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Metallurgy of the Rarer Metals – 2

ZIRCONIUM

METALLURGY OF THE RARER METALS

General Editor of Series
H. M. FINNISTON, B.Sc., Ph.D., A.R.T.C.
Head of Metallurgy Division, Atomic
Energy Research Establishment
Harwell, Berkshire

1 CHROMIUM
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ZIRCONIUM

by

G. L. MILLER

PH.D., B.SC., A.R.I.C., M.I.CHEM.E.

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TO

DR W. J. KROLL

PREFACE

THE reason for writing this book was a desire to collate the information on zirconium which has been flowing at an ever increasing rate from the technical press during the last few years. Wherever possible, and as the field is such an enormous one, it has not always been possible, I have examined the information critically in the light of my own experience obtained either as a result of my own work on zirconium or as a result of knowledge gained during several visits to the United States of America.

Historically, interest in zirconium may be divided into two parts. The first concerns a zirconium industry which was predominantly interested in zirconium for use in the form of refractories, vitreous enamels, and certain alloys. The second part is concerned with the present or rapidly approaching situation, where a new zirconium industry is developing and the metal, with or without alloying additions, will become of greater importance. It is this later interest with which the book is mostly concerned, the earlier aspect being covered in the first chapters.

The methods for the production of the metal are divided into three sections, each occupied by one chapter (*i*) Investigations leading up to the Present Production Methods, (*ii*) Commercial Production and (*iii*) Development. The first part covers the work of the investigators of 100–150 years ago who did so much with so little—helped no doubt at times by enthusiastic analysts. The second part describes the Kroll and iodide (van Arkel) processes, and the third the various attempts and suggestions that have been made to produce cheaper and better metal.

Melting is an important factor in the metallurgy of zirconium and it has been considered necessary to allocate a complete chapter to this subject, describing in fair detail the various melting techniques which have been employed.

The properties of the metal have been detailed under several sections and, in particular, a chapter has been devoted to the reactions of zirconium with the common gases. The outstanding property of zirconium—its resistance to chemical corrosion—deserved detailed treatment in a separate chapter.

I wish to thank my friends and colleagues for their generous help without which I could not have written this book. I particularly wish to thank Miss L. BRADLEY and Miss S. MONTGOMERY, and

K. J. BOADEN, F. G. COX, A. D. HARRISON and R. TITTERINGTON. I also wish to thank T. DEANS, Imperial Institute, B. FULLMAN, British Non-Ferrous Metals Research Association, and W. R. S. GARTON, Imperial College, for their kind assistance.

Finally, thanks are due to the many authors and publishers of papers for permission to reproduce original material, relevant sources being given in the bibliographies and indicated appropriately in the text.

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G. L. MILLER

5 August 1953

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HISTORY AND OCCURRENCE OF ZIRCONIUM

THE first reference to zirconium was in 1789 when Klaproth, a chemist, while analysing the precious stone jargon, found it contained an earth which he could not identify and which he later called *Zirkonerde*.

Klaproth's discovery was confirmed by several other chemists, and by 1797 another chemist, Vauquelin, had investigated the new earth which was then called zirconia, and given details of its preparation as well as the properties of some of its compounds. In 1824, Berzelius succeeded in isolating an impure form of the metal, but, despite many attempts, ductile metal in massive form was not produced until a hundred years later, when in 1925 van Arkel and de Boer evolved a technique which until recently was the only satisfactory method for the production of ductile metal.

Several methods have been devised for the production of metal of various grades of purity which, while satisfactory for certain commercial applications, could not be fabricated.

The development of the production of ductile zirconium is due mainly to Kroll, who, working in the laboratories of the U.S. Bureau of Mines, evolved a method of manufacture which was to be expanded to full scale commercial production.

1.1. OCCURRENCE

Zirconium is widely distributed in nature and while not one of the most abundant elements it ranks eleventh in the list of elements in the earth's crust. The zirconium content of the earth's crust is estimated to be more than 0·028 per cent, which is more than those of common metals such as copper, lead, nickel and zinc.

Zirconium is found in crystalline rocks (especially in granular limestone) in chlorites and schists, in gneiss, syenite, granite and beds of iron ore. It is found also in pegmatite, sandstone, ferruginous sands and in smaller amounts in a number of minerals.

The most widely distributed and abundant mineral containing zirconium is the silicate, known as zircon, 4[$ZrSiO_4$]. It forms tetragonal crystals with a density 4·6 to 4·8 and hardness on Moh's scale of 7·5. The zirconium content of the mineral varies from 61 to 66·8 per cent compared to 67·2 per cent theoretical content of normal silicate.

The main commercial source of zircon, before the development of the beach sands, was the decomposed pegmatites in places such as Madagascar and Brazil where zircon was obtained as large crystals weighing up to 15 lb.

Zircon is present in varied quantities in many igneous rocks, basalts and dolerites, and there are indications that it is universally present in granite and allied rocks. Its resistance to weathering and attrition explains its presence in the heavy residues of various rocks, and concentrates are to be found in the beach sands of many countries, in particular, New South Wales and Queensland, Florida, Brazil, India and Ceylon. (In the beach sands zircon is associated with ilmenite, rutile and monazite) and the zircon is recovered as tailings from the recovery of the titanium minerals.

The second most important zircon mineral is baddeleyite $4[ZrO_2]$, which is the native form of the oxide or zirconia. (The crystals have a density of 5·4 to 6·02 and a hardness on Moh's scale of 6·5.) The main deposits are in Brazil in a mountainous plateau, mainly composed of phonolite. The ore is divided into two classes, the alluvial pebbles known as 'favas' ranging in size from half an inch to three inches with a zirconia content of 90 to 93 per cent and a density of 4·8 to 5·2. The second class is a mixture and is known as zirkite, which ranges from a light grey material carrying a minimum of 73 per cent zirconia to a blue-black material with 80 to 85 per cent zirconia.

Numerous zirconium-bearing materials are described in the textbooks but the only two that matter as far as industry is concerned are zircon and baddeleyite.

Some confusion has been created by the use of trade names such as brazilite, zirkite and caldasite. The name brazilite was first used for an oil-bearing rock from Bahia and later mis-applied to baddeleyite. The name brazilite was revived in the United States of America about 1916 as a trade name for the fibrous and mamillated forms of baddeleyite from the Pocos de Caldas region of Brazil.

Zirkite and caldasite are ores consisting of fine-grained intergrowths of zircon and baddeleyite from the same district.

1.2. World Resources

The richest deposits of zircon occur as zirconiferous sands in Australia, and in 1948 as many as seven companies were engaged in exploiting these deposits.

Recently production of zircon concentrates in the U.S.A. has equalled the Australian production. Other sources of zirconium minerals are Brazil, Ceylon, Africa and Malaya.

World production of zircon is shown in *Table I*; these values are an amended version of those given by H. F. Pearson[8].

*Table I. World Production of Zirconium Ores in Tons**

Source	*1945*	*1946*	*1947*	*1948*	*1949*	*1950*
India	1,020	466	n.a.	n.a.	n.a.	n.a.
Malaya	182	—	—	—	n.a.	n.a.
Australia	15,180	12,403	21,576	21,889	20,675	21,535
Egypt	10	4	—	93	126	93
French West Africa	—	—	38	188	241	—
Madagascar	3	—	—	—	—	—
Brazil (*exports*)	746	4,382	3,915	3,581	2,243	950
U.S.A. (*estimate*)	—	—	—	—	n.a.	17,000
Total (*estimate*)	17,141	17,255	25,529	25,751	23,285	39,578

* All ores are zircon except the Brazilian which are baddeleyite-zircon.

1.2.1. *Australia*

Although displaced by the U.S.A. in 1949 from the position of the world's largest potential producer of zircon minerals, Australia held this position from 1934 until 1948. The production of ore expressed as zircon over that period rose from 28 to 21,811 tons with a total for the whole period of 136,083 tons. Exports to various countries are shown in *Table II*[5].

Table II. Exports of Zirconium-bearing Minerals from Australia

Exports of Zircon Concentrate in Tons

Destination	*1948*	*1949*	*1950*
United Kingdom	911	2,360	2,726
New Zealand	8	45	50
Canada	—	320	200
Other British countries	—	1	—
France	100	1,046	283
Netherlands	102	400	706
Austria	—	—	600
U.S.A.	11,766	13,302	14,489
Other foreign countries	—	309	556
	12,887	17,783	19,610

Table II—continued

Exports of Zirconium–Rutile Concentrate in Tons

Destination	*1948*	*1949*	*1950*
United Kingdom	—	4	201
Italy	—	50	—
U.S.A.	4,160	2,190	1,363
	4,160	2,964	1,564
Estimated zircon content	2,555	1,893	977

Exports of Zircon–Rutile–Ilmenite Concentrate in Tons

Destination	*1948*	*1949*	*1950*
United Kingdom	—	—	4
U.S.A.	180	—	—
	180	—	4
Estimated zircon content	133	—	3

The tables show that the U.S.A. continued to be the largest buyer of Australian zircon concentrate notwithstanding that she is a very considerable producer herself.

The most important sources of zircon are what are known as the beach sand minerals which are found mainly along the most easterly part of the Australian coast between Southport, 17 miles north of the Queensland-New South Wales border, and Ballina, 50 miles south of the border. Smaller deposits are known to occur farther to the south at intervals for several hundred miles and beaches have been worked at Yamba, 96 miles south and Woolgoola, 150 miles south of the border and at Swansea, 60 miles north of Sydney. Important deposits have been shown to exist on North Stradbroke Island and others have been located farther to the north, as far as Tin Can Bay at the south of Frazer Island.

The deposits belong to the group of zircon–rutile–ilmenite sands. They are known as black sand deposits and are the result of the concentration of the heavy mineral content, usually about 0·1 per cent of the beach sands, and occur where there is a suitable combination of coast orientation relative to prevailing winds and currents[4].

The deposits which are being worked in Southern Queensland are present in the form of beds or seams in the upper part of the beach and in the berm and dunes immediately behind the beach, as shown in *Figure 1*. Sections at right angles to the strand line have shown these seams to be wedge-shaped, gradually thinning out seawards and thickening landwards before tapering to a rather abrupt end. The average thickness of the seams is one to two feet but some have been found as much as five feet thick. Parallel seams may occur separated by layers of quartz sand.

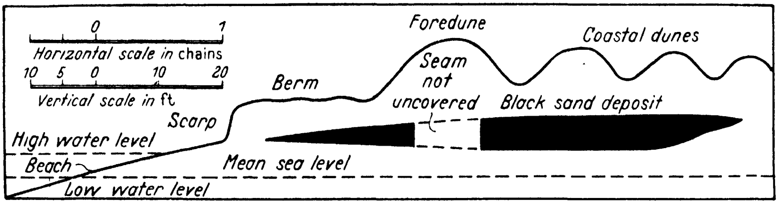

Figure 1. Section at right angles to strand line extending inland through northern end of Broadbeach Crown Land for 4·5 chains *showing the nature of the heavy mineral deposit.* (*For sake of clarity the thin layers of white sand which in places divide the lens into seams have been omitted.*)

The seams are generally well defined and for most of their extent almost horizontal. The beds vary in dimensions, but they are always longer in the dimension parallel to the strand line. Sections parallel to the beach have revealed lenticular beds with an average thickness of one foot extending for a distance of only 70 feet, while others of similar thickness have been traced for distances up to 250 yards and only slight evidence of their lenticularity has been seen[2].

Composition—The heavy mineral content of the deposits that have been worked ranges from 20 to 80 per cent, but probably averages in the feed to the concentrating tables 40 to 50 per cent by volume. The mineral composition of the heavy mineral concentrates obtained ranges, in general, from 44 to 70 per cent zirconia and 15 to 30 per cent each rutile and ilmenite. The zircon–rutile–ilmenite concentrate is remarkably free from other heavy minerals which seldom exceed a total of 5 per cent and are usually about 2 to 3 per cent.

Processing—The overburden, which is thin on the beaches but may be as much as 20 feet of dune sand in the deposits behind the beaches, is removed by bulldozers or other equipment. The heavy mineral seams thus exposed are mined either by selective hand-shovelling into motor lorries, or by overloader, diesel shovel, scoop or other power-driven appliance. At almost all workings some selection is practised and barren layers are discarded if possible.

All operators separate the heavy minerals, principally zircon, rutile and ilmenite, from the quartz which ranges from 20 to 90 per cent of the volume of sand mined, by mechanical concentration over Wilfley tables.

Some of the companies take from the top edge of the concentrates a small high-gravity cut consisting mainly of zircon, together with most of the monazite and other heavier minerals. This is re-tabled or otherwise concentrated and sold to the Commonwealth Government as a monazite concentrate.

Before 1948, most of the zircon exported from Australia was shipped as a black sand mixture containing zircon (50 to 90 per cent), ilmenite, rutile and monazite. Such mixed concentrates were subsequently beneficiated in the importing country, mainly the U.S.A. The Commonwealth Government acting under the provisions of the Atomic Energy Act of 1946 forbade the exportation of mixed concentrates as from March 1948 and from that date all exports of zircon were shipped as high grade (65 per cent ZrO_2) concentrates with the monazite and titanium minerals removed.

At first the export ban applied only to concentrates containing 0·5 per cent or more monazite and concentrates containing less were exported, but the Government did not favour the export of low grade material which, if concentrated, could demand a much higher price from the importing country and consequently as from 1st January 1950 export of all mixed concentrates was banned[1].

The highest grade zircon is obtained by a company which applies a flotation process to the table concentrates. The flotation product is dried and cleaned electromagnetically to produce a concentrate with 99·5 per cent zircon.

The other companies dry the table concentrate and pass it through electrostatic or electromagnetic separators. Details of the processes differ but they may be divided broadly into two systems:

(*1*) The dried concentrate is passed through electrostatic separators which split it into two portions, one containing rutile and ilmenite, the other zircon, garnet, monazite and other minerals. Each of these products is then passed through electromagnetic separators which remove the ilmenite from the rutile, and the monazite, garnet and other slightly magnetic minerals from the zircon.

(*2*) The concentrate is passed first through electromagnetic separators which remove the ilmenite, and in some cases also garnet and monazite. The resulting zircon–rutile mixture is then passed through electrostatic separators and the separate zircon and rutile concentrates obtained are each subjected to further electromagnetic cleaning.

The products of the various companies are zircon ranging from 93 to 99·5 per cent, rutile ranging from 95 to 97 per cent and a zircon–rutile (60:40 per cent).

Reserves—The deposits are widespread and have not yet been fully explored; however, estimates of the reserves have been made[4].

The deposits on the beaches are limited and could not be expected to maintain production at the 1947 rate (21,576 tons of zircon and 13,194 tons of rutile) for more than 10 years.

Fortunately, much larger reserves are contained in the deposits belonging to earlier sand dunes behind the beaches, particularly in the Byron Bay, New Brighton–Cudgera, Cudgera and Currumbin–Southport areas and on North Stradbroke Island.

Boring tests on Stradbroke Island indicate that while the average heavy mineral content is probably not more than 3 per cent (30 zircon, 25 rutile and 45 per cent ilmenite), the enormous quantities of sand promise very large reserves of zircon, rutile and ilmenite.

1.2.2. *United States of America*

Zircon is recovered in the U.S.A., as in most other countries, as a co-product or by-product in the production of ilmenite, rutile and monazite from the sands of elevated beaches. The ever increasing demand in recent years for titanium minerals has, in consequence, greatly expanded the output of zircon.

Between 1918 and 1928 the U.S.A. was a regular producer of zircon concentrates, but production ceased in 1928, to be revived in the last years of World War II.

The main production in the U.S.A. is from Florida. In April 1944 a company started operating near South Jacksonville and by 1948 was processing at the rate of 7500 tons of sand per day, which yielded a combined weight of zircon, rutile and ilmenite of approximately 4000 tons per month.

In December 1948 another company obtained a long term lease on State-owned ilmenite-bearing property near Starke, Florida. Operations on this site started in 1949 with a planned intake capacity of 25,000 tons of sand per day, this rate being approached by the end of the year. The heavy mineral fraction of the sand was reported as 4 to 4·5 per cent by weight, containing 45 per cent ilmenite and 14 per cent zircon. The principal minerals sought were leucoxene (altered ilmenite and rutile) and rutile with zircon being produced as a lesser co-product.

The site near Starke is leased by E. I. du Pont de Nemours and Co. and operated under contract by Humphreys Gold Corporation; they recover the zircon for their own account in a separate plant designed to treat the ilmenite-free tailings.

Unforeseen difficulties hampered earlier operations, coarse organic debris (logs and roots), and hard layers of sediment hampered dredging operations. Functioning of the Humphrey spirals in the concentrating plant was complicated by the presence of tannin-like substances which so darkened the mill-water that excessively wide cuts were required on the spirals to prevent undue loss of titanium minerals. Mill screens were clogged by roots and, finally, discharge of the dark mill effluent into streams aroused local protests.

Despite these difficulties the U.S.A. had attained self-sufficiency with respect to zircon, by the end of 1949. It should be noted, however, that this position is dependent on maintaining a stable titanium mineral industry.

By 1950, du Pont reported that the monthly sand output from the dredge slightly exceeded 500,000 tons, which is equivalent to about 3000 tons zircon on the estimate of 4 to 4·5 per cent heavy mineral containing 14 per cent zircon.

Reserves—Titaniferous black sands containing important quantities of zircon are extensively distributed through central and north-eastern Florida, from north east of Jacksonville to north west of Lake Okeechobee[9]. It is also reported that the reserves of zircon in this area are enormously large compared to U.S.A. requirements[7].

Zircon is abundant in the gold–monazite gravels flanking the granite areas of central Idaho, and with gradual development of monazite recovery in that region may eventually be producible in significant tonnage. Zircon is also abundant in central Californian gold gravels and may likewise eventually be recovered commercially.

1.2.3. *Brazil*

The chief zirconium ores produced in Brazil are the variety of baddeleyite known as brazilite, and the mixture of this mineral with zircon which is marketed as 'zirkite'. Brazil is the only known commercial source of baddeleyite in the world.

The deposits occur in the Plateau of Pocos de Caldas in the south western part of the State of Minas Gerais. The region has its boundary with that of the state of São Paulo.

There are two main zirconium districts in the plateau, Cascata and Pocinhos, the Serronte mine being the principal mine in the Cascata district while the Campo de Alemao or Taquary is the principal mine in the Pocinhos district[10].

The ore is present in alluvial, eluvial and vein deposits. The commercial grades vary from 70 to 99 per cent zirconium oxide. The material mined, caldasite, is mainly a mixture of baddeleyite and zircon. The ore occurs in four types:

(*i*) 'Favas' (alluvial zirconium)
(*ii*) Compact (from eluvial and vein formations)
(*iii*) Low grade (light, friable)
(*iv*) Mixed.

The highest grade ore is the large pebbles found in the gravels containing up to 90 per cent zirconium dioxide.

Mining is done by primitive methods with picks and shovels. Most of the ore is obtained from surface concentrates but some is mined from pits down to 20 metres in depth. All the vein material is transported to washing plants and concentrated by aid of water current, sieving, hand-picking and hand-jigging.

The plateau of Pocos de Caldas had produced, up to 1943, 33,000 tons of ore, all of which was exported.

The exports over the years 1935 to 1940 averaged 1000 to 1500 tons per year, the bulk of this being a 65 to 75 per cent ZrO_2 grade with a smaller quantity of 80 to 87 per cent grade.

Important deposits of zircon occur in the beach sands of the states of Bahia, Espirito Santo, and Rio de Janeiro, in association with monazite, the zircon being recovered as a by-product from the monazite operations.

Reserves—Reserves of baddeleyite in the State of Minas Gerais were estimated at 2,000,000 tons in 1936.

1.2.4. *Ceylon*

The beach sands at Pulmoddai and Tirukkovil, eastern Ceylon, are estimated to have a heavy mineral content of about 4,000,000 tons containing about 25 per cent zircon. Deposits in the western part of the island are thought to contain equally large reserves of heavy mineral[6].

1.2.5. *Malaya*

During the Japanese occupation 741 tons of zircon and 207 tons mixed monazite and zircon concentrates were recovered as a by-product of alluvial tin mining[3].

1.2.6. *U.S.S.R.*

The potentially commercial zircon mineral eudialyte (about 14 per cent ZrO_2) occurs in large tonnages in the Kola Peninsula in conjunction with the apatite deposits which are being operated.

1.2.7. *India*

The main deposits of heavy mineral beach sands in Travancore, Southern India, occur north from Quilon and at Manavala-Kurichi, 100 miles to the south, towards Cape Comorin. The zircon content of the black sand is up to about 7 per cent, the zircon concentrates containing about 67 per cent zirconia. The zircon is recovered as a by-product of the titanium and monazite operations.

Statistics on zircon production have not been published since 1946. During the period 1924 to 1946 the total production of zircon concentrate was 29,000 tons.

Reserves—A complete survey has never been made but reserves appear to be very large.

1.2.8. *Africa*

Small quantities (less than 100 tons per year) of zircon have been recovered from the ilmenite–zircon beach sands of Senegal, French West Africa, mainly between Rufisque and the mouth of the Saloum River.

At Tororo in Eastern Uganda the recovery of zircon and baddeleyite, as well as apatite, magnetite and pyrochlore, is being investigated.

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2

CONSUMPTION AND USE OF ZIRCONIUM

THE United States of America is the largest user of zirconium minerals (about 95 per cent of the Australian production is imported by the U.S.A. in addition to the bulk of the Brazilian output), and has an established zirconium industry[11]. Imports for recent years are shown in *Table III*[13].

*Table III. Zirconium Ore and Concentrates Imported for Consumption in U.S.A., 1946 to 1950**

Year	*Australia*†	*Brazil*	*Canada*	*India*	*Total*	
					Short tons	*Value $*
1946	14,379	2,431	4	—	16,814	453,458
1947	21,894	4,619	2	4,181	30,696	891,161
1948	14,320	3,553	2	279	18,154	571,161
1949	18,839	1,994	—	—	20,833	636,529
1950	15,988	697	141	—	16,826	431,107

* Concentrates from Australia are either zircon or mixed zircon–rutile–ilmenite, and those from Brazil are either baddeleyite or zircon. All other imports are zircon only.

† Imports of zircon, rutile and ilmenite from Australia until early 1948 were largely in the form of mixed concentrates. These mixed concentrates are classified arbitrarily by the U.S. Department of Commerce as 'zirconium ore', 'rutile', or 'ilmenite'. Total zircon contents of the 'zirconium ore' (as shown in *Table III*) and of the 'rutile' and 'ilmenite' concentrates are estimated as follows:

1946 11,535 tons
1947 22,727 tons
1948 13,873 tons
1949 14,623 tons
1950 15,098 tons.

Annual requirements of zirconium minerals for industry are estimated to be between 20,000 and 30,000 short tons. *Table IV* shows the imports of ore over the period 1947 to 1949 and, in addition, shows the exports of zirconium-containing materials[12]. (Values in this table refer to zirconium ore, the equivalent zircon content imported is given in the note below *Table III.*)

U.S.A. consumption in 1949 was estimated to have been around 20,000 short tons. This was distributed in the various sections of industry as follows: ceramics (except refractories) 32; refractories 20; oxides and chlorides 20; foundry sand 16; and alloys 12 per cent. Consumption of zirconium alloys amounts to several thousand tons a year.

Estimated requirements of various industries in Great Britain for 1948 was: refractories 43; vitreous enamels 22; and foundries 20 per cent[25]. The zircon concentrate imports into the United Kingdom are shown in *Table V*[24].

Table IV. Imports and Exports of Zirconium-bearing Materials by U.S.A. 1947 to 1949

Mineral product	*Quantity (short tons)*			*Value (thousand dollars)*		
	1947	*1948*	*1949*	*1947*	*1948*	*1949*
Zirconium ore	30,696	18,154	20,833	891	571	637
EXPORTS						
Zirconium ore	330	312	305	26	24	24
Metals and alloys	5	11	37	6	8	13
Other ores and concentrates	2,419	9,859	2,541	3,535	2,908	1,195
Other ferro-alloys	36,098	55,647	7,921	1,196	1,840	766
Other metals and alloys	2,320	2,795	921	1,462	1,465	651

Table V. Imports of Zirconium Ore (Zircon Sand) into the United Kingdom

Year	*1948*	*1949*	*1950*	*1951*
Tons	2,654	2,495	2,769	5,690

2.1. USES OF ZIRCONIUM

The large scale production of ductile zirconium metal has been developed during the past few years by the U.S. Bureau of Mines who in 1948 constructed a pilot plant capable of producing 15,000 lb of metal per year.

The fact that zirconium has a slight tendency to absorb slow neutrons, relatively high melting point, and good corrosion resistance indicates possible applications in the field of atomic energy, particularly for nuclear energy pile construction.

Since 1948 development of the production of zirconium metal has been rapid, and a plant has been built in the U.S.A. with a rated capacity of over 100 tons per annum while another is under consideration. The metal which will be produced for the Atomic Energy Commission must be free from hafnium, which has a high neutron absorption cross section. Zirconium with or without hafnium has outstanding corrosion resisting properties and may prove to be a most useful metal for chemical engineering purposes and other special applications. There has been little opportunity to test the metal for such applications since none of the metal produced at the U.S. Bureau of Mines has been available to industry.

Most of the zirconium which has been offered commercially has been available in two forms, powder or crystal bar. The powder form has been used mainly for flash light powders (now superseded by flash lamps), flares, fireworks, and detonators. In Germany large quantities of fine zirconium powder were used in ammunition primers and in time fuses for bombs, where it was found to have a decided advantage over other materials because when ignited no gas is evolved which could prevent the fuse from burning. Some powder has been used for electronic and powder metallurgical purposes. The crystal bar metal has been fabricated to sheet and wire for use in the electronic industry and for surgical purposes.

2.1.1. *Electronic applications*

Zirconium is an excellent getter[43], a fact that was noted by the early workers, de Boer and Fast, and recent experiments have confirmed their statement that zirconium will absorb or form solid solutions with oxygen up to 40 atomic per cent, and with nitrogen up to 20 atomic per cent without x-ray evidence of an actual compound being formed. This means that one gramme of zirconium (equivalent to 2 in^2 of 0·005-in sheet) will absorb 82 cm^3 of oxygen or 30·7 cm^3 of nitrogen at normal temperature and pressure or, expressed in terms of the conditions existing in a vacuum tube, 62,400 micron litres of oxygen and 23,350 micron litres of nitrogen per gramme of zirconium.

In design work it is desirable to use twice or more the volume of zirconium required by theoretical considerations to avoid possible disintegration due to weakening of the metal.

J. D. FAST[20] showed that the optimum temperature for absorption of hydrogen by zirconium is 300 to 400° C and for all other gases (except the rare gases) 1000 to 1500° C. Oxygen and nitrogen are absorbed in large quantities below these temperatures particularly if the thin film of oxide which prevents absorption at low temperatures is removed by heating the metal to 850 to 900° C in a vacuum, when the oxide dissolves rapidly into the metal producing an active surface which getters at temperatures as low as 600° C.

In power and transmitting tubes zirconium tabs can be welded to hot parts of the tube such as filament supports, cathode heat shields, *etc* or better still, the heat shields, anodes, *etc* can be fabricated from zirconium.

Zirconium will not alloy or amalgamate with mercury and can be used in mercury vapour or mercury arc rectifier tubes; zirconium has been used as a heat shield in a grid controlled mercury vapour rectifier with excellent results. It has also been used in sleeves over filament supports, and various arrangements have been devised for using the metal in close proximity to filaments or cathodes so that it will act as a getter whenever the tube is in operation, regardless of anode load and temperature.

Applications of this type, described by G. A. ESPERSON[19], are shown in *Figure 2.* Tests were made in experimental triodes having an emitter design similar to that shown in *Figure 2* (*b*) some with the zirconium cylinders and some without. The former showed a better vacuum during a 1000-hour life test as well as better emission. *Figure 3* shows the life performance of both types of tubes.

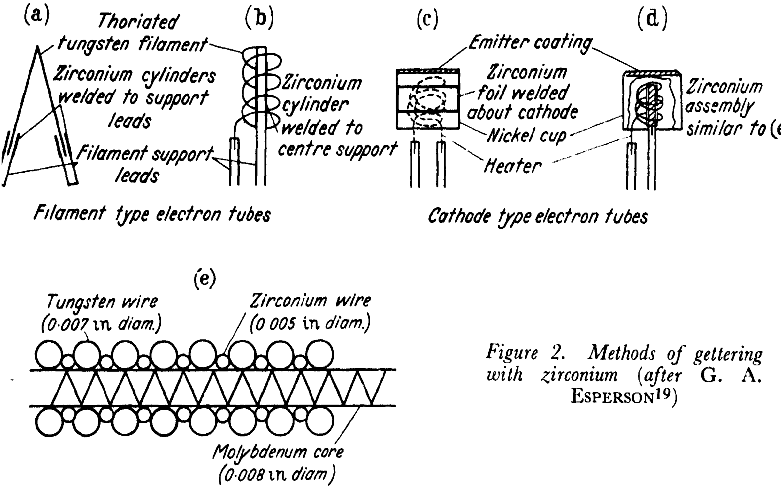

Figure 2. Methods of gettering with zirconium (after G. A. ESPERSON[19])

Although hydrogen is absorbed at a much lower temperature than oxygen and nitrogen it is possible to absorb all these gases with one getter by having a portion of it extending outside the area subject to heat by radiation—an alternative is to use two getters, one located at a point which will give a temperature of 900 to 1000° C or over and the other at a point which will give approximately 300° C.

The principal use for zirconium has been in power tubes but recent tube developments for radio, television and military requirements have tended to eliminate volatile getters and use zirconium which gives longer life and simplifies pumping procedures.

Zirconium is also used as a grid emission inhibitor. Powder in the form of zirconium hydride of fine particle size is usually employed. It is applied by forming a suspension with xylene, amyl

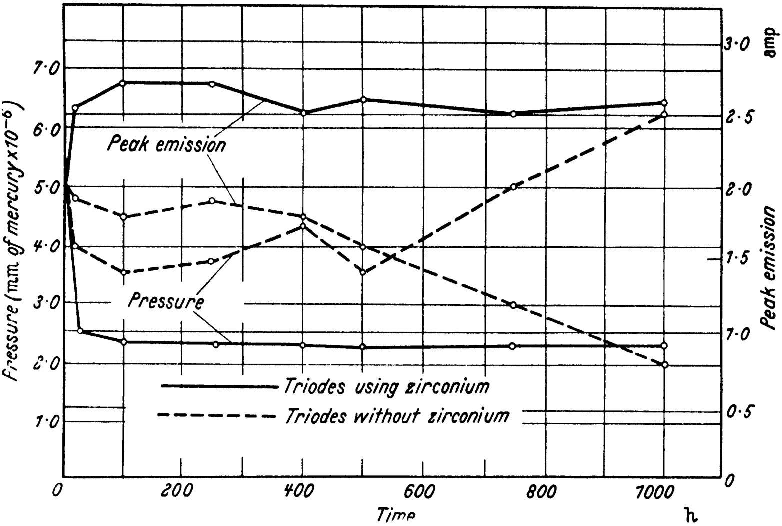

Figure 3. *Life versus pressure and peak emission* (*after* G. A. ESPERSON[19])

acetate or other suitable carrier and painted or sprayed on to the grid laterals, the carrier being removed by heating. Heat treatment at about 1100° C in a vacuum decomposes the hydride and fixes the zirconium coating to the plate.

