicated by the arrow in Fig. 251. Figure 253 shows unsatisfactory distribution of the fiber in a shaft machined from bar stock. Humfrey's reagent was used to etch these specimens.

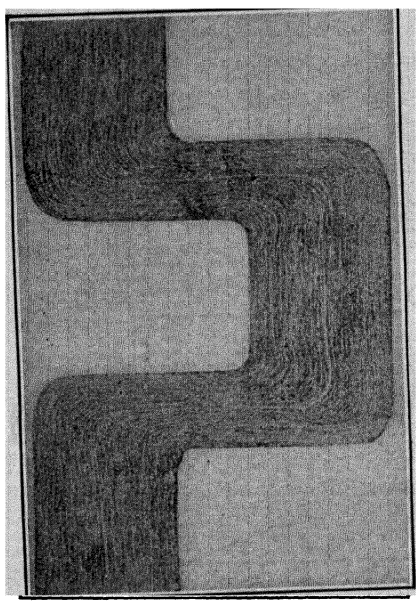


FIG. 255.—Reduced from direct ink print of forged crankshaft.

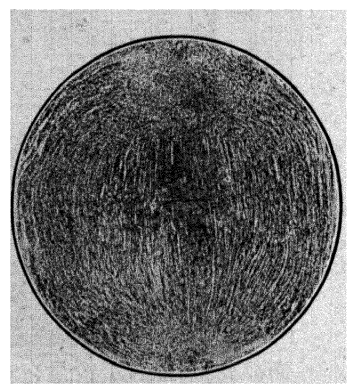


FIG. 256.—Reduced from printer's ink contact print of forged bar.

Contact Printing.—Instead of photographing deeply etched specimens, a reproduction of the details may be made by contact printing. A small amount of printer's ink should be placed on a glass plate and a squeegee roller should then be passed back and forth a number of times until the ink has been uniformly distributed over the roller. The ink is then transferred to the specimen. The specimen should be pressed firmly against a sheet of thick white paper, whereby the details of the etched surface will be reproduced. Figures 255 and 256 are macro-prints that were prepared in this manner.

Methods of Gear Manufacture.—In milling cutters and in gear blanks, the grain may be disposed in three ways,

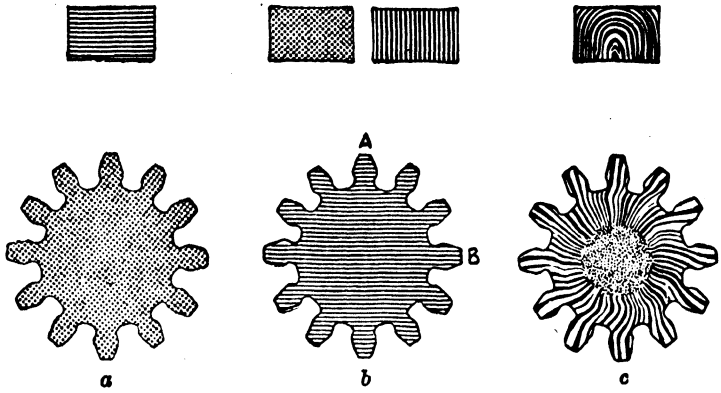


FIG. 257.—Three methods of forging gear blanks. (*Brearly.*)

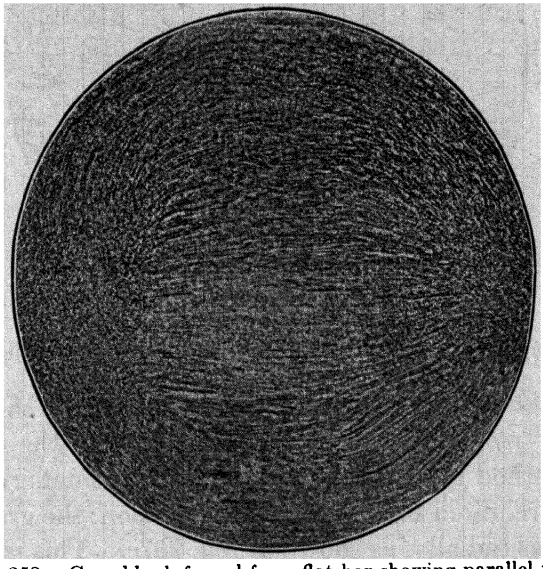


FIG. 258.—Gear blank forged from flat bar showing parallel fibers.

according to the manufacturing process used. The simplest method is to make the blank from a section cut off from the steel bar. In this instance, the gear blank will have the

direction of the fiber, as indicated in Fig. 257*a*. It is readily apparent that this direction is unfavorable for a gear that is to have maximum shock-resisting properties. Figure 257*b* illustrates the flat-bar method, in which the blow of the hammer is perpendicular to the direction of the fiber. A tooth at the position *A* has the fiber parallel to the pitch line and to the direction of the applied stress; this tooth will be greatly inferior in its shock-resisting

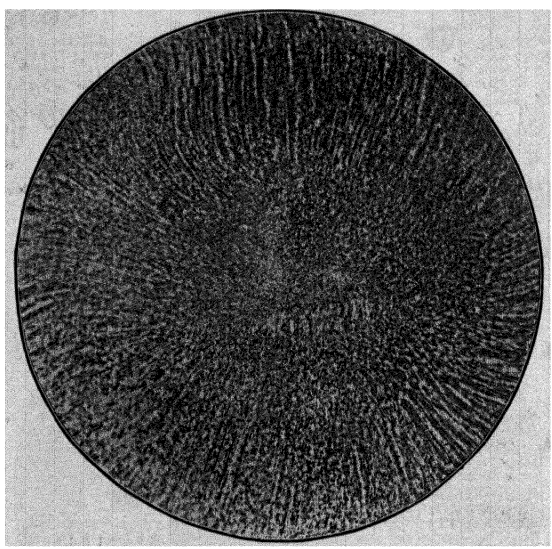


FIG. 259.—Gear blank forged from up-ended bar showing radial fibers.

properties to tooth *B*, where the direction of the applied stress is perpendicular to the direction of the fiber. A third method is to up-end a bar of much smaller diameter into the required blank. In this operation, the grain of the steel flows radially, as shown in Fig. 257*c*. This is the ideal method for making gear blanks or milling cutters, since the direction of the fiber in every tooth is such as to be most favorably disposed toward the working stresses; therefore such a gear or milling cutter will have maximum shock-resisting properties. Figures 258 and 259 show the direc-

tion of the fiber in gear blanks forged by the flat-bar and by the up-end methods, respectively.

The importance of the proper direction of fiber in tools, etc., particularly those which have to withstand shock, cannot be overemphasized. The effort required to break a

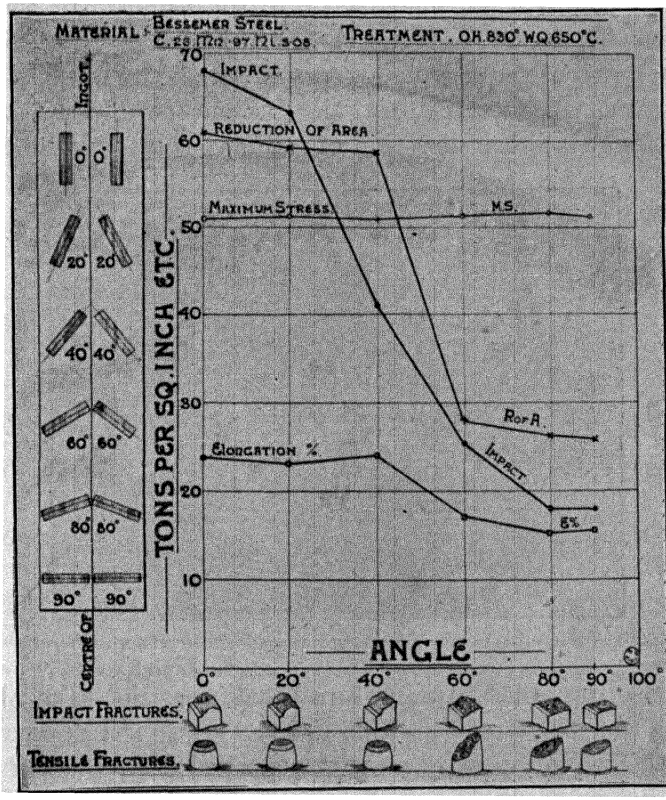


FIG. 260.—Influence of slag lines and fiber in relation to the direction of stress. (*Brearly.*)

notched bar across the grain may be from five to ten times as great as the effort required to break the bar along the grain.

Brearly obtained a quantitative idea of the influence exerted by the direction of the fiber on the mechanical properties of steel by rolling an ingot directly into a slab.

This slab was cut longitudinally down the center and duplicate test bars were cut parallel to the direction of rolling and also at varying inclinations up to and including one at right angles to the direction of rolling. The test bars were each oil hardened at 830°C. and tempered at 630°C. before being machined into the usual form of test piece. The test results are shown in Fig. 260. The maximum stress of the material is seen in this figure to be nearly constant, whether the test piece is cut parallel to or at right angles to the direction of rolling. This is invariably

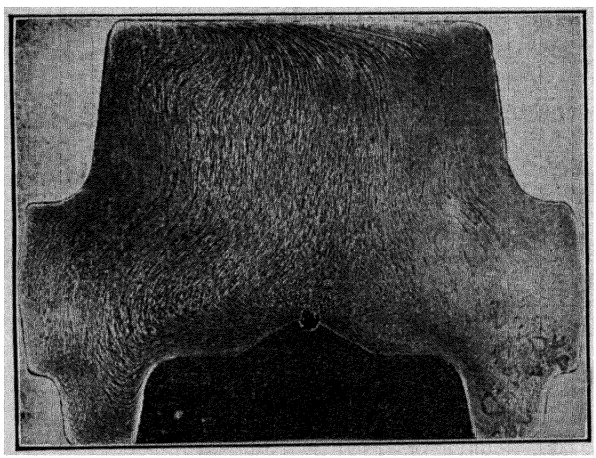


FIG. 261.—Direction of fiber in a forging as shown by Humfrey's reagent.

the case, provided a premature break does not take place owing to a slag streak or other defect. Both the elongation and the reduction of area show a marked decline when the fiber lies at an angle exceeding 40 degrees to the direction of the applied stress. The impact figure is greatly influenced by the direction of the fiber.

Figure 261 shows the direction of the fiber in a forging that has been etched with Humfrey's reagent.

One of the most common expressions used in accounting for fractures in crankshafts and similar articles is that the failure is due to the "crystallization" of the steel. This

erroneous idea undoubtedly originates from the appearance of the fracture, known as a *detail fracture* or a *fatigue failure*, although a better term would be *progressive failure*, produced as the result of alternations of stresses, in which part of the fracture appears more or less smooth and the remainder granular or crystalline. The steel, to begin with, is crystalline. If a piece of steel is subjected to a single stress, it will fulfill its requirements indefinitely, provided that a certain limit is not exceeded. This stress may be either tension, compression, or torsion. If, however, the material is subjected to stresses of similar values of compression and tension but repeatedly alternated, the article may ultimately fail. An example to illustrate this point is shown in Fig. 262. This specimen represents a section of a 2-inch shafting that was subjected to alternations of tension and compression in which the cycle was repeated thousands of times. A small crack started from the base of a V-thread and gradually penetrated into the shafting. Gradually, the usefulness of the cross section of the shafting decreased, until finally a point was reached at which so much of its usefulness had been destroyed that what remained as sound material was unable to withstand the final load applied. This part of the section, the lower part in Fig. 262, broke suddenly. The part of the shafting that appears smooth, owing to the constant rubbing of the fractured surfaces, the upper part in Fig. 262, represents the part of the section that failed gradually or progressively, while the granular part represents the sudden fracture. A microscopic examination showed the same structure over the entire cross section. The prevalent idea that steel "crystallizes" when subjected to alternations of stresses should be dismissed.

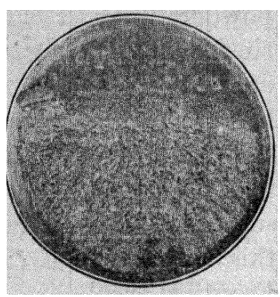


FIG. 262.—Detailed or progressive fracture showing the upper part worn smooth. The lower part shows the effect of a sudden break.

The list of etching reagents (p. 247) contains the formulas of the important macroscopic etching reagents. To this list should be added Fry's reagent, which has been used to bring out strain lines in mild steel. The formula and the method of using as advocated by Fry are as follows:

Concentrated hydrochloric acid.....	120 cubic centimeters
Water.....	100 cubic centimeters
Copper chloride (crystallized).....	90 grams

The specimen is first heated at 200°C. and is then rubbed with a cloth moistened with the solution and dipped in powdered copper chloride. The specimen is dried without rinsing in water, washed in alcohol, and again dried. The etched pattern consists of dark and light bands. These lines have been obtained only in mild steel and not on all mild steel with the same distinctness. The authors have used this solution according to directions but with little success. Jevons[1] has obtained excellent results by using this reagent with certain modifications in manipulation. From his results, it would appear that, by subjecting suitably prepared specimens to a preliminary low-temperature annealing, followed by a prolonged etching, strain-etch figures may be produced on many, but not all, steels. Beyond the fact that a fairly low-carbon content is apparently essential, no connection has as yet been shown between the chemical composition of steels and their ability to strain etch. Provided that permanent deformation has occurred, the actual degree of distortion has but little influence on the quality of the markings. Figure 263 shows strain lines on the fractured surface of a broach made from high-speed steel, improperly hardened and carelessly ground. It is an unusual case, as this specimen was not etched.

Macro-etching with Acids.—The macro-etching of steels with acids is frequently used in industry to reveal the structure for visual inspection. The most commonly used

[1] *Journal of the Iron and Steel Institute*, No. 1, 1925.

solution is one containing equal volumes of hydrochloric acid (sp. gr. 1.20) and water. A temperature of 70°C. is recommended.[1] A vigorous reaction takes place at this temperature without excessive evaporation of the solution. A mixture of 40 parts by volume of hydrochloric acid, 10 parts of sulphuric acid, and 50 parts of water may be used also to give satisfactory results. The time of etching

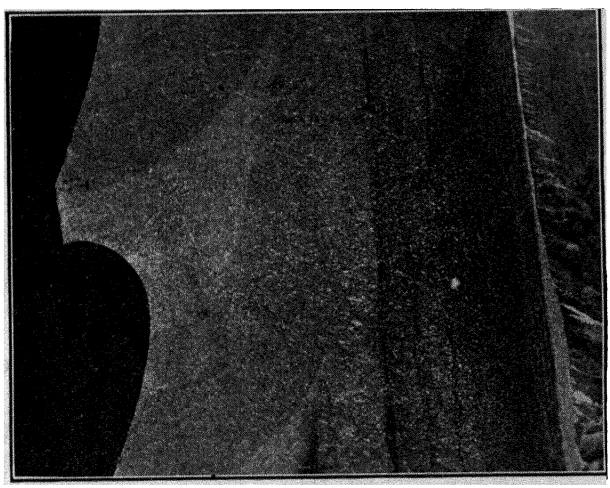


FIG. 263.—Strain lines (lighter V-shaped areas) on an improperly treated broach. Not etched.

depends on the type of steel and should be determined in order that all of the details will be revealed without the general destruction of the surface that will take place on prolonged exposure to the hot solution.

Unfinished or coarsely finished surfaces can be etched for the detection of surface defects such as seams, laps, grinding checks, etc. A machined surface is commonly used although a ground or polished surface free from toolmarks is to be preferred for etching to reveal the general structure. After etching, the specimen is washed and freed from the

[1] "Recommended Practice for a Standard Macro-Etch Test for Routine Inspection of Iron and Steel Metals Handbook, 1939 ed., p. 730.

dark deposit by scrubbing with a stiff brush, after which it is dried.

Figures 264 and 265 show the effects of the macro-etch on steel specimens representing two different lots of steel.

Macro-etching with acids can also be used to reveal grinding checks that are not visible unless subjected to such

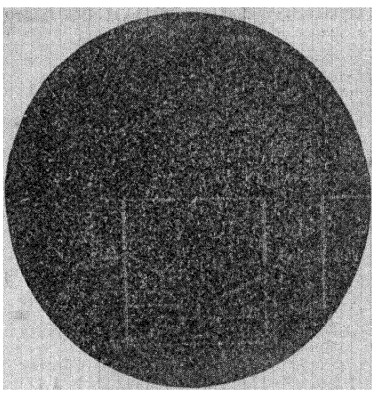


FIG. 264.—Steel of satisfactory quality. Etched with 50 per cent of hydrochloric acid. Three-fourths size.

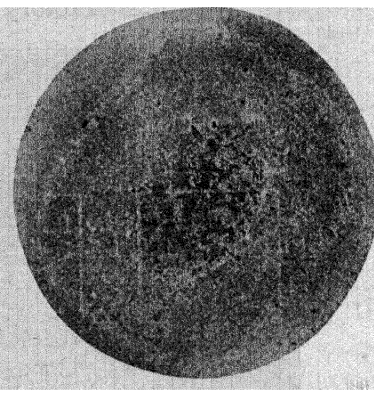
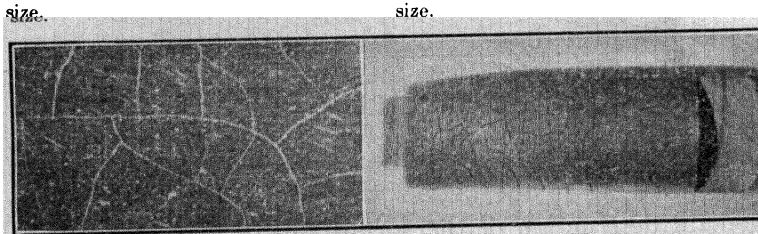


FIG. 265.—Steel of unsatisfactory quality. Etched with 50 per cent of hydrochloric acid. Three-fourths size.



a *b*

FIGS. 266*a* and *b*.—Grinding checks shown by acid etch.

action. Figure 266*b* shows grinding checks in a chuck jaw as shown after etching with a hot solution of 50 per cent hydrochloric acid. These grinding checks were due to the grinding of material that had been hardened but not tempered. The localized heating produced in grinding is sufficient in many cases to add additional stresses to material that is already in a highly stressed condition as the result of hardening, and thus produces grinding checks. The

careless grinding of properly heat-treated material may also produce these checks. This grinding may be faulty as the result of the use of grinding wheels that are too hard for the purpose or that are glazed, or because of the attempt to remove too much stock at one time. The faulty grinding of material that has been improperly hardened and tempered so that hardening stresses are present in the material may cause grinding cracks.

Detection of Cracks.—The roughly polished specimen is magnetized and then immersed in a light oil containing

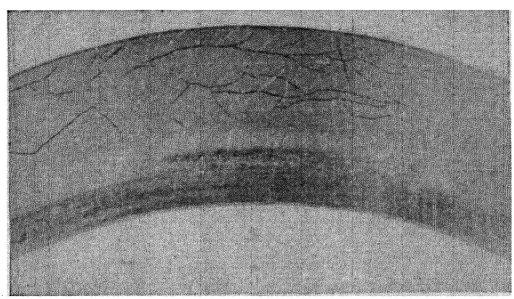


FIG. 267.—Quenching cracks in ball race revealed by Magnaflux method. (*De Forest.*)

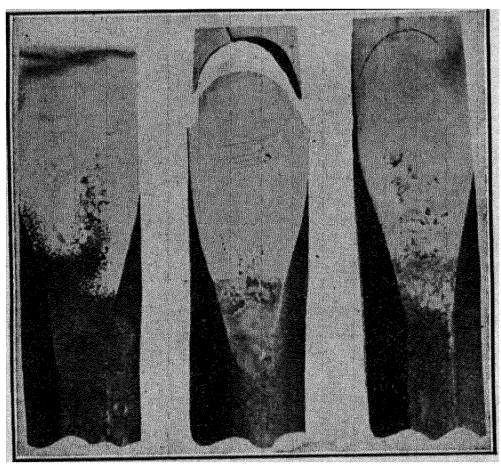
iron dust in suspension. Kerosene and cast-iron mud, such as is obtained from lapping disks, may be used. The iron particles bridge any slight discontinuity in the surface of the specimen and indicate accurately the system of surface cracks. The excess of iron rust must be removed by bathing the specimen in alcohol or clean kerosene.

The same method is used industrially and is known as the "Magnaflux" method.[1] The part is magnetized and then dusted with a special iron powder or covered with a suspension of the powder in a liquid such as carbon tetrachloride. When the part is tapped or shaken, the powder falls off unless a crack or a seam is present. Where such defects are present, they will be outlined by the powder and are made plainly visible. The appearance of a ball race

[1] See p. 293.

possessing quenching cracks is shown in Fig. 267. No cracks were visible before the treatment.

Sulphur Printing.—Printing paper having a matte finish is soaked in a 2 per cent solution of sulphuric acid, and then placed on a glass plate. The steel specimen is gently pressed upon the paper and then removed after about 30 seconds. The print is washed in water and fixed in acid hypo in the usual way. Sulphide areas are indicated by brown spots (see Figs. 244 and 245).



a *b* *c*

FIG. 268.—The chisel at the left is satisfactory. The two at the right show "thumb-nail" cracks. (*Nicholds.*)

Many types of failures, other than those just described, have been found in steel. Some of these are shown in Figs. 268 to 273. Figure 268 illustrates thumb-nail cracking, which may be caused by: (1) free cementite; (2) severe cold forging; (3) drastic hardening. *a* shows the sound forging while *b* and *c* illustrate the defects. Figures 269 and 270 show the connection between mechanical condition and hardening. Figure 269 is the photograph of one of a series of pieces, all of which cracked on hardening, the crack passing through, and probably originating in, the deeply stamped base of the numeral "1." Figure 270 shows

hardening cracks starting at the sharp corners of an incorrectly designed spline shaft. Figure 271 shows a magnet that has been strained in hardening and then cracked by the

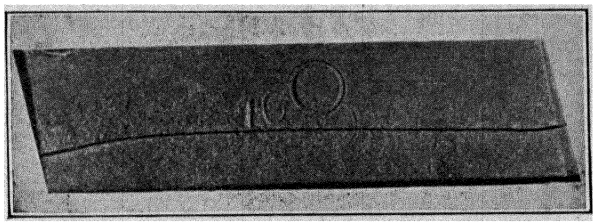


FIG. 269.—Hardening crack starting in the base of the numeral 1.