2.1.2. *Neurosurgical applications*

A special application for the high corrosion resistance of zirconium is illustrated by its use in surgery. Some of the small quantity of ductile zirconium, which was available before the development of the Kroll process, was used for this purpose. Zirconium has been compared with stainless steel, tantalum, silk and silver for various surgical applications. Tests were made in suturing, use of pegs, screws, skull plates and for haemostats in brain surgery. In all tests zirconium was found to cause no measurable reaction in muscle fascia, bone and brain. Zirconium compared favourably with tantalum in most applications and was definitely superior to silver in others[3–5].

J. CAUCHOIX and J. LAVARDE[15] also investigated the use of zirconium and other metals for neurosurgery and concluded that tantalum and zirconium were the most suitable metals, their properties being almost identical; tantalum was slightly more neutral electrically and zirconium less toxic.

2.2. COMMERCIAL ZIRCONIUM ALLOYS

Several zirconium alloys have been in commercial production for a number of years, some like the copper and magnesium alloys because the addition of zirconium confers peculiar properties and others like the iron and silicon alloys which are used as scavengers for steel.

2.2.1. *Aluminium–zirconium*

The aluminium–zirconium alloys are of little interest for their mechanical properties.

Corrosion resistant alloys containing magnesium, aluminium and zirconium have been patented by L. H. CANAC[14]. The alloys contained up to 3 per cent zirconium. The light emission of aluminium–magnesium alloys used for flash lamps is improved by the addition of zirconium[37]. M. D. SARBEY[34] claimed the addition of 0·5 to 15 per cent zirconium to such an alloy. Philips[30] claimed the use of a malleable alloy of aluminium–zirconium containing 1·5 to 2·0 per cent zirconium for use as grid wires in cathode vacuum tubes.

Aluminium–zirconium alloys are produced by the aluminothermic process, using zircon, zirkite or zirconia and boosting the heat of reaction with sodium chlorate or barium peroxide. The reaction with aluminium and potassium zirconium fluoride is vigorous but not uncontrollable. Good results are claimed for the prior fusion of the zircon, zirkite or zirconia with sodium fluoride before the reduction with aluminium.

2.2.2. *Copper–zirconium*

F. R. HENSEL[22] patented age hardenable copper–zirconium alloys with 0·1 to 5·0 per cent zirconium. It was claimed that an addition of 0·93 per cent zirconium to copper produced an alloy which when quenched from 950° C had a hardness of Rockwell B 10 and after aging 8 h at 450° C the hardness increased to Rockwell B 59. Double aging after cold work promotes the maximum aging effect[21]. The addition of zirconium to beryllium–copper alloys improves their strength at high temperatures[16]. The addition of 0·02 to 5·0 per cent zirconium to copper had little effect on the conductivity of the metal but considerably improved its tensile strength[29].

H. VON ZEPPELIN[39] produced a copper–zirconium alloy by reducing zirconium tetrachloride with magnesium in a copper container. The copper container is covered with molten salts contained in an iron crucible. During the reaction the copper crucible is melted and alloys with the reduced zirconium.

The production of copper–zirconium alloys by electrolysis is claimed by N. A. BELOZERSKÜ *et al.*[7]. A bath of the fused chloride and fluoride of zirconium was employed with a copper cathode; this melted down with the deposited zirconium to produce a low melting point alloy which collected on the bottom of the bath.

2.2.3. *Iron–zirconium*

As described below, zirconium–iron master alloys are used in the steel industry as deoxidizers and scavengers, in addition to which they give grain control.

J. W. MARDEN and M. N. RICH[27] quote references claiming that zirconium-bearing steels were particularly suitable for armour plate. More recently Bohler[9] claimed carbon steels containing zirconium for the same purpose.

Magnetic alloys containing iron and zirconium in addition to nickel are mentioned by F. RAFFLES[31] who claimed alloys with Zr 10, Ni 5 to 40, Al 5 to 20 per cent, balance iron. P. P. ALEXANDER[1] and F. KRUPP[26] mention magnetic alloys containing cobalt, nickel, zirconium and iron.

The alloys are produced by the electric furnace reduction with carbon or by the aluminothermic technique.

An alloy containing Zr 40, Si 45, Fe 15 and C about 0·03 per cent is prepared in the electric furnace from a mixture of quartzite, zircon and coal. The zircon sand is first mixed with tar to minimize loss during reduction.

2.2.4. *Magnesium–zirconium*

Zirconium exerts a most intensive grain refining effect on magnesium[42]. The grain size of ordinary pure magnesium when chill cast may vary from about 2 mm upwards, while the same metal containing an effective addition of 0·65 per cent zirconium, will in a very massive chill casting of dimensions 70 by 20 by 20 in^3 have a grain size from 0·05 to 0·15 mm.

The alloys possess outstanding mechanical and physical properties. They provide in both cast and wrought forms considerably higher proof stresses than have ever been obtained previously in commercially practicable magnesium-base alloys, combined with high ultimate stress values and good elongation. Two of the alloys have excellent properties at moderately elevated temperatures, being practically creep resistant at 200° C[36].

A high strength casting alloy *Elektron Z5Z* is considered the most suitable for structural purposes. Its composition is Zn 4·5, Zr 0·6 to 0·7 per cent and balance magnesium. In the cast state the proof stress is about 8 to 9 ton/in^2 compared to 4·5 to 5·0 ton/in^2 for the older magnesium–aluminium alloys. In the wrought state proof stress values may be as high as 19 ton/in^2. The alloy is suitable for use in structural applications up to about 150° C.

Elektron ZRE.1 alloy with composition: Zn 2·5, rare earth metals 2·5, Zr 0·6 per cent, balance magnesium, is practically creep resistant at 200° C and may be used at even higher temperatures. It is intended primarily for elevated temperature applications and is specified for a number of large and important castings for jet propulsion units. *MCZ* casting alloy with composition: rare earth metals 3·0, Zr 0·6 per cent, balance magnesium, is another alloy suitable for use at 200° C. The rare-earth-containing alloys are also notable for their high degree of pressure tightness due to the complete absence of porosity.

ZW3 with composition: Zn 3·0, Zr 0·7 per cent, balance magnesium and *ZW2* with 1·0 per cent less zinc are wrought general purpose alloys for high duty applications. These alloys possess excellent forming properties combined with good resistance to corrosion.

Various methods for introducing zirconium into magnesium have been described. H. VON ZEPPELIN[40] stirred a mixture of zirconium tetrachloride and other salts with the magnesium, but it is reported by A. E. WILLIAMS[42] that this was unsatisfactory for the production of the *Elektron* alloys as the reaction produced small centres of magnesium chloride contamination. Satisfactory results were obtained by adding zirconium metal to magnesium heated between 900 and 1000° C in an atmosphere of argon. This was too costly to be utilized on a commercial scale and the use of zirconium fluoride and fluozirconates was examined. A. E. WILLIAMS[42] states that the fluorides were more readily reducible than the chlorides.

The alloying of zirconium with magnesium was investigated by W. P. SAUNDERS and F. P. STRIETER[35] who used several zirconium-bearing materials for the additions including metallic forms of zirconium, zirconium chloride combinations, zirconium fluoride mixtures and master alloys. The metallic forms included zirconium sponge, fused zirconium, iodide zirconium as 0·005-in sheet, and zirconium powder (briquetted, briquetted and sintered, enclosed in gas-tight magnesium capsules, and briquetted with magnesium powder).

Zirconium tetrachloride was added in a briquetted form either alone or with additions of potassium chloride, or potassium chloride plus sodium chloride.

Zirconium tetrafluoride was added as powder, briquettes, with other fluorides, and with potassium chloride. Potassium zirconium fluorides, K_2ZrF_6 and $ZrF_4.KF$, were used, with other chlorides. Most work was done with a mixture of $K_2ZrF_6 + 20$ to 50 per cent potassium chloride.

Several master alloys of zirconium were investigated including 60–40 ZrMg, 28–71 ZrMg, 14–70 ZrZn and ferro-zirconium. Ferro-zirconium was used to check the fact that iron co-precipitates zirconium from magnesium melts, and as expected no soluble zirconium was present in the final alloy. Best results were obtained with a master alloy produced by the reduction of zirconium tetrachloride with magnesium. This material was prepared by reacting magnesium at 760° C with four times its weight of a proprietary flux containing about 50 per cent zirconium tetrachloride and 50 per cent potassium chloride. The metallic product contained 30 to 50 per cent of zirconium, balance magnesium, except for a small amount of residual chlorides. The final conclusions were that several of the materials tested could be used to produce magnesium–zirconium alloys. Sponge was satisfactory but difficult to get into solution, the fused metal and thin sheet were not successful, likewise none of the powder additions gave good results. The chloride additions were quite efficient but a large amount of material has to be handled. No comment was made about chloride impurities in the finished alloy. The fluoride additions were less efficient than the chlorides, requiring a higher alloying temperature.

Master alloys, and in particular a master alloy provided by reacting zirconium tetrachloride with magnesium, appear to be the most convenient medium for the introduction of zirconium into magnesium, but before arriving at a final decision costs must be considered.

2.2.5. *Nickel–zirconium*

H. S. Cooper[17] claimed a number of alloys containing zirconium and nickel or cobalt. The alloys were said to be tough and resistant to acids and alkalis and when heated to 1150° C formed tight, protective oxide skins. An alloy suitable for the production of cutlery was obtained by adding 2 to 10 per cent zirconium to nickel. Such cutlery was unaffected by acid fruit juice. It was also claimed by Cooper that alloys with 25 to 30 per cent zirconium may be used as high speed cutting tools.

W. ROHN[33] claimed alloys of cobalt–nickel–iron–chromium with additions of zirconium or titanium for use as exhaust valves in combustion engines. J. G. BOEKER[8] claims hard alloys with zirconium additions and F. R. HENSEL *et al.*[23] found that additions of zirconium to nickel–silicon bronzes produced beneficial degassing effects.

Cooper made his alloys by the aluminothermic process according to the equation quoted by Marden and Rich as follows

$$7Ni_2O_3 + 3ZrO_2 + 18Al = Zr_3Ni_{11} + 9Al_2O_3$$

It is noticeable that the nickel does not balance.

Zirkite was used as the source of the zirconium, being ground to pass a 200-mesh sieve before mixing with 200-mesh aluminium and nickel oxide. The mixture was fired in a nickel crucible lined with magnesia or alumina. The alloys could be collected as buttons or tapped off into moulds for remelting and adjusting to the desired composition.

2.2.6. *Silicon–zirconium*

This alloy together with ferro- and ferro-silicon–zirconium are the principal zirconium alloys used in ferrous metallurgy. The zirconium is a vigorous deoxidizer and scavenger and when added to steel quickly reduces the metallic oxides and scavenges non-metallic impurities, such as nitrogen and sulphur.

An alloy of manganese–silicon–zirconium is specially recommended for treating cast iron, where it acts as a powerful graphitizer, and also controls the chill.

Boron which is added to steel to produce deep hardening may be added in combination with silicon, zirconium and other reducing metals. Two alloys known as *Silcaz* and *Silvaz* are produced for this purpose. The composition of the first is: Si 35 to 40, Al 7, B 0·5, Ti 10, Zr 4, Ca 10 per cent, balance iron. The composition of the second is : Si 39 to 41, Al 6, B 0·5, Zr 6, V 6 per cent, balance iron.

Methods of production of the alloys have been examined by G. M. WAINSTEIN[41], and G. VOLKERT[38], and by V. ELYUTIN and R. GRIGORASH[18]. The alloys can be produced by carbon reduction in the electric furnace but difficulties are encountered due to the formation of zirconium carbide, which takes place because of an equilibrium between the silicide and carbon when the silicide reaches a composition of more than 50 per cent zirconium. The carbide formed can be reacted with either silicon or silicide containing more silicon than zirconium. According to F. M. BECKET[6], fresh ore rich in silica can be used. V. ELYUTIN and R. GRIGORASH[18] investigated the production of silico-zirconium from Russian ore containing 45 to 47 per cent zirconia by (*i*) aluminothermic reduction in the electric furnace, (*ii*) reduction with carbon, (*iii*) reduction with carbon and silicon (ferro-silicon) and (*iv*) aluminothermic reduction without the use of a furnace. Good results were obtained by the first method, negative results in the second, positive results with the third and possible results by development with the fourth method.

Calcium carbide has been used by L. RENAUX[32] as an alternative to carbon as a reducing agent in the production of silicon–zirconium alloys, and although some calcium is present in the alloy the zirconium content is considerably increased. Recent workers have checked and recommended the results obtained by Renaux[10, 38]

The carbon content of the commercial alloys is below 1 per cent, the other impurities being up to 5 per cent iron, above 1 per cent aluminium and with a zirconium content of about 38 per cent, the remainder being silicon.

J. L. ANDRIEUX[2] produced silicon–zirconium alloys by fusion electrolysis by the addition of zirconia to various fused silicates.

2.3. PYROPHORIC ALLOYS

Pyrophoric alloys of lead and zirconium have been produced[28]. These alloys are stable in air and suitable for appliances such as cigarette-lighter flints. Lead ingots are heated in an argon atmosphere with zirconium and titanium metal powders in a clay-graphite crucible. The temperature is raised to 1400° C and the melt cast by bottom pouring. The ingot contains: Zr 33·5, Ti 11·5 and Pb 53 per cent; it possesses good sparking characteristics.

2.4. REFRACTORIES

Zircon, zirkite and prepared zirconia are all useful refractory materials. The most commonly used is zircon because it is the cheapest. High grade zircon melts at about 2190° C, softens between 1600 and 1800° C and shows little shrinkage up to 1750° C.

Zircon exhibits many characteristics that make it very suitable for refractory purposes. In addition to the high melting and softening points already noted it has a low thermal expansion and good resistance to abrasion. Zircon is used where an acidic refractory is required while zirconia refractories are considered to be basic.

Various media have been used to bond zircon for the production of bricks, *etc.* Phosphoric acid, manganese oxide, cupric oxide, complex zirconium silicates, zirconates, silico-fluoride and ethyl silicate have all been used. Bricks have also been made by compressing a mixture of zircon sand and zircon flour with ammonium or calcium alginate jelly and, after drying, firing at about 1700° C[25].

The softening point under load of zircon bricks varies between 1590 and 1900° C according to the purity. The linear coefficient of thermal expansion of the bricks is about $4{\cdot}1 \times 10^{-6}$ per C°.

Zircon refractory bricks find special application as linings in glass furnaces because of their resistance to spalling. Another useful property is the resistance to wetting by molten aluminium which makes them particularly suitable for aluminium melting furnaces.

High grade zircon is used in the foundry for moulds and cores which have to withstand unusually high temperatures. Finely ground, it is applied to the surface of ordinary sand moulds and cores in order to produce a high grade finish on the casting as well as to reduce mould penetration.

Zirkite is used for the production of refractory bricks and refractory ware. In the latter, the ore is washed free from iron with hydrochloric acid. The bricks are fired at 1400 to 1500° C and the ware at 1700 to 1800° C.

Zirconium dioxide chemically prepared and free from impurities when ignited has a melting point of about 2715° C, a specific gravity about 5·74, and a coefficient of expansion of $8{\cdot}1 \times 10^{-7}$ per C°. As the thermal conductivity is also low zirconia refractories resist thermal shock.

Zirconium oxide is stable in both oxidizing and moderately reducing atmospheres but on prolonged heating it is liable to undergo inversion of the crystalline structure accompanied by a serious change in volume. However, small additions of lime and magnesia will stabilize the oxide and such stabilized refractories may be used up to 2400° C.

Zirconia and zircon are extensively employed in the ceramic industry for enamels, porcelains and glazes.

The large quantities of zirconia which were used as an opacifier in vitreous enamels have been considerably reduced by their displacement by other materials, mainly titania, but zirconia continues to find applications in porcelains and glazes.

Basic zirconyl sulphate is finding increasing use in tannage for the production of fine white leathers.

Zirconium compounds are used in the preparation of dyes, water-repellants and catalytic agents, and zirconia is also becoming important as an optical-glass polishing agent.

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3

EXTRACTION OF ZIRCONIUM FROM THE ORE

3.1. METHODS OF EXTRACTION

THE first step in recovering zirconium is to decompose the ore and this in the case of the silicate is a difficult task. Methods of decomposition have been summarized by J. W. MARDEN and M. N. RICH[10] and also by W. J. KROLL and A. W. SCHLECHTEN[6].

The methods used for decomposition of zirconium ores are classified as follows:—

(*a*) Removal of silica by volatilization
(*b*) Acid attack of pretreated ore
(*c*) Fluxing with alkalis
(*d*) Fluxing with nitre cake
(*e*) Hydrofluoric acid treatment and fluoride fusion
(*f*) Chlorination of ore.

3.1.1. *Removal of silica by volatilization*

The volatilization of silica when zircon is heated to a high temperature in the presence of carbon had been noted by the earliest workers on zirconium. According to C. MATIGNON[11] the zircon begins to dissociate at 1800° C; at 2126° C dissociation is complete and pure zirconia remains. This work was done without the aid of carbon; if carbon is present the silica is reduced to silicon monoxide which volatilizes and is oxidized rapidly on exposure to air, some of the zirconia is reduced to a lower oxide but when heated in air the dioxide is formed. A method for the production of commercial zirconium of about 98 per cent grade, by heat treatment with carbon to remove the silica has been patented[5].

3.1.2. *Acid attack of pretreated ore*

The ore is made more amenable to acid attack by some form of pretreatment such as sintering[14] or melting it[15] with calcium oxide, gypsum or calcium chloride[4]. The simplest method would appear to be that claimed by C. LORENZ [9] in a patent describing the heating of the ore to above 1000° C and quenching before attacking with acid. A similar method has been used successfully for the treatment of beryl.

Sulphuric and hydrochloric acids are used in the extraction. Extraction with hydrochloric acid makes possible the separation of the iron and aluminium by formation of $ZrOCl_2.8H_2O$ which is easily crystallized from concentrated solutions. By sulphuric acid treatment the silica is separated by filtering the leach and on the addition of further sulphuric acid, iron-free sulphate is re-dissolved and later precipitated as basic sulphate $Zr_4(SO_4)_2.(OH)_{10}.15H_2O$ which is roasted to oxide.

J. W. Marden and M. N. Rich[10] described a method for the treatment of zirkite ore (*i.e.* the commercial ore from Brazil containing baddeleyite mixed with varying amounts of zircon, *etc*) with sulphuric acid, which they considered simple and effective. Zirkite (presumably finely divided) is mixed with four times its weight of sulphuric acid and digested for one to two hours at 400° C. At the end of this period the temperature is carefully raised to about 650° C and held there for one hour or until all the free sulphuric acid has been removed.

The final temperature is rather critical and, if excessive, poor recoveries may be expected due to decomposition of the zirconium sulphate. The zirconium is recovered by leaching the roast with water and recoveries of 60 to 90 per cent are obtained.

3.1.3. *Fluxing with alkalis*

This method has been used on a commercial scale for making zirconia for use in the enamel, glass and porcelain industries where the presence of a small amount of residual alkalis in the oxide is regarded as an advantage and not a disadvantage. J. W. Marden and M. N. Rich[10], who tested the various published methods, favoured the fusion with caustic soda because it required a lower temperature and less time than the other methods. They added the finely divided ore, in the proportion of one to six, to the fused caustic soda, controlling the violent frothing by the rate of addition.

The fusion produced a clear liquid which was cooled, followed by crushing and leaching with water. Treatment of large quantities by this method would be difficult as the frothing is very troublesome, and fills the surrounding atmosphere with caustic spray which is most obnoxious.

Despite the slowness and higher temperature of the soda ash reaction it is to be preferred as a factory process.

The product of the caustic fusion contains most of the zirconium in the form of sodium zirconate and most of the silicon is present as sodium silicate, but there is present to a smaller degree sodium zirconium silicate. The fusion when cooled is crushed and leached with water. Sodium zirconate tends to hydrolyse and produces a gelatinous hydroxide which is difficult to filter, but this can be avoided by not allowing the washings to get too weak in caustic content. The insoluble residues consist of sodium zirconate containing titanium and iron hydroxides, and some sodium zirconium silicate. A commercial oxide may be recovered containing: ZrO_2 80 to 84, SiO_2 8 to 12, Na_2O 4 to 6 per cent. Alternatively, the insoluble residues after leaching may be treated with concentrated sulphuric acid and the solution evaporated to fuming to dehydrate the silica. After cooling, water is added and the diluted solution filtered free from silica, to produce a solution of zirconium sulphate, from which purified salts may be produced.

3.1.4. *Fluxing with nitre cake*

This was one of the original commercial methods for decomposing zirconium minerals. The fusion material used may be as much as twenty times the weight of the ore; less than 10 parts fusion material to one of ore does not give a clear fusion. The fusion is made in a graphite, silica or cast iron vessel, the finely divided ore being added gradually to the fused nitre cake. As with caustic soda considerable frothing takes place and additions must be kept small in order to keep the reaction under control. The cake when cool may be covered with concentrated sulphuric acid, which when heated will gradually dissolve the entire fusion including the silica. When cold the acid liquor is carefully poured into cold water, when the silica separates leaving zirconium sulphate in solution.

The alternative method for treating the fusion cake is to digest it with hot water and filter off the insolubles, recovering the zirconium from the filtrate, which contains in addition to zirconium, silica, iron, aluminium and much sodium sulphate.

3.1.5. *Hydrofluoric acid treatment and fluoride fusion*

Treatment with hydrofluoric acid is not suitable for large scale operations. The finely divided ore is digested with 40 per cent acid in lead dishes and finally evaporated to dryness to remove the silicon as tetrafluoride. The residue is boiled with water when the zirconium goes into solution and may be precipitated, after filtration, by the addition of caustic soda. An alternative method is to add concentrated sulphuric acid, after the digestion of the ore with hydrofluoric acid is complete, and evaporate to fumes of sulphuric acid. The residue is leached in water and filtered and the zirconium recovered from the filtrate.

The procedure with fluoride fusions is to mix the finely divided ore with four to six times its weight of sodium or potassium acid fluoride, and after gently heating to remove the moisture, raise the temperature until the whole mass is fused. When cooled the cake is crushed and leached with water containing a little hydrofluoric acid, and the insoluble alkali silico-fluoride separated by filtration, the zirconium being recovered as crystals of sodium (or potassium) zirconium fluoride which separates when the filtrate cools.

3.1.6. *Chlorination of the ore*

The production of zirconium tetrachloride by the chlorination of a mixture of zirconium ore and carbon, or zirconium carbo-nitride offers many advantages not only for the production of the tetrachloride but as a means of decomposing the ore as a preliminary to the preparation of other compounds. The chlorination of the ore-carbon mixture was studied by G. P. ALEXANDROV[1] who obtained a 90 per cent chlorination in six hours at 800° C.

A detailed account of the production of zirconium tetrachloride as practised in Germany has been published[12]. During the first years of the 1939–45 war, baddeleyite or native zirconia was chlorinated with a mixture of carbon monoxide and chlorine, but supplies of baddeleyite, which were imported from Brazil, ran out, and it was necessary to use zircon or natural zirconium silicate. Direct chlorination could not be achieved and for a time the zircon had to be treated chemically to produce a crude oxide which was amenable to chlorination.

Later it was discovered that a briquetted mixture of zircon and carbon could be chlorinated directly if some oxygen was introduced with the chlorine, which reacted with a part of the carbon to generate enough heat for the reaction to be self-sustaining at 800 to 1000° C.

Although details are not given it would appear that a charge of coke or charcoal was ignited in the bottom of the shaft and the briquettes fed on top of this. The heat provided started the reaction between the oxygen, added with the chlorine, and excess carbon in the briquettes, enough heat being produced to keep the mass at the required temperature. This method provided a simple means of heating the charge.

The chlorination furnace was lined with a brick with the trade name *Resistal* (good silica bricks are quite suitable for the purpose). The bottom of the furnace tapered off to a cone through which the chlorine and oxygen were introduced.

The briquette mixture was composed of 150 kg fine zircon, 60 to 75 kg powdered coal (20 per cent volatiles, 6 to 8 per cent ash) and 20 litres sulphite waste liquor (concentrated). The briquettes were calcined at 800° C in a rotary kiln, the finished briquette containing approximately 45 per cent zirconia. The use of sulphite waste liquor was not desirable because of its high calcium content which tended to cause sticking in the chlorinator. Coal tar pitch would have been preferable but was not available. The briquettes were charged through a cover on top of the furnace.

The vapours from the chlorinator gases passed into two condensers which consisted of cylindrical steel tanks with coned bottoms, with steel baffles to prevent the vapour short-circuiting the condensers. Cooling of the condensers was obtained by air convection.

The chlorine was fed at the rate of 10 to 15 cubic metres per hour and the oxygen at 5 m^3/h; this mixture gave a temperature of 800 to 1000° C, the latter being regarded as the top safe working temperature and if this was exceeded severe wear and attack of the refractories would be expected. The capacity of such a furnace was 300 to 400 kg per day of zirconium tetrachloride. No information on purity of the product is contained in the report.

W. J. KROLL[7] applied the chlorination process to a crude zirconium carbide or carbo-nitride. The carbide was prepared by heating a mixture of zircon and carbon in an arc furnace, the product being a metallic looking material which chlorinated more readily, and at a lower temperature than was required for zircon–carbon mixtures. The process is described fully as a part of the Kroll process for making zirconium sponge (see Chapter 6). In addition, methods of purification of the chloride, particularly the separation of iron, are described.

3.2. PREPARATION OF PURE ZIRCONIUM COMPOUNDS

Zirconium compounds of high purity are not readily produced owing to the great difficulty in separating the zirconium from the associated aluminium, titanium, iron and silica.

Titanium and zirconium have very similar chemical reactions and only a few methods of separation are available. Titanium may be separated by reducing it to the trivalent state, when it remains in solution.

Hafnium, which is present in all zirconium minerals, is not separated for normal operations but as hafnium-free zirconium is becoming of considerable importance a great deal of work has been reported in recent years and this is dealt with in Chapter 4.

The elimination of iron from zirconium solutions is usually achieved by employing the knowledge that zirconium compounds hydrolyse much more readily than similar iron compounds.

A compound of zirconium which may be usefully employed in separating it from other elements is the phosphate. Zirconium phosphate is insoluble in most strong mineral acids, which retain most other elements in solution. The zirconium phosphate after separation from impurities can be purified by dissolving the salt in hydrofluoric acid followed by precipitation as hydroxide with caustic soda.

The well defined compounds, potassium zirconium fluoride, K_2ZrF_6, and zirconium oxychloride, $ZrOCl_2.8H_2O$, may be used to obtain purification by crystallization.

The methods of purification are described under the following headings:

(*a*) Basic sulphate precipitation
(*b*) Oxychloride crystallization
(*c*) Precipitation with sulphur dioxide or sodium thiosulphate
(*d*) Precipitation as phosphate and subsequent treatment
(*e*) Purification by reprecipitation of hydrated sulphate
(*f*) Preparation of double fluorides.

3.2.1. *Basic sulphate precipitation*

This method, which depends on the precipitation of a basic zirconium sulphate, $4ZrO_2.3SO_3.14H_2O$, can be used to yield satisfactory results but only if certain conditions are obtained, in particular, the dilution or acidity of the sulphate solution is very critical. The acidity of the solution must be maintained throughout the precipitation at between 0·5 and 3·5 per cent with the temperature of the solution 39·5° C. As the hydrolysis proceeds the acid content increases due to the formation of free acid.

This method of purification has been applied to the product obtained by treating zirkite with sulphuric acid, and by variation of dilution, recoveries of 40 to 58 per cent were obtained. The basic sulphate so recovered contained only traces of impurities.

One of the difficulties in the basic sulphate process is the control of acidity due to the continuous increase in free acid as the precipitation proceeds, according to the equation

$$4Zr(SO_4)_2 + 19H_2O = 4ZrO_2.3SO_3.14H_2O + 5H_2SO_4$$

According to a recent patent[13] it is possible to overcome this difficulty by replacing the sulphuric acid by hydrochloric acid and adding soluble sulphates such as those of sodium, magnesium, aluminium, ammonium and other sulphates which do not precipitate during the hydrolysis. The addition of the SO_4 ions prevents an increase in acidity during hydrolysis by a buffering action, the Cl ions which are released during hydrolysis are converted to soluble chlorides and the SO_4 ions become attached to the hydrolysis product.

In one example the product of the roast of zircon and soda was dissolved in hydrochloric acid and 50 litres of solution obtained containing 85 g/l of ZrO_2 with a ratio 'active chlorine':ZrO_2, $=1{\cdot}95:1$. To this solution 0·55 mole of Na_2SO_4 per mole of ZrO_2 is added, *i.e.* 19 litres of a solution of sodium sulphate containing 142 g/l. Water is added to make up to about 85 litres and the solution boiled for two hours to complete the hydrolysis. The suspension is poured into 85 litres of cold water and the precipitate filtered and washed. The yield was 97·5 per cent of the zirconium present in the original solution and the product, when calcined, was extremely soft and with a low apparent density of 1·2.

3.2.2. *Oxychloride crystallization*

This is one of the best methods for purification; J. W. Marden and M. N. Rich[10] assumed it was too expensive to operate on a commercial scale because of the cost of the hydrochloric acid, but the method has been used to produce pure oxychloride on a large scale[12].

Zirconium tetrachloride produced by chlorination is dissolved in recycled 20 per cent hydrochloric acid. The concentration is adjusted so that the solution commences to crystallize at 65° C. The solution is allowed to stand 24 hours for settlement, while being maintained above the crystallizing temperature by hot water jackets. The clarified solution is cooled in rubber lined tanks to 20° C and the crystals separated and drained in a centrifuge, the mother liquor being recirculated.

The oxychloride may be dried at 85° C and supplied in this form to commerce or, if the oxide is required, the dried oxychloride may be ignited in air producing a very hard and granular product. If a fine oxide is required the oxychloride is dissolved in water and zirconium hydroxide precipitated by the addition of ammonia and the hydroxide ignited to yield a fine flour-like oxide.

3.2.3. *Precipitation with sulphur dioxide or sodium thiosulphate*

This method may be used to produce zirconium compounds free from iron. The precipitation of zirconium from sulphate solutions is hindered by the presence of sodium and potassium sulphates but, if these are present only to a small extent, an addition of sodium thiosulphate in excess will yield a good separation. There are four important conditions which must be satisfied before the sodium thiosulphate precipitation can be successful. These are:

(*1*) The solution must be only slightly acid and relatively low in sodium and potassium.

(*2*) The solutions should not be concentrated, a concentration of one part ZrO_2 to 50 parts water is favourable.

(*3*) The addition of thiosulphate should be made to the solution heated to about 70° C.

(*4*) After the addition of the thiosulphate the solution should be allowed to stand several hours to ensure complete precipitation.

Although J. W. MARDEN and M. N. RICH[10] showed that sodium thiosulphate could be used on a commercial scale, the cost, due to the large excess (500 per cent) of thiosulphate, was excessive and they investigated the possibility of using sulphur dioxide to replace the thiosulphate. They passed sulphur dioxide through a boiling dilute solution of zirconium obtained by dissolving sodium zirconate in hydrochloric acid and obtained complete precipitation.