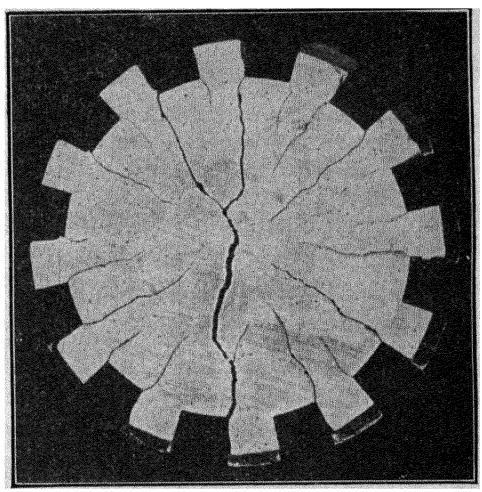


FIG. 270.—Hardening cracks starting at sharp corners.

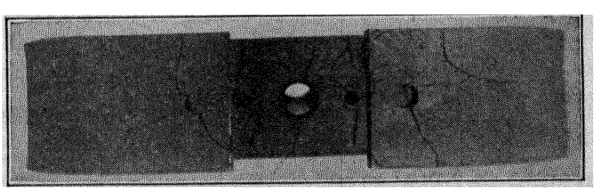


FIG. 271.—Magnet steel cracked by acid pickling after hardening. (*Nicholds.*)

pickling operation. Figure 272 illustrates the *fish-scale* type of fracture. This was found in a high-speed tool that had been hardened and later rehardened without an inter-

mediate annealing. Figure 273 is the macrograph of a broken die of high-carbon steel. The failure in this case was due to the separation of free carbon in the form of temper carbon.

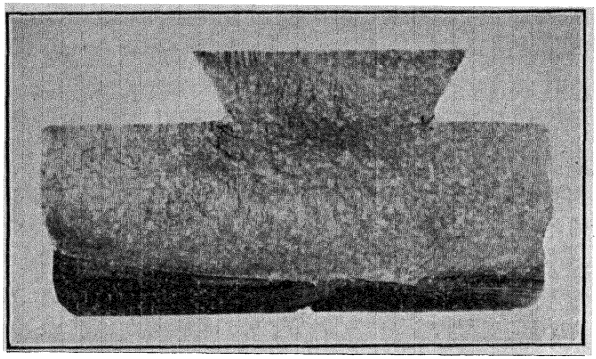


FIG. 272.—"Fish-scale" fracture in a high-speed steel, hardened twice without intermediate annealing.

The macroscopic examination of steel in the hands of an experienced metallographer is of the utmost value, but in this field of investigation, more than in almost any other, carelessness in manipulation and misinterpretation of surface appearances may lead to wholly incorrect conclusions.

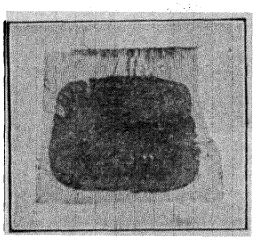


FIG. 273.—Fracture due to formation of graphitic temper carbon (black center).

The deep acid etching of hardened steel is not recommended since it often shows cracks after etching that were not present in the original material. The test, therefore, should be applied whenever possible to the unhardened steel in order that the results obtained will not be misinterpreted.

Preparation of Specimens.—As previously stated, specimens should be polished with No. 00 or No. 000 emery paper in most cases. A machined or ground surface is satisfactory for macro-etching with acids. A well-polished surface, such as for microscopic examination, is preferred

whenever Stead's reagent or that of Le Chatelier and Dupuy is used. It has been found advantageous to etch the specimen deeply with a 10 per cent solution of ammonium persulphate after polishing with 1G paper and then to pass directly to No. 000 paper before etching with the final reagent. All the specimens that were etched with Humfrey's reagent were prepared in this manner. This procedure is convenient in the case of large specimens.

In photographing deeply etched specimens, apply printer's ink to fill all of the hollows and then polish the reliefs with No. 000 emery paper. Excellent contrast will thus be obtained. Other specimens should receive a thin film of a light machine oil or glycerin before they are photographed.

MACROSCOPIC ETCHING REAGENTS

STEAD'S REAGENT

Cupric chloride	10 grams
Magnesium chloride	40 grams
Concentrated hydrochloric acid	20 cubic centimeters
Alcohol, sufficient to make	1000 cubic centimeters

Dissolve salts in smallest possible quantity of hot water (about 25 cubic centimeters), then add the acid and the alcohol.

Cover the specimen with a thin layer of the reagent. Shake off the layer of liquid after it has acted for about 1 minute and replace it with a fresh portion of the acid mixture. Repeat the operation until the desired results have been obtained; then wash first with hot water and, finally, with alcohol. Copper will deposit first on the phosphorus-free areas, so that the light areas represent phosphorus segregation. The specimen should be well polished. If the deposit becomes discolored, it may be brightened by rubbing briskly with a dry swab of cotton.

LE CHATELIER AND DUPUY REAGENT

Cupric chloride	1.0 gram
Picric acid	0.5 gram
Water	10.0 cubic centimeters
Concentrated hydrochloric acid	1 to 2 cubic centimeters
Alcohol	100.00 cubic centimeters

Use in same manner as Stead's reagent. Copper will deposit on the oxide-free or phosphorus-free areas first.

CANFIELD'S REAGENT

Nickel nitrate	5.0 grams
Cupric chloride	1.5 grams
Ferric chloride	6.0 grams
Hot water	12.0 cubic centimeters
Methyl alcohol	150.0 cubic centimeters
Nitric acid	1.0 cubic centimeter

Dissolve salts in the hot water, add acid and then the alcohol.

Cover the specimen with the solution and allow to remain until the desired effects have been obtained. White areas represent phosphorus segregation.

A record of the result may be obtained by soaking a developing paper (matte finish) in a 5 per cent solution of potassium ferricyanide in water, laying it face up on a piece of blotting paper, and then pressing the surface of the plated specimen against it, leaving it there for about a minute. The paper is then rinsed, fixed, and washed as usual. The areas that were not plated represent phosphorus segregation and will be recorded blue.

HEYN'S REAGENT

Copper-ammonium chloride	10 grams
Water	100 cubic centimeters

Immerse the roughly polished specimen in the solution, polished surface up. Care must be taken that the solution quickly covers the surface. Gently agitate the liquid. A coating of spongy copper forms over the face of the specimen. Remove this coating with a swab of wet cotton. High carbon, sulphur, and phosphorus areas will be darkened as a result of the etching.

HUMFREY'S REAGENT

Copper-ammonium chloride	100 grams
Concentrated hydrochloric acid	50 cubic centimeters
Water	1000 cubic centimeters

Polish specimen with No. 00 or No. 000 emery paper. Cover the specimen or immerse it in the neutral solution (Heyn's reagent) until a spongy deposit of copper has been obtained. Without removing this copper deposit, pour on Humfrey's reagent. Add fresh portions from time to time. If Humfrey's reagent is used directly without the preliminary treatment with Heyn's reagent, a copper coating will be obtained that adheres firmly to the specimen and produces unsatisfactory results.

Additional information concerning etching solutions for macroscopic examination is given in the appendix.

CHAPTER VII

LABORATORY METHODS[1]

In the study of alloys and in the construction of their diagrams, one of the most important factors to consider is the succession of heat changes that take place when the molten material passes into the completely solid state. In a few instances, notably in the cooling of steel, changes of great importance take place below the point of solidification of the alloy so that it is necessary in special instances to follow the cooling to very low temperatures. A study of these thermal changes necessarily involves three factors: (1) a method of melting the mixed metals; (2) a container in which the metals can be melted; and (3) an apparatus for measuring temperatures, especially temperature changes.

In order to study the heat changes that take place in alloys with low melting points, a convenient form of apparatus consists of a tube for holding the mixture of the metals in the form of chips, clippings, or drillings, a sand bath for insuring uniform and gradual heating of the tube, a suitable source of heat, and a thermometer (suitable for alloys with low melting temperatures), or a thermocouple in conjunction with a millivoltmeter or potentiometer.

The material and the shape of the container for the mixture of metals depend on the temperature at which the alloys melt, the properties of the melted alloys, and the shape of the furnace. For alloys with a low melting point (less than 700°C.), hard-glass tubes are useful, as the filling of the tube and the adjusting of the temperature-measuring

[1] See KEHL, G. L., "The Principles of Metallographic Laboratory Practice" McGraw-Hill Book Co., Inc., and VILLELA, J. R., "Metallographic Technique for Steel," American Society of Metals.

instrument can be watched. Tubes of porcelain or fused quartz are needed for alloys that melt above the softening point of glass. Thin-walled tubes of unglazed porcelain may be used for almost all metals. In a few instances, where the metal forms an oxide that is highly reactive chemically (*e.g.*, chromium oxide or manganese oxide), it may be necessary to use the much more fragile magnesia tubes. Fortunately, this expedient is seldom necessary.

A convenient size of container for the sand may be made from a steel tube about 5 inches long and from 2½ to 4 inches in diameter. This container can be made quite readily by threading one end of a short piece of steel pipe and screwing on a cap. The open end is fastened to a triangle of heavy iron or chromel wire so that the tube may be suspended over a burner by means of a ring and stand. The source of heat may be one or more Tirrel or Meker burners or, for very high temperatures, a blast lamp. Different types of furnaces may also be used for heating the sand containers.

The metals of which the alloy is to be made are weighed in the desired proportions and are generally mixed before they are introduced into the tube. In exceptional cases, it may be necessary to melt the less volatile component first, adding the more volatile metal in successive small amounts. The weight of material is determined by the accuracy desired in the final results. As a laboratory experiment or for a preliminary survey of the field to determine the general shape of the equilibrium diagram, 20 to 30 grams of the mixture will be sufficient. It must be emphasized, however, that, where great accuracy is required and where slight heat changes are to be detected, the amount of material must be greatly increased, often up to 400 or 500 grams. Since the metals used should be of great purity and are therefore expensive, it is seldom desirable to experiment with such large amounts of material.

There is sometimes a marked tendency for molten metals to separate into layers, especially if they differ considerably in specific gravities, and mix with difficulty or not at all. In such cases, the liquid mixture must be stirred during the course of the experiment. This can usually be done by means of a glass or porcelain rod having a circular bend at the bottom through which the thermometer or other temperature-measuring device can pass. This rod is moved slowly up and down during the cooling of the molten alloy.

It is necessary in all cases to protect the metals during the melting and during the solidification from the oxidizing effect of the air. In some instances this may be done by covering the surface with powdered charcoal, but it is usually more effective to melt the metals in an inert gas. Hydrogen, carbon dioxide, nitrogen, and argon have been used for this purpose. The gas passes from the generator or container into the melting tube through the bent glass or porcelain tubing. As a safety measure, if hydrogen is used, it is best to pass the gas through a small drying tube containing a number of disks of wire gauze. The gauze will cool the gas so that the danger of igniting the hydrogen in the generator or storage tank is eliminated.

The oxidizing effects are slight with the low-melting metals protected in this manner, so that it may be assumed that the composition of the resulting alloy is the same as the composition of the mixture from which it was made. This is not the case with easily oxidizable metals with high melting points, even under the most favorable conditions, so that the final composition of the alloy should be determined by chemical analysis.

Weight and Atomic Percentages.—In all industrial alloy work, and for most laboratory purposes, the metals are mixed according to their percentages by weight of the total amount of material used. It has been shown that some metals form intermetallic compounds. In this case a system based on the atomic relationships is more con-

venient. For example, a compound of tin and magnesium containing 70.95 per cent tin by *weight* is known. This percentage composition gives no indication of the relation of the atoms in the compound. If, now, the composition is indicated in *atomic per cent*, it will be found to be 33.33 atomic per cent tin and 66.66 atomic per cent magnesium, showing at once that the formula is $SnMg_2$. The following expression shows the method of converting weight percentage into atomic percentage:

A = atomic weight of first metal
B = atomic weight of second metal
p = weight percentage of A
q = weight percentage of B

Then

$$\text{Atomic per cent of } A = \frac{100p}{p + q\frac{A}{B}}$$

and

$$\text{Atomic per cent of } B = \frac{100q\frac{A}{B}}{p + q\frac{A}{B}}$$

Measurement of Temperature Changes.—A mercury thermometer will serve for the measurement of temperature changes in alloys melting at low temperatures, such as those of sodium, potassium, or the amalgams. Almost all alloy work, however, requires higher temperatures than can be determined in this manner, and some form of pyrometer is required. Many pyrometers of different kinds are available. One of these instruments will be considered as it illustrates the general method of use, and the principle may be applied with slight variation to any of the other pyrometers.

If two wires of dissimilar metals are joined at one end, and if this junction is put into a furnace while the other

ends (cold junction) are connected to a sensitive voltmeter or ammeter, the instrument will show that the temperature difference is causing an electric current to flow in the metallic circuit. The two wires form what is termed a *thermocouple.* The cold ends of the thermocouple, called the *cold junction,* are usually connected by flexible leads to the indicator. The circuit should be so arranged as to give a reading on the indicator that will show the electromotive force as a function of the temperature of the *hot junction* only. Since the indicator is dependent on the electromotive forces at both the hot and the cold ends of the couple and since the forces at these points depend on the temperatures of the two junctions, the temperature of the cold junction must also be taken into account in the final reading. Two wires, one of which is copper and the other a copper-nickel alloy (constantan), may be used for measuring low temperatures to 500°C. Iron-constantan is used for slightly higher temperatures to 950°C. A thermocouple made of two alloys, aluminum-nickel (alumel) and chromium-nickel (chromel), may be used for still higher temperatures to 1000°C., while for temperatures up to 1650°C. a rare-metal couple, one wire of which is platinum, the other an alloy of platinum and rhodium or platinum with iridium, is required. The two wires forming the couple must be insulated from each other by a protective tube of glass, quartz, porcelain, or other refractory material. This may be done also by wrapping one wire with asbestos thread or by encasing it in short lengths of capillary tubing of quartz or porcelain.

The recording instrument gives, either directly or indirectly, the temperature difference between the hot and the cold junctions of the thermocouple. The cold ends may be inserted in a jar where they are kept either at constant temperature or at some convenient temperature which may be determined from time to time and which will not vary more than a few degrees during the experiment. A con-

venient arrangement is to pass these wires through a stopper into a vacuum bottle. If ice is kept in the container during the experiment, no correction for the temperature of the cold junction is necessary. Otherwise, a correction must be made.

The instrument on which the temperatures are read is either a millivoltmeter or a potentiometer. Most of the millivoltmeters recommended for temperature work of this character are provided with two scales, one of which reads millivolts, and the other temperatures directly, either as degrees Centigrade or Fahrenheit. The temperature scale may be used with only a single pair of metals. Even then the reading varies somewhat with continued use of the thermocouple, so that, except for commercial work, the millivolt scale is almost always used in spite of the obvious advantages of a direct temperature reading.

Calibration is necessary in order to establish the relationship between the millivoltage as read and the temperature to which it corresponds. This can be done most simply by determining the millivoltages corresponding to the melting points of a series of pure substances and then constructing a plot, using the known temperatures as ordinates and the corresponding instrument readings as abscissas. The following list of pure substances with melting or boiling points is given for convenience, but any materials having definite melting points at suitable intervals may be used.

Pure Substances		Degrees Centigrade
Water	b.p.	100.0
Tin	m.p.	231.9
Sulphur	b.p.	444.5
Antimony	m.p.	630.5
Silver	m.p.	960.5
Copper	m.p.	1084.0

In locating the freezing points of the substances used in the calibration, it is convenient to follow the same procedure that is followed later in studying alloys themselves.

The pure substance, tin, for example, is heated until it is completely melted. The source of heat is then removed, and the molten material is allowed to cool slowly. Temperature, or millivoltage, readings are now taken at definite time intervals. If the temperature is high and is falling rapidly, intervals of 5 seconds are allowed between each consecutive reading of the millivoltmeter scale. When the cooling rate is normal (about 5 to 10° per minute), an interval of 10 seconds between readings will show any material changes in the cooling rate. At low temperatures, when the difference in temperature between the alloy and its surroundings is small, the cooling will be so slow that a much less frequent reading of the instrument is required. The frequency of readings is a question of judgment, but 10 seconds between readings may be taken as a reasonable interval. If the millivoltages are now plotted as ordinates and the time intervals as abscissas, a curve will be obtained showing a horizontal break at that millivoltage corresponding to the freezing point of the material in question. This horizontal line, which indicates not only the temperature of solidification but also the time taken for the material to solidify, varies in length with the amount of material used and with its latent heat of solidification. The constancy of this interval under the same conditions makes its determination of great value in making the alloy diagrams.

Various types of millivoltmeters are in use, some direct reading, some of the mirror type in which the deflection is magnified by reflecting a beam of light on a scale at some distance from the instrument, and still others of the recording type. Whichever instrument is used, the general method of study consists in establishing a connection between the temperature changes and the intervals of time during which these changes occur. Instead of using a millivoltmeter as a temperature-measuring instrument, a potentiometer may be used. This instrument measures the millivoltage without permitting any electric current to

flow in the line or in the thermocouple. This is done by balancing or opposing the electromotive force of the thermocouple with part of the electromotive force of a small battery, usually a dry cell. One of the disadvantages of the millivoltmeter is that a new calibration is required whenever the resistance of the leads and of the thermocouple changes. Such a condition does not exist with a potentiometer. Furthermore, automatic cold-junction compensation is usually provided in the case of the latter instrument.

Having considered the various factors involved in the study of the temperature changes taking place when an alloy is cooled, it may be helpful to summarize these factors in a brief description of an actual melting operation. The metals X and Y are weighed, preferably in a finely divided condition, such weights of the metals being taken as will produce an alloy of the required composition and in such amounts that the total weight will be 20 to 30 grams. This mixture is then placed in the container, which is embedded in the sand in the furnace tube. The stirring rod, the gas intake tube, and the thermocouple protector tube pass through a cork stopper or a suitably perforated brass cap. The insulated wires pass to a constant-temperature bottle (omitted when a potentiometer is used) and then, by copper leads, to a millivoltmeter or a potentiometer. Heat is applied to the sand bath and the metals are melted, after which the thermocouple tube and the stirring rod are introduced. The heat is then shut off and the instrument is read at definite time intervals until all the heat changes have taken place and the solid alloy is cooling at a uniform rate. The readings are carefully recorded. In the study of a binary (two-component) alloy, this operation is repeated with a series of metal mixtures of varying compositions. If the nature of the equilibrium curve is wholly unknown, mixtures are generally taken which vary in composition by 10 per cent

intervals from one pure metal to the other. The points representing the beginning and the final solidification of these alloys, with those representing the freezing points of the pure metals, will usually indicate the general shape of the equilibrium diagram. The necessary number of additional mixtures can be selected for study in the vicinity of the more essential points such as eutectics, intermetallic compounds, or other characteristic features suggested by the preliminary survey. In simple cases, a very few additional mixtures will give all of the necessary information, while in the more complex alloys 40 or 50 points are sometimes necessary to establish the diagram.

Plotting the Cooling Curves.—Various methods of plotting the experimental results are in use. Of these methods, the simple *time-temperature* curve is used more frequently than any other, although the *inverse-rate* curve has decided advantages when the heat effects are small. In this latter method, the ordinates represent the temperatures as in the simple cooling curve, but the abscissas represent the reciprocal of the rate of cooling, *i.e.*, the time necessary for the temperature to fall through a definite small interval, for example, 5 to 10°.

The detection of the critical points in steel, where only a small amount of heat is evolved or absorbed, requires a method in which the rate of heating or cooling is not affected by outside influences. In cooling, for example, the temperature of the metal at the critical point will be affected by the cooling of the furnace and by the evolution of heat at this point. The cooling in the furnace will tend to decrease the magnitude of the critical point while the evolution of heat will tend to increase it. If the former predominates, there will be a tendency to mask the critical point.

The use of a neutral body in conjunction with the material under test is resorted to in order to eliminate these objectionable influences. A double thermocouple is

used, one for each metal and so connected as to record the difference in temperature between the two. This temperature will be the same at all points except at the critical points, provided that the two materials have the same heat capacities and emissivities. Since the neutral body invariably differs from the test specimen with respect to these properties, a temperature difference will always be present between the two and the critical point will be indicated by abrupt temperature differences. The curves obtained

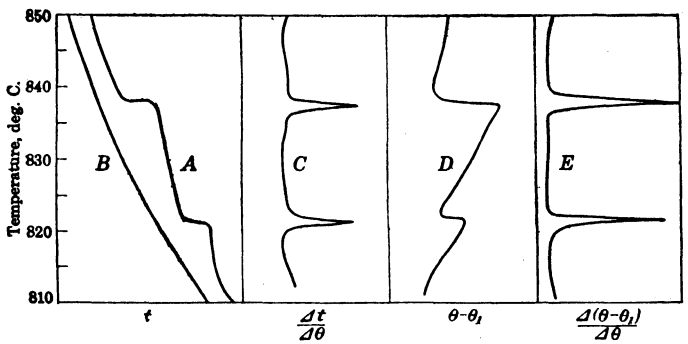


FIG. 274.—Different types of cooling curves. (*Desch.*)

will reveal the existence of even faint absorptions or evolutions of heat.

The neutral body should be free from transformations within the temperature range covered by the experiment. Nickel, austenitic manganese steel, or 25 per cent nickel steel may be used as the neutral body.

Figure 274 shows the different types of cooling curves. The time intervals are represented by t, the corresponding temperatures by θ, and the temperature difference between the test specimen and the neutral body by $\theta - \theta_1$. The curve B in the *temperature-time* curve represents the cooling of the neutral body. In the *derived-differential* curve successive falls of temperature are plotted as ordinates and

the corresponding rates of cooling for each degree of temperature as the abscissas.

Constructing the Diagram.—After plotting the individual cooling curves, a sheet of coordinate paper of suitable size is selected, and, using percentage compositions as abscissas and temperature arrests on the cooling curves as ordinates, a diagram is constructed as indicated in Chapter I. The relative lengths of any horizontal lines that may be found in the set of temperature-time cooling curves are next determined. These *time lines* are also plotted as an independent but closely associated part of the diagram.

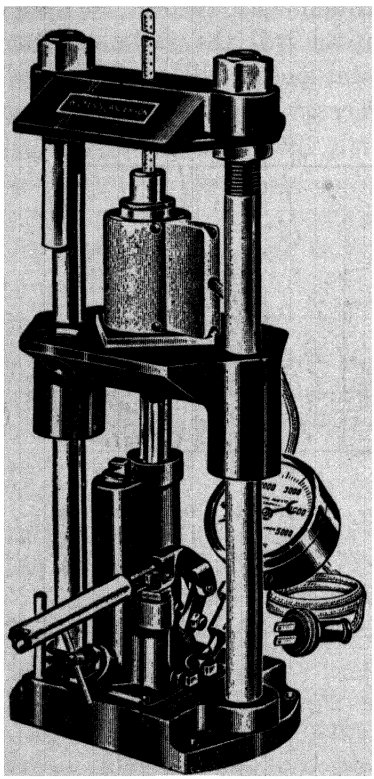


FIG. 275.—Bakelite mounting press.

Preparation and Microscopic Examination of the Polished Alloys.—The proper preparation of a specimen for microscopic examination necessitates the production of a flat surface free from scratches.

The selection of a representative sample is of paramount importance. Obviously, the sample should be characteristic of the material that is to be examined. Where a material has failed in service, it is important that a sample be taken near the failure and another at some distance from it for comparison. A convenient size is one about ½ to 1 inch square or round and ½ inch long.

Specimens may be obtained by cutting them off with a hack saw or power hack saw. Materials that are too hard

to be sectioned in this manner may be cut with an emery or a carborundum disk or fractured with a hammer.

Considerable difficulty is experienced in the polishing of small irregularly shaped specimens. A press to make possible the ready mounting of such specimens in bakelite, together with the technique of the subsequent polishing and etching, has been described by Krause[1] and Oesterle. Bakelite is an ideal mounting medium for specimens that are not affected by pressure or heat up to 140°C. Figure 275 shows a press[2] suggested by Oesterle for mounting specimens in bakelite. It gives excellent results. Figure 276 shows several mounted samples.

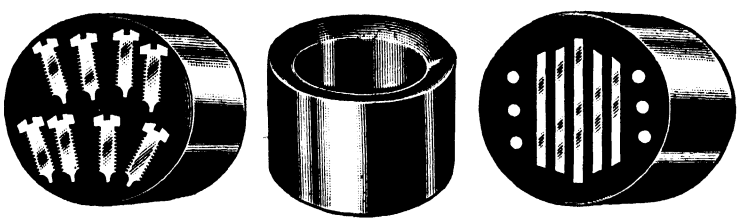


FIG. 276.—Specimens mounted in bakelite.

Lucas[3] has described the microtome method of sectioning for the preparation of soft metals for microscopic examination.

A longitudinal section is often preferred to a transverse one, especially when a study is to be made of the general quality of the material and of the effects of mechanical work. Both transverse and longitudinal sections should be examined in most cases.

Sections of wire and sheet metal may be conveniently mounted in bakelite, lucite, or tenite, as mentioned above, or in a fusible alloy of low melting point, such as Woods or

[1] KRAUSE and OESTERLE, "Press and Technique for Mounting Small Specimens," *Metal Progress*, **24** (1933).

[2] Manufactured by Adolph I. Buehler, Chicago, Ill.

[3] LUCAS, F. F., "Microtome Methods for Preparation of Soft Metals for Microscopic Examination," *Proceedings of the Institute of Metals Division, A.I.M.E.*, 1927.

Rose metal, by pouring the molten alloy around the section properly placed in a mold, a round metal tube, a malleable iron cap, or some other suitable receptable. The use of fusible metals is objectionable because of smearing. Pinch cocks that are provided with two screws such as are used by chemists are convenient for holding thin sections in position for polishing. A method that is frequently used is to clamp the specimen between two parallel steel plates about 2 inches long, ¾ inch wide, and ¼ inch thick, which are bolted together at the two ends. Tight contact can be made by

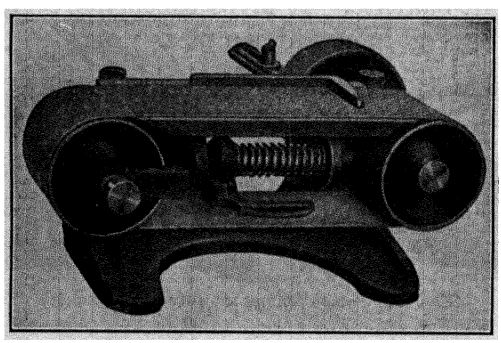


FIG. 277.—Belt grinder for rough grinding. (*Leitz.*)

inserting copper strips between the plates and the specimen. Hardened plates should be used in polishing hard specimens. The specimen is ground and polished even with the steel plates. In every case, the aim should be to prevent rounding of the edges of the specimens. A great deal of time is saved if the specimen is kept as small as possible, though still representative of the material to be examined.

The grinding may be done on two wheels, a medium wheel and a fine one. The specimen is then further polished by the use of emery paper. Endless emery belts supported on a machine shown in Fig. 277 are very convenient. The manufacturers supply belts of varying degrees of fineness for this purpose. This operation is followed by the use of suitable emery paper of grades Nos. 1, 0, 00 and 000,

respectively.[1] The use of one or more of these papers may be omitted, depending on the fineness of the final belts used and on the character of the specimens. In each step of the polishing operation, the specimen should be held in such a manner that the new polishing scratches will be at right angles to those produced in the previous operation. The polishing should be continued until all of the previous scratches have been eliminated.

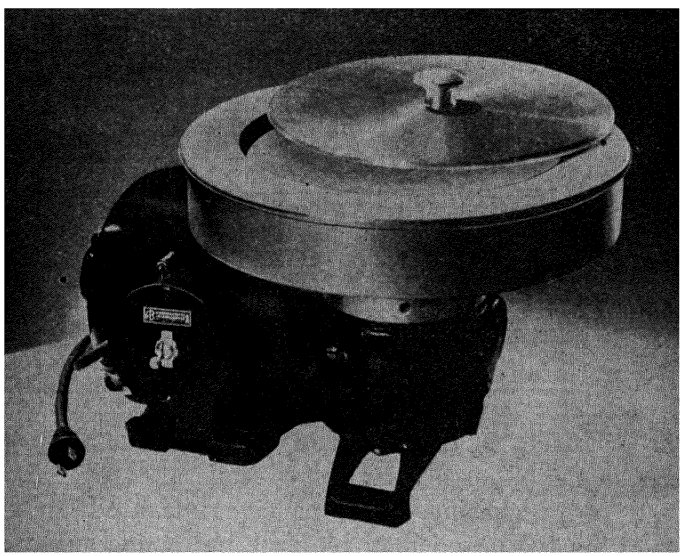


FIG. 278. Individual-motor-driven polishing wheel, single-speed type. (*Courtesy of Adolph Buehler.*)

Proper care in the rough polishing will save much time in the fine polishing. The specimen, in every case, should be cleaned by wiping or washing before passing from one polishing operation to the other.

Hand polishing may be used in the final stages by applying the suspensions of the abrasives to the polishing cloths, which have been stretched over wooden blocks. Mechanical polishing, however, is almost universally used. The types of polishing machines that are most commonly used

[1] These are the number designations used by Behr-Manning, Troy, N. Y.

have polishing disks that revolve either vertically or horizontally. A machine of the horizontal type is shown in Fig. 278. Automatic polishing machines are also available. The speed should be adjustable since a slow speed is preferred whenever soft metals or alloys are to be polished.

The first disk is covered with 12-ounce duck; while broadcloth and chiffon velvet or kitten's ear cloth are used on subsequent disks. If three disks are used, the order of the polishing cloths is 12-ounce duck, broadcloth, and finally chiffon velvet or other suitable material.

A suspension of No. 500 or No. 600 carborundum or alundum in water is used on the canvas. A suspension of the coarse alumina that is separated from the fine particles in the preparation of the final suspension may be used on the second disk, which is covered with broadcloth. A suspension of carborundum No. 600 may be used instead. A suspension of levigated alumina or rouge, preferably the former, is used on the final disk, and the specimen is held lightly until all of the remaining scratches have been removed. The specimen may be moved from the center to the periphery of the disk and then back, or it may be rotated in the opposite direction to that taken by the disk. Instead of purchasing the expensive levigated alumina, a less expensive brand may be used and a fine suspension obtained by shaking with water, allowing to stand 1 hour, and then siphoning off the fine suspension. The addition of a small quantity of soap to this suspension may serve as an aid in the polishing operation. It serves as a lubricant and holds the fine particles in suspension. The alumina, which settles to the bottom of the bottle before the siphoning of the fine suspension, may be shaken with water and siphoned off after allowing it to stand for a short time; this may be used on the disk preceding the one used in the final operation. The specimen, as well as the hands of the operator, should be thoroughly washed after each

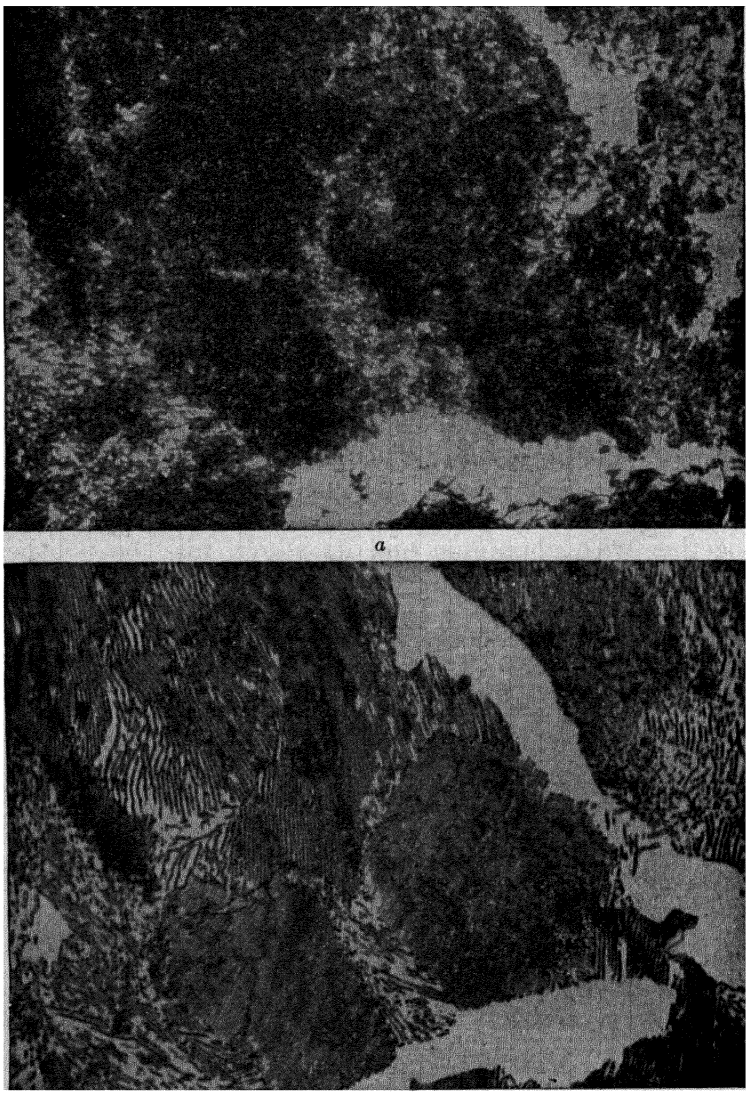
polishing operation in order that none of the abrasive may be transferred to the subsequent disk.

Specimens that are difficult to polish may be properly finished, etched, repolished with a very light suspension of alumina, and finally re-etched. Superficial scratches may be removed in this manner.

The proper polishing of a specimen cannot be overemphasized, since polishing pits may be erroneously interpreted as inclusions. Fig. 279*a* shows polishing pits, while Fig. 279*b* shows this same surface after it has been properly polished. Complete absence of disturbed metal on the etched surface must be obtained in order to reveal the true structure of the material. This is clearly shown in Fig. 279*b*.

Specimens to be photographed at high magnifications, together with aluminum and its alloys, may be polished according to the following method:

The specimen may be rendered plane by rubbing down on an oil stone. A solution of paraffin in benzol or a light oil should be poured onto the emery papers before using. The specimen should be freed from oil by means of xyloi or other suitable solvent. The specimen is then transferred to the polishing disks, the final polishing being done with magnesia free from carbonate on a cloth known as kitten's ear. Chiffon velvet may be used also but it is not so satisfactory. The magnesia should be dusted onto the cloth and then made pasty by the addition of distilled water. The paste is thinned by the gradual addition of distilled water during the polishing. The use of a finger in preparing the paste will give evidence as to the presence or absence of gritty particles which should be removed at this stage if present. Too great a speed of the disk should not be used. The polishing cloth should be freed finally from the abrasive by washing first with water and then with a dilute solution of hydrochloric acid to remove the magnesia so as to prevent



a

b

FIG. 279.—Effect of disturbed metal on appearance of coarse pearlite. Mag. 1000 ×.

a. Polished surface covered with layer of disturbed metal; structures like this were formerly called "sorbite" or "troosto-sorbite."

b. Same field after removing layer of disturbed metal by alternate polishing and etching; structure is unmistakably lamellar pearlite. (*Vilella.*)

the formation of magnesium carbonate. The cloth should be placed in a jar or wide-mouthed bottle containing distilled water, to which has been added a small amount of acid, until it is to be used again. Only the best quality magnesium oxide should be used, together with distilled water, since the presence of magnesium carbonate will give unsatisfactory polishing results. An intermediate polishing with alumina on broadcloth between No. 000 emery paper and the final operation is sometimes sufficient.

Vilella[1] recommends the use of canvas or billiard cloth saturated with paraffin, onto which the abrasive is applied. The billiard-cloth-paraffin laps are preferable for use with 600-mesh abrasive, while 12-ounce canvas impregnated with paraffin is recommended for coarser abrasives. The final polishing is done with levigated alumina on silk (hard, low-nap fabric). Fig. 280 shows the effect of the manner of polishing on the results obtained. The preparation of cast-iron specimens has been outlined also by Vilella.[2] The procedure is to polish in the usual manner up to No. 000 emery paper. This paper is smeared with soapstone on graphite before using. The wet polishing is done on the silk side of a heavy satin cloth, using alumina or magnesium oxide. Prevention of the dislodgment of the graphite flakes in cast iron is accomplished by this polishing procedure.

The specimen should be thoroughly washed after the final polish and then dried with either a soft cloth or lens paper or, preferably, by means of an air blast after washing with alcohol. The polished and dried surface should not be touched with the fingers.

The observer should acquire the habit of always examining the unetched specimen with the microscope. Nonmetallic inclusions, graphite in cast iron, temper carbon

[1] VILELLA, J. R., "Metallographic Technique for Steel," American Society for Metals.

[2] VILELLA, J. R., *Metals and Alloys*, **3** (1932).

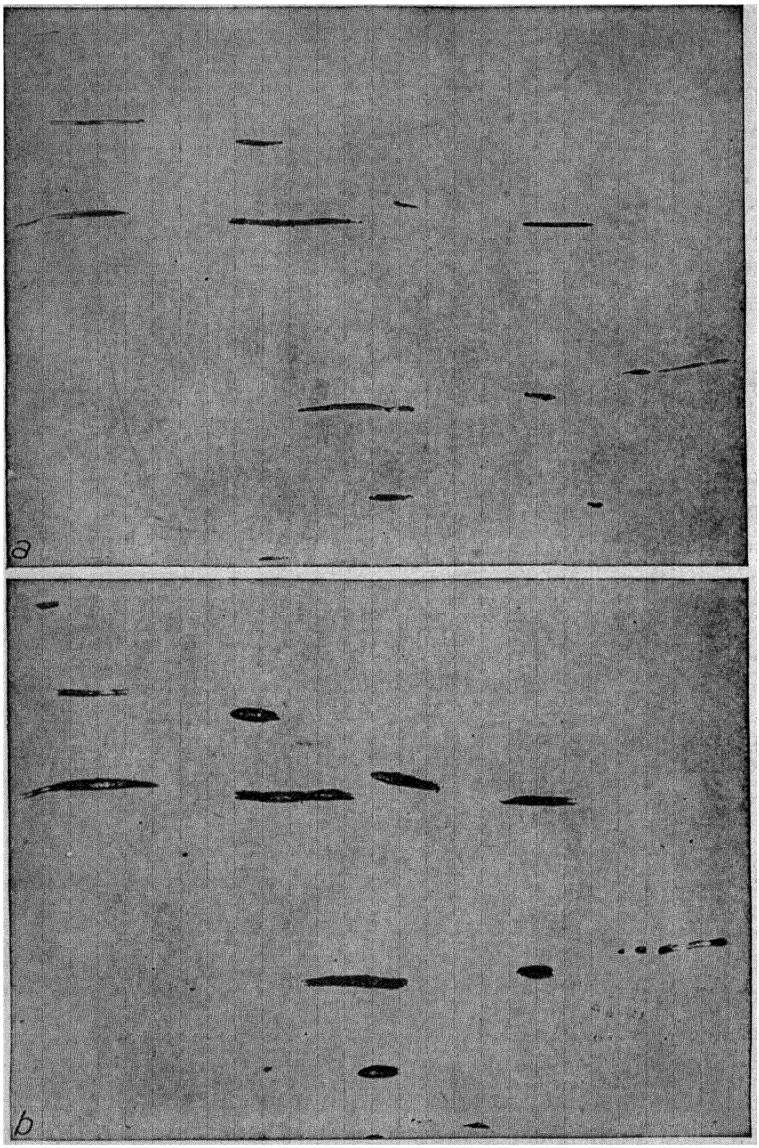


FIG. 280.—Preservation of inclusions. (*a*) Inclusions preserved intact by correct polishing. Rough polished on cloth-paraffin lap and finished on silk. Note gray color of inclusions. (*b*) Same field rough polished on plain cloth with 600 alundum and finished on broadcloth. Note enlarged pits. Mag. 150 ×. (*Vilella.*)

in malleable cast iron, besides flaws and cracks, may be detected before etching.

The structure of the metallic matrix is generally shown by etching the polished surface. Etching solutions are used which attack some of the constituents to a greater extent than others or leave some constituents unattacked. Relief polishing may cause the hard constituents to stand in relief so that the structure of the polished surface may be examined without etching. The hard constituents in Babbitt may be revealed in this manner, although etching will produce greater contrast between the matrix and the hard particles.

Electrolytic etching is performed by passing a weak electric current through a suitable electrolyte in which the specimen to be etched is made the anode and a piece of platinum, aluminum, or other suitable metal is made the cathode. The electrolytes used may be weak acids, weak alkalis, ammonium molybdate, sodium thiosulphate, etc. Adcock[1] has described this method of etching in considerable detail.

Heat tinting is the method used for producing temper colors on the polished surfaces of specimens by heating them in air until the surfaces are oxidized. The carefully cleaned specimen may be heated on molten tin at about 300°C. In this manner, phosphorus-rich areas in steel were studied by Stead. These areas became blue in color, whereas the remainder of the surface was colored a reddish brown. It is of great importance that the surface of the specimen should be carefully cleaned before heat tinting. Iron carbide in white cast iron colors deeper than iron phosphide. Cu_3P may be distinguished from Cu_4Sn in bronze as the phosphide becomes blue, whereas the Cu_4Sn becomes yellow on heat tinting.

The list of the etching reagents for the microscopic examination of both nonferrous and ferrous alloys as tabu-

[1] ADCOCK, *J. Inst. Metals*, **26** (1921), 361.

lated by the American Society of Metals is given in the appendix. The reagents that have been found most satisfactory for etching the various materials described in this book are given in conjunction with the photomicrographs.

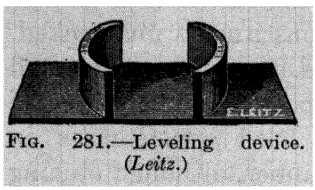
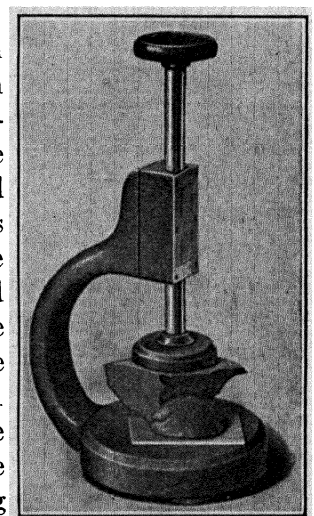


FIG. 281.—Leveling device. (*Leitz.*)

The specimens after etching should be carefully dried before examination. This may be accomplished by washing the specimen with hot water and then immersing in alcohol and finally drying by holding the specimen in front of an air blast or by wiping with a piece of linen, absorbent cotton, or lens paper. Immersion in absolute alcohol before drying is desirable for specimens that stain readily

A specimen to be examined microscopically must be mounted in a plane that is accurately perpendicular to the optical axis of the microscope. This is accomplished by placing the specimen on a mass of plasticine on a microscope slide or a similar slide made of brass and then making the surface of the specimen plane by means of the leveling devices shown in Figs. 281 and 282. In Fig. 281, a glass slide is used to force the specimen into the plasticine contained in the brass ring until the polished surface is in the same plane as the top of the ring.