3.2.4. *Precipitation as phosphate and subsequent treatment*

The precipitation of zirconium from solution as insoluble phosphate is used as an analytical method. If hydrogen peroxide is added to the acid solution before the addition of the precipitant, zirconium phosphate unlike other phosphates will still precipitate. The precipitate is difficult to filter and wash, and the process would be difficult to operate on a large scale. The conditions governing the precipitation are as follows[10]:

(*1*) The acidity of the hydrochloric or sulphuric acid solution of zirconium may vary from 3 to 20 per cent.

(*2*) The solutions must be very dilute in relation to zirconium.

(*3*) The presence of hydrogen peroxide is essential to prevent the precipitation of titanium.

(*4*) The precipitation is hastened by heating or agitation.

Marden and Rich describe the treatment of the fusion product of nitre cake and zirkite on a laboratory scale. The cake is extracted with hot water and the filtered solution treated with the calculated amount of disodium phosphate to precipitate the zirconium phosphate. After settling, washing, filtering and drying, the phosphate (one part) is fused with caustic soda (three parts). The fused cake is crushed, leached with hot water and finally the residue is treated with 1:3 hydrochloric acid which dissolves the iron and other impurities leaving the hydrated oxide of zircon which is dried to a product of about 98 per cent purity. This method is rather laborious and the result is not very satisfactory. J. H. DE BOER[3] purified the phosphate by washing the precipitate with hydrochloric acid and then redissolved the residue in hydrofluoric and hydrochloric acids, and reprecipitated the zirconium by pouring the acid solution into sodium hydroxide solution.

L. M. LARSEN *et al.*[8] describe a method for the precipitation of the phosphate in a granular form free from adsorbed mother liquor. Dilute sulphuric acid solutions of phosphoric acid and zirconyl sulphate are sprayed simultaneously into a 10 per cent sulphuric acid solution at 70 to 75° C to yield a dense, compact and easily filterable zirconium phosphate precipitate. One complete phosphate precipitation accompanied by thorough washing will eliminate most of the uranium, iron, manganese, and rare earth impurities. Larsen *et al.* also describe a method for the conversion of the phosphate to acid-soluble hydrate. The filtered phosphate is made into a slurry with water, any adsorbed acid being neutralized with sodium hydroxide solution and the slurry cooled with ice to 0 to 10° C. An ice-cold solution of sodium hydroxide and sodium peroxide is added to the phosphate slurry and the mixture digested at 50 to 70° C for about three hours until the intermediate, soluble peroxyzirconate, is completely decomposed to the insoluble peroxide hydrate which is filtered from the hot solution. The phosphate-free peroxide hydrate is soluble in sulphuric acid.

3.2.5. *Purification by reprecipitation of hydrated sulphate*

A new method for the production of zirconium compounds free from impurities except hafnium has been developed at the U.S. Bureau of Standards[2]. It is claimed that the zirconium is produced as the sulphate in good yield and high purity suitable for conversion to high grade oxide for commercial production of the metal.

The method of purification depends on the addition of concentrated sulphuric acid to a fairly concentrated solution of zirconium sulphate or chloride. A dense white crystalline precipitate of the sulphate $Zr(SO_4)_2,4H_2O$ is formed. Further purification is obtained by solution of the crystals in water followed by reprecipitation of the hydrated sulphate. For best results, one volume of concentrated sulphuric acid is added to two volumes of concentrated zirconium solution. The precipitate is collected on a sintered glass filter and washed with acid and acetone. A small amount of hydrochloric acid is added during recrystallization to prevent the precipitation of any iron that may be present. The solution used to wash the precipitate consists of 73 volumes of water, 40 volumes of concentrated sulphuric acid and 5 volumes of concentrated hydrochloric acid. The precipitate is washed several times with the mixed acid followed by washing with acetone. Alcohol cannot be used because it causes interference in subsequent recrystallizations.

In one test commercial zirconium chloride containing 0·3 per cent iron was treated by the method and gave a 70 per cent yield of high purity sulphate. The product contained less than 0·1 p.p.m. of iron, less than 0·1 p.p.m. of copper, less than 0·1 p.p.m. of silver and less than 10 p.p.m. each of calcium, magnesium, sodium and silicon. No other elements except hafnium were detected spectrochemically.

The sulphate was readily ignited to form high grade oxide which had the monoclinic form.

3.2.6. *Preparation of double fluorides*

Potassium zirconium fluoride may be prepared by dissolving zirconium oxide in hydrofluoric acid in lead vessels. To ensure solution of the oxide in the acid it is important that it should not have been ignited at a high temperature. The solution is filtered and the hot solution nearly neutralized with a solution of pure potassium hydroxide or carbonate. On cooling the solution, potassium zirconium fluoride separates as a heavy white crystalline precipitate.

The presence of sodium salts will cause the precipitation of sodium zirconium fluoride which is relatively insoluble, more flocculent and difficult to filter. The crystals of potassium zirconium fluoride are purified by further recrystallization, the crystals (25 g) being redissolved in hot water (100 g) containing a little hydrofluoric acid. The solubility of the potassium salt at room temperature is about 1·5 g in 100 g of water, at 100° C the solubility is 25 g in 100 g of water. At 2° C the solubility is only 0·78 g in 100 g of water.

The separation of impurities such as titanium and iron can only be achieved by repeated crystallization and it is better to start with a relatively pure oxide.

Titanium is particularly difficult to separate from the fluoride solutions as the solubility of potassium titanium fluoride, K_2TiF_6, is similar to that of the zirconium salt. Double fluoride prepared by this method had a purity of 99·99 per cent.

The sodium salt is best prepared by the double decomposition of the potassium salt with sodium chloride. The sodium salt has a solubility at 18° C of 0·387 g in 100 g of water and at 100° C the solubility is only 1·67 g, which makes it difficult to prepare by recrystallization.

The ammonium salt can be prepared by the same method as is used for the potassium salt, the hot solution of zirconium fluoride being precipitated by the addition of ammonia or ammonium carbonate. The ammonium salt may also be prepared by heating zirconium oxide with acid ammonium fluoride ($NH_4.HF_2$).

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4

SEPARATION OF ZIRCONIUM AND HAFNIUM

WHEN Coster and Hevesy discovered hafnium in 1923, and it was shown that this element had very similar chemical properties to those of zirconium with which it was invariably associated in nature, no one could have visualized the work that would be done to develop methods for the separation of the two elements. At first it was largely a matter of academic interest as the hafnium content (average of about 2 per cent) of zirconium did not detract from its industrial application, but in recent years, the problem has taken on a different aspect due to the knowledge that the presence of hafnium prohibited the use of zirconium for certain nuclear physical applications, for which it would otherwise be eminently suitable.

Many methods have been devised for the separation of zirconium and hafnium, including fractional crystallization, fractional precipitation, fractional dissolution, fractional distillation and sublimation, diffusion of volatile compounds, solvent extraction and electrolytic processes. F. HUDSWELL[8] studied the literature and arrived at the following conclusions:

(*i*) The phosphate precipitation method, one of the original means of obtaining the separation, has become more attractive since modifications have been introduced to produce granular precipitates.

(*ii*) The fractional crystallization processes, particularly those using the ammonium hexafluorides and the oxychlorides, will achieve separation but slowly.

(*iii*) Separation by fractional distillation of the halide additive compounds was an attractive method and a rapid one.

(*iv*) Solvent extraction processes and ion exchange techniques appeared most promising.

(*v*) Electrolytic methods are not very promising.

4.1. METHODS OF SEPARATION

As there appears to be little purpose in describing methods which are outdated, the latest techniques will be described together with a few of the older methods which may be considered as classical.

4.1.1. *Fractional precipitation*

The modified phosphate method for the separation of zirconium from hafnium is probably the best of the fractional precipitation techniques. It is described by E. M. LARSEN *et al.*[13].

It was already known that hafnium phosphate was less soluble than zirconium phosphate but the difference in solubility could not readily be utilized as a means of obtaining a separation because of the gelatinous nature of the phosphate precipitate. It was also difficult to convert the insoluble phosphate into soluble compounds for reprecipitation. Larsen *et al.* overcame both difficulties and obtained good concentrations of hafnium and zirconium by the following method. The precipitation of a granular, readily filterable phosphate was achieved by preparing three solutions (*1*) 10 per cent sulphuric acid, (*2*) a 2 to 5 per cent phosphoric acid solution in 10 per cent sulphuric acid and (*3*) a zirconyl sulphate solution containing 2 to 5 per cent zirconium dioxide also in 10 per cent sulphuric acid solution. The solutions of phosphoric acid and zirconium are added simultaneously, by means of an atomizer, to 45 litres of the dilute sulphuric acid solution at 75° C. The solution is stirred while the solutions are added at a carefully controlled rate. Heavy granular precipitates are obtained when the final liquor contains 3·5 to 20·0 g of phosphates per litre. The precipitate settles rapidly and is easily washed.

Before proceeding to the next precipitation it is necessary to convert the insoluble phosphate to an acid-soluble compound. Larsen achieved this by forming a slurry of the filtered phosphate and water, sodium hydroxide solution being added to neutralize any adsorbed acid, and the slurry cooled with ice to 0 to 10° C. Sodium peroxide is added to an ice-cold solution of sodium hydroxide and the alkaline solution added to the cold phosphate slurry. The mixture is digested at 50 to 70° C for about three hours until the intermediate soluble peroxyzirconate is completely decomposed to the insoluble peroxide hydrate.

The solution is filtered while hot to avoid crystallization of disodium hydrogen phosphate. The phosphate-free peroxide hydrate is dissolved in sulphuric acid solution and the phosphate precipitation repeated.

After seven such treatments, in each of which 55 per cent of the dissolved hafnium–zirconium was precipitated, the hafnium oxide content of the sample of mixed oxides was raised from 13 to 93 per cent. Four treatments gave a concentration equivalent to an increase from 59 to 97 per cent hafnium oxide.

A sample of mixed oxides containing 2 to 3 per cent hafnium oxide was fractionated by two successive precipitations in which 60 per cent of the total oxide was precipitated as phosphate. The remaining mother liquor when purified by oxychloride recrystallization gave a zirconium oxide free of hafnium.

4.1.2. *Fractional crystallization*

Fractional crystallization of the ammonium double fluorides and oxychlorides gave a satisfactory separation.

Diammonium hexafluo-salts are preferred to triammonium heptafluo-salts[1] since the difference in solubility between the zirconium and hafnium compounds is greater with the former salts. J. H. DE BOER and A. E. VAN ARKEL[1] fused ore with sodium bisulphate in a graphite crucible; the cooled melt was leached with water and the dissolved residue separated. The filtrates were treated with caustic soda solution to precipitate the zirconium and hafnium and the precipitate was dissolved in hydrochloric acid and evaporated to produce the oxychlorides, which were reprecipitated with ammonia, and the hydroxides dissolved in hot ammonium bifluoride. On cooling, the ammonium double-fluorides crystallized. Excess of ammonium bifluoride produced the triammonium heptafluoride salts $(NH_4)_3ZrF_7$ and $(NH_4)_3HfF_7$, but if the calculated amount was added it yielded the diammonium hexafluoride salts $(NH_4)_2ZrF_6$ and $(NH_4)_2HfF_6$.

Two schemes for the fractional crystallization were used. The first yielded crystals of zirconium practically free from hafnium, after two crystallizations from material which contained 1 per cent hafnium based on the zirconium content, but this method was slow to concentrate the hafnium in the mother liquor and simultaneous working-up of fractions was impossible. The alternative scheme gave quicker concentration of small quantities of hafnium and simultaneous manipulation of a whole horizontal row of fractions is possible, but this method results in the production of very small bulks of mother liquor at the end of each row and these have to be rejected after a few treatments.

G. HEVESY and V. T. JANTZEN[6] described the separation of zirconium and hafnium by fractional crystallization of the triammonium heptafluo-salts and indicated how laborious and exacting the work could be, stating that 650 crystallizations were performed in order to extract in a concentrated form the major part of the hafnium present in the mineral. G. HEVESY and E. MADSDEN[7] later used a similar procedure to that of de Boer and van Arkel to produce hafnium pure enough for atomic weight determination.

The solubilities of the hafnium and zirconium oxychlorides are increased in hydrochloric acid as the concentration of the acid increases. At 6·35N hydrochloric acid the solubility of $ZrOCl_2$ is 0·1037 gmole per litre, increasing to 0·334 when the acid concentration is 11·61N. The hafnium compound is less soluble and the corresponding values are 0·1030 and 0·1509 gmole per litre at acid concentrations of 6·48N and 11·28N respectively. All solubilities are measured[15] at 20° C.

The oxychloride salts are suitable for the final purification of hafnium produced by the potassium double fluoride method[19].

4.1.3. *Fractional distillation*

The fractional distillation method of separating hafnium from zirconium was used by A. E. van Arkel and J. H. de Boer[20]. When zirconium tetrachloride containing some oxychloride was distilled with phosphorus pentachloride several volatile liquid fractions were obtained. These liquids are addition compounds of zirconium and hafnium tetrachlorides with phosphorus oxychloride and phosphorus pentachloride. de Boer and van Arkel found that the analysis of these compounds corresponded to the formulae $2ZrCl_4.PCl_5$ and $2HfCl_4.PCl_5$ and $2ZrCl_4.POCl_3$ and $2HfCl_4.POCl_3$.

Since the hafnium tetrachloride addition compound with the phosphorus oxychloride has the lowest boiling point of all these compounds hafnium is enriched in the first distillates and is almost entirely absent from the residues.

The fractional distillation method of de Boer and van Arkel was investigated by D. M. Gruen and J. J. Katz[3]. Their work was chiefly concerned with the phosphorus oxychloride complexes since these have lower boiling points and greater thermal stability than the corresponding phosphorus pentachloride compounds. Analysis of the compounds indicated that instead of the formula $2ZrCl_4.POCl_3$ suggested by van Arkel and de Boer a more probable formula was $3ZrCl_4.2POCl_3$. The boiling points are 360 and 355° C for the zirconium and hafnium compounds respectively.

In one fractional distillation experiment 600 g of the zirconium tetrachloride-phosphorus oxychloride complex containing 2·5 per cent hafnium (on the weight of zirconium) was fractionated. The first fraction (35 g) contained 16 per cent hafnium (on the weight of zirconium). The residue after distilling off 40 per cent contained 0·12 per cent hafnium.

The vapour pressures of pure $3ZrCl_4.2POCl_3$ and $3HfCl_4.2POCl_3$ were determined in the range 0·1 to 1·0 atmosphere and are represented graphically in *Figure 4*.

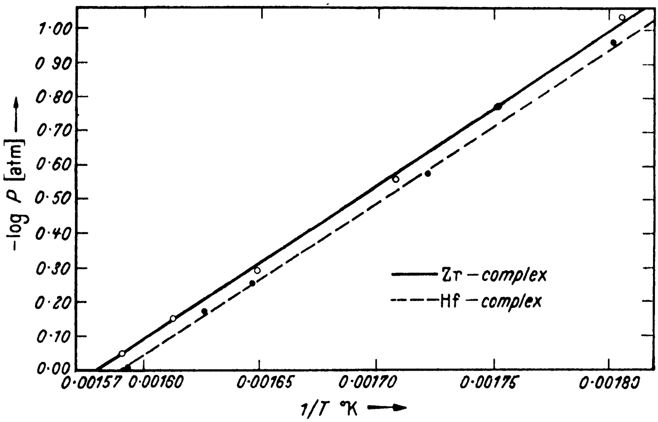

Figure 4. Vapour pressure of $ZrCl_4 - POCl_3$ *and* $HfCl_4 - POCl_3$ *complexes (after* D. M. Gruen *ond* J. J. Katz[3])

4.1.4. *Partition by solvent extraction*

W. Fischer *et al.*[2] found that the repeated fractional partition of zirconium hafnium thiocyanate mixtures between water and ether resulted in enrichment of the hafnium and it was possible by this method to produce high purity hafnium. Material containing 0·5 per cent HfO_2 when submitted to 6 to 8 fractionations yielded a 70 to 90 per cent product and at eight stages up to 95 per cent product; under optimum conditions 99·6 per cent purity was obtained.

The distribution ratio for zirconium and hafnium between 2M perchloric acid and various concentrations of thenoyltrifluoroacetone were determined by E. H. Huffman and L. J. Beaufait[9]. The equilibrium constants for zirconium and hafnium extractions were found to be $9{\cdot}4 \times 10^7$ and $4{\cdot}6 \times 10^6$ respectively at this acidity.

Two extractions with 0·025M thenoyltrifluoroacetone of a solution containing 59 per cent as much zirconium as hafnium, yielded 27 per cent of the original hafnium with a content of less than 1·2 per cent zirconium. Three extractions with 0·02M thenoyltrifluoroacetone of a solution containing 5·0 per cent zirconium, based on the hafnium content, gave a recovery of 50 per cent of the hafnium with zirconium content of 0·4 per cent.

The separation was also successfully accomplished by B. G. Schultz and E. M. Larsen[18] who extracted a hydrochloric acid solution of zirconium and hafnium with a benzene solution of trifluoroacetylacetone. The zirconium was preferentially dissolved into the benzene phase as the chelate compound, tetrakis-(1,1,1,-trifluoro-2,4-pentane-diono)-zirconium in a manner similar to that obtained in the extraction of a zirconium hafnium perchlorate solution with thenoyltrifluoroacetone.

A zirconium–hafnium solution containing only chloride anions was prepared; 'tracer' hafnium supplied by the Isotope Branch of the United States Atomic Energy Commission was used to follow the extraction process. The trifluoroacetylacetone was prepared by a Claison condensation between ethyltrifluoroacetate and acetone[5]. After preliminary experiments to determine the best operating conditions several separations were made. The concentration of the hydrochloric acid solution was 0·2N; this provided a hydrogen ion concentration high enough to prevent hydrolysis of the metal ions and yet low enough to permit extraction of an appreciable amount of material. The chloride concentration was such that the K_{Zr} and K_{Hf} values differed by a factor of about 10. The metal ion concentration was kept low and a fresh aqueous phase was prepared after each extraction by precipitating the extract with ammonia and redissolving in acid. The aqueous solution was equilibrated with an equal volume of benzene solution containing 0·025 to 0·075M trifluoroacetylacetone. In the purification of hafnium the major constituent is removed in the least number of fractions by the use of the higher diketone concentration in the benzene phase, while in the purification of zirconium the lower diketone concentration removes the zirconium with the least amount of accompanying hafnium. In two extractions hafnium in a zirconium–hafnium mixture was reduced from 1·56 to less than 0·1 to 0·05 mole per cent with 6·9 per cent yield of the original zirconium, and in six extractions the hafnium in a mixture was increased from 7·5 to 99·8 mole per cent with a 37·6 per cent yield of the original hafnium.

4.1.5. *Ion exchange*

Although the methods of separating zirconium and hafnium, which have been described, achieved a certain amount of success none of them appeared to be applicable to large scale economical operations for the production of the hafnium-free zirconium which was required for nuclear energy purposes. New methods were investigated and K. Street and G. T. Seaborg [17] were the first to give details of the ion exchange method. They reported that while making a rather cursory examination of the elution of tetrapositive ions from the cation exchange resin *Dowex 50*, with hydrochloric acid solution, they discovered an effective method of separating zirconium from hafnium and proposed it as a method for producing hafnium free from zirconium. The following experiment, involving only milligrammes of material serves to illustrate the usefulness of the technique. A mixture of 35 mg zirconium oxide and 15 mg hafnium oxide was dissolved in sulphuric and hydrofluoric acids, hafnium and zirconium tracer added and the mixture fumed to dryness. The residue was dissolved in hydrochloric acid and the hydrates precipitated with ammonium hydroxide, washed and redissolved in acid and the oxychloride crystallized by evaporation. 1 cm^3 of 250 to 500-mesh *Dowex 50* spheres, in the ammonium form, was suspended in 30 cm^3 of 2M perchloric acid and the oxychlorides added, a few milligrammes at a time over a period of 15 minutes, the mixture being continually agitated by air.

The use of dilute solutions in this acid concentration prevented appreciable polymerization of the zirconium and hafnium and about 80 per cent of each went on the resin. The slurry of resin was then placed on the top of an ion exchange column, 1 cm^2 in area and 30 cm long, which had been packed with the same resin, and washed with 6M hydrochloric acid to convert it to the acid form. On elution with 6M hydrochloric acid, two active peaks were observed—the first at about 60 ml due to hafnium, followed by a zirconium peak at about 100 ml. Approximately 66 per cent of the starting hafnium oxide was recovered containing about 0·1 per cent zirconium oxide.

The scale of operations was increased to gramme samples by I. E. NEWNHAM[16] who treated a 2 g oxide mixture containing 20 per cent hafnium oxide by the Street and Seaborg technique. The *Dowex 50* supplied as 100 to 200-mesh was packed in a column 150 cm high by 3·5 cm in diameter. The oxide mixture was converted to oxychloride crystals (2·8 g) which were slowly added to 1200 cm^3 of 2M perchloric acid containing 40 cm^3 of *Dowex 50*. The supernatant liquor was removed and the resin slurry added to the top of the exchange column. Elution with 6M hydrochloric acid was carried out at the rate of 0·5 cm^3/min. The hafnium content of successive fractions is shown below, in the order of collection:

Fraction No.	*Total* HfO_2 *recovered* per cent	HfO_2 *content of fraction* per cent
1	42	99·9
2	18	90
3	10	75
4	10	52
5	10	34

K. A. Kraus and G. E. Moore[12] obtained a partial separation of zirconium and hafnium when using a column 107 cm long by 0·0226 cm^2 packed with *Dowex-1* (a quaternary amine anion exchanger) and a mixture of 0·5M hydrofluoric acid and 1·0M hydrochloric acid as eluent. The experiment was performed with tracer concentrations of zirconium and 0·2 mg of hafnium. The hafnium was determined by delayed coincidence counting, taking advantage of the metastable ^{181}Ta. The estimated purity of the hafnium fractions was better than 95 per cent.

E. H. Huffman and R. C. Lilly[10] absorbed the ions on *Amberlite IRA-400* resin from dilute hydrofluoric acid solution and then slowly eluted the fluo-salts with 0·2M and 0·01M hydrochloric acid. As with the cation exchange method, zirconium is held preferentially on the column. One portion of the eluate containing 69 per cent of the starting material was found to contain no hafnium while another showed 0·02 per cent zirconium in 6·9 mg of hafnium (69 per cent of the starting material).

In the ion exchange methods which have been described the hafnium is eluted first from the column and B. A. J. Lister[14] pointed out that on economical grounds, for the purification of zirconium, it was much more favourable to elute the large quantity of zirconium and retain the very much smaller quantity of hafnium on the column.

The operations were confined to zirconium–hafnium mixtures in their naturally occurring proportions, *i.e.* about two per cent hafnium. In some of the work *Dowex 50* resin was used but later this was replaced by *Zeokarb 225* (Permutit Co. Ltd) which was similar in capacity and general exchange behaviour.

The overall elution curve was determined by the use of tracers and spectrographic analysis was made of selected oxide samples. Three columns were used (*1*) 60 cm by 0·8 cm diameter, containing about 20 g *Dowex 50* (200 to 250-mesh), (*2*) 60 cm by 1 cm diameter, containing about 30 g *Dowex 50* and (*3*) for larger scale runs 120 cm by 2·5 cm diameter, containing about 350 g of resin with particle size above 0·5 mm in diameter.

The use of hydrochloric, oxalic, nitric, perchloric and sulphuric acids as eluents was investigated. Hydrochloric acid was tested under the same conditions as those used by Street and Seaborg and some separation was obtained, but the elution was too rapid to achieve good resolution. By using slower elution with more dilute acid, a tenfold decrease in the hafnium content was obtained with complete recovery of the material.

The use of oxalic acid as eluent showed that the hafnium was held more strongly by the column but the separation was less than that obtained with hydrochloric acid.

Elution with nitric acid gave no apparent separation, although the single observed activity peak on the elution curve moved at a rate similar to that of the zirconium peak in runs with hydrochloric acid.

No separation was observed when perchloric acid was used as eluent.

Sulphuric acid elution proved to be the simplest and most satisfactory and was found to be applicable to the purification of either zirconium or hafnium and could be employed with starting materials of any composition. Gramme quantities of the two elements were separated by one passage through the column.

Lister pointed out that the disadvantage of the elution chromatography technique was the number of stages involved. He proposed a more useful separation, the 'breakthrough' technique whereby the mixture to be separated, in a suitable solvent, is passed through a column of resin, the mixture being fed continuously as the run proceeds. This method eliminates the impregnation step and so considerably simplifies the procedure.

Lister proceeded to test the 'breakthrough' technique using a column containing 350 g of resin and solution containing 2·5 g of zirconyl nitrate per litre of N sulphuric acid at a rate of about 200 ml per hour. Fractions of the eluate from the column were collected, the hydroxides precipitated and ignited and the oxides examined spectrographically for hafnium. It is seen from *Figure 5* that a small quantity of zirconium and hafnium leaked through into the eluate almost immediately, this concentration remaining approximately constant until the main zirconium breakthrough point at about 9 litres. Over this initial portion, the hafnium:zirconium ratio remains quite high at about the value of the feed solution. The concentration of hafnium in the eluate remains essentially constant until it begins to rise at about 18 litres (*i.e.* when 10 g of mixed oxides have passed through the column). Up to this point the oxides precipitated from the eluate contained overall about 0·1 per cent of hafnium oxide. The first 8·2 g of oxides had an overall hafnium oxide content of 0·047 per cent. The drop in zirconium content towards the end of the run is probably due to a fall in the flow rate. The slow uptake of zirconium was indicated by the decrease in eluate concentration noted at two points in the run after the flow had been stopped for some hours. Lister concluded that although the method is convenient and efficient for producing a low hafnium-content zirconium oxide, it does not give the clean separation

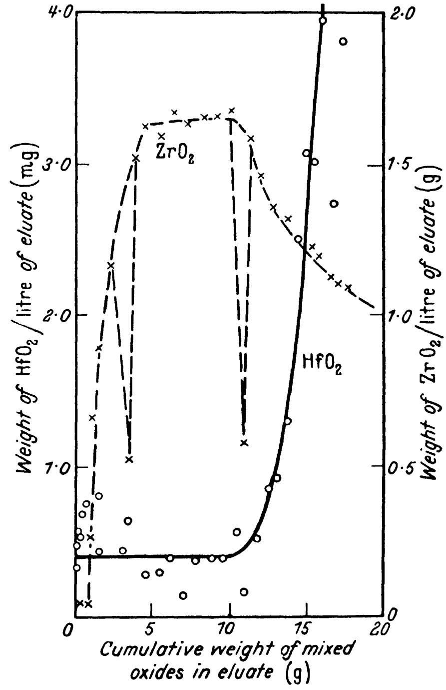

Figure 5. Eluate curves for 'break-through' run using N *sulphuric acid (after* B. A. J. LISTER[14])

(With acknowledgements to the Director, A.E.R.E., Harwell)

achieved by the normal elution method for the same amount of material processed.

4.1.6. *Adsorption methods*

Another method which operates on the principle that it is better to elute the large quantities of zirconium and retain the smaller quantities of hafnium in the column was discovered by R. S. HANSEN *et al.*[4]. It was found that silica gel adsorbs hafnium preferentially from a methanol solution of zirconium and hafnium tetrachlorides, and that the preference was so marked that it appeared good separations of the metals could be obtained in a column.

The possibility was investigated and the operating conditions determined as follows. A column is charged with activated silica gel which has been sludged with methanol. A solution of methanol containing zirconium and hafnium tetrachlorides in the proportion of one gramme chlorides per 5 ml of solvent is fed upwards through the column and the eluate collected, and by varying the conditions the zirconium can be recovered with the hafnium content as low as desired. The zirconium can be recovered by distillation of the methanol, solution of the residue in water and separation from common impurities such as iron, titanium and aluminium by crystallization of the oxychloride.

Curve *1* in *Figure 6* is typical of the results obtained with the smaller column, appreciably better results were obtained with larger columns as shown in curve *2*.

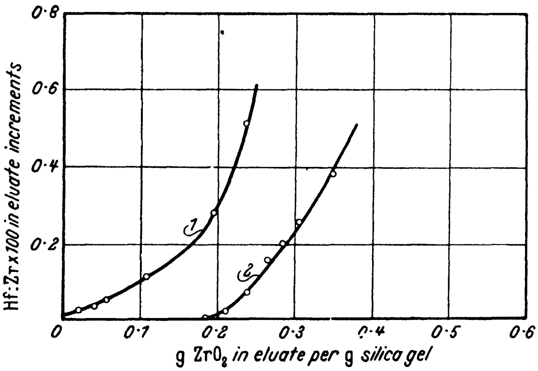

Figure 6. Comparison of column size in separation of zirconium and hafnium. 1: 50 mm *diameter* ×4 ft *long* – 1 kg *silica gel; 2:* 4 in *diameter* × 5 ft *long* – 8 kg *silica gel* (*after* R. S. HANSEN *et al.*[4])

To obtain the most satisfactory results it was found that (*i*) the silica gel (28 to 200-mesh) must be activated, (*ii*) methanol the most suitable solvent must be very thoroughly dried, (*iii*) concentrations of the tetrachlorides should be within the range 15 to 25 per cent, (*iv*) slow flow rates of the order 20 cm/h based on the empty column were satisfactory.

The charge of silica gel is related to the hafnium to be adsorbed; if the feed material has a Hf:Zr ratio of 0·02:1 and a product spectroscopically free from hafnium is desired this amount is not greater than 1 lb of zirconium dioxide per 5 lb of gel.

The gel is stripped by washing first with methanol, followed by 2·5M anhydrous hydrogen chloride in methanol. Nearly 90 per cent of the adsorbed hafnium can be recovered as an oxide containing 20:80 per cent $HfO_2:ZrO_2$. Alternatively, 60 per cent can be recovered as a 30 per cent hafnium oxide product or about 20 per cent as a 60 per cent hafnium oxide.

The final stripping is achieved by washing with aqueous 7N sulphuric acid solution, and the silica gel is reactivated for two hours at 300° C and is ready for use again.

The chromatographic separation of zirconium and hafnium on paper strips has been investigated by W. F. KEMBER and R. A. WELLS[11]. The method is not proposed as a means of recovering the separated elements but rather as a basis of a quantitative analysis of mixtures.

The salt is prepared in the form of mixed zirconyl and hafnyl nitrates. The solvent is prepared by adding slowly 30 ml of concentrated nitric acid to 70 ml of dichlorotriethyleneglycol. The separations were carried out by downward diffusion in the apparatus used for paper strip separations.

The most efficient separations were obtained with a total of 150 μg of the oxides when using a strip 3 cm wide of Whatman's *No. 1* paper or 300 μg on Whatman's *No. 3* paper. The solution (0·02 ml on *No. 1* and 0·05 ml on *No. 3* paper) was pipetted on to the paper, which, without drying, was immediately transferred to the extraction vessel. Drying the test spot caused deposition of an immobile basic nitrate. The chromatogram was allowed to run for 18 hours, a longer running time producing a wider separation but giving more diffuse bands.

After removal of the strip from the vessel, it was sprayed with a saturated solution of alizarin in ethyl alcohol containing 5 per cent by volume of 2N hydrochloric acid. The strip was then heated gently, but complete drying was avoided. The characteristic red bands of zirconium and hafnium lakes slowly appeared against the yellow background of the reagent.

It was found possible by this method to detect 2 μg of each metal and commercial zirconium nitrate clearly showed the presence of its proportion (about 2 per cent) of hafnium.

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5

PRODUCTION OF ZIRCONIUM METAL

5.1. Investigations Leading up to Present Production Methods

The production of zirconium metal in a pure state is considered a difficult task and even with the best equipment great care and skill are required to ensure that the metal is not unduly contaminated. It is not surprising that the first attempts to produce the pure metal, which were made over a hundred years ago, did not succeed and although the investigators sometimes claimed success, there is no doubt that their 'metal' contained considerable amounts of impurities such as oxide, nitride and carbide. Zirconium is a difficult metal to isolate and when it is isolated it is even more difficult to ensure that the metal is not contaminated by the common gases such as oxygen, nitrogen or hydrogen, because zirconium even at moderate temperatures has great reactivity towards these gases and many other substances, particularly those containing oxygen. As this applies to most of the refractory materials generally used for crucibles, there arises the problem of finding a crucible material to contain molten zirconium without contaminating the metal.

Before proceeding to describe the present methods of production of ductile zirconium some account will be given of the methods which were used by the many workers over the last hundred years.

As early as 1824, zirconium metal was produced by J. Berzelius[4]. The metal was badly contaminated with oxygen, not due to incomplete reduction, as the reaction was between potassium zirconium fluoride and potassium, but due to oxygen absorbed by the hot reactive zirconium. This oxygen mania of zirconium was to continue to be the main reason for the failure to produce ductile metal for nearly a hundred years after the work reported in 1824. In 1865 an interesting series of methods for producing zirconium metal was published by L. Troost[25]. In addition to repeating the reduction of potassium zirconium fluoride with sodium, mixed sodium chloride-zirconium chloride was subjected to reduction by magnesium or sodium, and sodium zirconium fluoride was similarly treated with aluminium. More interesting in view of present knowledge was the investigation of the reduction of zirconium tetrachloride vapour by sodium or magnesium and the fusion electrolysis work with double chlorides and double fluorides as the electrolytes. The best results obtained were poor, an amorphous 'metal' with a specific gravity of 4·15 indicating that it was little better than a lower oxide of zirconium.

In the fusion electrolysis it is reported that some particles were obtained which were at first thought to be metallic zirconium from their brilliant appearance but these were readily attacked by water.

Crystalline zirconium aluminide was obtained by reduction of potassium zirconium fluoride with aluminium, the crystals containing 27·5 per cent aluminium. An attempt to produce malleable zirconium metal by removal of the aluminium from the aluminide, obtained by the reduction of the double fluoride with excess aluminium, failed to give the desired result although a purity of 99·5 per cent was reported.

It was not until 1914 that malleable corrosion resistant zirconium was produced by D. LELY and L. HAMBURGER[15] in the form of small pellets by the reduction of zirconium tetrachloride with sodium in an evacuated steel tube. An important step in the process was the resublimation of the chloride shortly before reduction whereby the oxide formed by hydrolysis of the chloride, following absorption of moisture, was removed and did not contaminate the final metal.

Nearly ten years went by after the first production of ductile zirconium pellets before a compact ductile metal showing the true properties of zirconium was produced. It was in 1925 that A. E. VAN ARKEL[26], J. H. DE BOER and J. D. FAST[6] reported the technique which has since become so important and may become more important still. This technique is based upon the thermal dissociation of zirconium iodide. Similarly, work had been done with boron, silicon and tungsten, using the chlorides of these metals, but with zirconium, the iodide gave better results. The method has been described as the van Arkel process, the de Boer process, and even the Iodide process, but whatever the doubts about the use of the correct name there is little doubt that this method produced the first zirconium substantially free from oxide and nitride, and the excellent properties associated with the absence of small quantities of contaminants laid emphasis on the importance of excluding the common gases during production of the metal.

Many methods for the production of zirconium metal have been investigated and it was not for lack of interest that the production of pure metal, having ductility and corrosion resistance, took such a long time. The real trouble was the protection of the metal, during its production, from the atmosphere and it was mainly due to improvements in vacuum equipment that success was attained.

Another important point, to be remembered when considering the problem of the production of pure zirconium, is the high melting point which makes it difficult to produce a solid button of metal in the reduction process; instead, particles of metal dispersed in fused salts are the usual product of reduction.

The production of the first zirconium metal by J. Berzelius[4] and the eventual production of pure ductile metal by A. E. van Arkel[26] and his associates have been very briefly mentioned but in addition there were numerous workers endeavouring to produce pure metal by widely differing techniques which must not be overlooked or forgotten, for it is possible that one of these may form the basis of the process which many have sought—a process that will produce zirconium at a lower cost than the Kroll or Iodide process. (Most work has been done on reduction techniques with the zirconium in the form of oxide, halide, or double halide, and using sodium, calcium, magnesium, aluminium or carbon as the reducing agent. Electrolytic methods have also been investigated: fused double halides have been used as the electrolytes as well as aqueous solutions. Thermal dissociation of the halides was one of the final developments.)

5.2. Early Production Methods

In order to examine the methods more readily, they can be divided into groups: (*i*) reduction methods, (*ii*) electrolytic methods, and (*iii*) thermal dissociation methods.

5.2.1. *Reduction methods*

This section includes the methods used for the reduction of the chlorides and fluorides, or their double salts such as potassium zirconium fluoride, with metals and also the reduction of the oxides with metals and carbon.

Reduction of zirconium tetrachloride with sodium—The method used by D. Lely and L. Hamburger[15] to produce the first malleable zirconium by the reduction of tetrachloride with sodium has already been briefly described and although the metal was obtained only as small pellets in the form of discrete nodules intermingled with the other products of reduction, it represented a considerable advance in the quest for pure metal. The use of freshly sublimed chloride for the reduction is a feature of one of the present day production processes.

The reaction between the zirconium tetrachloride and sodium took place in a sealed pressure vessel, or bomb, a type of reaction unsuitable for large scale operations owing to the very high pressures developed. The method was used later by others[12, 21] and metal containing 96 to 99·3 per cent zirconium was claimed to have been obtained. It is interesting to note that it was used for the commercial production of zirconiumpowder. (See also Section 17.1.2.)

Reduction of chloride or double alkali chloride with magnesium—One of the earliest methods investigated, the reduction of the chloride or double alkali chloride by magnesium, was improved and made a commercial process. In this method a mixture of sodium and zirconium chlorides with magnesium turnings is heated slowly in an iron pot. The salts melt and the reaction proceeds quietly yielding a molten mixed salt of sodium and magnesium chlorides and reduced zirconium particles which settle to the bottom. The molten salts are decanted, leaving a cake of reduced zirconium with adhering salts. The cake is crushed and leached, first with water, then with dilute hydrochloric acid and finally with water to remove the acid before drying carefully at a low temperature. Zirconium powder is pyrophoric and must be handled with care. Vacuum drying may be employed but this does not eliminate the explosion hazard[29–32].

The final product contains a small amount of magnesium alloyed with the zirconium. The same method can be used for producing magnesium–zirconium 'alloys' of various compositions.

Reduction of potassium zirconium fluoride with potassium, sodium or aluminium—The use of fluorides has also been considered as the starting point in the production of zirconium, in fact it was the method used by Berzelius, who mixed potassium zirconium fluoride, K_2ZrF_6, with potassium and heated the mixture, in an iron tube, by means of a spirit lamp. The reaction, which was quiet, was assisted by occasional stirring with an iron rod. After cooling and crushing, the reduction product was leached with dilute hydrochloric acid and ammonium chloride and finally rinsed with water and alcohol. It is claimed that this method produced metal containing from 93 to 98 per cent zirconium and that the main impurity was oxygen introduced during the washing of the fine particles of metal.

A method similar to that used by J. BERZELIUS[4], in which sodium was the reducing agent, was used in Germany for the production of zirconium powder on a commercial scale[22]. Production attained the comparatively high figure of over 1200 kg per month. The potassium zirconium fluoride (90 kg) was mixed and melted with sodium, and potassium chloride (16·5 kg of each). The fused salts were crushed (1 mm sieve) and fed gradually to a bath of molten sodium (34 to 35 kg) heated to about 800° C in a steel vessel in an atmosphere of hydrogen. The reaction proceeded quietly as the additions were made. A mechanical stirrer assisted the reaction by continually presenting fresh sodium to the feed of salts. The temperature was controlled by the rate of addition. Heating was continued for about 2½ hours after the final addition when the stirrer was lifted clear of the reaction and the crucible and its contents allowed to cool under hydrogen. The hard product was crushed and ball-milled, leached with water until all the sodium fluoride was removed and then washed with dilute hydrochloric acid.

The zirconium metal powder was wet-screened under a stream of water and the final product of minus 200-mesh powder (25 to 30 kg) was dried in trays placed on pipes through which water at 60° C was circulated. The metal powder produced by this method is very fine and becomes partly oxidized during the washing operation and is, therefore, unsuitable for the production of ductile metal.

The reduction of potassium zirconium fluoride with aluminium was first attempted by L. WEISS and E. NEUMANN[35] who melted one part of the double fluoride in a carbon dish and then gradually added 1½ parts aluminium. The reaction was complete in about 15 minutes and the product allowed to cool under a layer of potassium chloride. A button of metal was obtained in the bottom of the crucible which when treated with caustic soda and hydrochloric acid yielded a crystalline alloy containing 72·2 per cent zirconium and 27·5 per cent aluminium.

Weiss and Neumann formed rods or pencils from the product. The rods, 6·4 cm long, 1·0 cm wide and 0·5 cm thick, were used as opposing electrodes in an arc furnace and, by passing a current, an arc was struck between the ends of the electrodes; the rods could be heated *in vacuo* or in any desired atmosphere. The arrangement is shown in *Figure 7*. The electrodes and furnace walls were water-cooled. The distance between the electrodes was controlled by adjusting a rack and pinion fitted to each electrode, the adjustment being observed through a sight glass in the side of the furnace. With a current of 60 to 70 A at 20 to 25 V and a distance of 2 to 3 mm between the electrodes a high temperature was obtained,

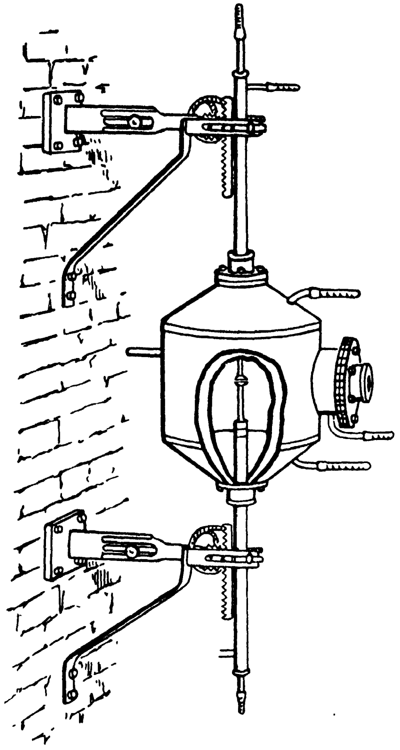

Figure 7. Vacuum arc furnace designed by L. WEISS *and* E. NEUMANN[35]

sufficient to volatilize the aluminium and melt the residual zirconium into globules. Despite this treatment the metal was still brittle. It is claimed that when the experiment was made with the zirconium–aluminium alloy in an atmosphere of nitrogen at about 10 mm of mercury pressure, globules of metal containing 99 per cent zirconium or better were obtained. In view of the reactivity of zirconium at high temperatures for nitrogen it is difficult to believe that such high purity could be obtained under the conditions described.

Some 10 years later J. W. MARDEN and M. N. RICH[17] investigated the results claimed by Weiss and Neumann. The first charge was made according to the equation

$$3K_2ZrF_6 + 4Al = 3Zr + 6KF + 4AlF_3$$

or 7·85 g K_2ZrF_6 to 1 g Al. This shows that Weiss and Neumann used an enormous excess of aluminium. The actual charge prepared was 10 g K_2ZrF_6 and 1·5 g Al which were mixed and heated in an *Alundum* crucible to 600° C in an Arsem vacuum furnace at a pressure of 1 to 2 mm of mercury (this furnace comprises a gas-tight steel casing with a graphite helix heating element). After heating for a short time at 1500 to 1600° C *in vacuo* the charge was allowed to cool. The product was a fairly pure, black, amorphous zirconium.

Further experiments were carried out using an excess of aluminium; this yielded an alloy containing about 10 per cent aluminium and if similar mixtures were reacted and heated to between 1750 and 2000° C in a vacuum the aluminium was volatilized, as well as the aluminium and potassium fluorides formed by the reaction. The metal recovered contained about 90 to 95 per cent zirconium with oxygen the main impurity. It was assumed that the poor vacuum was the main reason for the oxidation and an attempt was made to counteract this by the use of excess aluminium in the reaction mixture. The aluminium vaporized at the temperature of about 2000° C attained in the furnace and 'gettered' some of the residual gas in the furnace. The product was a sintered mass with a metallic appearance, which contained 95 per cent zirconium metal and 4 per cent zirconium oxide.

The reduction of the double fluoride of zirconium in the Arsem furnace was repeated by J. W. MARDEN and M. N. RICH[17] in an atmosphere of hydrogen at 1 mm of mercury pressure, a flow of purified hydrogen being passed through the furnace during the reduction and subsequent high temperature treatment. The product contained 98·9 and 99·7 per cent zirconium when the charge contained 200 and 80 per cent of the theoretical aluminium required for the reaction, but as the metal contained 1·7 and 0·2 per cent metallic impurities respectively, introduced from the fluoride and aluminium, the metal is remarkably pure.

Marden and Rich also repeated the work done by Weiss and Neumann with an arc furnace using electrodes prepared by pressing zirconium–aluminium alloy powder. The furnace was flushed with hydrogen and then evacuated to about 5 mm of mercury pressure before arcing. One of the best products contained 99·6 per cent zirconium.

Reduction of zirconium dioxide by calcium, magnesium, aluminium or carbon—The reduction of zirconium dioxide by calcium has received considerable study and metal containing up to 99·5 per cent zirconium has been reported. The reaction is said to take place in two stages. First

$$2ZrO_2 + 2Ca = CaZrO_3 + Zr + CaO$$

and later at about 1050° C the zirconate is reduced according to the following equation

$$CaZrO_3 + 2Ca = Zr + 3CaO$$

The method was first used by E. WEDEKIND[33] and later by O. RUFF and H. BRINTZINGER[24] who used sodium with the calcium in a bomb. J. H. DE BOER and J. D. FAST[7] also used calcium or calcium plus sodium to reduce zirconium dioxide. Wedekind used the calcium in the form of fine shavings which were mixed as intimately as possible with pure zirconia. The mixture containing an excess of calcium was heated in an iron tube under a reduced pressure of 0·1 to 0·5 mm of mercury. The charge was heated to the reaction temperature when the heat evolved was sufficient to continue the reaction. The reduced metal was dispersed as particles in the fused residue and to recover the metal powder it was necessary, after crushing, to leach successively with water, acetic acid, dilute hydrochloric acid and then again with water until the washings were free from chloride. The metal, after rinsing with acetone and drying *in vacuo*, contained 99·09 per cent zirconium and the yield was 97·5 per cent of the theoretical. Further treatment with calcium yielded not a purer, but a less pure product, due to oxidation during treatment. The metal powder produced by O. RUFF and H. BRINTZINGER[24], by using sodium–calcium instead of calcium, contained 97 per cent zirconium.

W. J. KROLL[13] improved the method for the calcium reduction of zirconia by performing the reduction in an atmosphere of argon under a flux of molten calcium chloride. The argon was at atmospheric pressure. It is possible to obtain metal of 99·5 per cent grade by this method but as there appears to be an equilibrium between zirconia and calcium it is not possible to remove all of the oxygen, and the metal is brittle.

D. B. ALNUTT and G. C. SCHEER[2] reduced zirconium with calcium in a bomb to produce metal suitable for purification by the van Arkel process. After leaching the reduced mass with acid to remove the lime, a metal with a total zirconium content of 98·3 per cent was obtained, the balance being substantially oxygen and nitrogen.

The most recent work on this process was done by G. MEISTER[18] who claimed very high purity but did not report the oxide content (for further details see Chapter 7).

A method for the reduction of zirconia by calcium hydride is claimed[1]. The advantage in using calcium hydride which is brittle and crushable, instead of calcium metal, is to obtain the reducing agent in a finely divided form without great difficulty, which can be mixed intimately with the zirconia. The hydride decomposes to calcium and hydrogen before the reaction temperature is attained. The resultant zirconium powder was of the same order of purity as that obtained with calcium metal. (See also Section 17.1.1.)

The use of magnesium as a reducing agent for zirconium dioxide was claimed by some of the earlier workers to give some success, but it is doubtful if the claims could be justified. A patent application[16] was granted covering the reduction of the oxide with magnesium in a sealed vessel filled with an inert gas. The removal of the ignited magnesia by acid extraction without attacking the zirconium would be a difficult task. More recent work on this method is described in Chapter 7.

The aluminothermic process of Goldschmidt was an obvious method to adopt for the reduction of zirconia, but the results were poor, some zirconium being produced intermingled with a slag composed of alumina and unreduced zirconia. It was considered that the reaction failed because there was insufficient heat evolved by the reaction

$$3ZrO_2 + 4Al = 2Al_2O_3 + 3Zr$$

and it was proposed[14] to boost the reaction by the addition of barium peroxide

$$ZrO_2 + 2Al + BaO_2 = Al_2O_3 + BaO + Zr$$

However, this addition failed to solve the problem, although 99·5 per cent purity was claimed for an aluminothermic reduction performed with the aid of chlorate[17].

Carbon is a common reducing agent for metals and was investigated for the reduction of zirconia. The best most workers appeared to have been able to do has been to produce an impure carbide. It was noticed at an early date that heating zirconia with carbon in an arc furnace eliminated silica, a reaction which has been usefully applied in more recent years to zircon for the production of a commercial grade of oxide and as the basis of zirconium tetrachloride production. One of the more interesting results was due to H. Moissan and F. Lengfeld[19], who heated zircon in a carbon crucible in an electric arc furnace. The product was metallic in appearance and contained about 5 per cent carbon. The silica had been removed during the heating. Moissan mixed this 'carbide' with powdered fused zirconia and heated it again and claimed that the product did not contain carbon and was zirconium metal containing a little oxide.

W. Rohn[23] later obtained a patent for a similar process; he claimed the reduction of oxides of metals such as silicon, titanium, zirconium, hafnium, vanadium, niobium, chromium and molybdenum by heating them with their respective carbides in a vacuum. The method has been confirmed for niobium by C. W. Balke[3] who claimed the production of pure ductile niobium by the reaction between niobium oxide and carbide.

The reaction between carbon and the mineral zircon was studied by E. Friederich and L. Sittig[11] who found that the first stage in the reduction process was the production of a lower oxide of zirconium, ZrO, at a temperature in the region of 1200° C and at higher temperatures carbide was obtained in varying degrees of purity.

Attempts to reduce zirconia by heating in an electric furnace with boron or silicon produced impure borides and silicides. One worker[28] claimed the reduction of zirconia by hydrogen operating at 5 atmospheres pressure and a temperature of 2500° C in the presence of a metal such as tungsten which absorbed the zirconium as it was produced. It is possible that some reduction occurred due to the presence of the tungsten, but this method is not feasible as a production process.

5.2.2. *Electrolytic methods*

L. Troost[25] who investigated so many methods for the production of zirconium included in his work an investigation of the electrolysis of the fused double fluoride and double chloride. Other investigators[8, 17] have followed Troost's[25] lead using the fluorides but difficulties were encountered because of the phenomenon, described broadly as anode effect, which is associated with fusion electrolysis and is due to the formation of a high resistance gas layer at the anode, indicated by sparking and hissing in the affected area. While anode effect may be avoided by addition of zirconium dioxide to the fused salt bath, it is difficult to produce the desired conditions without introducing oxide into the metal.

The use of the double chloride which was suggested by Troost was re-investigated[20] using a fused bath of aluminium chloride, potassium chloride,. and sodium fluoride to which additions of zirconium dioxide were made. In addition to the contamination by aluminium, considerable oxide was formed and the best result gave only 93 per cent zirconium.

Aqueous solutions would hardly be considered practical for the production of pure zirconium in view of the great chemical activity of the metal in the fine form in which it is usually produced by electrolysis. Nevertheless some work has been done and it is reported by W. E. BRADT and H. B. LINFORD[5] that although the method was not satisfactory some success was obtained by using zirconyl sulphate solution to which sodium sulphate was added to retard hydrolysis. The metal was produced in two forms, depending on the conditions in the cell, one a silver-white metal similar to nickel electroplate and the other composed of a black powder which would appear to be an oxide of zirconium. The compact white metal, which was examined on the spectrograph and showed strong lines of zirconium, was not assayed so it is impossible to state the metallic content, but it behaved rather oddly and oxidized slowly in air to white zirconium dioxide. However, heavier electrodeposits retained their silvery appearance for as long as three months. More recent developments are described in Chapter 7.

5.2.3. *Thermal dissociation methods*

The methods for the production of zirconium by thermal dissociation of its halides are based on the early work on boron and silicon when attempts were made to reduce their halides with the assistance of hydrogen in the high temperature of an electric arc. It was soon found possible to obtain the dissociation without the use of hydrogen and L. WEISS[34] demonstrated this with particular reference to tungsten trichloride. Zirconium tetrachloride was dissociated by contact with a hot tungsten filament and while at first there appeared to be a doubt about this claim[10] it was subsequently substantiated, although better results were obtained by using a zirconium filament which could be operated at a higher temperature than the tungsten which formed a low-melting alloy with the deposited metal. van Arkel, who originated the process which is known today by his name, showed that zirconium iodide was a much better starting material than the tetrachloride since it dissociated more readily to metallic zirconium and elemental halide. The dissociation method for metal deposition has been described by A. E. VAN ARKEL[26, 27] and by J. H. DE BOER and J. D. FAST[6, 7, 9]. The application of the technique as applied to the production of zirconium is described in Chapter 6.

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6

COMMERCIAL PRODUCTION OF ZIRCONIUM METAL

THE early methods used for the production of zirconium have been described and an attempt has been made to show some of the difficulties which were encountered as well as the versatility of the investigators.

Several reduction methods have been reported to produce metal of relatively high purity and there is one method, at least, which was used to produce commercial quantities of zirconium. All these methods yielded the zirconium as a metal powder, and although many attempts were made to use this powder for the production of ductile metal by various consolidation techniques, none of these was successful. Sometimes in a reduction experiment a small irregular piece of metal with a fair degree of ductility was obtained but in the main it is true to say that none of the metal possessed the virtue of ductility. Chemical analysis of the metal indicated that the impurities were not appreciable and at first it was not realized that the presence of a relatively small amount of oxide, nitride or carbide could exert such embrittling effects. It was not until about 1925, a hundred years after Berzelius made his experiments, that really satisfactory massive ductile metal was produced by van Arkel. This method is still used for the commercial production of zirconium and yields a very high grade of metal. One other method has been developed for the large scale manufacture of ductile zirconium, this is known as the Kroll process after its originator Dr W. J. Kroll at the U.S. Bureau of Mines, Albany, Oregon, who with his colleagues was also largely responsible for inaugurating the amazing development of titanium metal which has taken place in the last five years.

The development of the van Arkel process from 1925 to 1945 was not very rapid, and because of the high cost of production of the metal, applications appeared to be very limited, despite its outstanding corrosion resistance. There seemed to be no means of ending this dormant state where the high cost restricted development and the cost could not be reduced until the scale of production was increased, when a sudden impetus appeared, resulting from interest in zirconium metal as a material of construction for certain nuclear reactors. Zirconium has a high melting point, excellent corrosion resistance and a low thermal neutron absorption cross section, all important factors when considering nuclear energy applications. As a result of this interest the development of zirconium intensified and within a few years remarkable progress was made in overcoming the difficulties encountered in the large scale production of iodide zirconium. The same interest, which provided the momentum required to promote the van Arkel process, also provided the means which enabled Kroll and his colleagues to expand his process from a laboratory experiment to a production plant in a period of approximately half a decade.

6.1. THE VAN ARKEL OR IODIDE PROCESS

It has already been mentioned that the earlier work on the preparation of zirconium by thermal dissociation of the halide had been carried out on zirconium tetrachloride. This method was greatly advanced when it was discovered that the tetraiodide dissociated to the metal and halogen much more readily than the other halides. van Arkel and de Boer were responsible for this development but much of the later development was due to the work of investigators at the Foote Mineral Co. and the Battelle Memorial Institute.

In its simplest form the iodide process may be represented by the following equation

$$\begin{tikzcd}
\underset{\substack{\textit{solid}\\(\textit{impure})}}{\mathrm{Zr}} + \underset{\textit{vapour}}{2\mathrm{I}_2} \arrow[r, "200^\circ\text{ C}"] & \underset{\textit{vapour}}{\mathrm{ZrI}_4} \arrow[r, "1300^\circ\text{ C}"] & \underset{\substack{\textit{solid}\\(\textit{pure})}}{\mathrm{Zr}} + \underset{\textit{vapour}}{2\mathrm{I}_2} \arrow[ll, bend left]
\end{tikzcd}$$

This equation shows the production of pure zirconium from impure metal through the intermediate tetraiodide with the iodine being continuously regenerated to combine with more impure zirconium.

Only thermal energy is required to promote decomposition, and at a temperature of 1300° C the reaction is rapid. The reverse reaction, *i.e.* the combination of iodide vapour and zirconium metal takes place below 200° C. This reaction is usefully employed to provide pure zirconium tetraiodide using an impure zirconium metal as the starting material. Such low grade metal can be produced by the reduction of zirconia with calcium in specially designed equipment capable of withstanding high pressure and high temperature[1]. The reduced mass is crushed and digested in dilute hydrochloric acid. The metal is recovered in the form of a powder with a typical analysis, as follows: total Zr 98·3, Ca 0·02, Fe 0·008, Al 0·008, Si 0·002 per cent. This powder is satisfactory for certain purposes in the electronic industry but is useless for ductile metal manufacture since the balance of about 1·7 per cent is composed of oxygen and nitrogen which are present as embrittling oxide and nitride. The presence of impurities such as oxide or nitride does not affect the purity of the volatilized zirconium iodide, the oxide and nitride being non-volatile remain as residue, but it is essential that this metal powder should not contain appreciable quantities of elements such as titanium, silicon, thorium, boron, iron, aluminium, beryllium, hafnium or phosphorus, which form readily volatile iodides as these would accompany the zirconium iodide and contaminate the final product. The transfer of these impurities is not complete and with careful operation only small amounts of the metals mentioned are found in the final product.

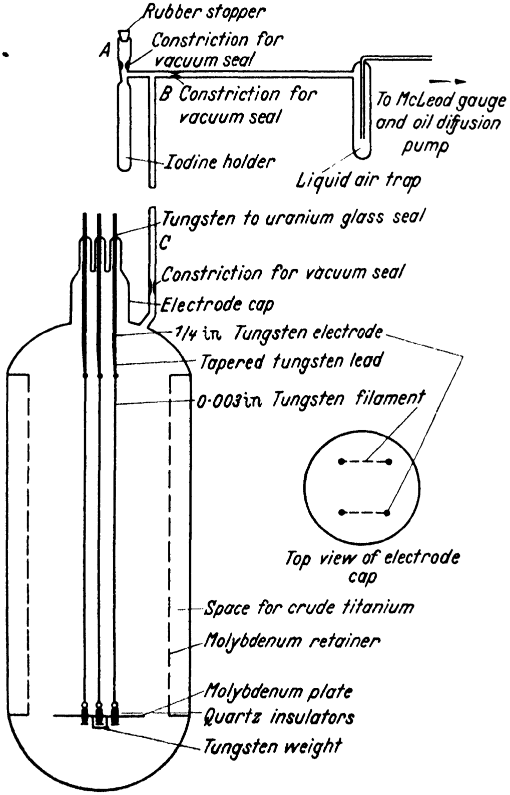


Figure 8. Schematic diagram of equipment used in producing iodide process titanium (after I. E. Campbell *et al.*[2])

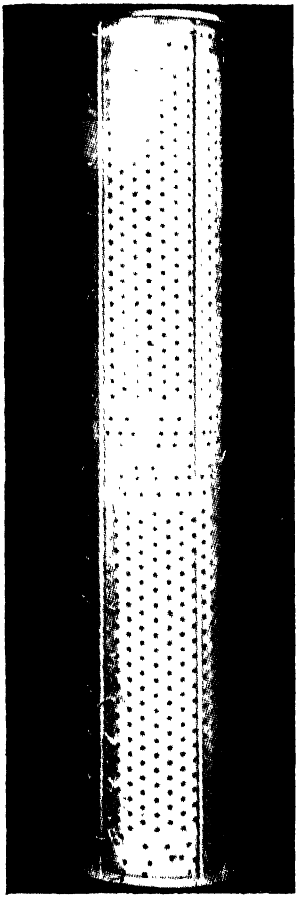


Figure 9. Molybdenum retainer used to support crude titanium

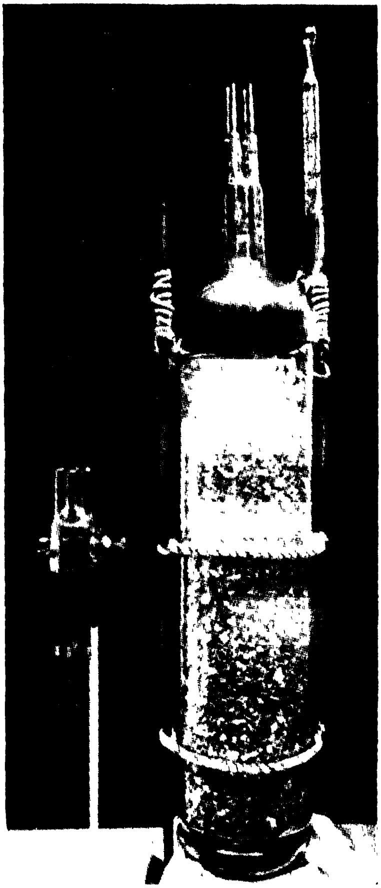


Figure 10. Large 7⅝-in *diameter de Boer bulb used in production of two* 24-in *titanium hairpins* (300 g *each*)

The apparatus used by de Boer and van Arkel to produce the first ductile zirconium was the basis of the more modern arrangement devised by the Battelle Memorial Institute, which was used for the production of ductile titanium[2]. The bulb, as it is termed, is shown in *Figure 8*. It contains a perforated molybdenum retainer, see *Figure 9*, which permits uniform distribution of the crude titanium throughout the bulb (a prepared bulb is shown in *Figure 10*) and also serves as a radiation shield.