FIG. 282.—Leveling press. (*Leitz.*)

Metallurgical microscopes[1] for the examination of opaque specimens differ from those used for the examination of transparent objects in that the stage is movable and a vertical illuminator holding either a plane glass reflector

[1] Much of this discussion of the optics of metallography has been prepared by W. Zieler (E. Leitz, Inc.).

or a prism is placed at the lower part of the tube and just above the objective.

In illuminators with a reflecting prism, a total reflecting prism is introduced into the course of the light rays close to the rear focal plane of the objective. In Fig. 283, a narrow bundle of light rays, on entering the prism perpendicular to the optical axis, is reflected and passes through

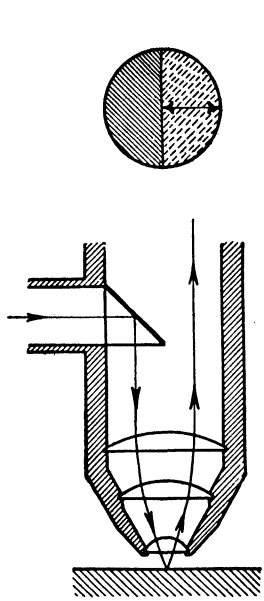


FIG. 283.—Vertical illumination with reflecting prism.

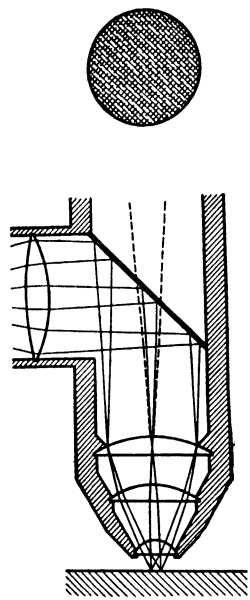


FIG. 284.—Vertical illumination with glass-plate reflector.

the objective. The prism covers only one-half of the cross section of the tube so that the other half is available for the formation of the image by the rays which, after reflection from the object, again pass through the objective. With the prism reflector, it is possible to produce images of excellent contrast but with a lack of satisfactory resolving power, especially at high magnifications. Since the resolving power depends upon the numerical aperture of the objective, as will be explained later, and since the prism,

covering half of the tube in the rear focal plane of the objective, reduces the numerical aperture in one direction to one-half of its full value, there must be also a reduction in the resolving power in this direction. This directional lack of resolving power becomes marked, especially at high magnifications. This type of illuminator is used only for low magnifications such as 50, 75, and 100 ×.

Resolving power and high magnification are so important that other methods of illumination are used. Instead of the prism, a plano-parallel glass plate can be inserted into the tube. This glass plate should be inclined 45 degrees toward the optical axis and must cover the entire cross section of the tube as shown in Fig. 284. If a narrow, concentrated beam of light falls upon this glass plate from a direction vertical to the optical axis, the plate will reflect a small part of it, while the greater part passes through and is ultimately absorbed by the inside wall of the tube.

The small reflected portion of the light passes through the objective onto the object. From there it is reflected and passes again through the objective to meet the glass plate a second time. This glass plate again reflects a small portion of the light but this time it is the part which passes through that is important. This portion of the light finally passes through the eyepiece and forms the image of the object. It is quite evident that with this method of illumination only a small part of the initial light is made available for the formation of the image and that this image, therefore, is not so light-powerful as that obtainable with the prism reflector. Nevertheless, there are strong light sources available, which produce enough light to make even the small part used for the formation of the image intense enough for visual observation and for photographing.

In comparing this method of illumination with that using the prism reflector, it will be noted that the entire aperture is available for the formation of the image so that the resolving power is not impaired. The images

produced by the plane glass reflector, however, do not show such good contrast as those produced with the prism reflector.

Increased contrast in the images produced by the plane-glass reflector can be obtained by eliminating the center portion of the incoming bundle of rays. This can be done by means of conical illumination. An opaque circular stop is introduced into the source of the rays before they fall on the reflector. A convex lens is placed at a certain distance from this stop. This lens forms a real image of the stop in the plane of the rear lens of the objective as indicated in Fig. 285. Thus the central portion of the rear lens is not illuminated at all. In their passage through the objective the rays meet other lenses which refract them so that they come closer and closer to the axis. At the same time their inclination increases and the internal reflections are not so objectionable.

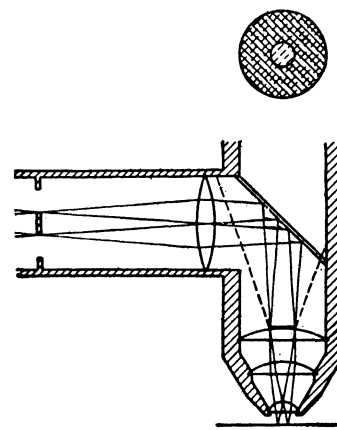


FIG. 285.—Conical illumination.

After the light has been reflected by the surface of the object, it passes through the objective a second time. These image-forming rays can pass through the center of the objective just as well as through the marginal parts and therefore the entire numerical aperture of the objective is available for image-forming rays.

It is possible with this method to produce images exhibiting good resolution and contrast. With conical illumination it is possible to increase the obliquity of the illuminating rays without detrimental effects but with a beneficial increase in resolving power.

Instead of the ring of light produced by the center stop, it is possible to create an almost parallel bundle of

rays which illuminates the object from one direction. If an iris diaphragm is placed in the plane of the center stop and if this iris diaphragm is contracted, its image will likewise appear in the plane of the rear lens of the objective. By laterally displacing this iris diaphragm it is possible to produce oblique illumination of any desired angle of inclination. This procedure will likewise result in an increase in contrast because the center portion of the rear lens is not illuminated.

Every method of illuminating the object so far described uses the objective for the double purpose of a condenser and as an image-forming system. The light passes through the objective twice. This means that the range of numerical aperture of illumination is always within the range of the numerical aperture of the objective. This principle may be called *direct illumination* because the light that is concentrated on the object is directly reflected and sent back into the objective to form the image. A perfectly polished plane metal mirror, when thus illuminated, will appear white. It is possible to arrange the illumination so that its numerical aperture is higher than that of the objective. An illuminator of this type is shown in Fig. 286. A large glass cube is introduced into the path of the rays. It is cut diagonally, polished, and cemented together. A ring-shaped silvered reflecting surface is provided on the dividing surface. The center portion of the incoming light is eliminated by a stop. The marginal rays are reflected and pass outside of the objective onto a spherical mirror which reflects them onto another spherical mirror. From there the rays converge and illuminate the object with an obliquity that is greater than the angular aperture of the objective. If the perfect mirror mentioned above is thus illuminated, no light passes into the objective and the field, therefore, appears entirely black. Light enters the objective only if a surface structure, owing to its inclination toward the plane of the object, reflects it in a

direction within the range of the angular aperture of the objective. This is a case of *indirect* illumination. The background remains dark and the structures appear lighter. This principle is called *dark-field illumination.* The images show excellent contrast. The very high numerical aperture

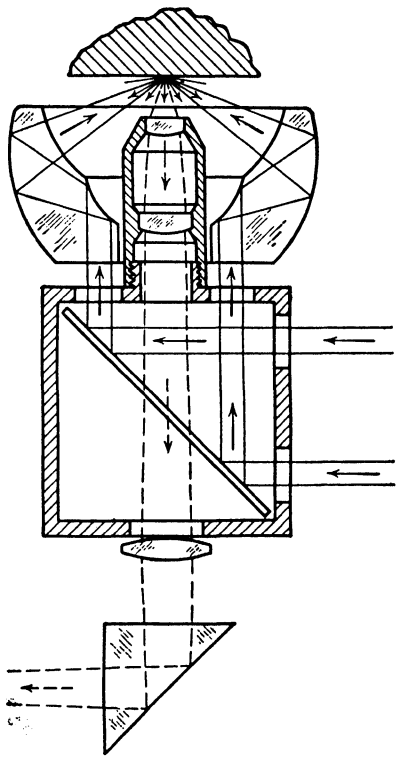


FIG. 286.—Diagram showing light passing through the dark-field condenser. (*Leitz.*)

of the illumination produces a considerable increase in the resolving power.

The microstructures of various materials can be permanently recorded by photographing them. Various types of photomicrographic apparatus are available for this purpose. The essential parts of a photomicrographic outfit consist of a microscope, the vertical illuminator, the

illuminating system, the camera, the optical bench, the table support, and the optical equipment.

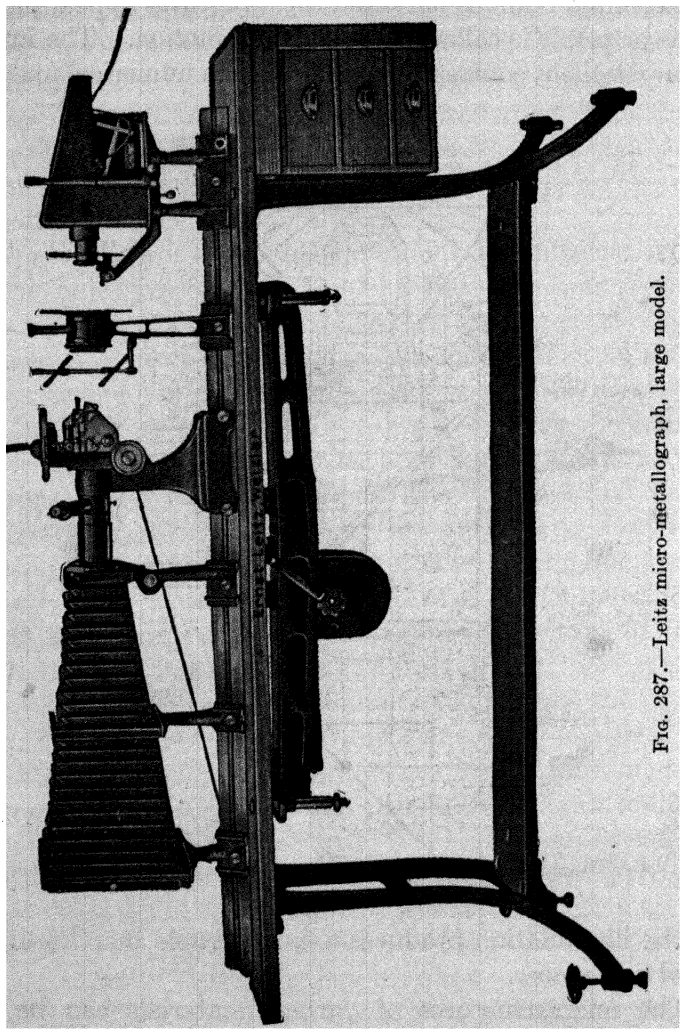
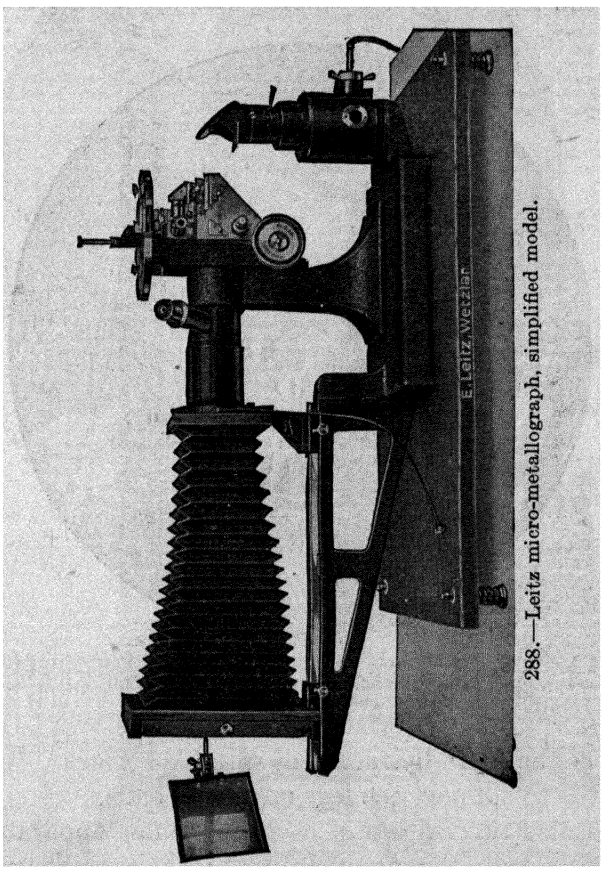


Fig. 287.—Leitz micro-metallograph, large model.

The microscope is generally of the Le Chatelier or inverted type. The camera is attached to the microscope by means of a light-tight connection. The image of the specimen is focused onto a ground-glass screen, final

focusing being done with the light filter in position and with the aid of a focusing glass.

The illuminant is generally an arc light in which the carbons are fed automatically. Another source of light is the "Point-O-Lite" or some similar lamp. Optically



288.—Leitz micro-metallograph, simplified model.

it is one of the finest sources of light. It operates on the principle of an arc lamp but is enclosed in a bulb. It can be used only with direct current. The positive electrode is a tungsten ball, which emits a very uniform and rather intense light. The negative electrode is a plate.

It is obvious that the camera and the microscope must be made free from vibrations. The various photomicrographic outfits are generally provided with shock absorbers. Apparatus not provided with such equipment may be made free from vibrations by placing thick sections of gum rubber under the legs or by suspending the apparatus from the

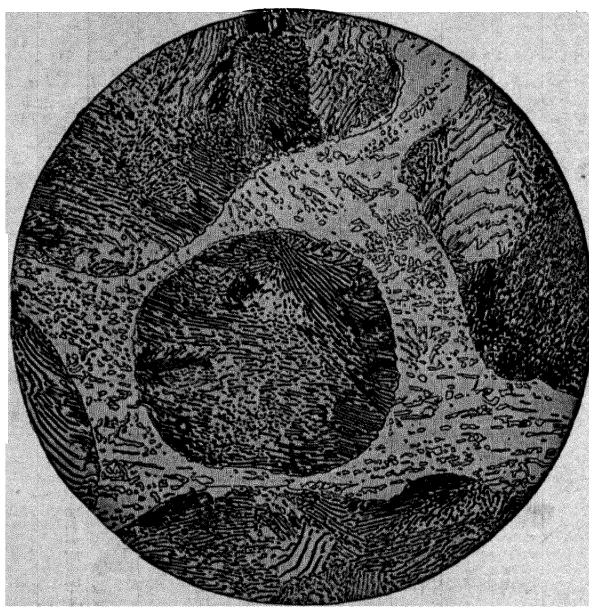


FIG. 289.—Gray cast iron. Bright-field illumination. Shows lamellar pearlite and phosphide eutectic. Nital etch. Mag. 500 ×. (*Zieler of E. Leitz, Inc.*)

ceiling of the room by means of suitable springs. Another method is to support the legs on tennis balls.

A detailed description of each particular apparatus can be obtained from the manufacturer. The reader is referred to their pamphlets for additional information.

Figure 287 shows the micro-metallograph as made by E. Leitz. A simplified outfit is shown in Fig. 288. Photomicrographs in Figs. 289 and 290 illustrate the structure of pearlite and phosphide eutectic in gray cast iron when

photographed, respectively, by bright-field and by dark-field illumination. The vertical illuminator is provided

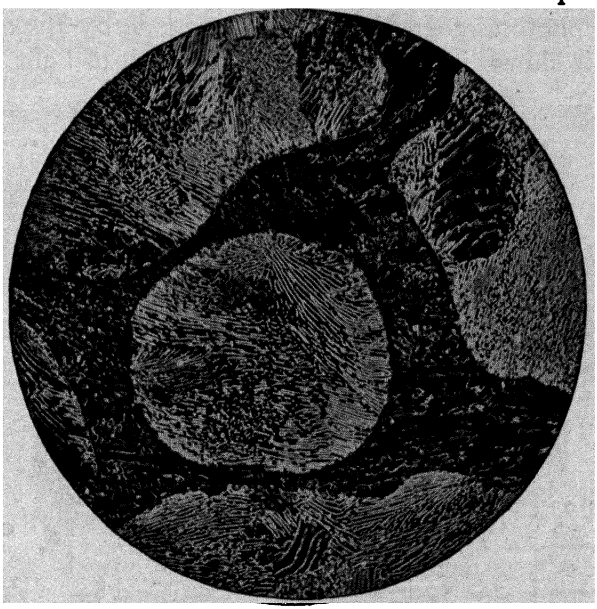


FIG. 290.—Same as Fig. 287 but with dark-field illumination.

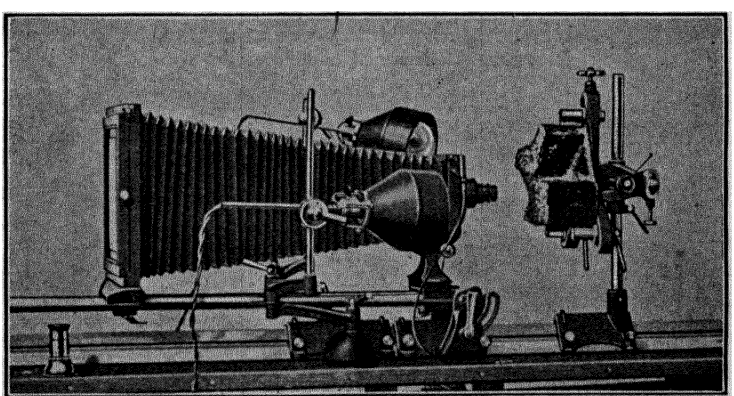


FIG. 291.—Arrangement for photographing large specimens. (*Leitz.*)

with a plane glass reflector and a prism mounted side by side on the same rod so that they can be interchanged quickly.

The arrangement for photographing large specimens is shown in Fig. 291.

The photomicrographic apparatus made by Bausch and Lomb is shown in Fig. 292, while the path of light is indi-

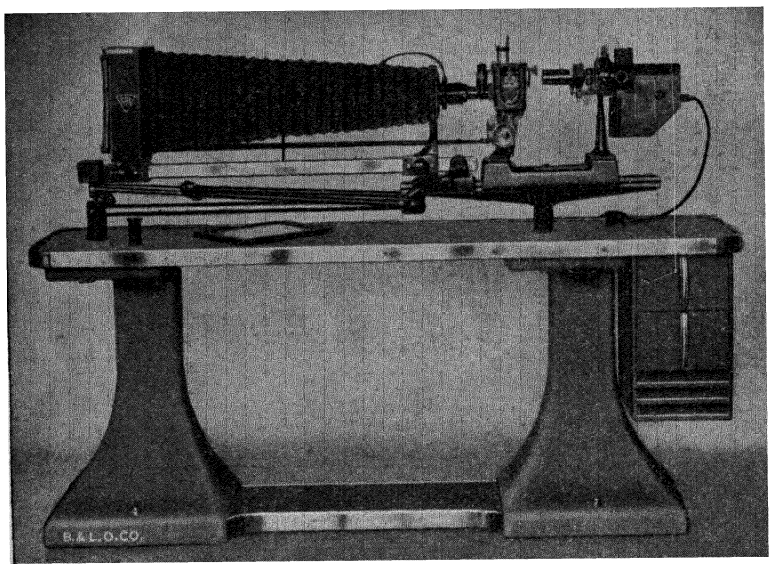


FIG. 292.—Bausch and Lomb metalloscope.

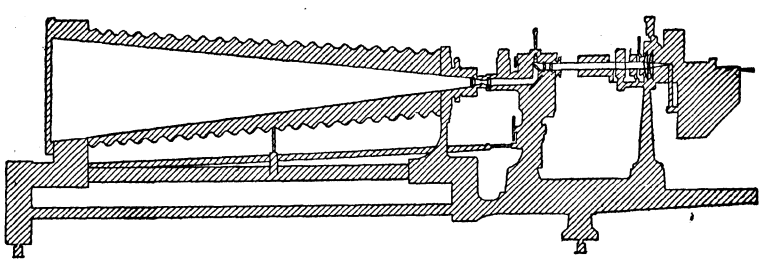


FIG. 293.—Path of light in Bausch and Lomb camera.

cated in Fig. 293. The microscope stand and the illuminating system are shown in greater detail in Fig. 294. The system is permanently aligned and is therefore simple to use. The rigid construction insures the permanence of the image in focus once it has been obtained. This appara-

tus is provided with shock absorbers, with an automatic arc lamp, and with arrangements for the use of vertical,

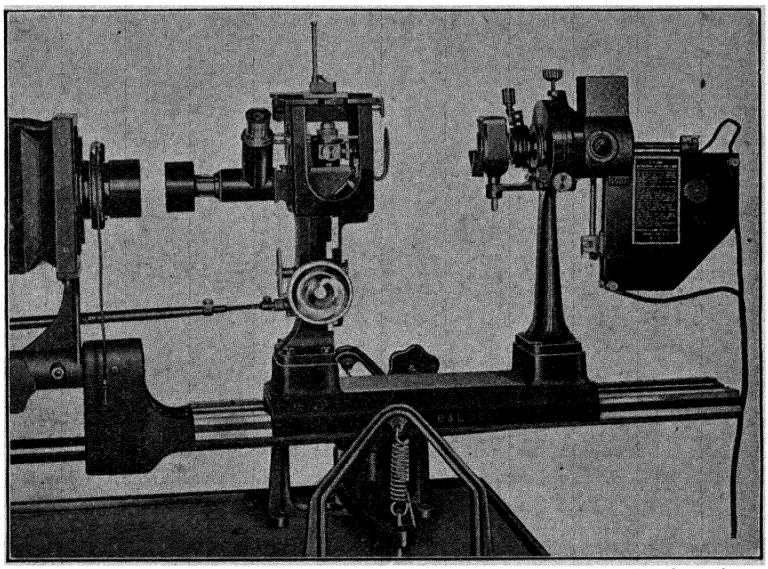


FIG. 294.—Metalloscope showing permanent alignment of the axis of condensing lens system on illuminating unit with center of vertical illuminator. (*Bausch and Lomb.*)

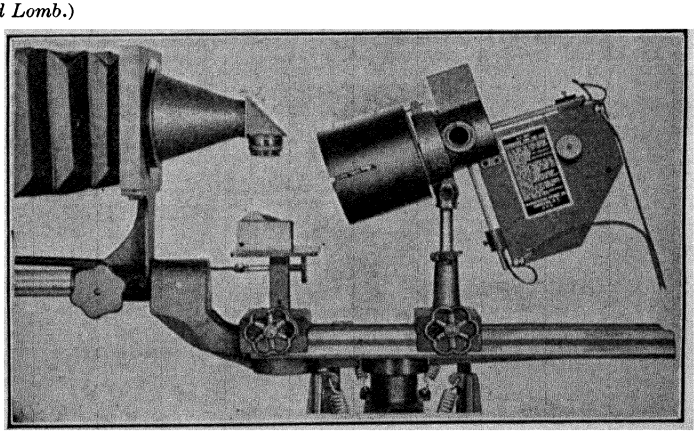


FIG. 295.—Attachments for macrophotography, showing arc-lamp unit tilted for oblique illumination. (*Bausch and Lomb.*)

oblique, and conical illumination. The attachments for photographing large specimens are shown in Fig. 295.