The procedure used in the preparation of iodide zirconium is as follows. The bulb is charged with the crude zirconium metal and the filaments lowered through the collar of the bulb and the electrode cap sealed to the collar. The bulb is then evacuated and sealed to the vacuum system as shown in *Figure 8*. The entire assembly is evacuated and the bulb heated to about 500° C for several hours to anneal the glass and to remove adsorbed gases. After the annealing and outgassing operation, the bulb is cooled to room temperature and helium is admitted through a liquid-air trap. A weighed quantity of iodine is added at *A*, while a counter flow of helium is maintained through the inlet. The open end of the iodine container is then sealed off and the iodine is chilled in a dry ice-alcohol bath. The unit is again evacuated to 10^{-4} mm of mercury, and then isolated from the vacuum system by closing the constriction at *B*. The iodine is now introduced into the bulb by heating its container with a soft flame and a second seal made at *C*. The bulb is then suspended in a *Nichrome*-wound furnace and heated to the operating temperature of about 200° C. This temperature is maintained overnight in order to ensure completion of the reaction between the iodine and the crude zirconium. After the incubation period, the filament is heated to about 1300° C when the iodide is dissociated and the zirconium is deposited while the liberated iodine returns to react with more crude metal. As the deposition proceeds it is necessary to adjust the current to maintain a constant temperature.

The whole success of the work is dependent on the skill of the operator, and the assistance of an experienced glass blower is essential for making the glass-metal seals for the electrodes which carry the current to heat the filament.

With titanium, and presumably with zirconium, it is possible to vary the temperature of the bulb over a wide range. The 'bulb temperature' appears to refer to temperature on the outside of the bulb and is controlled by cooling or heating as required, this temperature would be similar to the temperature of the crude metal or the 'iodination zone'. Bulb temperatures of 50 to 250° C give a reasonable rate of deposition and in this range there is little danger of the formation of the less volatile diiodide. In the range 250 to 450° C the deposition rate falls markedly due to rapid formation of diiodide which is not volatile even at these temperatures, but if the temperature is increased to volatilize the diiodide the reaction proceeds as readily as with the tetraiodide. It is noted with titanium di- and tri-iodides that disproportionation takes place readily and these reactions influence the deposition reactions. There is little doubt that the triiodide takes part in the deposition, particularly at the higher temperatures. Depositions of titanium have been made with bulb temperatures at 175 and 525° C and little difference in the nature of the deposits has been noted but there is an appreciable difference in the transfer of impurities. At the lower bulb temperature the deposited titanium contained up to 0·1 per cent iron operating with a crude metal containing 1 per cent while at the higher temperature iron transfer was negligible due to the instability of ferric iodide at this temperature. It was noted previously that silicon also transfers less readily at the higher bulb temperatures. The disadvantage of operating at the higher temperature is the danger of collapse of the apparatus.

It is customary to operate at a temperature of about 200° C when the iodine vapour reacts with the impure zirconium to produce volatile zirconium tetraiodide, leaving the impurities such as oxide and nitride as a residue. In order to obtain rapid dissociation of the iodide the filament must be at 1300° C or over. It is obviously difficult to obtain two quite different temperature zones within such small apparatus and yet the whole success of the process depends on such conditions being attained. If the impure metal should be permitted to exceed a certain critical temperature, which is slightly above 200° C, then zirconium diiodide is produced instead of the tetraiodide and as the diiodide does not vaporize very readily the process comes to a stop. This factor is not important for short runs but on long runs of 24 to 48 hours it is a problem to avoid overheating. For short runs heating is required to maintain the correct temperature conditions, while for long runs cooling becomes necessary. It is equally important to control the temperature of the filament to ensure the production of satisfactory metal and as the thickness of the filament is constantly increasing due to the deposition of the pure zirconium it is necessary to vary the power continuously. Increasing the size of the filament while maintaining the same temperature results in increasing the quantity of heat being radiated to the impure zirconium, and therefore the cooling of this metal must be increased gradually to maintain a steady temperature.

The filament temperature determines the rate of deposition but the maximum rate is actually determined by the safe working temperature of the filament which may burn out if excessive temperatures are used. The deposit obtained by operating at high temperatures is relatively smooth whereas at lower temperatures well developed crystalline faces are obtained which cannot be worked so readily in the later stages.

No published data are available for the deposition rates of zirconium but with titanium 24-in hairpin filaments of 0·3-in diameter weighing about 300 g are obtained in 30 hours. If optimum filament temperatures are maintained this time could be cut to 20 hours. The overall length of the bulb used to produce such titanium filaments was 35 in. The weight of crude metal was 13 lb and the iodine added was 100 to 300 g.

It is obvious that the simplicity indicated by the descriptive equation shown above is not realized in practice. The use of glass apparatus placed severe limitations on the iodide method for producing zirconium; not only was the result dependent on the skill of the glass blower but the bulbs had a habit of collapsing due to the heat radiated from the filaments.

As more zirconium was required for the expanding electronic industry it became apparent that the use of glass limited the technique to the laboratory and the small production obtained resulted in enhanced costs. The use of metal to replace glass was desirable, but the corrosive conditions due to the iodine vapour were severe. Molybdenum was satisfactory but considered to be too expensive and most of the ordinary metals were useless, but eventually tests showed that certain alloys were satisfactory and aluminium wire formed a reasonably satisfactory gasket for sealing the vessel.

The introduction of metal vessels with modifications to the cooling system and other improvements resulted in the production of filaments from 0·25 to 0·4 in in diameter in lengths up to 24 in. The filaments are known as 'crystal bars' because of their highly crystalline appearance. When the bars are bent a distinct creaking noise is heard similar to 'tin cry'. The metal possesses the property of cold ductility and can be drawn to fine wire or rolled to thin sheet before work hardening is appreciable.

6.1.1. *Pilot plant operations of van Arkel process*

In the following description of a van Arkel production unit a metal reactor has been used. The details given refer to the method as applied to the production of titanium, but with a few minor modifications the description may be applied equally well to the production of zirconium. As has already been stated molybdenum would be satisfactory but it is rather expensive although it might be used as a lining if the difficulties of welding could be overcome, and as it would have an almost unlimited life it would be economical. The relatively high iron content of iodide metal

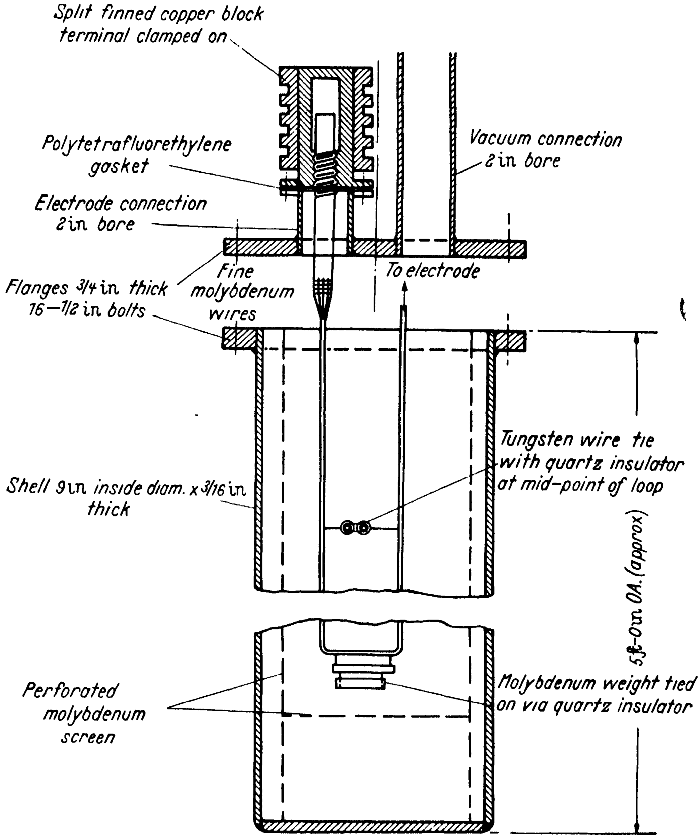


Figure 11. Details of apparatus for iodide process titanium

may indicate that the metal used for the construction of the reactors is not entirely satisfactory.

The reactor consists of a cylindrical vessel with a closed end and a cover for the top which is sealed by means of a copper gasket. (Recent U.S.A. press reports on zirconium operations suggest that gold is the ideal gasket material.) There are three openings in the cover, one connects to the vacuum pump, and also holds the device for feeding the iodine into the reactor. The other two are used to hold the electrode connections to the filament. The arrangement is shown in *Figure 11.* The electrodes are made of stout tungsten rods connected to copper terminals fitted with radiator fins, and the electrode connections are sealed to the reactor by *Fluon* (*Teflon*) jointing rings which also provide electrical insulation. The reactor shown in *Figure 11* was used for the production of titanium and all the following data apply to titanium, but with zirconium the only variation would be to modify the temperature of the bath and instead of an oil bath a salt bath would have to be used.

Titanium wire of about 0·1-in diameter is used as the filament, the hairpin, formed by connecting the ends to the tungsten electrodes and allowing the wire to hang below, is about 8 ft overall. The ends of the filament are tied to the tungsten electrode by means of fine molybdenum wire. The filament is weighted by means of a piece of molybdenum tied to a silica tube which is in turn tied to the bottom of the filament. The filament is also tied across the middle to prevent it from bowing outwards, when the current is applied, and touching the sides of the molybdenum radiation shield. The molybdenum shield is in the form of a perforated sheet inserted around the inside of the reactor leaving an annular space which is packed with titanium sponge. After charging, the reactor is heated by means of a resistor furnace which heats all of the vessel except the cover to a temperature of 600° C while it is maintained under a vacuum, the pressure being not more than one micron. This treatment is continued until the vessel is completely degassed, an operation that may take up to three days. When the vessel is degassed it is allowed to cool and is sealed by a valve before it is disconnected from the vacuum pump, lifted out of the furnace and lowered into a deep oil bath which covers the whole reactor including the protruding electrode connections.

The next step is to introduce the iodine; this is done by giving a sharp blow to the anvil fitted on the metal diaphragm above a glass phial containing the iodine, which is supported on a metal ring in the pipe connection from the cover. The phial has a pip turned at right angles so that when the anvil strikes the phial the pip is broken and the iodine and broken phial are discharged into the reactor. Originally the phial was simply dropped into the reactor but there were occasions when it did not break, but with the new arrangement there is no doubt about the tube being broken. The oil bath is maintained at 150° C first by heating and later by cooling.

It has not been found possible to measure the temperature of the filament because of fuming, but by tests and experience it is possible to control the temperature by means of the applied voltage. Deposition starts at about 1100° C and the temperature is maintained at 1300° C. Typical values are, starting voltage 45 and amperage 57. A schedule is arranged by which the voltage is adjusted to give an increase of about 10 to 15 A/h. The deposition proceeds for three days, during which time the oil bath temperature is carefully controlled. The final readings are 17 V and 700 A. After cooling, the reactor is opened and the cover is lifted off with the hairpin of titanium suspended from the electrodes. The hairpin is now about $\frac{5}{8}$-in diameter and with an overall length of 8 ft weighs about $5\frac{1}{2}$ lb. The charge of titanium sponge weighs 70 lb and the iodine 200 g. A typical analysis of titanium crystal bar produced by this equipment is:

O_2	60 p.p.m.	Ni	10 p.p.m.	S	47 p.p.m.
H_2	<10 p.p.m.	Cu	21 p.p.m.	Si	50 p.p.m.
Fe	600 p.p.m.	Cr	<5 p.p.m.	Mo	<10 p.p.m.
N_2	100 p.p.m.	C	200 p.p.m.	W	<10 p.p.m.

The process is very difficult to control and it is only after considerable experience that successful results can be obtained. One difficulty that arises is due to bad packing of the titanium sponge which may result in a void being formed in the titanium around the reactor. The presence of the void would result in excessive cooling at this spot, leading to cooling of the filament at a point opposite the void. If this cooling is appreciable the reaction may be reversed, the iodine vapour attacking the filament and rapidly severing it.

6.1.2. *Examination of van Arkel process*

A report[12] has recently been published by W. M. Raynor of the Foote Mineral Co. describing efforts to determine the factors limiting the rate of reaction and the optimum operating conditions to permit maximum production. The apparatus used is shown in *Figure 12*, the tube being constructed from *Inconel* (this is the first known disclosure of the material of construction). The apparatus includes a thermocouple well, fitted into the bottom of the tube because it has been found that the temperature of the outside of the tube could not be used as an indication of the true temperature of the crude zirconium sponge. The optimum temperature of the filament was 1200 to 1300° C and investigations described indicated that 460° C was the optimum sponge temperature while an addition of 24 g iodine per pound of crude zirconium appeared to give the best rate of production.

Further improvements in the iodide process, which were the direct result of research sponsored by the U.S. Atomic Energy Commission, have resulted in the manufacture of zirconium filaments up to 1·7 in in diameter and 12 ft in length, but these dimensions are not considered economical owing to high power cost coupled with heat-dissipation problems and it is probable that commercial developments would be better directed towards the production of

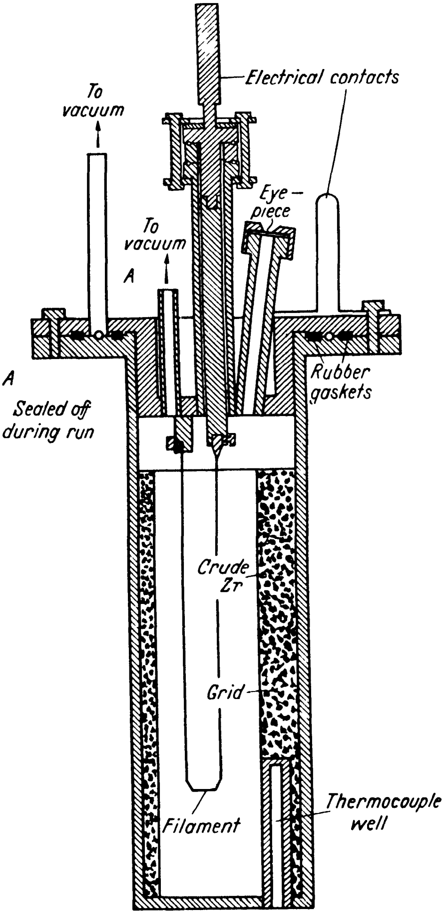


Figure 12. Zirconium deposition tube (after W. M. RAYNOR[12])

longer lengths of smaller diameter crystal bar, *i.e.* not exceeding 1 in in diameter.

The present iodide process for the production of pure zirconium is based upon the use of an intermediate zirconium, either coarse powder as produced by the calcium reduction of zirconia, or metal sponge from the Kroll process. This policy of operating with an expensive and comparatively pure metal as an intermediate is a major factor in preventing the process becoming a commercial proposition, and endeavours are being made to use other intermediates. One possibility is the use of zirconium carbide but this intermediate like any other must not contain any element which will be vaporized with the zirconium tetraiodide.

Many of the difficulties encountered in operating the iodide process are due to the use of one vessel for the two operations, iodination and dissociation, and it has been shown that the use of separate chambers not only simplifies control but makes possible semi-continuous operation of the process[4].

A fundamental study of the iodide or 'hot-wire' process was made by R. B. HOLDEN and B. KOPELMAN[3]. They divided the process into four steps (*a*) synthesis of zirconium tetraiodide at about 300° C, (*b*) transport of the tetraiodide to the hot filament, (*c*) thermal decomposition and (*d*) transport of the liberated iodine back to the feed zirconium. Steps (*b*) and (*d*) were combined and termed the gaseous transport step. The first part of the investigation was to measure the probability that a zirconium tetraiodide molecule will decompose upon striking a hot surface. Pure zirconium tetraiodide was introduced into an evacuated glass apparatus containing a molybdenum filament or target which was heated to various temperatures. The zirconium decomposed during the experiment and the amount was determined by analysing the target for zirconium. The quantity of zirconium tetraiodide impinging on the target was controlled by maintaining the iodide crystals in a closed chamber at a carefully controlled temperature which determined the pressure of the vapour. The vapour passed through an effuser of special design which permitted a calculation to be made to determine the fraction of tetraiodide which impinged on the target.

These experiments show that the probability of a zirconium tetraiodide molecule decomposing when it impinges once upon a surface at 1300 to 1500° C in a vacuum is nearly unity.

It was also shown by further experimenting that the step which determines the speed of the hot-wire process is the rate of transport of the gaseous reactants. This applies when the feed zirconium is not appreciably less reactive than the crystal bar used in the experiments. The result indicates that the speed of the iodide process could probably be accentuated by increasing the velocity of gases.

An interesting and unexpected finding was that the synthesis of the zirconium iodide from the iodine and feed zirconium which proceeds very slowly while the filament is unheated, increases rapidly as soon as the filament becomes hot enough to emit light. It was assumed that the effect was a photochemical one due to the action of the light, from the filament, on the iodine.

6.1.3. *Purity of iodide process zirconium*

Commercial iodide zirconium contains approximately 2 to 3 per cent hafnium which is associated with zirconium in the mineral and which is not normally eliminated in the processing. A recent analysis of iodide zirconium was published[11] by the Foote Mineral Co., as follows: Hf, 2·4; Ti and Fe, 0·1 each; H_2, 0·02; Si, Al, Ni, Ca, Cu, O_2 and N_2, 0·01 each; Mg 0·003 per cent. The hafnium and titanium would be iodized and deposited as readily as the zirconium and must have been present in the crude metal. The relatively high iron value emphasizes one of the drawbacks in the iodide process. Recent analysis of iodide zirconium indicates that material of a much higher purity than that quoted by the Foote Mineral Co. is being produced.

6.2. THE KROLL PROCESS

The Kroll process for the production of ductile zirconium is based upon the reduction of zirconium tetrachloride vapour with molten magnesium. The reduction of zirconium tetrachloride with magnesium is not novel, as von Zeppelin had already demonstrated the reduction of the tetrachloride with magnesium in the presence of sodium chloride, but by means of the modifications suggested by Kroll it was possible to produce ductile metal.

As with the iodide process for the production of zirconium, it is possible to illustrate the main reaction by a simple equation

$$\underset{\textit{vapour}}{ZrCl_4} + \underset{\textit{liquid}}{2Mg} = \underset{\textit{solid}}{Zr} + \underset{\textit{liquid}}{2MgCl_2}$$

The main difference in the reaction is that whereas in the iodide process the zirconium is obtained free from the other product of the reaction, in the Kroll process the zirconium is associated with the magnesium chloride which is produced simultaneously, and it is necessary to recover the metal by further treatment.

The process proposed originally by Kroll consists of several steps which are denoted as follows: (*a*) carburization of zircon, (*b*) chlorination of the carbide, (*c*) purification and densification of the crude chloride, (*d*) reduction of the pure chloride with magnesium, (*e*) separation of the salts from the reduced zirconium, and (*f*) melting the metallic sponge.

W. J. KROLL *et al.* described these operations in several papers[5–7] and emphasized the importance of preventing zirconium satisfying its extreme activity towards oxygen, nitrogen, *etc* in order to avoid contamination of the final metal with embrittling oxide or nitride.

Failure to prevent contamination with such impurities had been the main reason for the failure of other workers to obtain ductile metal.

The earlier work on the reduction of zirconium tetrachloride with magnesium is particularly mentioned and Kroll shows how this method, which depended upon the reaction between solid chloride and magnesium turnings mixed together, was prone to failure because the oxygen introduced by hydrolysis of the extremely hygroscopic tetrachloride was ultimately transmitted to the reduced metal. As the chloride could contain as much as 1 per cent oxygen the resultant metal was brittle. In the Kroll process the zirconium tetrachloride is resublimed under such conditions that not only are the oxygen and other impurities eliminated, but the condensed chloride is recovered as a dense mass offering a minimum of surface area to the atmosphere during its short period of exposure before proceeding to the reduction step, where the dense chloride is again sublimed so that its vapour is exposed to the reducing action of molten magnesium.

6.2.1. *Carburization of zircon*

Zirconium tetrachloride may be produced directly from zircon (zirconium silicate) by passing chlorine gas over a heated mixture of zircon and carbon, but if the zircon and carbon are first reacted at a high temperature to produce zirconium carbo-nitride, this material will react exothermically with chlorine at a lower temperature than that required for the zircon–carbon reaction. There is the further advantage that most of the silica is eliminated by the carburization step, the silica being reduced to silicon monoxide which is volatile at the temperature attained in the electric arc furnace used for the carburization process. The carbo-nitride contains zirconium in a much higher concentration than the zircon ore, with 75 to 80 per cent zirconium combined with about 5 per cent each of silicon and carbon and 1 to 2 per cent each of oxygen and nitrogen.

A mixture of 83 parts by weight of zircon and 17 parts carbon is fed to the arc furnace when an intense reaction occurs yielding large volumes of vapour containing silicon monoxide which rapidly oxidizes to dioxide in the air. The product is a dense block with a metallic appearance, having a golden-yellow fracture. All loose adhering material is returned for further treatment.

Good carburizing yields a product containing 5 per cent carbon or just over and with a high zirconium content indicating the presence of little oxide. Such material chlorinates readily and completely. Badly carburized material is usually low in carbon and high in oxide and when chlorinated leaves a residue which contains a considerable amount of zirconium.

6.2.2. *Chlorination of the carbide*

There are various types of chlorinators[10] and the one shown in outline in *Figure 13* is typical of that used for the production of zirconium tetrachloride. The equipment is in two parts, a vertical furnace for the actual chlorination and a condenser to collect the chloride. The furnace may be lined with silica brick which has an extraordinarily long life under the severe conditions, but for smaller furnaces carbon is very satisfactory. The heating element shown in the illustration is a split-rod resistor formed by making a saw-cut along a graphite rod to within a few inches of the end. Special water-cooled connections are made to the two legs of the hairpin and the current passes down one and up the other; this type of resistor is ideal for the smaller chlorinators. The outer casing is made of nickel to withstand corrosion by chlorine and the same metal is employed in the construction of the condenser and most of the other parts.

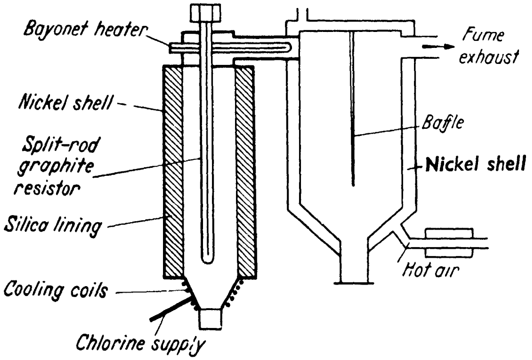


Figure 13. Chlorinator and condenser (after G. L. MILLER[10])

The condenser is heated by a hot air jacket and a temperature of about 100° C maintained on the walls, this ensures that silicon tetrachloride is not condensed but passes out of the exhaust with the waste gases. Chlorine is supplied from cylinders of liquid chlorine and the flow is adjusted to the feed of carbide.

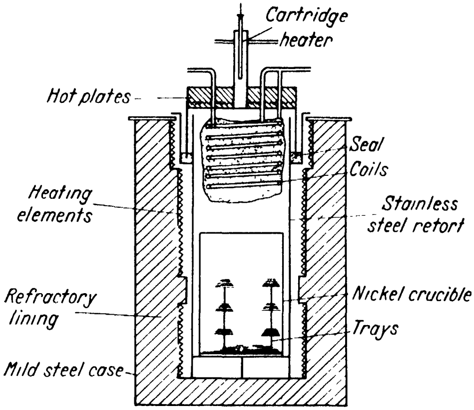
It is most important that the pipe connecting the furnace and the condenser should be of ample size, short length, and preferably heated in order to minimize the danger of the chloride being deposited at this point.

The chlorinator is run continuously and the zirconium carbonitride crushed to a suitable size is fed in at the top of the furnace which is maintained at about 500° C. The zirconium chloride passes over into the condenser and is condensed as a loose fluffy powder which contains small amounts of impurities such as iron, chromium, silicon and zirconium oxide.

6.2.3. *Purification and densification of the crude chloride*

The light crude zirconium chloride is purified and densified by resublimation in specially designed equipment[10] shown in *Figure 14.*

Figure 14. Densifier (*after* G. L. MILLER[10])



The charge of crude chloride is placed in a nickel crucible and lowered into a stainless steel vessel, which has a special cover fitting into a bismuth–lead alloy seal contained in an annular trough round the top of the main stainless steel vessel. The cover carries steel cooling coils which are used to condense the sublimed chloride. The stainless steel vessel is placed in a furnace heated in three horizontal zones by metallic resistors. The bismuth–lead alloy is melted and the cover lowered into it; the alloy when cooled forming a gas-tight seal. The vessel is then partially evacuated by means of a water ejector pump (a mechanical vacuum pump is better but a lime-trap must be included in the system to absorb the fumes which would otherwise damage the pump) and filled with hydrogen, and the operation repeated in order to remove as much air as possible. The bottom heating zone is used to heat the chloride to about 200° C to remove residual silicon tetrachloride and reduce the ferric chloride to the non-volatile ferrous chloride and so tend to prevent its sublimation. The bismuth-lead seal is remelted and the temperature of the bottom heaters raised to about 400° C when the zirconium chloride volatilizes and collects on the cooling coils; all other parts of the furnace including the cover are maintained above the sublimation temperature of the chloride. The operation is carefully controlled so that the rate of volatilization coincides with the rate of condensing in the cooling coils. The successful accomplishment of this operation is only possible with an experienced operator. The cover, resting in the molten bismuth–lead alloy, may act like a safety valve and rise and fall depending on the pressure within the vessel. At the end of the operation the seal is frozen by cooling and the whole allowed to cool to about room temperature.

After cooling, the seal is remelted and the cover with the purified zirconium chloride attached to the coils is removed. The chloride is now much denser than the original material, and pure. Most of the iron, chromium and zirconium oxides are left as a residue in the nickel crucible. This purification step is very important, particularly as it provides a means of removing oxide which would normally be left as an impurity in the finished metal. It is essential that the purified chloride be in contact with the air for as short a time as possible.

Various methods for the purification of zirconium tetrachloride have been claimed. One example[9] claims the use of zirconium sulphide to eliminate small amounts of iron and aluminium. Zinc, magnesium or calcium sulphides can be used to replace zirconium sulphide. The metallic sulphide is intimately mixed with the zirconium tetrachloride and heated to the sublimation temperature of the chloride. With a mixture of one part zirconium sulphide and nine parts zirconium tetrachloride a purified chloride containing less than 0·001 per cent iron was produced. Separation of iron and chromium from the chlorination products of zircon ores is claimed in a recent patent[8]. In the preamble of the patent it is stated that the purification by reduction of the ferric chloride to ferrous chloride by hydrogen is not complete, the limit of the reduction at the ordinary sublimation temperature being 0·2 per cent iron, calculated as iron in the zirconium tetrachloride.

The patent claims that zirconium tetrachloride with very low iron contents can be obtained by passing the vapours of the crude chloride, in the absence of free chlorine, over zinc, cadmium or manganese. Alternatively these metals as powders may be mixed with the crude chloride before sublimation. Impure zirconium chloride containing 1·1 per cent iron yielded purified chloride containing 0·01 and 0·001 per cent iron when mixed with three and ten times, respectively, the amount of zinc powder required for the reduction of ferric to ferrous chloride. No appreciable contamination of the product by zinc chloride can occur due to the low vapour pressure of this chloride at the operating temperature.

In practice purified zirconium tetrachloride containing about 0·1 per cent iron can be produced by the method described by Kroll using hydrogen to reduce the ferric iron to ferrous. Although this value may rise to 0·4 per cent if sublimation is rapid, the iron is not present as an unreduced ferric chloride but almost wholly ferrous chloride. During the sublimation of the chloride in the reduction vessel or reactor the ferrous iron is almost completely left as a residue and does not contaminate the metal as shown by iron contents in the sponge of the order 0·03 to 0·05 per cent.

6.2.4. *Reduction of pure chloride with magnesium*

The actual reduction of the purified chloride is carried out in a vessel similar to that used for the purification of the crude chloride[10], see *Figure 15.* A steel crucible containing pure magnesium ingots

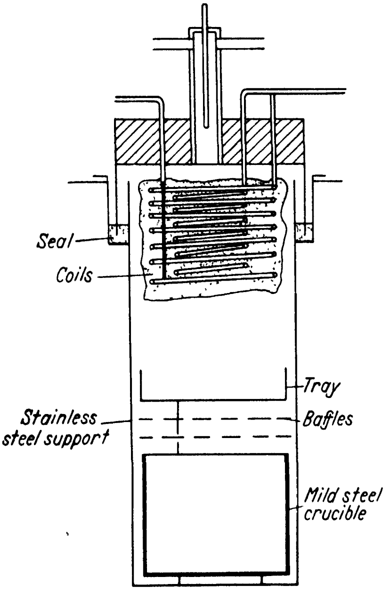


Figure 15. Set-up for reduction (after G. L. Miller[10])

is lowered into the bottom of the stainless steel vessel and the cover, with its coil carrying the block of pure zirconium chloride, is lowered into the annular trough containing molten bismuth–lead alloy which is then cooled to form a seal. Baffle plates and a tray are placed on top of the crucible containing the magnesium, to reduce radiation of heat and collect any oxide which might be present in the chloride and which would drop off the coil as sublimation of the pure chloride proceeds.

The vessel is evacuated and filled with argon or helium; this gas is evacuated and the vessel refilled with the inert gas. The seal is melted and the top cover floated, buoyed up by the pressure of the inert gas.

The next step is to melt the magnesium by using the bottom heater while the cooling on the coil is maintained in order to prevent any sublimation of chloride at this stage. It is important to heat the magnesium to a temperature above the melting point of magnesium chloride, otherwise there is the danger that the first stage of the reduction of the zirconium tetrachloride vapour results in the formation of a solid crust of magnesium chloride on top of the molten magnesium. This crust forms a barrier between the chloride vapour and the magnesium until the temperature rises sufficiently to melt the crust, when there is a sudden intensification of the reaction due to the production of zirconium chloride vapour. The condition is difficult to control because the temperature of the magnesium would rise as a result of the accelerated reaction and this in itself would make matters worse. The result of failure to control the reaction, an example of which possibility has just been described, leads to a reaction between magnesium vapour and zirconium tetrachloride vapour. The product of this reaction is a very fine pyrophoric powder which collects in various parts of the apparatus; it ignites at the first opportunity and may result in the complete loss of the reduced zirconium. In addition to the production of pyrophoric zirconium powder the excessive temperature resulting from the accelerated reaction may lead to contamination of the zirconium by iron from the steel crucible used to contain the magnesium.

Despite the difficulties which have been indicated it is possible with careful manipulation of the heating and cooling equipment to control the reaction between the molten magnesium and zirconium tetrachloride vapour so that excessive temperatures are avoided and little, if any, vapour phase reaction takes place.

6.2.5. *Separation of salts from reduced zirconium*

After reduction of the zirconium tetrachloride the apparatus is cooled under an inert gas atmosphere and after breaking the seal the cover is removed and the steel crucible containing the products of the reaction lifted from the vessel. The reduced zirconium is intermixed with fused magnesium chloride and in addition some magnesium will be present resulting from the use of an excess of this metal which is added to ensure complete reduction of the zirconium tetrachloride. The zirconium may be recovered by cutting the reduced mass out of the crucible followed by leaching with water and dilute hydrochloric acid. This treatment yields zirconium as a powder with a high purity except for about 0·2 per cent oxygen and 0·5 per cent magnesium. Since contamination by oxide is almost inevitable if zirconium powder is leached with water and it is impossible to remove the last 0·5 per cent magnesium from the zirconium by acid leaching, these conclusions clearly indicate that some other method must be used to separate the zirconium from the magnesium and the magnesium chloride. At the time this work was proceeding, titanium, which was being produced on a pilot-plant scale by a process very similar to that used for zirconium production, was being recovered by an acid leaching operation. Kroll, who was largely responsible for the development of both titanium and zirconium production, realizing the objections to the leaching technique, devised an entirely new method for the recovery of the reduced zirconium. The method is based upon a heat treatment in a vacuum, whereby the magnesium chloride is removed from the zirconium, partially by melting and partially by distillation while the magnesium metal is distilled and collected on condensers.

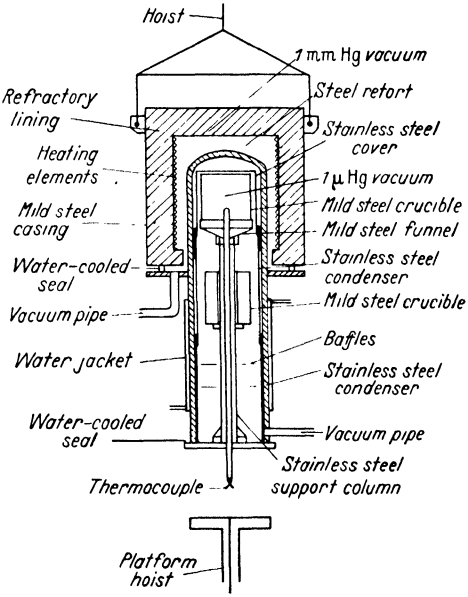


Figure 16. Salts separator (after G. L. Miller[10])

The process is carried out as follows[10]. The crucible containing the reduced mass is inverted and supported on a stout stainless steel tube and pushed up into a steel retort (see *Figure 16*). A cover plate on the end of the steel tube is clamped over the open end of the retort to form a seal. A portable furnace is lowered over the top section of the retort and is sealed around the bottom by means of a a water-cooled joint. The retort and the furnace are evacuated, the former by an oil diffusion pump backed by a rotary pump and the latter by a rotary pump only. To maintain high vacuum in the retort it is necessary to use a cold trap to prevent contamination of the pump oil with water. When the pressure in the retort is about 0·1 micron of mercury, and in the furnace is about 1mm (evacuation of the furnace ensures that there is no danger of the retort collapsing) the resistance heaters in the furnace are switched on and the temperature raised to 650 to 700° C as indicated by a thermocouple inserted in the crucible as shown in *Figure 16.* At this temperature there is a rise in pressure to 50 microns of mercury and high pumping capacity is essential to remove gases, including water vapour, which are evolved during the heating. When the pumps have recovered the pressure steadies at less than one micron. Heating is increased and the temperature raised to about 885° C and maintained for several hours. It is important to avoid exceeding a temperature of 900° C otherwise the zirconium tends to become alloyed with the steel crucible, and the metal touching the crucible will be contaminated with iron. During this soaking period the magnesium chloride melts and drips from the crucible and collects in a steel pot or crucible supported on the tube below the charge in the cooler part of the retort. The magnesium distils, with some magnesium chloride, and is collected on the cold surface of a stainless steel sheet wrapped round the inner surface of the lower part of the retort. When the salts are removed the apparatus is allowed to cool to 60° C, the furnace being lifted off the retort to accelerate cooling.

Although the zirconium is cool it is not safe to expose it to the atmosphere because the surface of the metal is very active in its present state and it is necessary to condition or slightly oxidize the surface by gradually breaking the vacuum with air. The final safety precaution is to evacuate the air and then fill the retort with inert gas and cool to 20° C before opening it and removing the crucible. The metal is obtained in a spongy mass attached to the sides and bottom of the crucible from which it is removed with the aid of a chisel. In this state the metal is known as 'sponge zirconium'.)

6.2.6. *Blending zirconium sponge*

S. M. Shelton and E. D. Dilling[13] describe the handling of zirconium sponge, which varies from batch to batch and also within the same batch. *Figure 17* shows the three types of sponge which are obtained. Sponge *A* is a dense massive material making up about 35 per cent of the total. It is low in magnesium and chloride. Sponge *B* is formed during the initial reaction. It occurs as a plate representing about 20 per cent of the total weight. The iron content of this sponge is higher than that of the others. Sponge *C* is porous and very light. It is 35 per cent of the total weight. This type is lowest in impurities but contains considerable amounts of magnesium and chlorides.

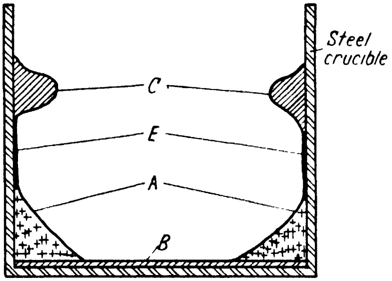


Figure 17. Reduction crucible with various sponge types indicated (*after* S. M. Shelton *and* E. D. Dilling[13])

The sponge is removed from the crucible, type *C* being removed without breaking, but *A* and *B* must be broken before removal. As occasional batches tend to ignite, the crucible is kept flooded with argon during the chiselling operations. The pieces of *A* and *B* sponge are cleaned of black deposit before crushing, pieces too large to handle are cut with a chisel.

A gyratory crusher is used to crush *A* and *B* sponge to minus ¼ in. *C* sponge is chopped in a rotary-tooth mill.

Split samples of about 3 lb are briquetted in a 4-in die under 200 tons total load and samples for analysis taken by drilling six holes with a multiple-point ⅜-in drillhead through the briquette. The sponge, after crushing, is blended in 2000-lb lots.

6.2.7. *Shipping zirconium sponge*

Zirconium sponge can be shipped safely in argon-filled steel drums in wooden crates.

6.2.8. *Composition of Kroll zirconium*

Various values have been given for the impurities in zirconium metal produced by the Kroll process and often it is not clear whether they refer to sponge or ingot. Often the analysis is given for zirconium which has been melted in a graphite crucible and no mention is made of the fact that the carbon present is almost solely due to contamination during melting and can be avoided by using the more recently developed arc melting technique. The analysis of the three types of zirconium sponge described by S. M. SHELTON and D. DILLING[13] are shown in *Table VI.*

Table VI. Analysis of Three Types of Zirconium Sponge

Procedure	*A* p.p.m.	*B* p.p.m.	*C* p.p.m.
Chemical			
Fe	400	2100	300
Ti	30	50	<30
N_2	10	40	<10
Mg	550	600	4000
Cl	230	350	2600
Spectrographic			
Al	150	150	60
Fe	100	>600	80
Mn	10	30	<10
Si	<20	>20	<20
Ti	<50	<50	<50
Mo	<10	<10	<10
Cr	20	20	<20
Cu	5	5	10
Mg	>100	>100	>100
Ni	<5	<5	<5
Pb	60	60	15
Sn	1	2	<1
Zn	<50	<50	<50
B	<0·5	>0·5	>0·5
Cd	<0·5	—	—
As	<50	—	—
P	<100	—	—
V	<50	—	—
Bi	<1	—	—
Co	<5	—	—
Sb	<50	—	—
Ag	<0·5	—	—
Be	<1	—	—

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7

ZIRCONIUM PRODUCTION DEVELOPMENT

ALTHOUGH the standard Kroll and van Arkel processes produce zirconium which is satisfactory as far as the properties of the metal are concerned, they are both complicated techniques which are expensive to operate. If full advantage of the unique properties of zirconium is to become available to industry the metal must be produced at a more reasonable price. Attempts have been made in the last few years, and are still continuing, to modify the Kroll and van Arkel processes for both zirconium and titanium production.

New processes, some based on earlier work, have been examined and while most of these have little hope of becoming commercial propositions there are a few that may well be the basis of the zirconium industry of the future. There is also the possibility that when the Kroll method is applied on a larger scale a number of the production difficulties may become less important and costs very considerably reduced.

7.1. MODIFIED KROLL PROCESSES

7.1.1. *Combination of purification and reduction steps*

W. J. KROLL and his colleagues[13] at the U.S. Bureau of Mines investigated the possibility of carrying out the purification and reduction of zirconium chloride simultaneously instead of preparing a batch of the dense chloride and then transferring this to another vessel for reduction as in the standard method. The apparatus used is shown in *Figure 18.* The crude zirconium tetrachloride is heated in hydrogen in the purification vessel and distilled directly into the reactor vessel. The cooling coil shown is employed as a means of controlling the pressure if it tends to become excessive. The chloride vapour reacts with the magnesium and when the reaction slows down the bulk of the magnesium chloride is expelled from the reaction vessel through the siphon shown in the arrangement by applying a pressure of helium. A further charge of molten magnesium is introduced from a special pot through a tap hole, assisted by a pressure of helium, and the reaction continued. Most of the salt is drained from the sponge at the end of the reaction and

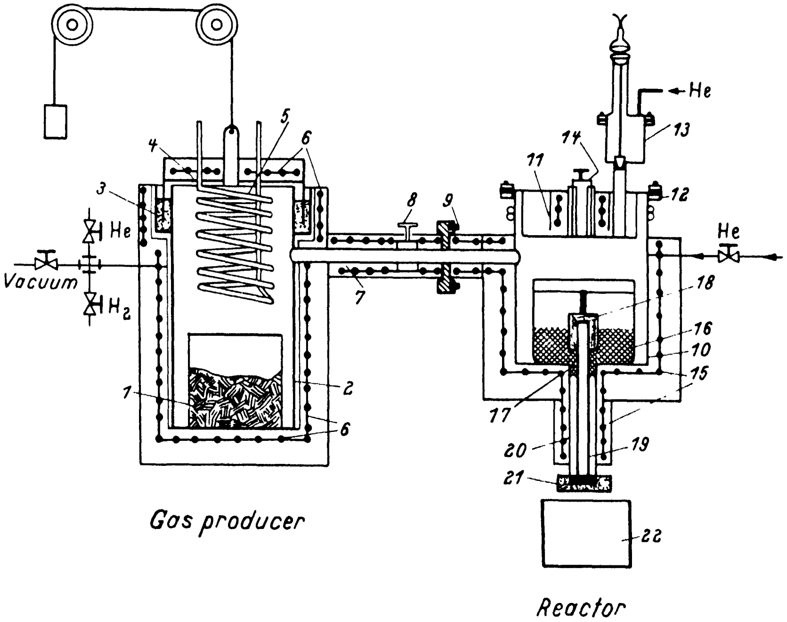

Figure 18. Combined purification and reaction vessels. 1. Nickel can with raw zirconium chloride powder. 2. Iron shell of the gas producer. 3. Trough with lead alloy seal. 4. Floating top. 5. Water-cooled coils. 6. Heating elements. 7. Heated transfer pipe for gaseous chloride. 8. Heated stopcock. 9. Heated flange. 10. Heat-resisting steel shell of the reactor. 11. Inserted top. 12. Water-cooled rubber gasket and bolts. 13. Magnesium ladle held under helium. 14. Heated lead alloy safety valve. 15. Heating elements of the reactor. 16. Reaction crucible with siphon. 17. Threaded joint. 18. Siphon. 19. Siphon outlet. 20. Drain pipe. 21. Lead joint. 22. Mould for the salts. (After W. J. KROLL *et al.*[13])

the remainder together with the excess magnesium removed by the usual vacuum treatment.

The apparatus and technique used for this work are unsuitable for large scale operations but they served to demonstrate that the standard Kroll process can be considerably improved. The next development would be to carry out the purification and reduction in one vessel and omit the nuisance of the connecting pipe. The technique of draining the molten salts from the sponge has been applied successfully to titanium.

S. M. SHELTON and E. D. DILLING[19] described the combined operation of purification and reduction using the arrangement shown in *Figure 19.*

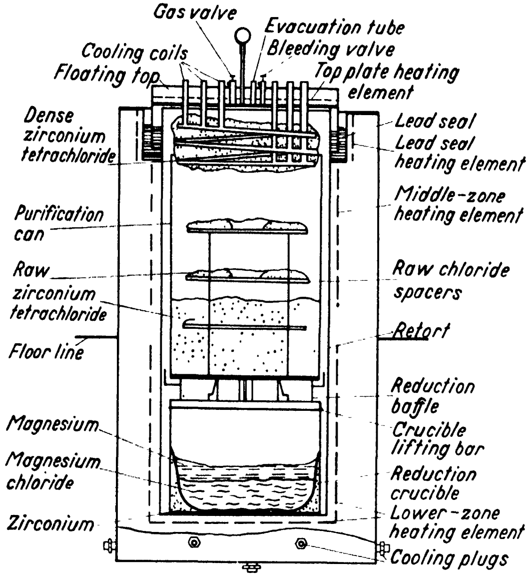

Figure 19. Assembly of combined purification–reduction furnace (after S. M. Shelton *and* E. D. Dilling[19])

7.1.2. *Use of a mixture of magnesium and sodium as a reducing agent*

In the apparatus which has been described for the combined purification and reduction of zirconium chloride, W. J. Kroll *et al.*[13] also investigated the effect of using magnesium–sodium mixtures as the reducing agent. The mixtures varied from 5 per cent sodium and 95 per cent magnesium to 80 per cent sodium and 20 per cent magnesium, with a 20 per cent excess of reducing agent as magnesium added to ensure complete reduction of the chloride.

It was observed that the reaction with sodium started at temperatures as low as 500° C, and even with the higher proportions of sodium the heat evolution was not excessive although it was not possible to predict what the result would be with large batches. When over 15 per cent sodium was used, salt eutectics were formed which melted out of the reduced mass long before the residual magnesium and magnesium chloride were removed. No secondary evaporation of the sodium salt occurred and no sodium was found in the distillate, indicating that the excess magnesium did not reduce the sodium chloride formed in the reaction.

The results of the investigation indicated that sodium could be used to replace part of the magnesium in the reaction but until large scale trials can be made it is not possible to indicate the usefulness of this modification. The main advantage to be gained by using magnesium–sodium mixtures is to form a low melting point eutectic of NaCl–$MgCl_2$ which could be removed more readily from the sponge than magnesium chloride.

7.1.3. *Adaptation of Kroll process to continuous working*

A method for the continuous reduction of titanium tetrachloride with magnesium has been investigated[14]. Although the method has not been tested for zirconium a similar procedure could no doubt be used. The process consists of two main steps.

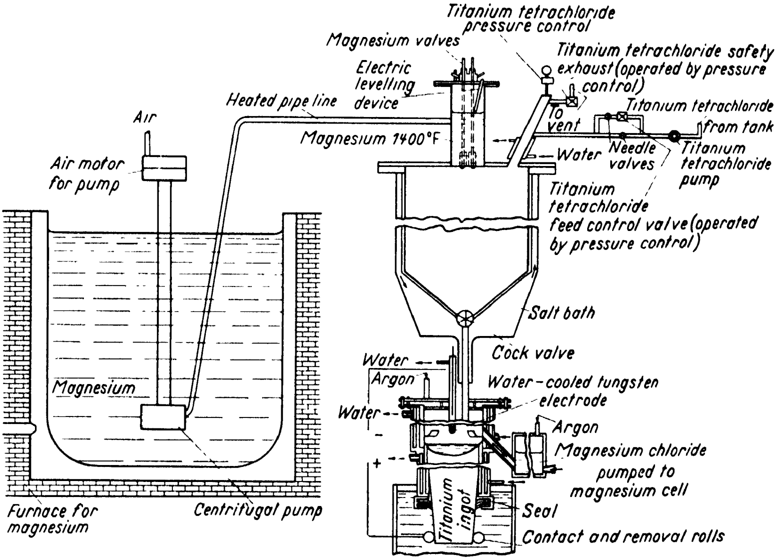

Figure 20. General arrangement of a proposed pilot plant unit for making continuous titanium ingots from titanium tetrachloride and magnesium (after P. J. MADDEX *and* L. W. EASTWOOD[14])

(*1*) The continuous addition of molten magnesium to titanium tetrachloride vapour in a reduction chamber heated to 760 to 870° C. The reaction products consisting of molten magnesium (89 per cent by volume) and solid titanium particles (11 per cent by volume) flow continuously into an arc furnace where the next step is carried out.

(*2*) In the arc furnace the titanium is melted and collected as molten metal while magnesium chloride and unreacted magnesium are volatilized, condensed and removed from the furnace chamber and the molten titanium is cooled and forms an ingot which is withdrawn continuously from the bottom of the furnace.

The feasibility of the process was studied at the Battelle Memorial Institute, and while the two main steps were carried out separately, the investigators concluded that the method could be applied to continuous large scale production using a pilot plant such as that shown in *Figure 20.*

7.2. REDUCTION OF TITANIUM AND ZIRCONIUM TETRACHLORIDES BY HYDROGEN

The halides of some metals can be dissociated thermally and this is the basis of the van Arkel process; in some cases hydrogen is used at a high temperature to reduce the halide. Titanium bromide has been reduced[21] by hydrogen at 1300° C.

The possibility of reducing titanium tetrachloride by hydrogen in an arc furnace has been examined by L. D. JAFFEE and R. K. PITLER[10]. While the conclusions are not directly applicable to zirconium there is a close similarity.

A process which would use the cheapest reducing agent possible to produce titanium unencumbered with reaction products is very attractive, and it is claimed by Jaffee and Pitler that starting with hydrogen saturated with titanium tetrachloride vapour at 25° C, where the vapour pressure of the chloride is 12·6 mm of mercury and maintaining the overall pressure at one atmosphere, 99¼ per cent of the chloride would be reduced to titanium at thermodynamic equilibrium.

An arc furnace designed for melting titanium was used to test the theoretical data. After evacuating and flushing with argon an arc was struck on a piece of titanium and commercial hydrogen, dried by passing over silica gel (apparently no attempt was made to deoxidize the gas), was bubbled through commercial titanium tetrachloride and the gas stream directed into the zone of the arc. Unfortunately after 10 minutes the arc went astray, burnt a hole in the copper crucible and terminated the experiment. Instead of repeating the experiment before forming conclusions the investigators compared the weight and titanium content of the metal used at the start with that recovered, and showed a profit of 13·96 grammes (on an original charge of about 300 g) equivalent to the reduction of 430 litres of tetrachloride at 12·6 mm of mercury.

Despite the failure to complete the experiment satisfactorily the authors saw no reason why the process should not be scaled up to the size of a 30-ton steel melting arc furnace.

The reduction of zirconium tetrachloride by hydrogen has been studied at the U.S. Bureau of Mines by W. J. KROLL and his

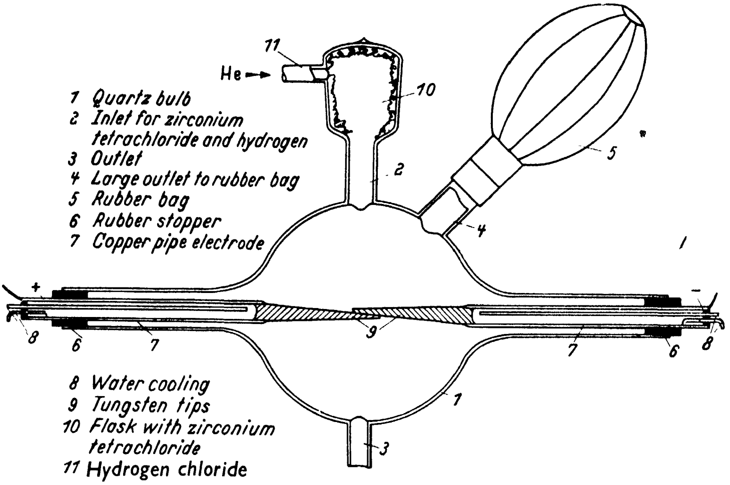

Figure 21. Apparatus for hydrogen reduction of zirconium chloride in a tungsten arc (after W. J. KROLL *et al.*[12])
(Reprinted from U.S. Bureau of Mines *Report of Investigations 4915*).

colleagues[12]. Purified hydrogen is used in the apparatus shown in *Figure 21* which consists of a special quartz tube with two adjustable water-cooled tungsten electrodes which are used to strike an arc in an atmosphere of hydrogen and zirconium tetrachloride vapour. The zirconium tetrachloride is introduced into the main tube by vaporizing from a side bulb. Equilibrium of the gas with the atmosphere is maintained by using a rubber balloon attached to the apparatus. The reaction produces a powder, some of which collects on the walls. This powder contains up to 26 per cent zirconium, the balance being mainly tungsten. Some dense black powder collects on the electrodes; this when leached assayed 75·8 per cent zirconium.

Kroll concluded that the efficiency of the process was low and that excessive quantities of power and high purity hydrogen would be required for the reduction.

The reduction of titanium or zirconium tetrachlorides by hydrogen is most attractive on paper but there are many problems to be solved if commercial operation is to become possible. The mixture of tetrachloride vapour and hydrogen for complete reduction would be very dilute in regard to chloride and a temperature in the region of 2000° C would be necessary. Assuming material capable of withstanding such a high temperature in an atmosphere of zirconium or titanium chloride, hydrogen chloride and hydrogen can be found, there is still the problem of removing hydrogen chloride.

If the process is to be economical, large volumes of pure dry hydrogen must be recycled with as little loss of heat as possible, and the circuit must include means for maintaining the purity of the hydrogen, in particular, removing the hydrogen chloride.

7.2.1. *Arc dissociation of zirconium halides*

J. H. MOORE and W. O. DI PIETRO[16a] studied the dissociation of the zirconium halides and concluded that very low pressures were required for the dissociation of the tetrachloride, and decided that, although more expensive, it was better to operate with the

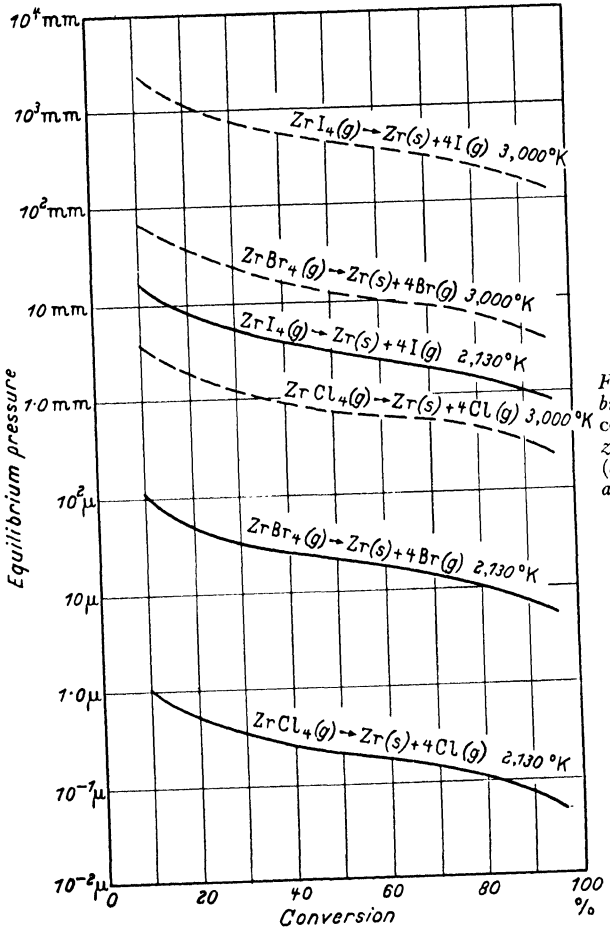

Figure 22. Equilibrium pressure/per cent *conversion for zirconium halides* (*after* J. H. MOORE *and* W. O. DI PIETRO[16a])

tetraiodide as a starting material. The results of the preliminary work in determining the equilibrium pressure/conversion data are shown in *Figure 22*.

Several small scale arc dissociation experiments were made with zirconium tetraiodide. Yields of metal, calculated from the weight of tetraiodide vaporized and the ingot weight gain, varied from 8 to 52 per cent. On the basis of these results a larger unit was constructed. The tetraiodide was produced in units capable of yielding 25 lb of halide. Iodine was introduced into a vaporizer on top of a vertical column packed with zirconium sponge (¼-in pieces). The iodine vapour passed down the column of zirconium sponge which was contained in a stainless steel tube heated by an external winding. The tetraiodide was collected in a porcelain enamelled condenser at the bottom of the column. The reaction column was maintained at 760° C during the run.

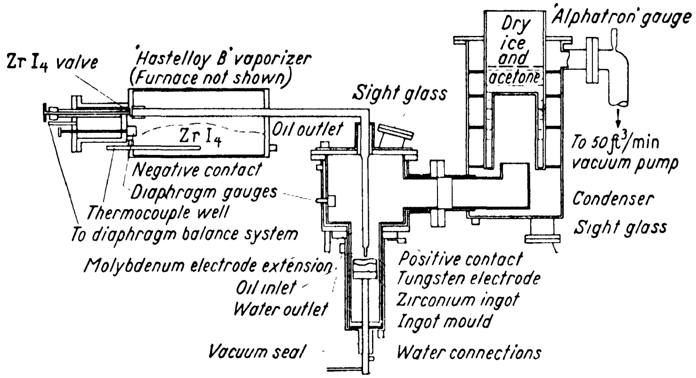

Figure 23. Large arc dissociation unit (after J. H. Moore *and* W. O. di Pietro[16a])

The arc dissociation unit was designed to produce up to 2 lb o zirconium. The unit is shown in *Figure 23*. In a typical run a charge of 25 lb of tetraiodide was placed in the vaporizing chamber, and the head containing the valve and molybdenum foil diaphragm gauge was sealed. The zirconium starting-ingot and the hollow electrode were weighed before closing the dissociation chamber. The unit was then pumped down to 20 to 30 microns of mercury pressure, and the coolant was added to the condenser. The vaporizing chamber valve was left open until the temperature of the chamber reached 200 to 235° C to ensure removal of adsorbed gases and iodine. The valve was then closed and the chamber heated to 540° C when the arc was struck and a pool of molten metal formed on top of the starting ingot. The feed valve was opened and the dissociation started. During the run the arc voltage was usually 22 to 30 V, the arc current 700 to 1000 A and the exhaust line pressure about 250 microns of mercury. Upon completion of the run the unit was allowed to cool and the yield of metal calculated by determining the changes in weight of the remaining tetraiodide, the ingot and the electrode.

(After initial difficulties were overcome the dissociation was operated without much difficulty.) Moore and di Pietro claimed that the attack of the iodine vapour on the copper crucible was overcome by using the design shown in *Figure 23*.

Much difficulty in striking the arc was encountered initially. It was found that a thermionic arc had to be established quickly, to avoid the formation of a glow discharge which could become destructive by degeneration to an arc to parts of the furnace other than the ingot. Arcing could be accomplished successfully by (*i*) striking under 5 to 10 mm of argon, (*ii*) striking at low pressure but maintaining a very short arc length until a molten pool was formed, or (*iii*) striking at low pressure and increasing the short circuit current considerably.

A series of twenty runs was made and much useful information was collected. Two runs were made under a partial pressure of argon of about 30 mm, one gave no yield and the other 8 per cent compared to 40 per cent obtained under comparable conditions without the inert gas. A variation in iodide feed rate from 0·62 to 22·7 lb per hour resulted in a variation of conversion from 97·7 to 16·4 per cent, and a yield from 41·2 to 255 g per hour.

The back reaction was checked by feeding iodine instead of iodide, with the dissociation chamber at 70 microns pressure. A 7·3 per cent conversion of iodine to iodide was obtained.

Graphite and tungsten were tried as electrode materials. The graphite contaminated the zirconium with carbon, while the tungsten failed if the current density was allowed to exceed about $5kA/in^2$.

The zirconium was contaminated with about 0·35 per cent iron and 5·5 per cent nickel due to reactions of iodine with the vaporizing chamber which was constructed from *Hastelloy B* (Ni 65, Mo 28 and Fe 5 per cent).

Approximately 15 kW were required in the arc to maintain a molten pool and the dissociation reaction. Theoretically, about 1·4 kWh per pound would be required for complete dissociation.

It was concluded that the process was feasible, but successful operation would depend on certain problems being overcome.

The diaphragm gauge was not entirely successful and a more efficient pumping system for removing iodine vapour from the reaction zone appears to be necessary for an improvement in conversion: 40 per cent against a theoretical conversion of about 90 per cent at the melting point of zirconium. Constructional materials for the vaporizing chamber which would not be attacked by the iodine vapour would have to be found.

7.3. REDUCTION OF ZIRCONIUM OXIDE WITH CALCIUM AND MAGNESIUM

The reduction of zirconium oxide with calcium was one of the original processes investigated by E. WEDEKIND[24], O. RUFF and H. BRINTZINGER[17] and J. H. DE BOER[5]. The method was also used by D. B. ALNUTT and C. L. SCHEER[1] for the production of low grade (98 per cent) zirconium for purification by the van Arkel process. None of the metal produced was pure. Attempts have been made to improve the results obtained by the earlier workers. Calcium and magnesium have been compared as reducing agents for titanium dioxide[4] and while not directly applicable to zirconium dioxide the reaction is similar. Titanium dioxide prepared by treating a dilute solution of pure titanium chloride with ammonia, was mixed with the reducing metal (calcium was in the form of fine filings and the magnesium as powder) and briquetted at 32 ton/in^2. The extent of reduction of the oxide was determined *in vacuo* at different temperatures up to 1200° C. Reduction of the oxide with calcium begins at a lower temperature than with magnesium and goes to titanium metal without the formation of intermediate products. With magnesium the reduction did not proceed beyond the production of titanium monoxide (TiO) after passing through the oxide (Ti_3O_4). The results were confirmed by x-ray analysis.

The conclusion that titanium dioxide could not be reduced beyond the monoxide by magnesium at 1200° C is contradicted by G. MEISTER[16] who prepared pure zirconium by reducing the oxide with magnesium as well as calcium in a molybdenum crucible in an argon atmosphere. The mixtures were heated in a special glass bulb by means of a high frequency coil as shown in *Figure 24*. Excessive vaporization of calcium and magnesium which occurred at 1000 to 1200° C was suppressed by the use of the inert gas. The analysis of the metal powder for impurities showed an average of: C 0·02, Si 0·02, Fe 0·04, Ca 0·10 and Ti 0·01 per cent. No value is given for oxygen, presumably because of the difficulty in determination.

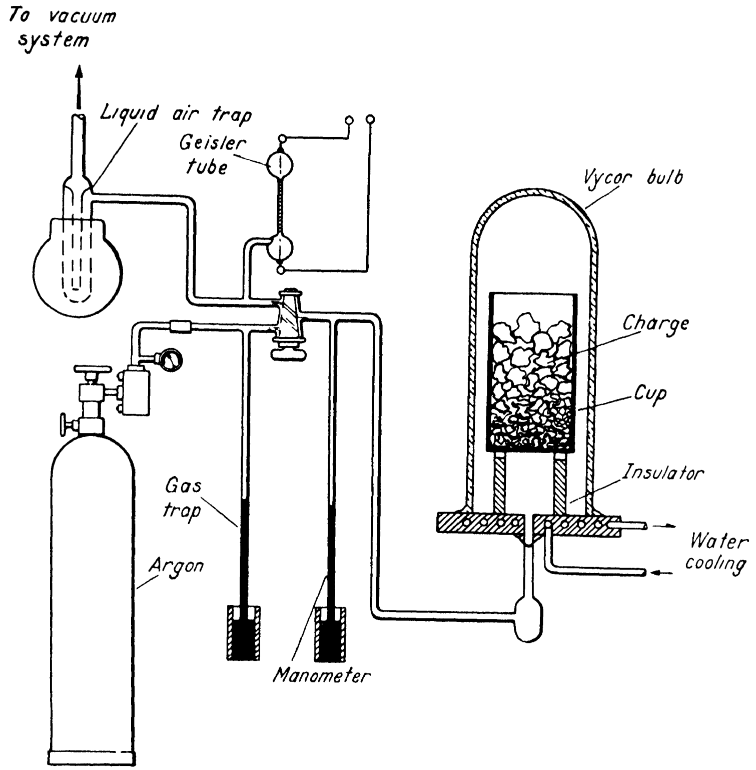

Figure 24. Apparatus used to produce pure zirconium (after G. MEISTER[16])

The metal must have been reasonably pure as it could be pressed and sintered in a vacuum to yield a compact with Rockwell hardness B90. When melted *in vacuo* 'on a suitable refractory' the metal was harder (no data given) presumably due to contamination resulting from attack of the molten metal on the refractory.