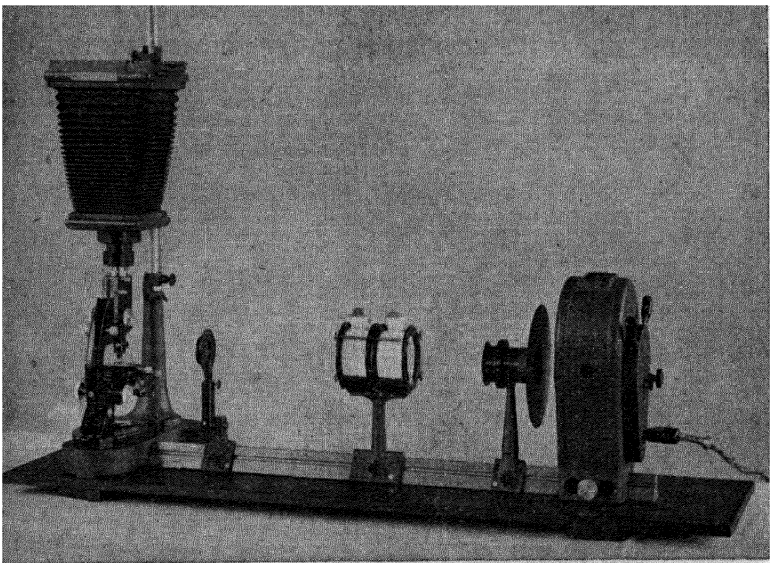


FIG. 296.—Vertical camera with table board and optical bench. (*Zeiss.*)

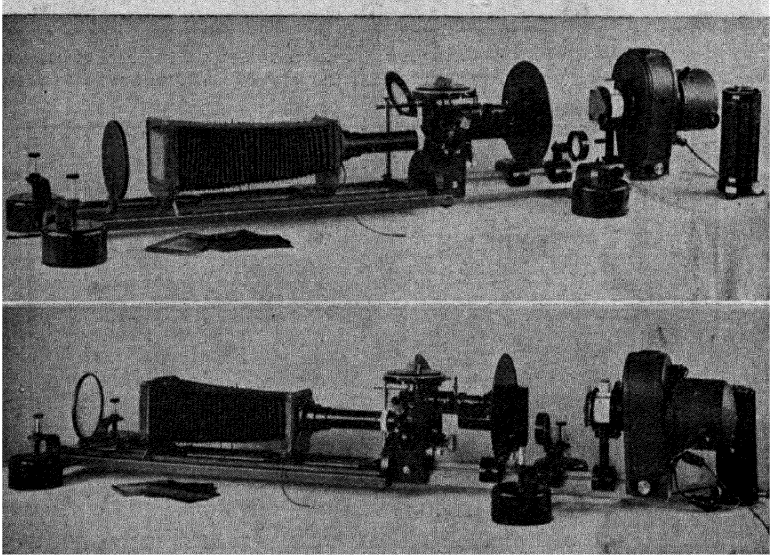


FIG. 297.—Zeiss metallograph, "Neophot."

The two types of apparatus manufactured by Carl Zeiss are shown in Figs. 296 and 297. Both are excellent for photomicrography.

The Leitz microcamera attachment shown in Fig. 298 provides a simple and practical means of obtaining photographic records. The apparatus attaches to any microscope stand in place of the eyepiece without the use of



FIG. 298.—Microcamera. (*Leitz.*)

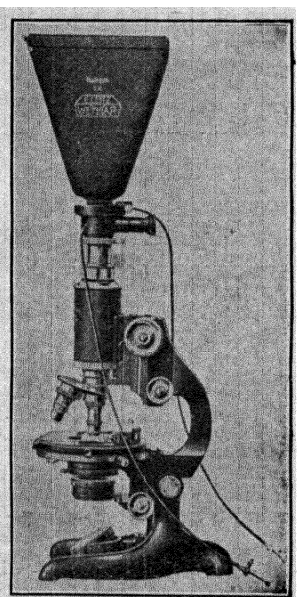


FIG. 299.—Microcamera attachment connected with microscope. (*Leitz.*)

adapters. An inspection tube provided with a prism permits a view of the image during the actual exposure. Figure 299 shows the attachment applied to a microscope.

The lens system of a microscope consists of the objective and the eyepiece. The objective may be an achromat, a fluorite system, or an apochromat. An objective should be free from spherical and chromatic aberration. In spherical aberration, the rays passing through the outer edge of the lens and those coming through the center do

not come to a focus at the same point along the optical axis. As a result the image lacks sharpness. Chromatic aberration is due to the dispersion of light in passing through the lens, with the result that light of different wave lengths comes to a focus at different points along the optical axis so that images are not coincident. Also, color fringes are often obtained, owing to inequality in the size of the images. Figures 300 and 301 by Patterson[1] show the corrective effect of an apochromatic objective on chromatic and spherical aberration. It is obvious that the highest efficiency and correction in regard to color and resolving power are obtainable with the apochromatic objective.

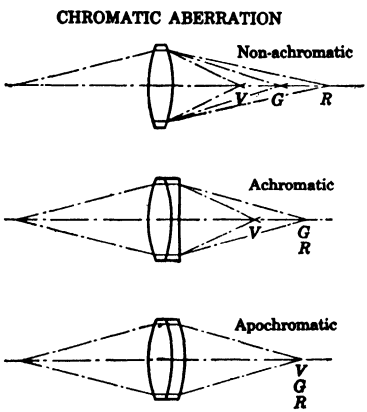


FIG. 300.—Shows effect of apochromatic lens on chromatic aberration. (*Patterson.*)

The resolving power or the ability of a lens to make visible the fine details of a structure increases with the "numerical aperture" (N.A.) of the objective, which serves as a measure of the amount of light gathered and brought to a focus. Cedar oil is used with the oil-immersion objective since a wider angle of rays is collected in this case than by the use of the dry objective. Figure 302 shows the theory of numerical aperture. The light ray R_1 is shown as leaving the object at an angle of 30 degrees, passing through air and just entering the extreme edge of the front lens of the objective. A similar ray R_2 passing through oil will be bent and will fall within the edge of the lens and will occupy the position of R_3. Obviously, it is possible for rays of light leaving the object at angles greater than 30 degrees to be

[1] PATTERSON, W. L., "Optics of Metallography," Transactions A.S.S.T., **11** (1921).

bent sufficiently in passing through the oil to pass into the objective.

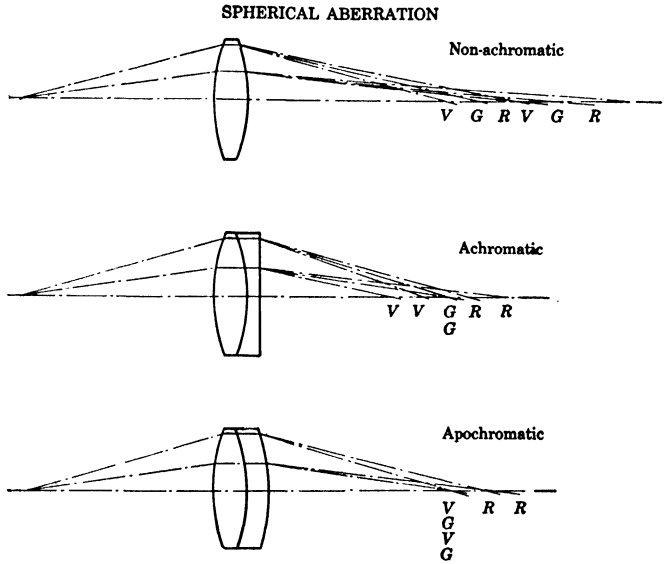


FIG. 301.—Correction for spherical aberration. (*Patterson.*)

The resolution of a structure is dependent upon the numerical aperture and the wave length of light. The greater the N.A. and the shorter the wave length (λ) of the light, the greater will be the resolution. The maximum resolving power is expressed by this formula: Resolution = $\lambda/2$N.A. If the wave length is 0.00053 millimeter for green light and N.A. is 1.00, the resolution is 0.00053/2 = 0.000265 millimeter. This means that an objective with a N.A. of 1.00 under the most favorable conditions can show as separate lines the lines in an object that are 0.265 micron apart. Another method of expressing the resolving power is in lines per inch

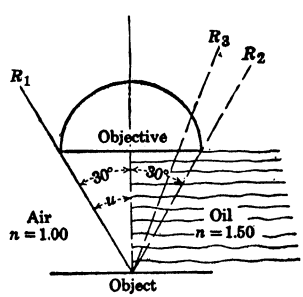


FIG. 302.—Sketch illustrating theory of numerical aperture. (*Patterson.*)

and is defined numerically by the following formula: $N = 2\text{N.A.}/\gamma$, N being the number of lines per inch, γ equaling the wave length of light in inches.

Lucas[1] has designed a special metallographic camera built by Zeiss in which an objective with a high N.A. is used in conjunction with monochromatic light of short wave length from a mercury-vapor lamp. This apparatus is intended for very high magnifications. Visual focusing is not possible with this equipment and special objectives must be used.

Bausch and Lomb have introduced special objectives which, when used with a special light and filter, make possible the visual focusing of "semi" ultraviolet light with a wave length of 365 millimicrons as compared with the true ultraviolet wave length of 275 millimicrons. Greater resolution with more clearly defined structural lines is obtained with this equipment than with the regular apparatus. Such structures as spheroidized cementite and pearlite are rendered very distinct.

If an image is formed of an object, the latter being plane and vertical to the optical axis, the image is not exactly in one plane but shows a certain curvature. Curvature of the field is often confused with spherical aberration. These two defects are not related to each other. Whereas spherical aberration always results in a lack of sharpness of the image, the field may be curved even though no spherical aberration is present. In this case each part of the image may be brought into perfect focus, but when the center portion is in sharp focus the edge of the field is out of focus and vice versa.

Achromatic objectives show a certain curvature of the field so that, when the center is in focus, the periphery is out of focus. They also show spherical aberration at the edge of the field. If an attempt is made to focus at the

[1] LUCAS, F. F., "A Precision High Power Metallographic Apparatus," *Metal Progress*, **24** (1933).

periphery, the sharpness will never be so good as the best sharpness obtainable in the center. Apochromatic objectives have an even higher curvature of the field but no spherical aberration at the edge of the field. On focusing at the periphery, the best sharpness obtainable will be just as good as the optimum in the center. Apochromatic objectives do not require green light since their correction is almost equally good within the entire visible spectrum. Achromatic objectives perform to their best advantage in green light. The fluorite objectives perform to best advantage in green light but the quality of the image is remarkably good even in other colors.

It is necessary to call attention to the fact that apochromatic objectives are not always the most desirable for metallographic work. These objectives show one unavoidable fault even though they may possess a high degree of correction. The perfection of the correction can be obtained only by combining a comparatively great number of individual lenses. In passing through these lens components, the light undergoes a number of transitions from air to glass and vice versa. Each transition causes a partial reflection at the border surface, thus increasing the haze and reducing the contrast.

Recently a new type of objective has been developed. This objective is corrected for infinity.

The eyepieces, just as the objectives, are compound lens systems. The best known type is the Huygens eyepiece. Although they were originally intended for visual observation only, the slight theoretical decrease in the quality of the image is negligible when they are used in photomicrography. These eyepieces should be used with achromatic objectives, especially when low and medium magnifications are used.

Compensating eyepieces are recommended for apochromatic objectives. These eyepieces are corrected for color. Other eyepieces have been designed that correct both for the color and for the curvature of the field, while a

special type of eyepiece, known as a *projection eyepiece*, has been designed so that the eye lens is in a focusing mount. This mount is provided with a scale and an index mark for setting the eye lens at the correct distance for each bellows extension. An increase in the flatness of the field can be obtained by a lens system known as an *amplifier*. It has the slight disadvantage, however, that it cannot be used for visual examination. Also, an amplifier of slightly different correction and magnification must be used as the focal length of the objective decreases.

The selection of the optical equipment for photomicrography, as well as the bellows extension to be used, is worthy of mention. If the desired magnification has been decided upon, the objective should be so selected that its numerical aperture is about $\frac{1}{500}$ to $\frac{1}{1000}$ that of the magnification. The type of objective used determines the type of eyepiece to be selected. The eyepiece as well as the bellows extension participates in the total magnficiation obtained.

It is always preferable to select an eyepiece of low magnification and a long bellows extension instead of an eyepiece of high magnification and a short bellows extension.

Filters are used in all photomicrographic work. Those which transmit only narrow bands of the spectrum of visible light lead to pictures of much better definition and contrast than can be obtained without them. A green filter or a combination of a yellow filter to cut out blue and violet light and a green filter to eliminate the red is most commonly used. In special cases blue or violet filters are used, especially with apochromatic objectives. Yellow or red filters should be avoided because the longer wave lengths of these colors decrease the resolving power.

Photographic plates that will give good negatives may be obtained. Panchromatic plates are sensitive to red light and therefore require a special safety light. It is much

more convenient and more advantageous to use a plate that is particularly sensitive to green, but not to red, light. Orthochromatic plates are of this type. Cut films are also used. They are easy to file and are unbreakable.

The time of exposure may vary from a few seconds to 10 or 15 minutes, depending on the source of light, the nature of the specimen, the color of the filter, and the kind of plate, as well as the optical system used and the setting of the camera. The operator soon recognizes these factors so that he can estimate the length of exposure with considerable accuracy. When the conditions are entirely unknown, the following test method will save time and plates: Expose, as usual, for a few seconds. Instead of shutting off the light, as would be done ordinarily, push in the opaque screen, which is used to cover the plate in the holder, about ½ inch in order to shut off a portion of the exposed plate. After another short interval, push in the screen another ½ inch. Repeat this operation until the opaque screen has completely covered the plate. When the plate is developed, it will show a series of bands, each of which represents an exposure for a somewhat longer time than the one preceding it. Select the correctly exposed strip from the banded negative, record its time of exposure, and use substantially the same length of exposure for photographs taken under similar conditions.

Directions for the preparation of developing solutions are supplied by the manufacturers and are generally included in each box of plates.

A developing solution that gives good results for plates, films, and paper is the following:

Metol	2.0 grams
Sodium sulphite anhydrous	35.0 grams
Hydroquinone	6.0 grams
Sodium carbonate anhydrous	58.0 grams
Potassium bromide	0.7 gram
Water	1000.0 cubic centimeters

Dissolve the metol in 50 cubic centimeters of water, then add the remaining chemicals in order. The solution may be used full strength or it may be diluted with an equal volume of water.

A solution that will give extreme contrast is as follows:

Solution A	
Hydroquinone	25 grams
Potassium metabisulfite	25 grams
Potassium bromide	25 grams
Water	1000 cubic centimeters

Solution B	
Potassium hydroxide	50 grams
Water	1000 cubic centimeters

Mix equal parts of A and B and use at approximately 18°C. Maximum development occurs in 2 minutes or less.

After the development has been completed, the plates are passed through water and then into a hypo bath made by dissolving 500 grams of sodium thiosulphate in 2000 cubic centimeters of water. An acid hardener is generally added to this solution, especially for use in hot weather, the formula of which is as follows:

Water	150 cubic centimeters (5 fluid ounces)
Sodium sulphite (dried)	28 grams (1 ounce)
Potassium alum	28 grams (1 ounce)
Glacial acetic acid	30 cubic centimeters (1 fluid ounce)

The effect of the fixing solution is to dissolve the unreduced silver salt. After the grayish white color has disappeared from the back of the plate, the plates should be left in the bath an equivalent length of time to complete the fixing. All traces of hypo should be removed by washing thoroughly in running water, an hour generally sufficing. The plates are then placed in a rack for drying.

Sometimes negatives may be underexposed or overexposed. In the former case, detail is lacking, so that it is better to make another exposure rather than to treat the

poor negative. An overexposed negative is too dense and may be reduced in the following solution:

SOLUTION A

Water	30 cubic centimeters, or 1 fluid ounce
Potassium ferricyanide	1 gram, or 15 grains

SOLUTION B

Water	1000 cubic centimeters, or 32 fluid ounces
Sodium thiosulphate (hypo)	28 grams, or 1 ounce

Mix A and B and immerse the plate in the solution until sufficiently reduced; then wash thoroughly and place in rack to dry.

Photomicrographs require the greatest possible detail in printing so that a glossy paper is commonly used. Glossy Azo Nos. 3 and 4, as well as other brands, give good results.

After the prints are washed, a brilliant finish may be obtained by placing them face down on a ferrotype plate and pressing into firm contact by means of a print roller. The ferrotype board should be clean. Any tendency of the prints to stick to the board may be prevented by rubbing the surface with a few drops of oil or with a solution of paraffin in benzol. The board should then be polished with a soft cloth before the prints are placed on its surface. The prints may be trimmed to any convenient size. A circular print may be made by the use of a revolving print trimmer and a metal mask. Black paper masks are commonly used. The dry prints may be mounted on suitable cards for examination and filing. Dry mounting tissue is excellent for attaching the prints. A mounting card of the type shown in Fig. 303 will prove satisfactory.

Magnetic Testing.[1]—Magnetic methods of test have been greatly extended during the past five years. Several systems that have been worked out in laboratory form for

[1] This brief discussion of magnetic testing was written by Dr. A. V. de Forest, Professor of Mechanical Engineering, Massachusetts Institute of Technology.

some time are now in commercial use, and the limitations of the various tests are becoming established. The following description covers only methods of commercial interest. From the point of view of magnetic research, many other laboratory tests are in use.

Magnetic tests offer the great advantage that they are in general rapid, nondestructive, and may be applied to the finished product, and not solely to a specimen representative of the product. In the case of materials used because

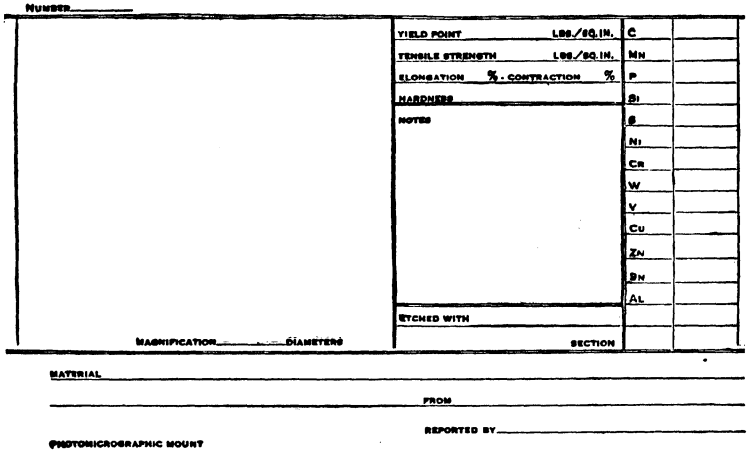


FIG. 303.—Photomicrographic mount. Original card is 5 by 7 in.

of their magnetic behavior, such as transformer steels, magnet steels, and the like, magnetic measurements are made under the same general conditions under which the steel is used in service, and the measurement is then a primary one, giving results in finite numbers that define the relative merit of the specimen.

Magnetic tests are also used to determine the suitability of steel for mechanical purposes.

Two completely distinct types of tests are in use: one a continuity test to discover defects such as cracks, seams, blowholes, or inclusions, and the other a test that determines whether the structure of the steel, its strength, hard-

ness, and grain are similar to a standard. This process of determining the structure of steels is known as *magnetic analysis.*

One form of the continuity test is in daily use for locating dangerous fatigue cracks in used railroad rails. In the Sperry test a heavy current is passed longitudinally through the rail, and where a defect occurs a change-of-potential drop can be measured. Instead of measuring this drop, however, the transverse magnetic field due to the variation in current density is used. A coil is carried at constant speed over the head of the rail, and changes in the magnetic field are amplified by a vacuum-tube circuit and recorded. In service the test apparatus is carried in a rail car. Both tracks are tested at once, at a speed of about six miles per hour. The sensitivity of the equipment allows defects to be found which occupy only 1 per cent of the area of the rail head. Unfortunately, however, the test is not purely one of continuity of the metal in the rail; sudden structural changes, such as are caused by wheel burns, will also record on the apparatus. It is now known that transverse fissures, as in the case of other fatigue cracks, grow slowly, and periodic inspection locates a great percentage of the cracks before they have become dangerous.

Another form of continuity test which has reached general use is known as the *Magnaflux test.* Under proper magnetizing conditions a small local pole is produced at the extreme edge of surface cracks of any kind. The usual indicator for this polar effect is finely divided iron or a magnetic iron oxide. Where extreme refinement of the detecting powder is necessary, the iron dust may be suspended in a liquid. Oil, water, or, in some cases, carbon tetrachloride is used. For other purposes the dust is used dry and is more effective when coated with a nonmagnetic layer surrounding the iron particles. This powder method has been particularly effective for the detection of surface seams, grinding cracks, quenching cracks, and shrinkage

cracks in welds, and in locating incipient fatigue cracks in used machinery. Where safety is important as in airplane parts and engines, this testing is particularly desirable and is in extensive use. The result of using this test for incipient fatigue cracks is important as the actual cause of the defect can be far more readily discovered if the part is examined before the evidence is destroyed. After failure has occurred, accurate examination is in many cases impossible. This test is also in general use on large forgings such as those for turbine rotors. The depth to which cracks can be detected depends on the material and its physical shape. In favorable cases as with thin-wall tubing, interior defects can be located on the outside by the disturbance created in a circular magnetic field generated in the wall of the tube.

Another important continuity test is one in which a very strong direct-current field is produced between the poles of a heavy magnet and the distribution of this flux is measured by search coils mounted in the pole pieces. In case of a slight change in the magnetic reluctance of material between the poles, a condition of dissymmetry is created which may be used as an indication of local internal defects. This test is somewhat similar to the Sperry rail test and is used primarily by the General Electric Company on turbine rotor wheels.

In the history of magnetic analysis there have been many failures to progress from apparently successful laboratory applications to commercial shop conditions. This is primarily due to the many variables that arise in practice and in large volumes of metal as compared with those variations known and studied under ideal laboratory conditions. As the practical metallurgist becomes more familiar with the possibilities of magnetic methods, this convenient form of test will be applied more widely.

The varieties of magnetic analysis all proceed from the observation that if two specimens of steel are identical

as to their magnetic properties they are identical as to their mechanical properties. Unfortunately the reverse is by no means true, and specimens may differ markedly in magnetic properties without any indication of differences in the mechanical properties as usually measured. The principal reason for this condition is that the magnetic measurements are usually affected by the state of internal stress, which exerts a negligible effect under most conditions of mechanical testing. Magnetic tests of this type are purely secondary in that the magnetic properties are of no importance in themselves, but must be interpreted in the light of experience. It is necessary that the test specimen on which experience is based be of the same material and have the same method of preparation as the material tested; for instance, heat-treated bolts could readily be magnetically compared with each other as long as the composition is uniform, but a change in the composition of the steel or in the heat-treating process would result in large magnetic differences that might or might not be indicative of mechanically imperfect bolts.

The simplest form of this test, and the earliest in point of commercial application, is an alternating-current bridge in which the impedance of a coil surrounding the test specimen is balanced either against a standard specimen in a similar coil or against a synthetic standard of equal impedance. As an indicator of unbalance an alternating-current galvanometer may be used, or the current may be passed through a rectifier and measured as a direct current. The galvanometer may be replaced by an oscillograph and additional information obtained from the wave form of the magnetizing current. Using this method, attempts have been made to interpret the many variations in magnetic properties into the corresponding mechanical behavior. In certain cases this analysis can be successfully carried out; in others, under commercial conditions, the confusion of variables becomes too great. This balanced alternating-

current system of test is primarily applicable to large quantities of similar materials, for instance, razor-blade stock, wire, bar-stock, tubing, and similar products. In the case of these items certain peculiarities of magnetization may be indicative of longitudinal defects such as seams. This is particularly true in the case of cold-drawn bars and the method is in commercial use as a defect indicator for such products. In this case the defect seems to produce a greater magnetic difference in cold-drawn stock than in the same bar annealed. The seam, therefore, probably changes the conditions of internal stress, the magnetic results serving as an indication. A change in the internal stress distribution may also be caused by some harmless mechanical variation such as local straightening or a local hammer mark. Quite obviously care must be used to discriminate between harmful and harmless causes of the magnetic change that is used as a test indication. Strict attention must be paid to the uniformity of cross section and of composition and heat treatment of the stock to prevent confusion.

Similar apparatus, but with special methods of magnetization, is in use in the ball-bearing industry; raceways, balls, and rollers can very conveniently be tested in this manner. If the magnetic readings are interpreted in terms of Rockwell hardness variation, reliable average measurements can be made to one-tenth of one Rockwell division. The magnetic indications also show irregular internal stress conditions regardless of the actual hardness of the surface. These variations are hard to calibrate as the equivalent mechanical tests are poorly developed.

An extension of this method consists in differentiating between the different harmonics generated by alternating-current magnetization. It has been found, particularly in the case of tubing, that longitudinal defects have a greater proportional effect in the case of certain harmonics than in the fundamental wave.

Instead of the use of an oscillograph for such measurement of harmonics, a filter system may be used which will measure the energy developed by the various harmonics present in the wave form. This method, however, is as yet primarily a laboratory one.

In certain fields, particularly for small parts of magnetic material, high-frequency magnetization is used and a number of types of oscillating circuits have been devised which give valuable indications of slight changes in composition and heat treatment. Tests of this type can also be applied to nonmagnetic materials, measuring in this case the electrical resistivity of the test specimen. A very high degree of comparative accuracy is possible and small changes in the amount and direction of cold work can be discovered. This system in general is similar to the Hughes induction balance of 50 years ago.

In the correlation of magnetic with mechanical methods of test, the greatest obstruction to progress has been the absolute lack of methods of mechanical testing, which depend on the condition of the material before deformation beyond the elastic limit has been imposed. Mechanical tests give only figures on metal greatly different from its original condition. Magnetic tests, on the other hand, deal with the material as it is manufactured, quite a different substance. Close agreement between the two conditions is not to be expected.

X-ray Methods.[1]—In connection with laboratory methods, a brief reference should be made to the use of x-rays which have become a most useful aid in the study of the metallic state. Broadly speaking, x-rays may be used in two ways, the first of which is classified as the application of *radiography* and the second as the application of *x-ray diffraction.*

Radiography is based on the ability of x-rays to penetrate solid and other opaque matter, a fact that is due to the

[1] This section on x-rays has been rewritten by Dr. Morris Cohen, Assistant Professor of Physical Metallurgy, Massachusetts Institute of Technology.

short wave length of x-radiation. The method consists in passing a beam of x-rays (produced by 100,000 volts or more) through the metal object to be examined and then observing the emergent beam with the aid of a photographic plate or film, since x-radiation, although invisible, affects a sensitized emulsion as does ordinary light. This furnishes a shadowgraph of the interior of the metal object. Since the penetration of a given x-ray beam depends on the kind, density, and thickness of the material through which it passes, it is evident that the parts of the beam passing through such defects as blowholes, shrinkage cavities, internal cracks, and the like will be less absorbed and so will produce darker spots on the plate than those portions of the emergent beam that have passed through solid metal. The presence of large inclusions and segregations can be detected in the same way. In this manner, the interior of a metallic specimen may be examined without injury to the part.

The radiographic method finds a wide application in the examination of castings and forgings and so is an excellent means of plant control. Porosity, sand inclusions, serious segregation, and shrinkage cracks or "pipes" are some of the internal flaws commonly detected by radiography. Not only can defective castings and forgings be rejected before being put into service, but also the manufacturing technique can be modified immediately to eliminate the flaws.

The application of radiography to the examination of welds is of great importance. The detection of gas pockets, slag inclusions, and imperfect union of the welded metals has resulted in marked improvements in welding technique. This nondestructive method of weld testing has been found to give so satisfactory an indication of the condition of the weld that it has led to a large increase in the use of pressure vessels and structural shapes. The boiler code of the American Society of Mechanical Engineers requires

that all welded boilers must be radiographically tested before they are put in service. Figure 304 shows two welds which appeared satisfactory from the outside, but which showed serious defects when examined by the *x*-ray.

With modern *x*-ray equipment using 400,000 volts, which is approximately the maximum commercial tube voltage, thicknesses of steel up to 4½ inches can be tested. For greater thicknesses gamma rays emitted from radium emanation are now used. Gamma rays differ from *x*-rays only in that their wave length is much shorter so that they

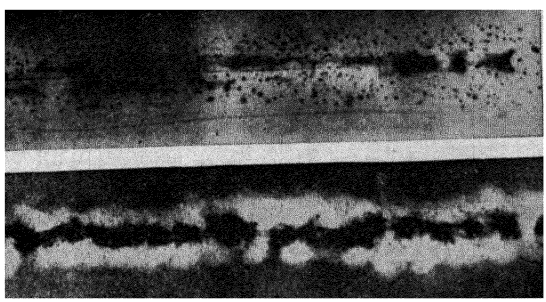
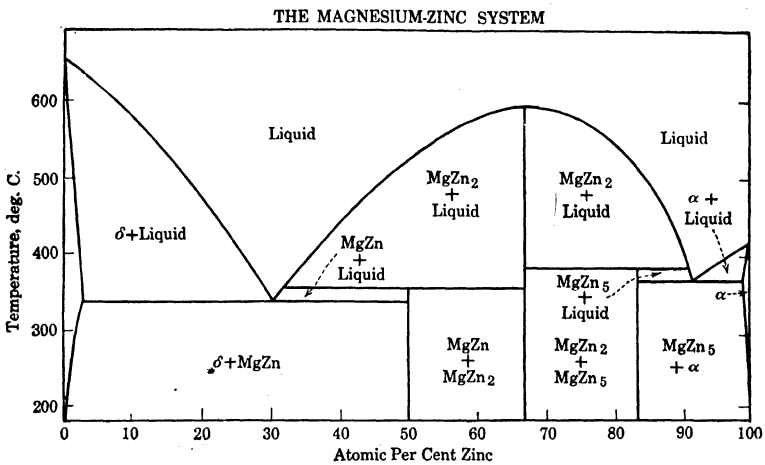


FIG. 304.—Radiograph of defective welds showing porosity and imperfect joining of metals. (*Norton.*)

have much greater penetrating ability. These rays will give satisfactory shadowgraphs through 10 inches of steel in 10 hours.

The second and far more complicated application of *x*-rays is based upon the fact that all metals and alloys are crystalline (see p. 52), and therefore the atoms in each grain form various sets of parallel planes which are able to reflect *x*-rays striking them at certain angles. Since *x*-rays penetrate the metal, they are reflected not merely from the surface, but also from an appreciable depth below the surface. The reflected *x*-ray beams are allowed to fall on a photographic film and produce an array of lines, the arrangement of which is characteristic of the arrangement of the atoms in the space lattice. In addition, the



Film No.	Atomic Per Cent Zn	Atomic Per Cent Mg	$\sin^2\theta$ 0.3 0.4 0.5 0.6	Phases Present
1	0.0	100.0		Mg (*s*)
2	7.2	92.8		δ (*s*)+MgZn (*w*)
3	42.0	58.0		MgZn (*m*)
4	45.2	54.8		MgZn (*m*)
5	49.4	50.6		MgZn (*s*)
6	56.5	43.5		MgZn (*w*)+$MgZn_2$ (*w*)
7	65.4	34.6		$MgZn_2$ (*s*)
8	70.5	29.5		$MgZn_2$ (*m*)+$MgZn_5$ (*w*)
9	82.5	17.5		$MgZn_2$ (*w*)+$MgZn_5$ (*m*)
10	83.6	16.4		$MgZn_5$ (*s*)
11	95.0	5.0		$MgZn_5$ (*w*)+Zn (*s*)
12	100.0	0.0		Zn (*s*)

POWDER PHOTOGRAMS OF THE MAGNESIUM-ZINC ALLOYS
Chromium Radiation (Unfiltered)

Notation: *s* = strong, *m* = medium, *w* = weak.

FIG. 305.—*X*-ray diffraction patterns of the solid phases existing in the magnesium-zinc system. (*Cohen.*)

lattice parameters and atomic distances can be determined from a measurement of the spacing of the lines on the x-ray film.

This method of x-ray diffraction has been very valuable to the metallurgist in his study of alloy systems since solid solutions and intermetallic compounds also have characteristic crystal structures. Figure 305 illustrates the application of x-ray diffraction to the identification of the solid phases existing in a complex equilibrium diagram. X-rays are also used to study phases transformations during heat treatment, to determine grain orientations after plastic deformation, and to measure internal stresses resulting from quenching, welding, and cold working. Since the lattice parameters of solid solutions vary with the composition, the x-ray measurement of lattice parameters provides an excellent means for determining solid solubility curves.

APPENDIX

TABLE I

Suggested outline of a brief laboratory course in Metallography.

NONFERROUS

1. *Cadmium-bismuth Series.*—The prepared specimens range from 10 Cd-90 Bi to 90 Cd-10 Bi, all of which should be carefully examined. The report should include the equilibrium diagram, cooling curves, and sketches of three representative specimens, the etching reagent used, and a brief statement as to the commercial uses of the alloys.

2. *Copper–copper oxide Series.*—Examine and report as in the Cd-Bi series.

3. *Copper-silver Series.*—Examine and report as in Cd-Bi series.

4. *Matte and Slag.*—Prepare and examine specimens of copper matte and copper slag. Remember that the former contains Cu, Fe, and S, with probably some magnetite. The latter contains silicates of Fe and Ca with probably some other materials. Learn what you can regarding the constituents and cover in the report. Give sketches.

5. *Brass.*—(*a*) Compare the structures of cast 60-40 and 70-30 brass. (*b*) Forge cold a piece of cast α-brass reducing the cross section to less than one-half. Cut the specimen in two, heat one piece to 800°C. and cool in air. Compare the two pieces.

6. 60–40 *Brass* (*Muntz Metal*).—Heat three pieces at 825°C. for ½ hour. Quench one in cold water, cool one in air, and cool one in the furnace. Etch with a freshly prepared mixture of equal volumes of concentrated NH_4OH and H_2O_2. Compare the structures.

7. 70–30 *Brass* (*Cartridge Brass*).—Examine one piece of cold-worked α-brass. Heat one at 650°C. and one at 800°C. for ½ hour. Compare the structures.

8. Polish and etch a specimen of duralumin.

FERROUS

1. *Wrought Iron.*—Examine longitudinal and transverse sections.

2. *Cast Steel.*—Examine the original cast steel and the original material after it has been reheated slightly above Ac_3 for 1 hour and cooled in air. Compare the two structures. Forge a specimen of cast steel to reduce its cross section about one-half. Cut into two pieces longitudinally. Heat one slightly above Ac_3 for 1 hour, cool in air. Examine the structures.

3. *Hot-rolled Steel.*—Treat seven specimens from a steel bar as follows:
(*a*) Original untreated.
(*b*) Heat at proper temperature for ½ hour and quench in water.
(*c*) Heat as in (*b*), quench in water, reheat at 300°C. for ½ hour.
(*d*) Heat as in (*b*), quench in water, reheat at 600°C. for ½ hour.
(*e*) Heat as in (*b*), and cool in the furnace.
(*f*) Heat as in (*b*), and quench in oil.
(*g*) Heat as in (*b*), and cool in air.

4. *Case-hardened Steel.*—Examine carefully several prepared specimens.

5. *Overheated Steel and "Burnt" Steel.*—Examine prepared specimens.

6. *Cast Iron.*—Examine specimens of white, gray, and malleable cast iron.

7. *Macroscopic Examination of Steel.*—Make macroscopic studies of various types of steel showing segregation, etc., as directed.

8. *Photomicrography.*—Photograph a series of properly polished and etched specimens, develop the negatives, prepare and mount the prints on suitable cards.

9. Examine various commercial alloys, bronzes, aluminum alloys, high-speed steels, and the like. Examine and make formal report of the causes of failure of defective alloys.

TABLE II

Journals[1]

American Institute of Metals—1906–1918 (incorporated with American Institute of Mining Engineers, 1919). Deals with the production and metallography of nonferrous alloys.

American Institute of Mining Engineers. Includes the metallography of iron and steel and since January, 1919, has published the nonferrous metallography formerly printed in American Institute of Metals.

American Society for Metals (American Society for Steel Treating until 1934). The society publishes Transactions and Metal Progress and now covers both nonferrous alloys and steel.

American Society for Steel Treating—1920 to 1934. Deals with the manufacture, microscopic examination, and especially the heat treatment of iron and steel. Contains papers of scientific and of practical interest.

American Society for Testing Materials—1899 to date. In the metals section will be found much information on the physical properties and metallography of alloys.

Archiv für Eisenhüttenwesen—1926 to date. Valuable for ferrous metallography.

Bureau of Standards, United States. Publishes frequent valuable monographs on various branches of metallography.

[1] This list is by no means complete but it contains the journals usually available.

Journal of the Institute of Metals (British)—1919 to date. A semi-annual publication of the society which covers for nonferrous alloys the field occupied by the Iron and Steel Institute in the steel industry.

Journal of the Iron and Steel Institute (British)—1896 to date. Deals with the preparation and metallography of iron and steel. Published semi-annually.

Metals and Alloys—1929 to date. An excellent journal including papers on nonferrous and ferrous alloys. The abstract section is especially valuable.

The Metallurgist—(Supplement to The Engineer). Deals with applications of Metallography.

Metallwirtschaft—1921 to date. Especially useful for technical information concerning methods of manufacture, prices, and patents.

Mitteilungen aus den Eisenhüttenschen Instituts Aachen—Wust—1906 to date. A series of valuable contributions to theoretical and industrial metallography.

Zeitschrift für Metallographie. Published original articles in English, French, Italian, and German and included abstracts of all metallographic articles.

Zeitschrift für Metallkunde—1919 to date. A successor to the Zeitschrift für Metallographie but dealing primarily with the general properties of nonferrous metals and alloys.

In addition to the journals devoted primarily to the properties of metals the following journals frequently publish important articles on metallography:

Chemical and Metallurgical Engineering, Metallurgie, Revue de Métallurgie, Stahl und Eisen, Zeitschrift für anorganische Chemie.

TABLE III

The Common Industrial Alloys.—The industrial alloys now number several thousand.[1] The following table includes a few of those most commonly used. The composition, even of the alloys listed, varies between fairly wide limits with a corresponding variation in physical properties and applications.

The information given under Uses is intended merely to indicate the general nature of the alloy.

Name	Composition, per cent	Uses
Admiralty metal	Cu 70 Zn 29 Sn 1	Condenser tubes for use with salt water. Marine fittings.
Alpax	Al 92–89 Si 4–11	General castings. Has lower shrinkage than Al-Cu alloy.
Aluminum alloy—No. 12	Al 92	This alloy with slight variations in composition is the standard aluminum casting alloy used in the United States.
S.A.E.—No. 30	Cu 8	
Aluminum brass	Cu 70–68 Zn 27–31 Al 1–3	Propeller blades, rudder frames, sea valves.
Bronze		
Aluminum	Cu 90 Al 10	Hard, non-corrodible. Used in parts exposed to tanning, sulphite and similar corrosive liquors.
Bearing	Cu 70–90 Sn 1–10 Pb 0–15 Zn 0–27	Bearings of various sorts.
Gear	Cu 89 Sn 11	Used for heavy gears usually against steel.
Gun	Cu 88 Sn 10–8 Zn 2 Pb 2	Strong valves and fittings.
Phosphor	Cu 80–77 Sn 8–10 Pb 0–15 P 0–1.0	Bearing metal, wire, rods, steam fittings.

[1] A list of compositions of more than 1500 alloys is give in "International Critical Tables," Vol. II, p. 370.

TABLE III (*Continued*)

Name	Composition, per cent	Uses
Plastic	Cu 70–50 Pb 30–50 Ni trace	Bearing metal.
Silicon	Cu 96 Si 1–4	Telegraph wires, electrical work, rivets, range boilers, fans.
Babbitt metal	Sn 70–90 Sb 7–24 Cu 2–22	Bearings and antifriction lining for bronze or steel bushings.
"Genuine"	Sn 88.9 Sb 7.4 Cu 3.5	
Bell metal	Cu 80–75 Sn 20–25 (Sometimes Ag, Ni or other metals)	Bells, gongs, etc.
Brass		
Gilding metal	Cu 99–80 Zn 1–20	Cheap jewelry, gold paint.
Dutch metal	Cu 80–76 Zn 20–24	Thin sheets as substitute for gold leaf.
Standard	Cu 73–66 Zn 27–34	Brass for cold working. Sheets, tubes, cartridges.
White	Cu—less than 45	Ornamental castings not requiring strength.
Brazing metal	Cu 85 Zn 15	
Britannia metal	Sn 95–90 Sb 5–10 Cu 1–3	Cheap table ware.
Chromel (Nichrome)	Ni 70–85 Cr 15–30 (approximate)	Resistance wire for heating units, crucibles, triangles, tongs. (Patented.)
Copper-beryllium Beryllium bronze	Cu 97–98 Be 2–3	Heat treated to give 200,000 lb. per square inch tensile strength. Used for pump parts, springs, and nonsparking tools.
Cupro-nickel	Cu 98–52 Ni 2–48	Projectile driving bands, rifle bullet caps, electrical resistances, condenser tubes.