The production of crude zirconium and titanium by the reduction of the respective oxides with magnesium is claimed in a recent patent[7]. With titanium, powdered oxide is mixed with magnesium in the form of chips, shavings or powder and preferably a proportion of magnesium chloride which facilitates removal of the magnesia. The mixture is placed in a container and covered with a layer of lime. The container is sealed, evacuated and filled with argon to a pressure of 3 to 5 lb/in^2, and heated to 900 to 1000° C when a reaction occurs raising the temperature to at least 1300° C. After cooling, the reaction mass is leached with dilute sulphuric acid to yield metal containing 92 per cent titanium. With zirconium, metal containing 90 to 95 per cent zirconium is obtained. The crude metal may be further reduced with calcium.

Two advantages are claimed for the double reduction using magnesium and calcium. First, by far the greater part of the reduction is obtained with a comparatively cheap metal and secondly, as calcium has a greater affinity for nitrogen, less of this impurity is present in the final titanium or zirconium.

7.4. ZIRCONIUM METAL PRODUCTION BASED ON DISPROPORTIONATION OF LOWER HALIDES

A method for the production of zirconium metal, which has received little attention as far as published literature is concerned but which no doubt is being investigated, is based on the disproportionation of the lower halides.

R. C. YOUNG[25] prepared zirconium tribromide by the reduction of the tetrabromide with aluminium in a *Pyrex* tube in an atmosphere of hydrogen. The aluminium was heated to 450° C and the tribromide collected as a black to blue mass in the cooled zone immediately after the hot aluminium. The aluminium bromide was carried beyond this zone. After all the unchanged tetrabromide had been removed the tribromide was heated to 310° C and the temperature gradually raised to 390° C when tetrabromide collected at the end of the tube leaving a lustrous black mass of dibromide. The reactions involved are shown by the following equations:

$$\begin{aligned} ZrBr_4 + Al &\rightarrow ZrBr_3 + AlBr \\ ZrBr_3 &\rightleftharpoons ZrBr_4 + ZrBr_2 \end{aligned}$$

If the decomposition of the zirconium tribromide is carried out at too high a temperature zirconium metal will be formed due to the reaction

$$2ZrBr_2 \rightarrow ZrBr_4 + Zr$$

This takes place very slowly at 350° C but at 400° C and above, the decomposition proceeds quite rapidly. The method could be applied to the purification of zirconium by using crude zirconium instead of aluminium to reduce the tetrabromide.

The method described by Young for the tetrabromide could equally well be applied to the cheaper tetrachloride. O. RUFF and R. WALLSTEIN[18] investigated the reduction of zirconium tetrachloride in a vacuum with aluminium. The trichloride was formed at 300° C and it disproportionated into the di- and tetra-chloride above 330° C. The dichloride like the dibromide can be disproportionated. When heated above 600° C, the dichloride yields the tetrachloride and metal. All reactions are carried out *in vacuo* and are illustrated as follows:

$$\begin{aligned} ZrCl_4 + Al &\rightarrow ZrCl_3 + AlCl \ (300^\circ\ C) \\ 2ZrCl_3 &\rightleftharpoons ZrCl_4 + ZrCl_2 \ (\text{above } 300^\circ\ C) \\ 2ZrCl_2 &\rightarrow ZrCl_4 + Zr \ (\text{above } 600^\circ\ C) \end{aligned}$$

No reports are available on investigations designed to produce zirconium metal by either of the above methods although it is known that metal has been produced during experiments in the laboratory. The advantages of such a method for zirconium production are similar to those of the van Arkel or iodide method—(*a*) the metal would be recovered free from salts, (*b*) the halide is recycled. The use of aluminium instead of crude zirconium is much to be preferred on a cost basis and gives the method an advantage over the iodide process. However, recovery of the metal in a suitable form would be a problem, and there would be a tendency for the reaction to produce fine powder which would be difficult to recover free from oxide unless melted before exposure to the atmosphere. Insufficient data are available to indicate whether the rate of reaction is economic. A well designed and instrumented plant with careful supervision would certainly be essential for controlling the complex operations. The production of pure aluminium from scrap by employing a disproportionation method, has been described by P. GROSS[8]. It has been shown on pilot plant scale that when aluminium trichloride at an elevated temperature is passed over liquid aluminium a small portion of the trichloride reacts according to the equation

$$AlCl_3 + 2Al \rightleftharpoons 3AlCl$$

The monochloride on cooling reverts to trichloride and metallic aluminium. As it is considered that large scale production of pure aluminium by this process is feasible it would indicate that the economical production of zirconium by a similar method is not impossible.

7.5. CALCIUM REDUCTION OF ZIRCONIUM FLUORIDE

The reduction of zirconium oxide with calcium is not very satisfactory owing to the difficulty in obtaining complete reduction. The recovery of the metal from reduction products is also difficult.

The use of zirconium tetrachloride is much more favourable than the oxide since the chloride produced can be removed without leaching. Unfortunately zirconium tetrachloride is very hygroscopic and great care must be exercised to ensure that the chloride remains free from water which could contaminate the reduced metal with oxide.

Fluorides in general are less hygroscopic and their use for reduction purposes has become prominent with the knowledge that uranium fluoride is being reduced successfully by calcium to produce very pure metal. The technique appeared to offer a possible method for the production of the rare earth metals and successful application is reported[6].

The fluorides may be prepared by reacting the rare earth oxides with acid ammonium fluoride to produce the double fluoride which is decomposed with the liberation of ammonium fluoride and the formation of rare earth fluorides. The formation of oxyfluorides is avoided by operating *in vacuo* or in a current of nitrogen.

In the reduction of uranium fluoride with calcium it was found necessary to boost the reaction by adding a small amount of iodine which provided additional heat by the exothermic formation of calcium iodide. The calcium iodide facilitates the reaction by lowering the melting point of the slag.. Iodine has also been used for the reduction of the rare earth fluorides. A charge of the following composition was found most suitable, 150 g of mixed fluorides, 70 g iodine and 80 g of calcium turnings (15 per cent excess). The reaction made in a crucible lined with calcium fluoride produced a button of *Mischmetall* weighing 75 g representing a metal recovery of about 78 per cent.

A feature of this technique is that the lining in the reactor vessel is shaped like a funnel so that the metal collects in the bottom and may be recovered as a button free from slag. As a precaution the reaction is cooled in an argon atmosphere by placing a steel cover on top of the reactor and maintaining a slight pressure of gas.

The successful application of the calcium reduction to both uranium and the rare earth fluorides suggests that this method may well be adapted to the reduction of zirconium fluoride. The production of zirconium fluoride is a relatively simple matter using the technique which has been described for the rare earths.

7.6. ELECTRODEPOSITION OF ZIRCONIUM

The early attempts to produce zirconium metal by electrodeposition have been described and, while there appeared to be little hope that an economical process for the production of pure zirconium could be developed, work has continued.

7.6.1. *Electrodeposition from aqueous and non-aqueous solutions*

Aqueous and non-aqueous solutions of zirconium were electrolysed by M. N. HOLT[9] in an attempt to produce zirconium and zirconium alloys. Holt realized that there was little hope of recovering a metal as reactive as zirconium from an aqueous solution but he wished to prove the matter one way or the other.

Various aqueous and non-aqueous solutions were tried. The first bath was composed of zirconyl chloride and ammonium carbonate which had been reported[11] to give a film of zirconium on the cathode when electrolysed at 8 to 20 A/dm^2 at 27° C. Despite a thorough investigation the results showed that while a deposit was obtained which had a dull metallic appearance it weighed only 2 mg, dissolved in nitric acid and gave an excellent reaction for iron and a slight one for zirconium.

The bath used by W. E. BRADT and H. B. LINFORD[3] containing zirconyl sulphate, with an addition of sodium sulphate to retard hydrolysis, gave difficulties when prepared according to directions, but by variation of the quantity of zirconyl sulphate a very thin silvery deposit was obtained on a gold cathode. This deposit disappeared as it was washed and dried.

Several other aqueous solutions were tested including solutions of zirconyl sulphate in aqueous fluoboric acid, boric acid, oxalic acid, tartaric acid and trisodium phosphate but none was satisfactory.

Non-aqueous solutions of zirconium were examined by Holt and first of all he decided to use a modified form of a bath which had been used successfully for plating aluminium[2]. The aluminium bath was composed of aluminium chloride and bromide, benzene, xylene and ethyl bromide. A similar bath using zirconium chloride and bromide instead of the corresponding aluminium salts, failed to give an electrodeposit of zirconium. The zirconium salts had a very limited solubility in benzene and xylene.

Other aluminium plating baths were tried and a wide variety of organic reagents; zirconium tetrachloride was used with the organic nitrogen derivatives, ethanolamine, triethanolamine, di- and tri-ethylamine, aniline, pyridine, quinoline, *etc.* Formamide was considered a possibility as it had been suggested for the electrodeposition of metals and alloys, but although zirconium tetrachloride was soluble in molten formamide and the melt was a good conductor, the result was no better than before. Ethyl, *iso*butyl and *iso*amyl alcohols, formic and acetic acids, benzene, chloroform and bromobenzene, glycerine, ethylene glycol, *iso*amyl acetate, ether, chloroform, hexachloropropylene and acetyl acetone used with zirconium tetrachloride did in some cases yield baths with fair conductance, particularly with ethyl alcohol, ethylene glycol and acetic acid, but success was not obtained. Zirconium tetrachloride appeared to be slightly soluble in liquid ammonia and electrolysis produced a dull deposit which contained zirconium.

In no case did Holt obtain a weighable deposit of pure zirconium although several of the baths yielded deposits with a metallic appearance, but these deposits oxidized immediately they were exposed to the atmosphere. In a few cases weighable deposits of zirconium and iron were obtained. In view of the extensive field covered by Holt there appears to be little prospect of producing zirconium by electrodeposition from solutions.

7.6.2. *Electrodeposition from fused salts*

The production of zirconium by electrodeposition from a fused salt bath was one of the earliest methods to be studied in the laboratory. L. TROOST[23] used the double chloride and double fluoride and claimed some success. J. W. MARDEN and M. N. RICH[15] repeated the work using the potassium zirconium double fluoride and after electrolysis the fused bath, containing zirconium dispersed throughout the salt, was allowed to cool, crushed and leached to remove the salts. The residue was 'fairly pure amorphous zirconium in the form of the usual black powder'.

In the production of zirconium by electrolysis there appears to be little doubt that the metal is deposited but owing to its reactivity it is difficult to separate from the salts, without contaminating with oxide. The problem in electrolytic work is to produce the metal as fairly coarse particles which are not readily attacked by air or water during the leaching operations.

Successful production of zirconium by electrodeposition from a salt bath has been claimed[20] by workers at Horizons Inc. Of the two reports issued the first describes the production of zirconium with a purity of 99·7 per cent (this presumably includes hafnium). The oxygen content is claimed to be as low as 0·09 per cent. This value is not particularly low for oxygen, but good for this type of process which includes recovery by aqueous leaching.

The bath used by Horizons Inc. was a fused mixture of potassium zirconium fluoride, K_2ZrF_6, and sodium chloride, the electrolysis being performed under the protection of an argon atmosphere at temperatures up to about 1000° C. After electrolysis the deposited zirconium was recovered by leaching.

The second report shows that when the first deposits of metal were arc-melted, they behaved badly in the arc and the metal produced had poor corrosion resistance and when worked only reduced 40 per cent at 760° C before edge cracking developed. The spectrographic analysis of the metal showed that most of the impurities were in the third place of decimals; these included Si, Al, Cu, Mn, Pb, Mo, Ni, Cr and Sn, while Mg was much less. The major impurities were Fe 0·08, Ti 0·027 and Hf 0·94 per cent (hafnium is not normally regarded as an impurity).

It was established that the cause of the fuming during melting, and the black deposit obtained, was the presence of residual salts, mainly fluorides present in the metal.

The second report covers the work done to improve the quality of the zirconium. In addition to checking more carefully the purity of the salts used in the electrolysis, particularly with regard to moisture and oxide content, the purity of the inert gas was the subject of careful control. It was found that improved working was obtained by lowering the operating temperature for the electrolysis from 950 to 1000° C to 750 to 800° C and, in particular, the metal contained less carbon, nitrogen and oxygen.

The presence of fluorides in the first metal indicated that an improved washing technique was necessary and after some experimenting it was found that by washing with dilute sulphuric acid, complete removal of the salts could be assured and metal treated in this manner did not fume or give a black deposit when melted in the arc furnace.

The electrolytic cell used in the earlier experiments is shown in *Figure 25.* The new cell is a modified version of the one used in the first series of experiments and contains five to six pounds of electrolyte and, in a period of two to three hours electrolysing, is capable of producing 120 to 300 g of metal. The cell and heating element are enclosed in a steel casing with a cover to seal the top during degassing. The casing is packed with lamp black for conservation of heat. The heating element is a cylinder of graphite slotted alternately from top and bottom. All internal parts are made of graphite, including the crucible to contain the electrolyte which is of 5-in diameter by 9-in depth.

The sequence of operations is as follows: (*a*) evacuation at a temperature of 1000 to 1300° C to degas the apparatus, (*b*) back fill with pure argon, (*c*) the crucible which has been charged with sodium chloride is cooled to approximately the electrolysis temperature and the potassium zirconium fluoride added through the cathode opening, (*d*) the carbon cathode is lowered into the fused

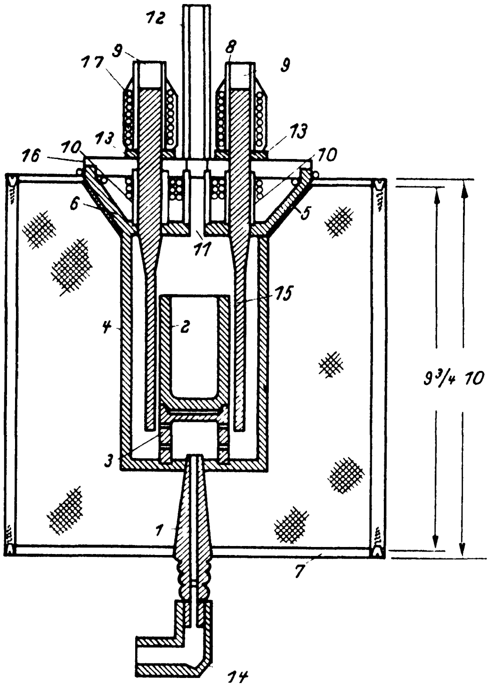

Figure 25. Improved carbon resistance heated furnace and electrolytic cell. 1. Carbon argon inlet. 2. Carbon crucible. 3. Carbon pedestal. 4. Carbon 'can' liner. 5. Carbon dish. 6. Carbon head. 7. Steel casing. 8. Copper leads for element. 9. ½-in *copper rod—element power leads. 10. Carbon sleeves. 11. Cathode entrance. 12. Cathode protector tube. 13. Carbon ring seats. 14. Carbon elbow-argon inlet. 15. Resistance element. 16. Graphite-plate. 17. Copper cooling cores (after* M. E. SIBERT *and* M. A. STEINBERG[20])

bath for pre-electrolysis, (*e*) the carbon cathode is removed and replaced by a molybdenum rod-carbon cathode (made by screwing a molybdenum bar into a carbon rod) and electrolysis is continued, (*f*) the cathode is withdrawn from the bath but allowed to cool in argon before withdrawing, (*g*) the deposit is washed and the zirconium powder recovered.

The pre-electrolysis stage lasts about one hour and is intended to purge the bath of impurities such as iron, copper, nickel, *etc.*

The deposition of the zirconium is obtained with a current between 100 and 200 A, and at a potential varying from 3 to 10 V. The rate of deposition is about 0·83 g metal per ampere-hour.

The argon purification train shown in *Figure 26* provides for a constant flow of purified gas but the arrangement does not provide for sudden surges. The passage of the gas is as follows: (*i*) calcium hydride (300° C) to absorb oxygen and nitrogen, (*ii*) copper oxide (550° C) to convert liberated hydrogen from the hydride to water, (*iii*) phosphorus pentoxide and magnesium perchlorate (room temperature) to remove moisture and finally (*iv*) titanium sponge (850 to 1000° C).

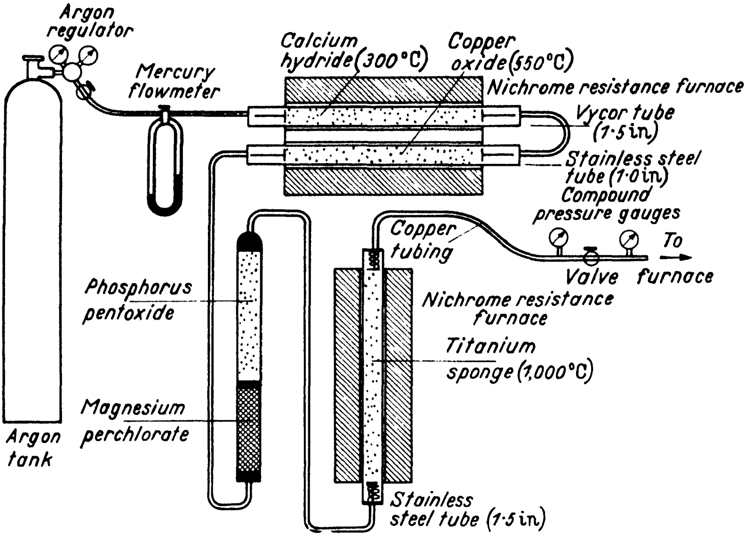

Figure 26. Argon drying and purifying train for electrolysis cell (after M. E. Sibert *and* M. A. Steinberg[20])

The leaching technique found to be most successful is as follows. The cathode after removal from the cell is washed repeatedly in a large excess of hot water to dissolve all occluded sodium chloride and potassium zirconium tetrafluoride. Hot water is used because of the low solubility of the double fluoride in cold water. It is surprising that hot water can be used to wash such a reactive powder without oxidation. Washing and crushing of the deposit is continued until all but the last traces of salts are removed when a final wash with dilute sulphuric acid is used. The powder receives a final water wash, a rinse with alcohol and is dried *in vacuo.*

During the investigation the ratio of potassium zirconium fluoride to sodium chloride was varied from 18·5 to 81·5 to 21 to 79. The yields obtained were, in general, between 80 and 90 per cent with a current efficiency of about 50 per cent.

7.6.3. *Properties of electrolytic zirconium powder*

The zirconium powder produced by Horizons' electrodeposition from fused fluoride is quite coarse. A typical screen analysis is shown in *Table VII*, this shows that over 50 per cent by weight of the powder is coarser than a 200-mesh Tyler sieve (plus 0·074 mm).

Despite the modifications and improvements claimed in the second report, the spectrographic analysis of a sample of the new

Table VII. Sample Screen Analyses of Electrolytic Zirconium
(Tyler Ro-Tap Testing Sieve Shaker 20 min)

Mesh (Tyler)	*Opening* mm	*Sample weight* g	Per cent
35	0·417	26·3	22·9
80	0·175	15·9	13·9
100	0·147	8·6	7·5
150	0·104	16·9	14·7
200	0·074	13·7	11·9
325	0·043	15·7	13·7
<325	—	17·6	15·4

metal, when compared with the values obtained in the earlier work, shows that although some impurities are lower others are higher; in particular, iron is slightly higher (0·085 compared to 0·080 per cent), titanium has increased fourfold (0·10 compared to 0·027 per cent) and aluminium more than tenfold (0·073 compared to 0·006 per cent). The chemical analysis of the same sample showed: C 0·027, O_2 0·16 and N_2 0·0018 per cent. This sample appears to have been higher in oxygen than the average; several samples were assayed for oxygen and nitrogen and gave values varying between 0·033 to 0·184 per cent oxygen and 0·0012 to 0·012 per cent nitrogen. The average value for oxygen on eleven samples was 0·08 per cent and for nitrogen, 0·004 per cent.

Compacts of the powder melted by 'drip-melting' produced massive metal with a hardness of 81 Rockwell B. The metal was cold rolled to 71·5 per cent reduction before edge cracking occurred.

The corrosion resistance of the melted zirconium to water vapour at 315° C was poor and this is attributed to the presence of metallic impurities such as iron and titanium which were introduced from the original potassium zirconium fluoride, in spite of the care in purification.

M. A. STEINBERG, M. E. SIBERT *and* E. WAINER[22] review the literature on the electrolytic preparation of zirconium metal before proceeding to describe their own investigations on this subject. Most of their work has been described above but the latest report details the investigation of various bath compositions. The best bath compositions for zirconium plating were: one containing 35 parts sodium chloride, 65 parts calcium chloride and 5 to 25 parts potassium zirconium fluoride with 3 parts of zirconium dioxide; the other contained 100 parts of sodium chloride and 25 parts of potassium zirconium fluoride. The latter was eventually shown to give the purer zirconium and had the further advantage that the salts were all water-soluble.

For the production of crystalline zirconium the inert atmosphere carbon resistance furnace previously described was used. High purity of gas and salts was essential. The bath was a mixture of potassium zirconium fluoride and sodium chloride as already mentioned in Sibert's earlier report. *Table VIII* gives the operating conditions and properties of the zirconium produced.

Table VIII. Operating Conditions for the Electrolytic Production of Crystalline Zirconium

Bath		*Cathode material*	*Temp.* °C	*E (Av.)* V	*C.D.* A/dm^2	amp. hrs.	*Rockwell hardness*	*Carbon* %	*Nitrogen* %	*Oxygen* %	*Character of deposit*
K_2ZrF_6	NaCl										
35	65	Mo	1040	4	50	20	—	—	—	—	*Bulk powder + dendrites*
35	65	Mo	1025	6·5	270	18	34 (C)	—	—	—	*Needles to* ⅛ in *long*
18·5	81·5	Mo	1000	5	270	47	35 (C)	—	—	—	*Coarse dendritic*
35	65	Mo	1000	5	200	300	—	—	—	0·09	*Dendritic*
18·5	81·5	Ti	1000	5	250	300	34 (C)	—	—	—	*Very coarse*
26	74	Mo	950	5·2	425	350	—	0·038	—	—	*Dendritic*
27	73	Mo	920	7·1	500	300	81 (B)	0·027	0·018	0·161	*Dendritic, coarse*
20	80	Mo	860	6	450	300	81 (B)	—	0·004	0·039	*Hexagonal C.E.* 51%*
20	80	Mo	860	6	360	225	79 (B)	—	0·002	0·042	*Hexagonal C.E.* 61%*
20	80	Mo	795	3·1	400	300	—	—	0·012	0·061	*Hexagonal C.E.* 58%*

* Current efficiency.

The description of the process in Steinberg's latest report is little different from that already given from the earlier work. The pre-electrolysis cycle is described and after withdrawal of the graphite cathode, a metal cathode in a graphite holder is inserted. The metal may be molybdenum, titanium or steel provided the metal is kept cathodic and below the bath level.

The deposit is withdrawn on the cathode just clear of the bath and allowed to cool in argon to about 150° C or less; this takes four to six hours. The washing technique used to recover the metal differs from that given in the first report which described the use of dilute sulphuric acid as a final wash. Instead 10 per cent hydrochloric acid is employed as the first wash followed by water and alcohol and final drying in air.

It was concluded that the following conditions were necessary to obtain successful production of electrolytic zirconium:

(*1*) Use of an inert atmosphere cell
(*2*) Purification of the potassium zirconium fluoride
(*3*) Use of inert crucible anode

(*4*) Lowering of operating temperature from 1000° C to 800 to 850° C.

The first three conditions could yield zirconium but the last condition was essential to produce ductile metal.

Undoubtedly the zirconium powder produced by Horizons Inc. is the best that has been made by electrolysis but despite attempts to improve the quality the metal did not pass the corrosion test. Even if the purity problem can be overcome the process appears to offer no advantage over the Kroll method as it suffers from the same defect—production of the zirconium mingled with salts which have to be removed; in fact, it is simpler to remove magnesium chloride than potassium zirconium fluoride, which must in any case be recovered. The Kroll method yields the zirconium in the form of a comparatively dense sponge which is not ideal but much better than the powder recovered by washing the electrolytic deposit. If powder metallurgy methods are contemplated for fabrication then zirconium in the form of powder would be an advantage.

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8

STRUCTURE

8.1. Crystallographic Properties

8.1.1. *Allotropic modifications*

Zirconium has two allotropic modifications. The alpha form is close packed hexagonal and is stable up to 862° C. The beta modification which is stable from this temperature to the melting point (approximately 1860° C) is body centred cubic[8].

		Alpha	*Beta*
Crystal structure—		Close packed hexagonal	Body centred cubic
Schoenflies space group—		D_{6h}^{4}	O_{h}^{9}
Coordination number—		6, 6′	8′
Lattice constants—	a	3·230 ±0·002 Å[33]	3·62 Å[4]
	c	5·133 ±0·003 Å[33]	—
Axial ratio—	c/a	1·589	—
Interatomic distances—	d_1	3·16 Å[2]	3·22 Å[2]
	d_2	3·12 Å[2]	

Atomic diameter—According to J. G. Becker[2] Goldschmidt's atomic diameter for coordination number 12 is 3·19 for alpha and 3·22 Å for beta zirconium.

Free volume—The free volume[24] of zirconium at the melting point is $24{\cdot}3 \times 10^{-27}$ cm^3.

8.1.2. *Alpha–beta transition*

The transition from alpha to beta zirconium was first discovered by C. Zwikker[36] by electrical resistance measurements.

The transition temperature was determined by R. Vogel and W. Tonn[34] as 862 ± 5° C by thermal analysis. W. G. Burgers[4], who studied the transition extensively, first reported that the beta form was body centred. Later he used x-ray crystallographic methods to determine the orientation of the new phase with respect to the old one at the transition point[5, 6], and found that the transition of beta into alpha zirconium takes place through a combination of shifts and expansions parallel to definite crystal axes and not through grain growth. Thus the transition is to some extent a cooperative one. Further investigations by W. G. Burgers and J. J. A. P. van Amstel with the aid of the electron microscope confirmed the results obtained by x-ray studies[7, 9, 10].

The transition process has also been studied by F. Förster and E. Scheil[15] using a cathode ray oscillograph and by this means they were able to observe effects due to groups of atoms 'flapping-over' as they described it, from one form to the other as the temperature was slowly changed.

C. F. Squire and A. R. Kaufmann[30] determined the changes in magnetic susceptibility (*Figure 33*), electrical resistance (*Figure 31*) and specific heat (*Figure 30*) with rising temperature and noted the discontinuity which occurred at the same temperature, the transition temperature, in every case.

Mechanical treatment has little effect on the transition[11] but absorption of oxygen, nitrogen and hydrogen has an effect in each case. Both oxygen and nitrogen raise the transition temperature very considerably while hydrogen lowers it. (See also Chapter 12.) Many other alloying elements have an effect on the transition temperature.

E. T. Hayes and A. R. Kaufmann[16] studied the alpha–beta transformation of zirconium to determine whether it was martensitic or of the nucleation and growth type. No conclusions were reached on the manner of transformation although important observations were made.

The methods of investigating the transformation which are described by Hayes and Kaufmann were (*a*) high speed thermal analysis, (*b*) high speed resistivity measurements and (*c*) attempts to determine habit relationships.

It was observed that the transformation of pure zirconium differed from that of impure zirconium as the acicular microstructure obtained by quenching from above the transformation temperature is absent when the zirconium is sufficiently pure. In addition, with the impure zirconium, discontinuities are found in the resistivity curves taken during rapid cooling (about 3200 C° per sec) through the transformation range. It appeared that an impurity content of about 0·07 to 0·10 per cent oxygen appears to be necessary to obtain the acicular microstructure and discontinuities in the resistivity curves.

The temperature at which transformation begins can be depressed by increasing the cooling rate, but not suppressed.

A. D. Schwope[28] compared the properties of zirconium, titanium and iron, all of which possess allotropic transformations and discussed the effect of alloying elements on the transformations. A selection of possible metallic alloying elements is shown in *Figure 27* with their effect on transformation. The results are similar to those obtained with iron and titanium. Elements such as niobium, tantalum, molybdenum, tungsten, vanadium, uranium, chromium, manganese, iron, cobalt, nickel and copper, with a larger number of outer *d* electrons which can be expected to be eutectoid formers, enlarge the beta field and lower the transformation temperature. Elements such as boron, aluminium, tin, germanium, antimony, lead, thallium and indium with a smaller number of outer *d* electrons can be expected to raise the transformation temperature.

The elements oxygen, nitrogen and carbon are alpha-stabilizers and raise the transformation temperature.

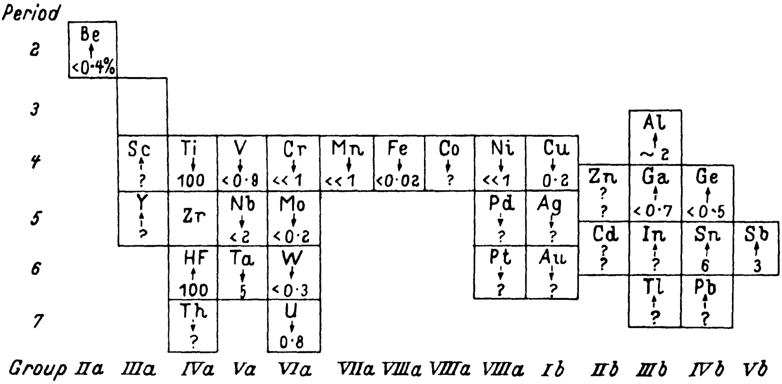

Figure 27. Solubility of alloying elements and their effect on the transformation temperature of zirconium. Arrow indicates direction of transformation shift upon alloying; dashed arrow indicates predicted shift, solid arrow indicates measured direction. Note: numerals below arrows indicate maximum solubility in alpha zirconium (atomic per cent) (*after* A. D. Schwope[28])

8.2. Atomic and Nuclear Properties

Atomic number 40

Atomic weight[17, 3] Chemical scale 91·22
Physical scale 91·24

Packing fraction[12, 26] $-(6\cdot5 \pm 0\cdot9) \times 10^{-4}$

8.2.1. *Electronic configuration*

The electronic structure of the free zirconium metal is compared with those of neighbouring elements in the Periodic System in *Table IX*.

Table IX. Electronic Structures of Free Atoms ($Z = 36$ *to* 42)[25]

Element	*Atomic number* Z	*Principal and secondary quantum numbers*								
		$n = 1$	2	3		4			5	
		$l =$			0	1	2	3	0	1
Kr	36	2	8	18	2	6	—	—	0	—
Rb	37	2	8	18	2	6	—	—	1	—
Sr	38	2	8	18	2	6	—	—	2	—
Yt	39	2	8	18	2	6	1	—	2	—
Zr	40	2	8	18	2	6	2	—	2	—
Nb	41	2	8	18	2	6	4	—	1	—
Mo	42	2	8	18	2	6	5	—	1	—

The free atom of zirconium has four electrons outside the krypton-like core, two in $4d$ and two in $5s$ quantum states, *i.e.* there are four electrons which in the solid state may act as conduction electrons. Some of these four electrons may remain tightly bound to the krypton-like core, which would reduce the effective valency to less than four. In the solid condition the $4d$ and $5s$ energy levels are likely to become hybridized so that if the effective valency of zirconium is four, there may no longer be two $4d$ and two $5s$ electrons.