TABLE III (*Continued*)

Name	Composition, per cent	Uses
Constantan	Cu 60 Ni 40	Used with copper or iron to make thermocouples.
Delta metal	Cu 60 Zn 40 Mn 0.5–2	See Sterro metal.
Dow metal	Mg 85–92 Al 8–15	Standard magnesium alloys. Used as castings or forgings.
Duralumin	Al 95.5 Cu 3.0 } Approx. Mn 1.0 } comp. Mg 0.5	Strongest and best of aluminum alloys. Used in airplane and automobile parts.
Fusible metals		
Lipowitz	Bi 50 Pb 27 Sn 13 Cd 10	These and other ternary and quaternary alloys are used for fuse plugs for automatic sprinklers.
Woods	Bi 38 Pb 31 Sn 15 Cd 16	
German silver	.....	See Nickel silver.
Gun metal	Cu 92–88 Sn 8–12	Gears, heavy hydraulic castings.
Hercules metal	Aluminum brass with Fe	Same as Aluminum brass with added toughness.
Invar	Fe 64 Ni 36	Low coefficient of expansion. Used in clocks, precision instruments.
Magnalium	Al 90–94 Mg 10–6	Scientific instruments. Balance beams.
Magnolia metal (Lead-base babbitt)	Pb 78 Sb 16 Sn 6	Antifriction, bearing alloy.
Manganese bronze	Cu 56 Zn 41 Sn 0.5 Fe 1 Mn 0.5 Al 1	Propeller blades. Noncorrodible and great wearing qualities.
Manganin	Cu 82 Mn 15 Ni 2.3 Fe 0.6	High electrical resistance and low temperature coefficient.

TABLE III (*Continued*)

Name	Composition, per cent	Uses
Monel metal	Ni 68 Cu 27 Fe, Mn, Si 5	Almost noncorrodible. Used for propeller blades, wire, sheets, valves, pumps, etc.
Muntz metal	Cu 60 Zn 40	Sheathing for ships, bolts, nuts, condenser tubes.
Naval brass	Cu 60 Zn 39 Sn 1	Properties like Muntz metal. Less easily corroded by sea water.
Nickelin	Cu 74.5 Ni 25 Fe 0.5	Resistance wire.
Nickel silver (German silver)	Ni 18–25 Zn 20–30 Cu (Remainder)	Table ware, cheap jewelry, base for silver plating.
Palau	Pd Au	Substitute for platinum in chemical crucibles, dishes, etc. (Patented.)
Pewter	Sn 85–90 Sb 15–10	Platters, bowls, cups, etc.
Platinite	Fe 54 Ni 46 C 0.15	Same coefficient of expansion as glass. Used as substitute for platinum in equipping incandescent lamps.
Platinoid	Cu 60 Zn 24 Ni 14 W 1–2	High resistance wire but not suitable for heating coils.
Platinum-iridium	Pt 90 Ir 10	Standard meter and other standards. Thermocouple with platinum.
Rheotan	Cu 52 Zn 18 Ni 25 Fe 5	High resistance but not suitable for heating coils.
Shot metal	Pb 99 As 1	Casting bullets and small shot.
Solder		
Soft	Pb 67 Sn 33	Plumber's solder.
Medium	Pb 50 Sn 50	

TABLE III (*Continued*)

Name	Composition, per cent	Uses
Hard	Pb 33 Sn 67	
Silver	Ag 10–80 Cu 16–52 Zn 4–38	High melting solder
Speculum metal	Cu 70–65 Sn 30–35	Takes a high polish. Formerly used in reflectors for telescopes.
Steel		
Plain carbon	C 0.05–0.15	Boiler plate, rivets, sheet steel, case-hardening stock.
	C 0.15–0.25	Structural work, bridges, shafting.
	C 0.25–0.40	Axles, connecting rods, piston rods.
	C 0.4–0.75	Rails, steel castings.
	C 0.6–0.8	Cutlery, woodworking tools, drills.
	C 0.8–1.0	Springs, lathe tools, drills.
	C 1.0–1.2	Large lathe tools, axes, knives.
	C 1.2–1.5	Saws, files, balls for bearings, razors.
Chromium	Cr less than 3	Projectiles, files.
Chromium-tungsten	C 0.65–0.75 W 13.5–18.5 Cr 3.5–4.5 V 0.75–2.0	High-speed tools. May be run at 500°–600°C. without losing their edge.
Chromium-vanadium	C 0.25–1 Cr 0.8–1.1 V 0.15	Gears, springs, general automobile parts.
Manganese	Mn 12–14	Used on sharp railroad curves, frogs, switches, etc., where wear is hard.
Nickel	Ni 3–4	Drive shafts, crankshafts, gears, and other automobile parts.
Nickel-chromium	Ni 1–4 Cr 0.45–2	Armor plate, automobile parts subject to heavy stresses.
Silicon	Si less than 5	Has high permeability and low hysteresis. Used in dynamo construction.

TABLE III (*Continued*)

Name	Composition, per cent	Uses
Stainless.....	Cr 13–20	Used in cutlery, containers for corrosive liquids, etc.
	Cr 8–25 Ni 8–25	General purpose corrosion-resistant metal.
Sterro metal..... (Aich's metal, Delta metal)	Cu 60 Zn 38 Fe 2	Strong as mild steel and not easily corroded. Used in hydraulic cylinders, sea-water valves.
Type metal.....	Pb 60–85 Sb 8–20 Sn 5–35	
"Y" alloy.....	Al 92.5 Cu 4 Ni 2 Mg 1.5	Used for general castings. Retains strength at higher temperatures than No. 12.

TABLE IV.—ETCHING SOLUTIONS FOR MACROSCOPIC EXAMINATION*

Etching reagents	Composition	Used to show	Remarks
Hydrochloric acid	Use concentrated hydrochloric acid, or HCl, 1 part; water, 1 part. Heat to 212°F.	Segregation and the like.	Etch for at least ½ hour or until defects, if any, are brought out.
Sauveur's reagent	3 water; 2 sulphuric acid (conc.); 1 hydrochloric acid (conc.)	Segregation and the like.	Add H_2SO_4 to water, then add HCl and keep near boiling point, adding more HCl as necessary. A pyrex baking dish makes a good container. Etch for at least ½ hour or until defects, if any, are brought out.
5 per cent picric acid	Add 5 grams picric acid, $C_6H_2(NO_2)_3.OH$, to 95 c.c. alcohol, C_2H_5OH.	Segregation and the like.	Etch for 4 to 5 hours.
Ammonium persulphate	Add 1 to 2 grams ammonium persulphate, $(NH_4)_2S_2O_8$, to 10 c.c. of water.	Variations in crystalline structure as well as segregation.	One of the best reagents for developing crystalline variations and segregations in iron and steel.
Various reagents containing copper chloride proposed by:			
1. Heyn,	Add 10 grams copper-ammonium chloride, $CuCl.NH_4Cl.6H_2O$, to 100 c.c. of water.	Segregation (portions high in carbon, sulphur, and phosphorus will darken). Neumann lines, etching pits, etc.	A somewhat weaker solution is better, the specimen being etched two or three times in a fresh solution if necessary. A coating of spongy copper forming may be removed with a swab of wet cotton. 0.5 per cent solution of ammonium persulphate will facilitate removal of adherent copper film.
	Cupric chloride, $CuCl_2$, 10 grams. Magnesium chloride, $MgCl_2$, 40 grams. Hydrochloric acid, HCl, 10 c.c. Water H_2O, 20 c.c. Alcohol, C_2H_5OH, to 1000 c.c. Dissolve salts in least possible amount of hot water and make up to 1000 c.c. with absolute alcohol.	Segregation.	Apply drop by drop to small specimens until structure is developed. Wash in boiling water and then alcohol or wash off the deposited copper with ammonia to obtain greater contrast. Absolute methyl alcohol may be used if ethyl is unavailable.

* From the *Handbook of the American Society for Steel Treating.* (*Reproduced by permission.*) A complete and detailed discussion of etching reagents will be found in the 1939 edition of the "Metals Handbook," American Society for Metals.

TABLE IV.—ETCHING SOLUTIONS FOR MACROSCOPIC EXAMINATION (*Continued*)*

Etching reagents	Composition	Used to show	Remarks
2. R. H. Canfield	Nickel nitrate crystals, 5 grams. Cupric chloride, 1.5 grams. Ferric chloride, 6 grams. Dissolve salts in 12 c.c. of hot water. The amount of water present in the solution largely determines the speed with which it works. If desirable to have it work slowly, add 150 c.c. of methanol. A few c.c. of nitric acid may be added.	Segregation of impurities, especially phosphorus.	The specimen is immersed in the solution to a depth of a few millimeters. After 90 seconds, it should show the effect of the plating, although it sometimes takes several minutes. Pure metal takes the plating. The color of the deposit shows a wide range from purplish red to pale brown. Ghost lines and segregations show up perfectly white. When the plating is complete rinse and dry the specimen quickly. Phosphorus print; Soak a piece of photographic paper for several minutes in a 5 per cent solution of potassium ferricyanide in water. Lay it face up on a blotting paper and press the surface of the plated specimen against it, leaving it there for a minute. For this purpose the plating should be fairly thin. After rinsing the paper and fixing in the usual manner a record in blue is obtained of the places which did not take the plate. These blue places contain the impurities, presumably phosphorus.
3. Le Chatelier and Lemoine	Cupric chloride, $CuCl_2$, 10 grams. Magnesium chloride, $MgCl_2$, 40 grams. Hydrochloric acid, HCl, 20 c.c. Water, H_2O, 180 c.c. Absolute alcohol, C_2H_5OH, 1000 c.c.	Segregation, etc.	Applied like Stead's reagent. Contrast can be increased by electrolysis using a single battery cell, keeping current below 50 milliamperes. Absolute methyl alcohol may be used if ethyl is unavailable.
4. Rosenhain and Haughton	Iron chloride, $FeCl_3$, 30 grams. Hydrochloric acid, HCl, 100 c.c. Cupric chloride, $CuCl_2$, 10 grams. Stannous chloride, $SnCl_2$, 0.5 gram. Water, H_2O, 1000 c.c.	Segregation, etc.	The copper adheres firmly. Pearlite areas remain bright. Ferrite darkened by deposited copper, the purest parts darkening the fastest. To avoid pitting dilute the reagent.
5. Le Chatelier and Dupuy	Ethyl alcohol, C_2H_5OH, 100 c.c. Water, H_2O, 10 c.c. Cupric chloride, $CuCl_2$, 1 gram. Picric acid, $C_6H_2(NO_2)_3.OH$, 0.5 gram.	Segregation, etc.	Amount of hydrochloric acid to be added varies with the material under examination.
6. Oberhoffer	Ethyl alcohol, C_2H_5OH, 500 c.c. Water, H_2O, 500 c.c. Stannous chloride, $SnCl_2$, 0.5 gram. Cupric chloride, $CuCl_2$, 1 gram. Ferric chloride, $FeCl_3$, 30 grams. Hydrochloric acid, HCl, 50 c.c.	Segregation, etc.	
7. Humfrey	Copper ammonium chloride, 120 grams. Hydrochloric acid, HCl. ± 50 c.c. Water, H_2O, 1000 c.c.	Segregation, etc.	Addition of hydrochloric acid causes copper deposit to adhere. Etching therefore starts with a neutral solution until all scratches have disappeared. Then in successive applications the acidity is increased to a maximum. After wiping away deposited copper and drying, the surface is lightly rubbed with fine emery paper and relief portions brought out in strong contrast. The section may be printed with ordinary printers ink applied by a roller to the surface.
8. Dickenson	First etch with 10 per cent nitric acid, HNO_3; then re-etch with iron chloride, $FeCl_3$, 40 grams. Cupric chloride, $CuCl_2$, 3 grams. Hydrochloric acid, HCl, 40 c.c. Water, H_2O, 500 c.c.	Segregation, etc.	

* From the *Handbook of the American Society for Steel Treating.* (*Reproduced by permission.*)

TABLE V.—ETCHING SOLUTIONS FOR MICROSCOPIC EXAMINATION*

(a) For Normal Iron and Steel

Etching reagents	Composition	Proposed by	Used to show	Remarks
Picric acid[1] (*a*)	Picric acid, $C_6H_2(NO_2)_3.OH$ 4 grams. Ethyl alcohol, absolute, C_2H_5OH, 95 c.c.	Igevsky.	General structure of iron and steel.	Bottle should be well stoppered.
(*b*)	Picric acid, $C_6H_2(NO_2)_3.OH$, 5 grams. Ethyl alcohol, 95 per cent, C_2H_5OH, 100 c.c.	Igevsky.	General structure of iron and steel.	Bottle should be well stoppered.
Nitric acid[2] (*a*)	Nitric acid, conc., HNO_3, 5 c.c. Absolute methyl alcohol, CH_3OH, 95 c.c.	Boylston.	General structure of iron and steel.	A weaker solution, 1 per cent, is better for heat-treated steels, especially for those containing martensite or troostite.
(*b*)	Nitric acid, conc., HNO_3, 10 c.c. Ethyl alcohol, C_2H_5OH, 90 c.c.	Sauveur.	General structure of iron and steel.	
Iodine-iodide	Iodine, I, 1.25 grams. Potassium iodide, KI, 1.25 grams. Water, H_2O, 1.25 c.c. Alcohol, C_2H_5OH, to make 100 c.c.	Stead.	General structure of iron and steel.	
Tincture of iodine	Iodine, I, in alcohol, C_2H_5OH, in varying proportions as required.	Osmond.	General structure of iron and steel.	Bottle should be well stoppered and kept in dark place.
Hydrochloric acid	Hydrochloric acid, HCl, sp. gr. 1.19, 1 c.c. Alcohol, C_2H_5OH, 100 c.c.	Martens and Heyns (1904).	.....	For hardened steel especially. May dilute with 500 c.c. distilled water and use weak electric current.
Potassium bitartrate	Potassium bitartrate, $KCH_4H_4O_6$.	LeChatelier.	Ferrite.	

(b) For Hardened Steel[3]

Nitric acid in amyl alcohol.	Nitric acid (conc.)$_4$, HNO_3, 4 c.c. Amyl alcohol, $CH_3(CH_2)_4.OH$, 96 c.c.	Kourbatoff.	Structures of hardened steel.	In 5 minutes troosto-sorbite is brown, austentite yellow, martensite white.
Alcohol and acid solution in acetic anhydride (*a*)	(1) 1 part amyl alcohol, $CH_3(CH_2)_4.OH$, 1 part ethyl alcohol, C_2H_5OH, 1 part methyl alcohol, CH_3OH. (2) 1 part of 4 per cent nitric acid, HNO_3, in acetic anhydride, $(CH_3.CO)_2O$. Mix (1) and (2) just before using.	Kourbatoff.	Structures of hardened steel.	Colors troostite and troosto-sorbite
(*b*)	2 parts methyl alcohol, CH_3OH. 2 parts ethyl alcohol, C_2H_5OH, 2 parts amyl alcohol, $CH_3(CH_2)_4.OH$,	Kourbatoff.	Troosite.	
	1 part butyl alcohol, $CH_3(CH)_3OH$, 3 parts of 4 per cent nitric acid, HNO_3, in acetic anhydride, $(CH_3.CO)_2O$.	Kourbatoff.	Structures of hardened steel.	Colors austenite, martensite, and troostite differently.
Alcoholic solutions of nitric and picric acids.	4 per cent nitric acid, HNO_3, in methyl alcohol, CH_3OH, to which is added .10 its volume of 4 per cent picric acid, $C_6H_2(NO_2)_3.OH$, in ethyl alcohol, C_2H_5OH.	Kourbatoff.	Troosto-sorbite and martensite needles.	In 10 minutes colors troosto-sorbite and martensite needles.
Nitric acid and nitrophenol	1 volume 4 per cent nitric acid, HNO_3, in ethyl alcohol, C_2H_5OH, and 3 volumes saturated solution of nitrophenol, $NO_2.C_6H_4OH$, in ethyl alcohol, C_2H_5OH.	Kourbatoff.	Structures of hardened steel.	Differentiates the various constituents.
Hydrochloric acid and orthonitrophenol.	1 volume of saturated solution of orthonitrophenol in alcohol C_2H_5OH. 2 volumes of 20 per cent hydrochloric acid, HCl, in amyl alcohol, $CH_3(CH_2)_4.OH$.	Kourbatoff.	Structures of hardened steel.	Colors troosto-sorbite and martensite needles.
Nitric acid and nitraniline.	1 volume of nitric acid, HNO_3 in alcohol, C_2H_5OH and 3 volumes of saturated solution of nitraniline, $NO_2.C_6H_4NH_2$.			
Meta-nitrobenzol sulfonic acid.	5 per cent meta-nitrobenzol sulfonic acid in alcohol.	Benedicks.	Martensitic and austenitic steels.	Darkens martensite more than austentite.

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TABLE V.—ETCHING SOLUTIONS FOR MICROSCOPIC EXAMINATION (*Continued*)*

(*c*) *For Carbides, Etc.*

Etching reagents	Composition	Proposed by	Used to show	Remarks
Sodium picrate	Picric acid, $C_6H_2(NO_2)_3.OH$, 2 grams. Sodium hydroxide, NaOH, 24.5 grams. Water.....73.5 c.c.	Kourbatoff.	Cementite and other carbides, etc.	Use boiling 5 to 10 minutes. Cementite colored; also iron tungstide (Fe_nW) and iron tungsten carbide (Fe_2W_2C) in tungsten steels while tungsten carbide (WC) is unattacked. This reagent is most easily made up by adding a 5 per cent water solution of picric acid to a 25 per cent solution of NaOH. The acid should be added slowly while stirring to prevent precipitation of sodium picrate crystals, and the mixture should always be alkaline as tested with litmus paper.
Neutral sodium picrate	Neutral Sodium picrate, $C_6H_2(NO_2)_3.Na$.	Matweieff.	Cementite and iron phosphide.	Solution used boiling 20 minutes. Iron phosphide attacked, cementite unattacked.
Hydrogen peroxide and sodium hydroxide.	10 c.c. commercial hydrogen peroxide, H_2O_2. 20 c.c. 10 per cent sodium hydroxide, NaOH in water.	Yatsevitch.	Structure of high speed steel and free carbide.	Use fresh; 10 to 12 minutes. Tungsten carbide darkened.
Sulphurous acid	Sulphurous acid, saturated solution, 3 or 4 c.c. Water or alcohol to make 100 c.c.	Hilpert and Colver-Glauert.	Structure of non-pearlitic steels and pig iron.	Use 7 seconds to 1 minute.
Ferricyanide solution (*a*)	Potassium ferricyanide, $K_3Fe(CN)_6$, 10 grams. Potassium hydroxide, KOH, 10 grams. Water 100 c.c.	Murakami.	Carbides and tungstides in tungsten and high-speed steels.	Use hot.
(*b*)	Use 1 to 4 grams of $K_3Fe(CN)_6$ instead of 10 as above.	Comstock.	Nitrides.	Use hot. Cementite blackened; pearlite is turned brown; and massive nitrides remain unchanged.

(*d*) *For Alloy Steels*

Copper sulphate	4 grams copper sulphate. 20 c.c. hydrochloric acid. 20 c.c. water.	Marble.	Structure of stainless steel.	
Saturated solution of ferric chloride.	Saturated solution of ferric chloride in HCl, to which a little HNO_3 has been added.	.....	Structure of stainless steel.	Use full strength.
Ammonium persulphate	2 parts of 50 per cent solution of HCl. 2 parts of 15 per cent solution of ammonium persulphate. 1 part of a concentrated alcoholic solution of O-nitro-phenol.	.....	Structure of stainless steel.	
Aqua regia	3 parts HCl. 1 part HNO_3.	.....	Structure of stainless steel.	The mixture should stand 24 hours before using. It is used full strength for rapid work but requires very careful handling.
Acid ferric chloride	Ferric chloride 10 grams. Hydrochloric acid 30 c.c. Water to make 120 c.c.	Curran.	Structure of stainless steel.	This ordinarily used diluted with an equal amount of water, applying with a piece of cotton, rubbing gently, then washing with water and finally with alcohol. The time will vary but is rarely over 30 seconds. The time is lengthened by using a more dilute solution, allowing closer control of the depth of etching. With very dilute solutions, electrolytic etching works very well, using 1.1 volts (an ordinary dry cell).
Mercurous nitrate	Hydrochloric acid 100 parts. Water 100 parts. Mercurous nitrate 7 parts.	.....	Structure of stainless steel.	Heat to effect complete solution but use cold.
Ferric chloride	Ferric chloride, $FeCl_3$, 5 grams. Hydrochloric acid, HCl, 50 c.c. Water, H_2O, 100 c.c.	.....	Structure of austenitic nickel steels.	
Electrolytic etching	Sodium hydroxide, NaOH, 0.5 gram. Water, H_2O, 100 c.c. Use low electric current.	.....	Structure of stellite, high-chrome steels, etc.	On 110-volt D. C. circuit use two 4 c.p. lamps in series connected with two wire terminals, platinum wire preferable. Flood specimen's surface with solution. Make contact with one wire at side and dip the other with the solution moving it around to obtain uniform etch.

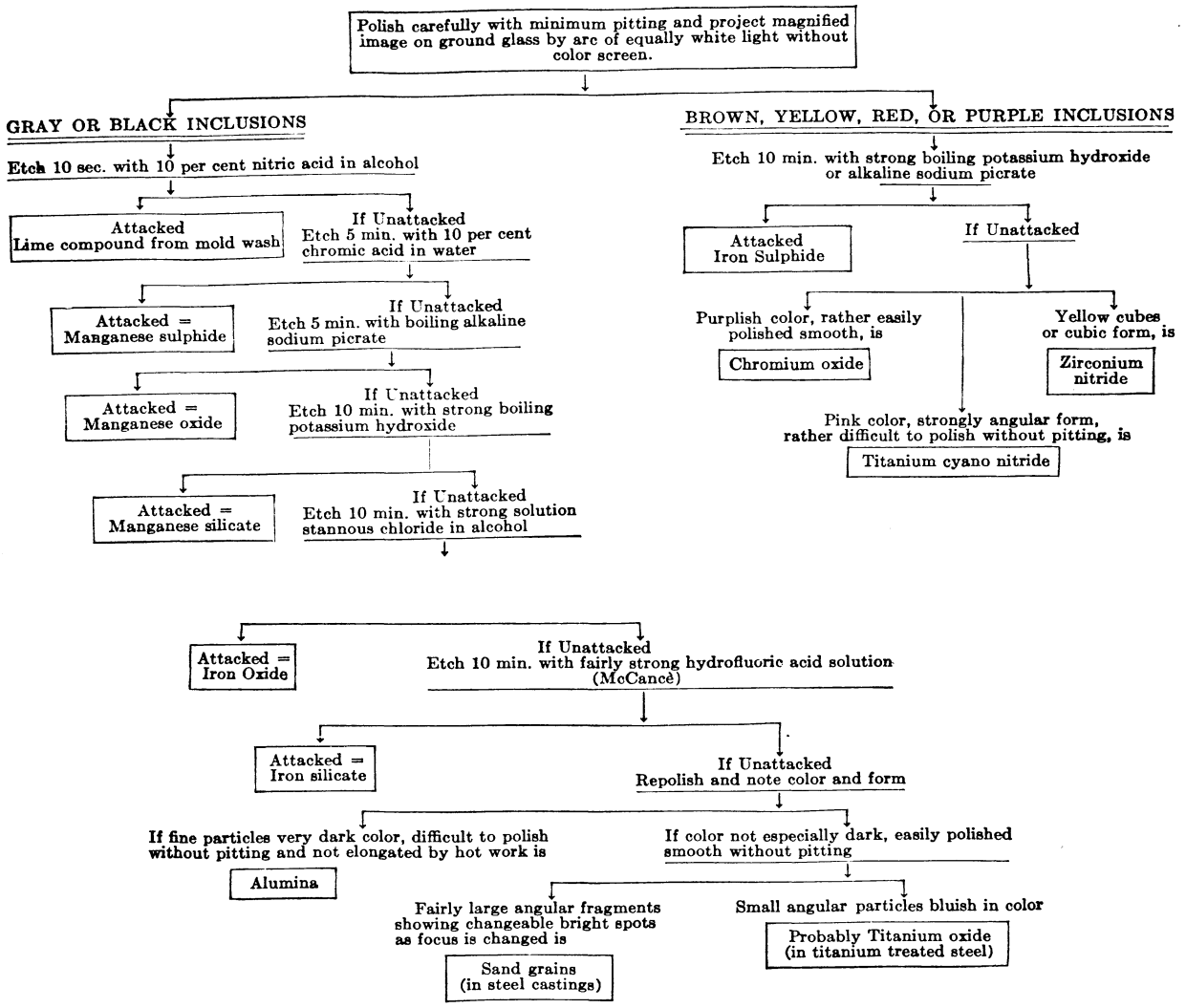
[1] The term *picral* is frequently applied to any solution of picric acid in alcohol.
[2] The term *nital* is frequently applied to any solution of nitric acid in alcohol.
[3] Not frequently used. Added for general information.

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TABLE VI.—METHOD FOR THE IDENTIFICATION OF NONMETALLIC INCLUSIONS IN IRON AND STEEL[1]

BY CAMPBELL AND COMSTOCK

Revised Form



[1] *Proceedings*, American Society for Testing Materials, Vol. 1, 1923, p. 521.

TABLE VII.—ETCHING SOLUTIONS FOR NONFERROUS METALS*

Etching Reagents and Methods.—The following list gives the principal reagents which have been found especially suitable for different nonferrous metals and alloys:

Copper

Ammonium persulphate, copper-ammonium chloride, ammonium hydroxide and hydrogen peroxide.

Brasses

Ammonium persulphate, ferric chloride, ammonium hydroxide with hydrogen peroxide.

Copper-aluminum Alloys

Ammonium persulphate, ferric chloride, nitric acid, copper-ammonium chloride.

German Silver

Ammonium persulphate, ferric chloride.

Nickel, Monel Metal, Etc.

Merica's solution (nitric and acetic acids).

Aluminum and Light Aluminum Alloys

Sodium hydroxide, hydrofluoric acid, hydrofluoric with hydrochloric acid.

Lead, Tin, and Their Alloys (White Metal, Etc.)

Chromic acid with nitric acid, hydrochloric acid, silver nitrate, ferric chloride.

Zinc and Alloys Rich in Zinc

Iodine, chromic acid with nitric acid.

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Etching Reagents for Copper*

Reagent	Composition	Remarks
Ammonium hydroxide and hydrogen peroxide.	Equal volumes of concentrated ammonium hydroxide and hydrogen peroxide (3 per cent solution). (Sometimes better results are obtained by increasing the proportion of ammonium hydroxide.)	Swab surface of the specimen with cotton, which has been previously dipped in the solution. Slow swabbing of the surface is most effective. To prevent oxidation the specimen should be placed in running water as soon as swab is removed. Only freshly prepared solutions are of value.
Ammonium hydroxide and hydrogen peroxide.	Hydrogen peroxide.....10 c.c. Ammonium hydroxide (conc.).....40 c.c.	A satisfactory etching reagent for cast copper. Apply reagent to surface of polished specimen with swab and rub briskly until mirror-like surface is obtained.
Ferric chloride for copper products.	Ferric chloride..... 15 c.c. (Saturated solution of ferric chloride and water.) Hydrochloric acid (conc.)..... 30 c.c. Water.....200 c.c.	For copper products, such as sheets, rods, etc., use the above reagent and method as given for cast copper but with a final immersion for a few seconds in this ferric chloride solution.
Sulphuric acid.....	Sulphuric acid (sp. gr. 1.84)..... 1 part Hydrogen peroxide (3 per cent solution) .....20 parts	Approximate time of etching—1 to 1½ minutes.
Sulphuric acid.....	Sulphuric acid (sp. gr. 1.84)..... 1 part Potassium dichromate (saturated solution).....10 parts	Approximate time of etching—30 to 60 seconds. This method emphasizes the occurrence of cuprous-oxide inclusions.
Sulphuric acid.....	Sulphuric acid (sp. gr. 1.84)..... 1 part Potassium permanganate (4 grams per 1000 c.c. of water)...10 parts	Approximate time of etching—1 to 1½ minutes.
Ferric chloride.....	Ferric chloride..... 10 grams Hydrochloric acid (sp. gr. 1.19)..... 30 c.c. Water.....120 c.c.	Approximate time of etching—30 seconds. Both methods are satisfactory for low magnifications. The alcoholic solution produces the better contrast.
Ferric chloride.....	Same, in 120 c.c. of alcohol.	
Potassium arsenate.....	Ammonium hydroxide (conc.).....1 part Potassium arsenate (saturated solution)...3 parts	Etch for about 24 hours. This method emphasizes the oxide inclusions.
Potassium permanganate.	Ammonium hydroxide (conc.).....2 parts Potassium permanganate (4 grams per 1000 c.c. of water)....3 parts	Etch for 2 or 3 minutes. The etching is best carried out just as the solution begins to change to a brown color, due to formation of manganese dioxide; otherwise, an obscuring film may result on the specimen.
Nitric acid.....	Nitric acid (sp. gr. 1.42).	The time of etching is very short. A satisfactory etch may be produced, but it is difficult to control the intensity of attack.
Chromic acid.....	Chromic acid (saturated solution).	Etch from 1 to 1½ minutes. This reagent emphasizes the grain boundaries and also the oxide inclusions.

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ETCHING REAGENTS FOR COPPER (*Continued*)

Reagent	Composition	Remarks
Silver nitrate.....	2 per cent solution.	Etch from 20 to 30 seconds. The film of deposited silver must be removed by a swab of cotton. The presence of oxide inclusions is emphasized by the etching.
Copper-ammonium chloride.	Copper ammonium chloride..... 5 grams Water.....120 c.c. Add ammonium hydroxide (conc.) until precipitate which forms redissolves, giving a clear blue color.	Etch from 30 to 60 seconds. One of the most satisfactory etching reagents for copper.
Ammonium persulphate..	10 per cent solution.	Etch from 1 to 2 minutes. A very satisfactory etching reagent for copper. The surface of the specimen should be free from any trace of grease.

Etching Reagents for Copper Alloys (Brass, Bronze, German Silver, Etc.)*

Reagent	Composition	Remarks
Nitric acid	Nitric acid (conc.).....50 c.c. Water.....50 c.c.	Immerse sample in the solution until the structure is revealed, then wash with water and dry with alcohol. This reagent is likely to cause pitting. For copper and its alloys, this reagent is satisfactory for microscopic examination.
Ammonium hydroxide and hydrogen peroxide.	Hydrogen peroxide..... 7 c.c. Ammonium hydroxide..43 c.c.	Satisfactory for copper alloys, chiefly the yellow brasses, containing copper, lead, and zinc.[1]
Ammonium hydroxide and hydrogen peroxide.	Ammonium hydroxide (conc.).....10 c.c. Hydrogen peroxide... 1.0 c.c. (Equal volumes are often used with excellent results.)	Suitable for wrought brass, bronze, German silver, etc. Place 10 c.c. of strong ammonium hydroxide in a watch glass and add 1 or 2 c.c. of hydrogen peroxide (3.6 per cent). The solution is applied to the surface of the specimen with a wad of cotton, rubbing gently until the grain structure appears.
Grard No. 1	Ferric chloride.... 0.5 grams Hydrochloric acid. 50 c.c. Water.....100 c.c.	For cast gun metal, use the above ammonium hydroxide solution to show dendrites. Then flood specimen with Grard No. 1 until the alpha darkens slightly. The eutectoid remains a bright blue-white color and shows up in marked contrast.
Grard No. 2	Ferric chloride..... 19 grams Hydrochloric acid (conc.)..... 6 c.c. Water.....100 c.c.	
Ferric chloride	Ferric chloride..... 10 grams Hydrochloric acid (sp. gr. 1.19)..... 30 c.c. Water.....120 c.c.	Suitable for brasses, bronzes, German silver, copper-aluminum alloys, and phosphorus bronze.
Ammonium persulphate.	10 per cent aqueous solution. (Made just before using.)	This reagent is improved by adding a few drops of ammonium hydroxide just before using. One of the most satisfactory reagents for copper-alloys. The surface of specimen should be free from grease.
Heyn's solution	Copper-ammonium chloride..... 5 grams Water.....120 c.c.	Add ammonium hydroxide until precipitate which forms redissolves. Suitable for copper-aluminum alloys.

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[1] For copper-zinc, copper-tin, and copper-zinc-tin alloys, this solution, with a final immersion of the specimen in a ferric chloride solution, gives satisfactory results. The ferric chloride solution may be varied in strength, according to the judgment of the user.

Etching Reagents for Nickel, Monel Metal, Cupro-nickel and Nickel-silver Alloys*

Reagent	Composition	Remarks
Merica's solution	Nitric acid (70 per cent).50 c.c. Acetic acid (50 per cent).50 c.c.	Nickel and its alloys frequently show pits with colored rings or holes when etched with a 50 per cent aqueous nitric-acid solution. Merica's solution gives much better results. This is a very satisfactory etching reagent for cast, cold-drawn, and annealed nickel.
International Nickel Co.	Nitric acid.....20 to 40 c.c. Acetic acid (75 per cent).....30 to 40 c.c. Acetone.....30 to 40 c.c.	
Hydrochloric acid	Hydrochloric acid (conc.)	This reagent is excellent for cast and cold-drawn nickel but requires about 1 hour for etching.
Sulphuric acid	Sulphuric acid (sp. gr. 1.84).....1 part Potassium dichromate (saturated solution)...5 parts	This reagent gives excellent results for electrolytic nickel. Etch for about 4 minutes.
Nitric acid	Nitric acid (conc.)	This reagent, which is suitable for electrolytic and cold-drawn nickel, gives good contrast. Etch for about 5 seconds.
Sulphuric acid	Sulphuric acid (sp. gr. 1.84)..... 1 part Hydrogen peroxide (3 per cent solution)....10 parts	For cast nickel, this reagent gives good results. Etch for 30 seconds.
Ferric chloride[1]	Ferric chloride..... 10 grams Hydrochloric acid (sp. gr. 1.19)..... 30 c.c. Water.....120 c.c.	This reagent gives good results for cold-drawn nickel. Etch for about 2 minutes.

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[1] For nickel-silver alloys, a 15 to 20 per cent solution of ferric chloride gives good results. The polished surface of the specimen is immersed in the solution until a slight dullness appears, which should signify that it has been etched sufficiently. However, when the structure is not homogeneous, *i.e.*, cored, the cores are highly emphasized.

Etching Reagents for Aluminum and Aluminum Alloys*

Reagent	Composition	Remarks
Sodium hydroxide.....	Sodium hydroxide....0.1 to 20 per cent Dissolve in water (a few c.c. of alcohol are added to slow up the action).	The alcoholic solutions have a slower action. The more dilute solutions are useful for differentiating constituents.[2] Sodium hydroxide reagents leave a black deposit which can be removed by washing the specimen in water and then momentarily immersing in concentrated chromic or nitric acid.
Sodium hydroxide.....	Sodium hydroxide... 10 grams Water.....100 c.c.	This reagent is suitable for developing the structure of zinc-bearing aluminum alloys.
Sodium hydroxide.....	Sodium hydroxide....0.1 to 1.0 per cent Dissolve in water.	This solution swabbed on the surface of the specimen brightens $FeAl_3$; with prolonged swabbing this constituent etches to a brownish coloration.[3]
Hydrofluoric acid.....	Hydrofluoric acid.....0.1 to 20 per cent Aqueous or alcoholic solution.	The 1, 2, and 8 per cent solutions are used most frequently. A black deposit is formed by etching, which is removed by immersing momentarily in concentrated nitric acid. $CuAl_2$ and $FeAl_3$ are darkened by hydrofluoric acid.[4]
Hydrofluoric and hydrochloric acids.....	Water.....90 c.c. Hydrofluoric acid (conc.).....10 c.c. Hydrochloric acid (conc.).....15 c.c.	Reveals grain size in an excellent manner. Etch from 30 to 90 seconds.
Nitric acid.....	1 to 25 per cent aqueous solution.	A 20 per cent aqueous solution heated to 160°F. is excellent for distinguishing $CuAl_2$. The specimen is immersed for 2 or 3 seconds and then immediately quenched in cold water. $CuAl_2$ is colored brown, while $FeAl_3$ and most of the other constituents are not affected.[5] A 4 per cent alcoholic solution is recommended for aluminum-zinc alloys.
Ferric sulphate.....	Ferric sulphate .5 to 10 per cent Dissolve in water.	With a 10 per cent solution, etch 45 seconds, or about 3 minutes, with a 5 per cent solution. $CuAl_2$ is colored brown. $FeAl_3$ is not affected.
Sodium carbonate.....	A saturated solution of sodium carbonate is made up, and for use a few drops are added to about 25 c.c. of water.	The solution is brought to boiling, and the previously warmed specimen is immersed in it for only a second or two. Wash at once and dry.
Sulphuric acid.....	10 to 20 per cent aqueous solution.	The reagent is heated to 160°F. Immerse specimen for a few seconds and then quench in cold water. $FeAl_3$ is stained black.
Villela's etch.....	Hydrofluoric acid..... 2 parts Nitric acid..... 1 part Glycerin..... 3 parts	Etched by immersion.

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ETCHING REAGENTS FOR WHITE METALS (LEAD, TIN, OR ZINC BASE)*

Reagent	Composition	Remarks
Nitric acid	2 per cent alcoholic solution.	For alloys rich in tin.
Nitric acid	5 per cent aqueous solution.	For alloys rich in lead.
Hydrochloric acid	5 per cent aqueous solution.	For alloys rich in zinc.
Hydrochloric acid	Either a concentrated or dilute solution may be used, depending upon the composition of the alloy.	Used for white metals high in tin. When a concentrated solution is used, dip the specimen in the acid for a few seconds; wash thoroughly and dry quickly.
Chromic oxide and sodium sulphate.	Chromic oxide.... 20 grams Sodium sulphate.. 1.5 grams Water.....100 c.c.	This is an excellent etching reagent for both cast and wrought zinc.
Chromic acid	94 per cent nitric acid. 6 per cent chromic acid.	A few drops of this solution is added to 100 c.c. of water just before using. Used for zinc.
Iodine	Iodine..... 1 part Potassium iodide..... 3 parts Water.....10 parts	Suitable for alloys rich in zinc or cadmium.
Silver nitrate	5 per cent aqueous solution.	Suitable for alloys of lead, tin, antimony, bismuth, and antifriction alloys. The black deposit left on the surface is washed off.
Ferric chloride	Ferric chloride..... 10 grams Hydrochloric acid (sp. gr. 1.19) ..... 30 c.c. Water.....120 c.c.	Very satisfactory etching solution for alloys of antimony, lead, and babbitt metals.

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Reagents for Miscellaneous Etching*

Reagent	Composition	Remarks
Glycol etch	Diethylene glycol. 75 per cent by vol. Concentrated nitric acid 1 per cent by vol. Water 24 per cent by vol.	Suitable for magnesium and its alloys. Etch for about 10 seconds.
Ammonium hydroxide	(1) Boil in ammonium hydroxide and hydrogen peroxide or hydrogen peroxide alone.	These three reagents are used for tungsten.
Sodium hydroxide	(2) Electrolytic etch. 15 per cent sodium hydroxide. 20 milliamperes per square centimeter.	Etch about 5 minutes.
Potassium ferrocyanide	(3) 2.5 per cent aqueous solution. Add a few drops of ammonium hydroxide just before using.	The specimen is gently polished with a piece of broadcloth or rubber which has been moistened with this solution.
Aqua regia	Nitric acid 1 part Hydrochloric acid 5 parts Water 6 parts	Suitable for gold, silver, platinum, and alloys rich in gold. Use at about 60°F.

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TABLE VIII.—TEMPERATURE CONVERSION TABLE (CONDENSED)
Degrees Centigrade to Degrees Fahrenheit.
Degrees Fahrenheit = 9/5 Degrees Centigrade + 32°.
Degrees Centigrade = 5/9 (Degrees Fahrenheit − 32°).

Degrees→ Centigrade ↓	0	10	20	30	40	50	60	70	80	90
	Degrees Fahrenheit									
0	32	50	68	86	104	122	140	158	176	194
100	212	230	248	266	284	302	320	338	356	374
200	392	410	428	446	464	482	500	518	536	554
300	572	590	608	626	644	662	680	698	716	734
400	752	770	788	806	824	842	860	878	896	914
500	932	950	968	986	1004	1022	1040	1058	1076	1094
600	1112	1130	1148	1166	1184	1202	1220	1238	1256	1274
700	1292	1310	1328	1346	1364	1382	1400	1418	1436	1454
800	1472	1490	1508	1526	1544	1562	1580	1598	1616	1634
900	1652	1670	1688	1706	1724	1742	1760	1778	1796	1814
1000	1832	1850	1868	1886	1904	1922	1940	1958	1976	1994
1100	2012	2030	2048	2066	2084	2102	2120	2138	2156	2174
1200	2192	2210	2228	2246	2264	2282	2300	2318	2336	2354
1300	2372	2390	2408	2426	2444	2462	2480	2498	2516	2534
1400	2552	2570	2588	2606	2624	2642	2660	2678	2696	2714
1500	2732	2750	2768	2786	2804	2822	2840	2858	2876	2894
1600	2912	2930	2948	2966	2984	3002	3020	3038	3056	3074
1700	3092	3110	3128	3146	3164	3182	3200	3218	3236	3254
1800	3272	3290	3308	3326	3344	3362	3380	3398	3416	3434
1900	3452	3470	3488	3506	3524	3542	3560	3578	3596	3614
2000	3632	3650	3668	3686	3704	3722	3740	3758	3776	3794

TABLE IX.—MELTING POINTS AND ATOMIC WEIGHTS OF THE MORE IMPORTANT METALS AND METALLOIDS

Element	Symbol	Atomic weight	Melting point, °C.
Aluminum	Al	26.97	658.7
Antimony	Sb	121.76	630.5
Arsenic	As	74.91	814.0
Barium	Ba	137.36	850.0
Beryllium	Be	9.02	1285.0
Bismuth	Bi	209.00	271.0
Boron	B	10.82	2300.0
Cadmium	Cd	112.41	320.9
Caesium	Cs	132.91	26.0
Calcium	Ca	40.08	851.0
Carbon	C (Diamond)	12.01	3500.0
Cerium	Ce	140.13	775.0
Chromium	Cr	52.01	1550.0
Cobalt	Co	58.94	1490.0
Copper	Cu	63.57	1083.0
Gallium	Ga	69.72	30.0
Gold	Au	197.2	1063.0
Indium	In	114.76	155.0
Iridium	Ir	193.1	2409.0
Iron	Fe	55.84	1535.0
Lanthanum	La	138.92	826.0
Lead	Pb	207.21	327.4
Lithium	Li	6.940	186.0
Magnesium	Mg	24.32	651.0
Manganese	Mn	54.93	1243.0
Mercury	Hg	200.61	−38.9
Molybdenum	Mo	95.95	2620
Nickel	Ni	58.69	1452.0
Osmium	Os	190.2	2700.0
Palladium	Pd	106.7	1555.0
Phosphorus	P	31.02	I—44, II—590.0
Platinum	Pt	195.23	1773
Potassium	K	39.096	62.5
Rubidium	Rb	85.48	38.5
Ruthenium	Ru	101.7	2450.0
Selenium	Se	78.96	220.0
Silicon	Si	28.06	1427
Silver	Ag	107.880	960.0
Sodium	Na	22.997	97.5
Sulphur	S	32.06	I—112.8 II—119.0 III—95.5
Strontium	Sr	87.63	771.0
Thallium	Tl	204.39	303.0
Tellurium	Te	127.61	452.0
Tin	Sn	118.70	232.0
Titanium	Ti	47.90	1800.0
Tungsten	W	183.92	3370.0
Uranium	Ur	238.07	1690.0
Vanadium	V	50.95	1710.0
Zinc	Zn	65.38	419.4

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