8.3. ISOTOPES

Table X. Stable Isotopes[31]

Mass No.	*Abundance* Per cent	*Thermal neutron absorption cross section* barn
90	51·5	0·1
91	11·2	1·5
92	17·1	0·2
94	17·4	0·07
96	2·8	0·05

These nuclides have been identified as products of fission of ^{235}U induced by slow neutrons.

Table XI. Artificial Radioisotopes of Zirconium[31]

Mass No.	*Half life*	*Mode of decay and radiation*	*Energy of radiation* MeV	*Correctness of mass no.*	*Existence of element*
86	17 h	*K*		*Probable*	*Certain*
87	1·6 h	β^+	2·10	*Certain*	*Certain*
		γ	0·6, 0·3		
88	85 d	*K* γ	0·41	*Probable*	*Certain*
89	4·4 min	*IT*	0·59	*Certain*	*Certain*
isomeric		β^+	0·9, 2·4		
states		γ	1·5		
89	78 h	*K*	0·91	*Certain*	*Certain*
		β^+	0·92	*Radiation emitted by short-lived daughter*	
		γ			
93	$\sim 5 \times 10^6$y	β^-	0·06	*Probable*	*Certain*
95	65 d	β^-	0·39, 1·0; e^-	*Certain*	*Certain*
		γ	0·73, 0·92		
97	17 h	β^-	1·91	*Certain*	*Certain*
		γ	0·75	*Radiation emitted by short-lived daughter*	

The nuclides 93, 95 and 97 have been identified as products of fission of ^{235}U induced by slow neutrons.

K = *K*-electron capture
IT = isomeric transition
e^- = internal conversion electron
β^+ = positive beta particle
β^- = negative beta particle
γ = gamma radiation

8.4. NEUTRON ABSORPTION

For thermal neutrons the absorption cross section is 0·4 barn. This value was determined[3] on a sample of zirconium oxide containing less than 200 parts per million of hafnium and two parts per million of the rare earths as indicated by spectrographic analysis.

In a private communication to BOULGER[3], H. S. POMERANCE gave the results of further investigations of the cross section of zirconium on re-purified samples. He gave the following values for the atomic cross section for thermal neutrons.

Sample 1 0·40 barn.

(This sample was free from impurities.)

Sample 2 0·33 barn.

(Uncorrected for hafnium content.)

0·26 barn.

(After correction for 0·14 per cent hafnium.)

Sample 3 0·31 barn.

(Separated isotopes measured separately and totalled.)

Prior to these determinations zirconium was generally believed to have a relatively high absorption cross section for thermal neutrons although H. Volz[35] and L. Seren[29] had reported low values. The variation in cross section values probably resulted from variation in hafnium contents. Pure hafnium is reported[3] as having an absorption cross section to thermal neutrons of 101 barns and a sharp resonance in the total cross section of about 2000 barns at 1eV. Consequently small hafnium contents have an important influence on the nuclear properties of impure zirconium.

The scattering cross section of zirconium is given by H. B. Fairchild[14] as 8·2 barns, he also stated that the absorption cross section of zirconium is less than niobium and steel and twice that of aluminium and 40 times that of beryllium.

The total neutron cross section of zirconium as determined by Barschall is shown in *Figure 28.*

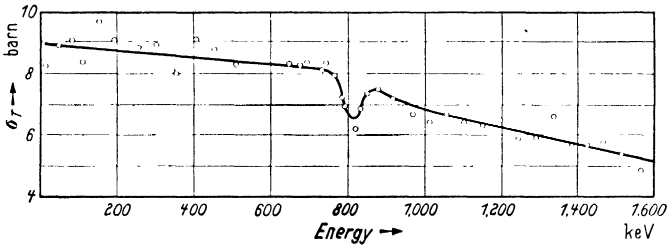

Figure 28. Total neutron cross section of zirconium measured by H. Barschall et al. (after F. W. Boulger[3])

8.5. X-Ray Data

X-Ray spectra[32]—Excitation potentials (kV) for x-ray spectra for zirconium:

K 18·0 and *L* 2·51

Emission lines[1]—In kX units:

K Series			*L Series*					
α_2	0·78851	Strong	l	6·899	Very weak	β_2	5·5742	Medium
α_1	0·78430	Very strong	η	6·5939	Very weak	β_3	5·6186	Weak
β_3	0·70083	Very weak	α_2	6·0567	Weak	β_4	5·6517	Very weak
β_1	0·70028	Weak	α_1	6·0567	Very strong	β_6	5·6927	Very weak
β_2	0·68850	Very weak	β_1	5·8236	Strong	γ_1	5·3738	Weak

K absorption edge 0·68738

L_{III} absorption edge 5·5610

Mass absorption coefficient (μ/ϱ) *including scattering*[18]—

Radiation	*Wavelength*	*Coefficient*
Ag K_α	0·5604 Å	61·1
Rh K_α	0·6149	80·9
Mo K_α	0·7097	17·2
Cu K_α	1·5392	143
Ni K_α	1·6565	173
Fe K_α	1·9344	260
Cr K_α	2·2869	391

Atomic absorption coefficient—

$$\mu_\alpha = \frac{\mu}{\varrho} \times \frac{\text{Atomic weight}}{\text{Loschmidt's number}}$$

Radiation	*Wavelength*	*Coefficient* $\mu_\alpha \times 10^{25}$
Ag K_α	0·5604 Å	911
Rh K_α	0·6149	1208
Mo K_α	0·7097	257
Cu K_α	1·5392	2120
Ni K_α	1·6565	2570
Fe K_α	1·9344	3880
Cr K_α	2·2869	5830

8.6. Optical Spectra

In the zirconium atom the K, L, and M shells are already filled, *i.e.* they contain the full complement of electrons allowed by the Pauli principle, and the arc spectrum of the element arises from the four remaining valence electrons. The spectrum is thus fairly complex. An extensive analysis of 1600 observed lines, in the range 2089 to 4277 Å, has been performed by C. C. Kiess and H. K. Kiess[20] who have labelled by spectroscopic term symbols, and by assignments to electron configurations, some 80 per cent of them. In a later paper by W. F. Meggers and C. C. Kiess[21] wavelength measurements and classifications are extended to 10,739 Å. The zirconium I ionization potential of 6·95 V is derived from the energy level classification, the latter being supported by the Zeeman effect studies of C. C. Kiess and H. K. Kiess[20] and of P. M. Sancho[27].

An analysis of the first spark spectrum (zirconium II) has been made by C. C. Kiess and H. K. Kiess[19] who give a line list for the range 1744 to 6787 Å, classifications being given for 735 lines. The ionization potential of the Zr^+ ion is derived as 14·03 V.

For complete lists of arc and spark lines reference must be made to the papers cited; complete tables of derived energy levels identified to date are given by C. E. Moore[22]. The following gives the lines which are important for purposes of spectrochemical identification and estimation by emission methods.

8.6.1. *Sensitive lines of zirconium*[13]

Wavelength Å	*Relative intensity*	*Wavelength* Å	*Relative intensity*	*Wavelength* Å	*Relative intensity*
3391·975	10	3572·473	7	4688·448	8
3438·230	10	3601·193	10	4710·075	9
3496·210	9	4575·515	7	4739·478	9
3519·605	9	4633·985	8	4772·312	8.
3547·682	8	4687·803	10	4815·629	7

Though the line 4687·803 Å has been quoted as the 'most sensitive line' or '*raie ultime*', it has been emphasized by H. DINGLE[13] that some care must be exercised in choice of lines used for deciding on the presence or absence of zirconium in a sample.

Of diatomic molecules containing zirconium, the most important spectroscopically is ZrO. This emitter is responsible for extensive band systems covering the near ultraviolet, visible and infra-red regions, which are readily produced by introduction of the oxide into an arc. Details of positions and intensities of the bands are to be found in *Identification of Molecular Spectra* by R. W. B. PEARSE and and A. G. GAYDON[23]. Some of these bands occur prominently in the absorption spectra of late-type (*S*) stars.

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9

PHYSICAL PROPERTIES OF ZIRCONIUM

9.1. MASS

9.1.1. *Density*

With 2·5 per cent hafnium[4]	6·52g/cm^3
Hafnium-free zirconium[1]	6·49 ± 0·001g/cm^3

R. M. TRECO[27] calculated the density of various types of zirconium from x-ray data as follows:

Oxygen-free iodide zirconium	6·507 g/cm^3
Low hafnium iodide zirconium	6·504 g/cm^3
Kroll sponge zirconium	6·489 g/cm^3
High hafnium iodide zirconium	6·574 g/cm^3
Graphite-melted Kroll zirconium	6·605 g/cm^3

9.2. THERMAL PROPERTIES

9.2.1. *Melting point*

With hafnium	1830 ± 40° C[4]
Hafnium-free zirconium	1845° C[1]

9.2.2. *Boiling point*

3577° C [19]

9.2.3. *Vapour pressure*

$$\log P\,(\text{atm}) = -(31{,}066/T) + 7{\cdot}3351 - 2{\cdot}415 \times 10^4 T$$ [23]

L. L. QUILL[19] quotes temperatures for various partial pressures:

10^{-4} atm	10^{-3} atm	10^{-2} atm	1 atm
2450° K	2700° K	3000° K	3850° K

9.2.4. *Allotropic transition temperature*

863 ± 3° C[4]

The transition temperature may be raised or lowered by the presence of other elements.

9.2.5. *Thermal expansion, linear coefficient*

5·2 ±0·6 × 10^{-6}/C°	at room temperature[4]
2·9 ±0·3 × 10^{-6}/F°	at room temperature
5·4 × 10^{-6}/C°	20 to 200° C[15]
6·4 × 10^{-6}/C°	200 to 300° C
6·9 × 10^{-6}/C°	300 to 400° C
7·9 × 10^{-6}/C°	400 to 500° C
8·4 × 10^{-6}/C°	500 to 600° C
8·9 × 10^{-6}/C°	600 to 700° C

N.B.—Temperature coefficients which are higher by factors of 1·8 to 3 have been reported for the same range.

The thermal expansion values for hafnium-free zirconium annealed at 1000° C[1] are as follows:

−183° C	−5·66 × 10^{-6}/C°	538° C	6·10 × 10^{-6}/C°
−70° C	−5·88 × 10^{-6}/C°	760° C	5·97 × 10^{-6}/C°
204° C	6·23 × 10^{-6}/C°	871° C	5·76 × 10^{-6}/C°
316° C	6·23 × 10^{-6}/C°		

Expansivity along the hexagonal axis is more than twice as great as along the basal axial directions[17].

Tentative coefficients calculated from x-ray data of specimens with a preferred orientation[2] are:

$$\bar{\beta}_{\parallel} = 7{\cdot}9 \times 10^{-6}/\mathrm{C}^{\circ} \quad (25 \text{ to } 200^{\circ}\ \mathrm{C})$$

$$\bar{\beta}_{\perp} = 4{\cdot}7 \times 10^{-6}/\mathrm{C}^{\circ} \quad (25 \text{ to } 200^{\circ}\ \mathrm{C})$$

Cold worked zirconium approached the value $\bar{\beta}_{\perp}$ whereas annealed (transformed) zirconium showed a value equal to $\frac{1}{3}(\bar{\beta}_{\parallel} + 2\bar{\beta}_{\perp}) = 5{\cdot}8 \times 10^{-6}/\mathrm{C}^{\circ}$.

Recent expansion coefficient values for zirconium containing 2·4 per cent hafnium at 25° C are as follows[22]:

True (instantaneous) linear:

6·15 × 10^{-6} ±0·01 per cent/C° (‖ to *c* axis)
5·69 × 10^{-6} ±0·01 per cent/C° (⊥ to *c* axis)

True linear for heterogeneous orientation: 5·85 × 10^{-6}/C°.

In *Figure 29* is shown the mean linear expansion coefficient for zirconium combining the low temperature data of H. D. Erfling[10] and the high temperature data of R. B. Russell[22].

Determinations by G. B. Skinner and H. L. Johnston[24] give the values for the mean coefficient of expansion in the temperature range 298 to 1143° K. These are:

5·5 × 10^{-6}/C° along the *a* axis 10·8 × 10^{-6}/C° along the *c* axis

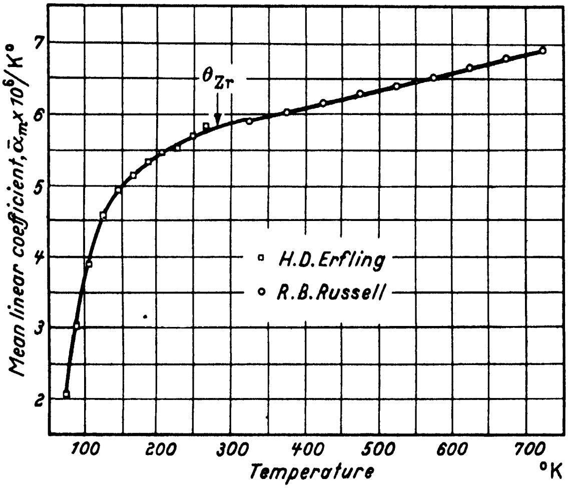

Figure 29. Mean linear coefficient of expansion for zirconium as a function of temperature (after R. B. RUSSELL[22])

the mean coefficient being intermediate between the two values above, 7·2 × 10^{-6}/C°.

9.2.6. *Thermal conductivity*

Iodide crystal bar, 0·04 ± 0·002 cal/cm²/cm/C°/sec at 125° C [4].

Kroll (graphite-melted metal), 0·035 ± 0·002 cal/cm²/cm/C°/sec at 125° C[4].

The thermal conductivity is decreased by about 10 per cent for each one atomic per cent of oxygen contained in the zirconium[28].

9.2.7. *Specific heat*

0·067 ± 0·001 cal/g/C° at room temperature[4, 25].

Hafnium-free zirconium 0·0693 cal/g/C° (25 to 100° C)[1].

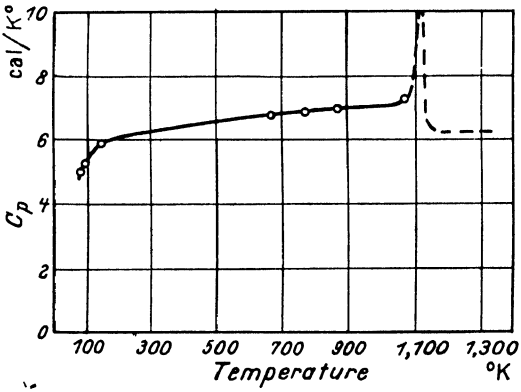

Figure 30. Specific heat per mole *of zirconium against temperature (after* C. F. SQUIRE *and* A. R. KAUFMANN[25])

C. F. SQUIRE and A. R. KAUFMANN[25] investigated the change in specific heat with the rise in temperature and obtained the results illustrated in *Figure 30*.

9.2.8. *Heat capacity*

The molal heat capacity values of zirconium reported by F. W. BOULGER[4] are slightly different from those reported by S. S. TODD[26] which are quoted here. Todd corrected for the hafnium content and found, for zirconium, this amounted to an increase of one per cent. This difference is very similar to the differences in the results reported by Boulger and Todd.

Values of molal heat capacity for zirconium (mol. wt 91·22)

T °K	53·2	56·8	60·8	65·6	70·6	75·4	79·8	84·1	94·9	104·5
C_p cal/K°	2·418	2·640	2·873	3·134	3·383	3·609	3·789	3·945	4·296	4·562
T °K	115·0	124·1	135·1	146·2	156·0	166·1	176·0	186·2	196·1	206·3
C_p cal/K°	4·796	4·971	5·172	5·293	5·409	5·510	5·606	5·672	5·737	5·802
T °K	216·4	226·2	236·4	246·0	256·7	266·4	276·4	286·6	296·8	(298·16)
C_p cal/K°	5·861	5·905	5·948	5·981	6·042	6·083	6·127	6·149	6·168	(6·186)

The high temperature heat capacity values were determined by J. P. COUGHLIN and E. G. KING[8], as follows:

T °K	390·3	477·5	585·6	694·6	780·4	877·3	968·5
$H_T - H_{298 \cdot 16}$ cal/mole	605	1195	1970	2775	3400	4140	4845
T °K	1073·7	1082·0	1098·4	1104·4	1124·7	1147·5	1165·8
$H_T - H_{298 \cdot 16}$ cal/mole	5680	5795	5855	5925	6160*	6685*	7115*
T °K	1182·1	1208·3	1231·1	1253·0	1294·0	1335	1371
$H_T - H_{298 \cdot 16}$ cal/mole	7355*	7620	7790	7940	8260	8530	8925

Results marked with * are in the transition region.

9.2.9. *Entropy*

F. W. Boulger[4] quotes the entropy value of zirconium as

9·18 ± 0·08 cal/mole/K° at 25° C (298·16° K)

S. S. Todd[26] determined the value to be

9·28 ± 0·08 cal/mole/K° at 25° C (298·16° K)

9.2.10. *Enthalpy*

(Heat function or heat content) referred to 0° C[4]

at 100° C	5·0 cal/g
at 200° C	12·0 cal/g
at 300° C	19·2 cal/g
at 400° C	26·9 cal/g
at 500° C	35·0 cal/g
at 600° C	43·5 cal/g

9.2.11. *Latent heat of fusion*

5·5 kcal per mole[19] (doubtful)

9.2.12. *Latent heat of vaporization*

120 kcal/mole[19]
142·150 ± 0·35 kcal/mole[23]

9.3. ELECTRICAL PROPERTIES

9.3.1. *Volume conductivity*

(Iodide zirconium) 4·1 per cent International Annealed Copper Standard copper at 20° C[13].

9.3.2. *Electrical resistivity*

Crystal bar	45 microhm/cm[4]
Kroll graphite-melted metal . .	54 microhm/cm[4]
Crystal bar as deposited . .	40·5 microhm/cm[1] at 0° C
Cold swaged hafnium-free crystal bar	43·2 microhm/cm at 0° C
Annealed at 700° C . . .	39·6 microhm/cm at 0° C
Annealed at 800° C . . .	39·7 microhm/cm at 0° C

R. M. Treco[28] reported 39·84 microhms at 0° C for pure degassed annealed metal. He also noted the rise in resistivity with oxygen absorption (see *Figure 86*).

9.3.3. *Temperature coefficient of resistivity*

44·0 ± 1·0 × 10^{-4}/C°, 0 to 200° C[4]

Hafnium-free crystal bar as deposited

$43{\cdot}5 \times 10^{-4}$/C°, 0 to 200° C
$29{\cdot}3 \times 10^{-4}$/C°, 0 to 800° C

Hafnium-free crystal bar cold swaged

$39{\cdot}2 \times 10^{-4}$/C°, 0 to 200° C
$25{\cdot}0 \times 10^{-4}$/C°, 0 to 800° C

C. F. SQUIRE and A. R. KAUFMANN[25] plotted the electrical resistance against temperature and obtained the curve in *Figure 31.*

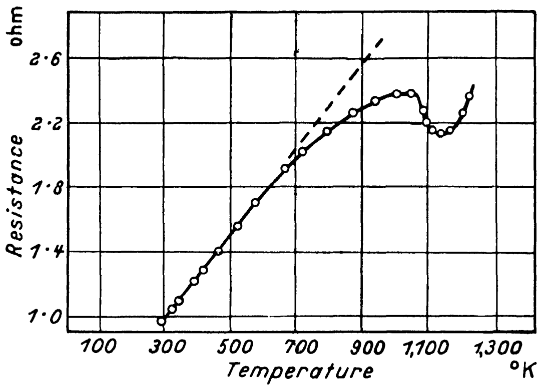

Figure 31. Electrical resistance of zirconium against temperature (after C. F. SQUIRE *and* A. R. KAUFMANN[25])

9.3.4. *Pressure coefficient of resistivity*

The resistance decreases under pressure as expressed by P. W. BRIDGMAN[7].

$$\Delta R/R_0 = -0{\cdot}431 \times 10^{-6}p + 6{\cdot}7 \times 10^{-12}p^2 \text{ at } 30^\circ \text{ C}$$
$$\Delta R/R_0 = -0{\cdot}601 \times 10^{-6}p + 5{\cdot}8 \times 10^{-12}p^2 \text{ at } 75^\circ \text{ C}$$

More recent work by P. W. BRIDGMAN[6] gives the value

$$\Delta R/R_0 = -0{\cdot}39 \times 10^{-6}p + 5{\cdot}5 \times 10^{-12}p^2 \text{ at } 250^\circ \text{ C}$$

where p is expressed in kg/cm².

9.3.5. *Superconductivity*

A. E. VAN ARKEL reported[29] that zirconium was not superconductive even at 1·1° K. N. KÜRTI and F. SIMON[16] found a discontinuity in the conductance/temperature relationship at 0·7° K. T. S. SMITH and J. G. DAUNT[24a] reported T_c in zero magnetic field $= 0{\cdot}546^\circ$ K ($H_f = 0{\cdot}374^\circ$ K).

Slope of magnetic threshold curve
at $T=T_c$ in gauss/C° 170 ($H_f=230$).
Magnetic threshold curve for zirconium is
parabolic with $H_c=33{\cdot}8$ gauss.

9.3.6. *Electrochemical equivalent*

(With valency of 4) 0·2363 mg/coulomb

9.3.7. *Thermoelectric power*

Zirconium–silver[18]—

$$Q = A + Bt \text{ mV/C}^\circ$$

where $A = 11{\cdot}3$ and $B = -0{\cdot}033$ between 100 and 400° C.

The thermoelectric power/temperature curve goes through a maximum at 0° C; B is positive at lower temperatures[14].

Zirconium–platinum—H. K. ADENSTEDT[1] determined the e.m.f. values of a zirconium–platinum couple for temperatures up to 950° C and obtained the curve shown in *Figure 32.*

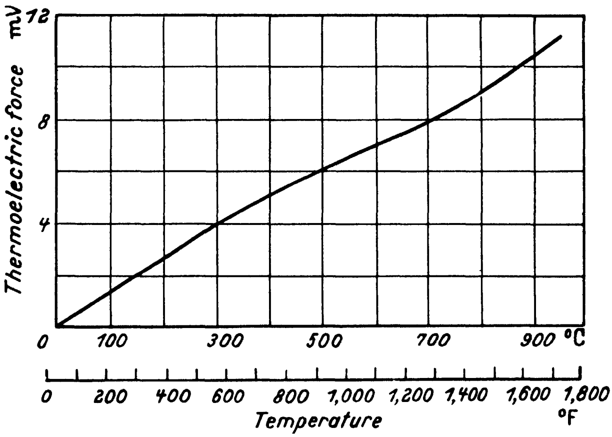

Figure 32. Thermoelectric force of zirconium–platinum thermocouple (Zr +, Pt – ; *after* H. K. ADENSTEDT[1])

9.4. OPTICAL AND THERMIONIC PROPERTIES

9.4.1. *Spectral emissivity*

C. ZWIKKER[31] and J. H. DE BOER[9] investigated the brightness temperature and total radiation of zirconium at high temperatures.

Their results may be summarized as follows:

T° K	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000	2100	2130
Brightness temperature $\lambda =$ 6520 Å	957	1059	1151	1242	1332	1432	1513	1602	1691	1779	1866	1952	1980
Total radiation watt-cm^2	1·68	2·27	3·03	4·06	5·40	7·29	10·0	13·4	17·5	22·0	28·0	34·2	36·5

The coefficient of specific emissivity for wavelengths between 5410 and 6520 Å was measured as follows:

at 5410 Å 0·50 (alpha)	0·46 (beta)[30]
at 6520 Å 0·48 (alpha)	0·43 (beta)[30]
at 6500 Å 0·32 (solid)	0·30 (liquid, unoxidized)[21]
at 6520 Å 0·436 (alpha, 820 to 840° C)	0·426 (beta, 1020 to 1540° C)[5]

Oxidation may explain the discrepancy between values for solid samples. It is considered that the probable value for the oxide formed on a smooth surface is 0·40 although values from 0·18 to 0·43 have been reported[21].

9.4.2. *Photoelectric threshold*

The photoelectric threshold of zirconium is 3200 Å and increases to 3400 Å with dissolved oxygen and nitrogen according to H. C. Rentschler and D. E. Henry[20].

9.4.3. *Electron emission*

J. H. de Boer[9] recalculated the values obtained by C. Zwikker[31] and obtained the following data for the electron emission of zirconium:

T° K	1500	1600	1700	1800	1900	2000	2100	2130
Electron emission mA/cm^2	0·02	0·18	1·30	8·4	40·5	160	520	720

9.4.4. *Work function*

4·1 eV[32, 3]

9.5. MAGNETIC PROPERTIES

9.5.1. *Susceptibility*

C. F. Squire and A. R. Kaufmann[25] reported that zirconium is paramagnetic and that the susceptibility increases linearly with

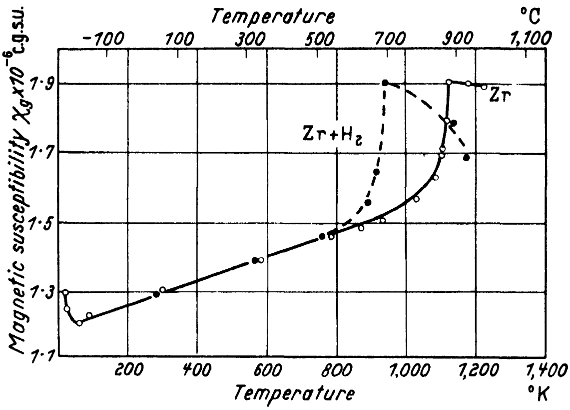

Figure 33. Paramagnetic susceptibility of zirconium as function of temperature, and effect of dissolved hydrogen (after C. F. SQUIRE *and* A. R. KAUFMANN[25])

temperature from 20° K until the allotropic transformation occurs, as shown in *Figure 33.*

K. HONDA[12] reported in 1910 that zirconium was diamagnetic with a susceptibility of $-0{\cdot}45 \times 10^{-6}$ c.g.s. electromagnetic units. Although quoted frequently this result is now considered to be erroneous because of the doubtful purity of the metal then available.

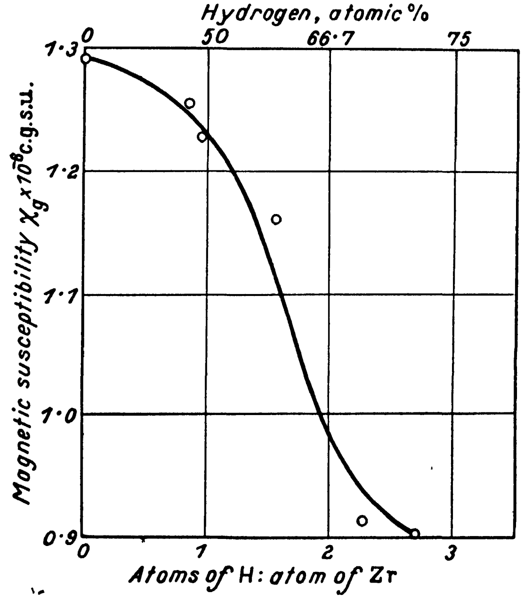

Figure 34. Magnetic susceptibility of zirconium–hydrogen system as function of hydrogen concentration at 295° K (22° C) (*after* C. F. SQUIRE *and* A. R. KAUFMANN[25])

9.5.2. *Effect of quenching and of hydrogen content on susceptibility*

According to C. F. SQUIRE and A. R. KAUFMANN[25], quenching from above the critical temperature does not affect the magnetic susceptibility of zirconium at room temperature. The susceptibility is affected by the hydrogen content as shown in *Figures 33* and *34*.

Specimens containing hydrogen showed a Curie point at 585° K. Hydrogen changed the lattice from hexagonal close packed to tetragonal face centred in the experiments by J. FITZWILLIAM, A. R. KAUFMANN and C. F. SQUIRE[11].

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10

MECHANICAL PROPERTIES OF ZIRCONIUM

THE published data for the mechanical properties of zirconium sometimes show considerable variations due to differences in the purity of the metal under examination.

10.1. MODULUS OF ELASTICITY

F. W. BOULGER[4] states that the modulus of elasticity of zirconium is not known with exactitude but is probably slightly higher than that of aluminium. From available data Boulger estimated the modulus for different conditions as follows:

Annealed, or as-deposited iodide zirconium

$$11{\cdot}3 \pm 2{\cdot}3 \times 10^6 \text{ lb/in}^2$$

Cold worked about 75 to 90 per cent (iodide):

Parallel to rolling direction . .	$12{\cdot}8 \pm 2{\cdot}4 \times 10^6$ lb/in^2
Transverse to rolling direction .	$11{\cdot}8 \pm 1{\cdot}7 \times 10^6$ lb/in^2

W. M. RAYNOR[18] for iodide zirconium, cold reduced 65 per cent, from turned crystal bar, and annealed, gave the following range for wire and rod from 0·065 to 0·156 in

$$9{\cdot}5 \text{ to } 12{\cdot}0 \times 10^6 \text{ lb/in}^2$$

M. B. REYNOLDS[20] gives the following results:

Kroll zirconium	$13{\cdot}9 \times 10^6$ lb/in^2
Crystal bar zirconium . . .	$12{\cdot}8 \times 10^6$ lb/in^2

A. D. SCHWOPE and S. J. STOCKETT[23] found the modulus of zirconium sheet to be:

Parallel to rolling direction . .	$13{\cdot}9 \times 10^6$ lb/in^2
Transverse to rolling direction .	$14{\cdot}0$ to $14{\cdot}2 \times 10^6$ lb/in^2
At 45° to rolling direction . .	$13{\cdot}6 \times 10^6$ lb/in^2

10.2. LONGITUDINAL WAVE VELOCITY

Kroll zirconium	$4{\cdot}62 \times 10^5$ cm/sec[20]
Crystal bar zirconium . . .	$4{\cdot}65 \times 10^5$ cm/sec[20]

10.3. SHEAR WAVE VELOCITY

Kroll zirconium	$2{\cdot}34 \times 10^5$ cm/sec [20]
Crystal bar zirconium . . .	$2{\cdot}25 \times 10^5$ cm/sec [20]

10.4. SHEAR MODULUS

Kroll zirconium	$5{\cdot}24 \times 10^6$ lb/in^2 [20]
Crystal bar zirconium . . .	$4{\cdot}76 \times 10^6$ lb/in^2 [20]

10.5. POISSON'S RATIO

M. B. REYNOLDS[20] gives Poisson's ratio for Kroll zirconium as 0·33 and for iodide 0·35.

A. D. SCHWOPE and S. J. STOCKETT[23] found the ratio to be between 0·32 and 0·35.

10.6. TENSILE PROPERTIES

As already mentioned the strength and ductility of zirconium specimens vary considerably, depending on their purity and prior history.

Figure 35 is useful for estimating the relationship between strength and elongation in tensile tests for samples in different conditions but without deliberate alloying additions.

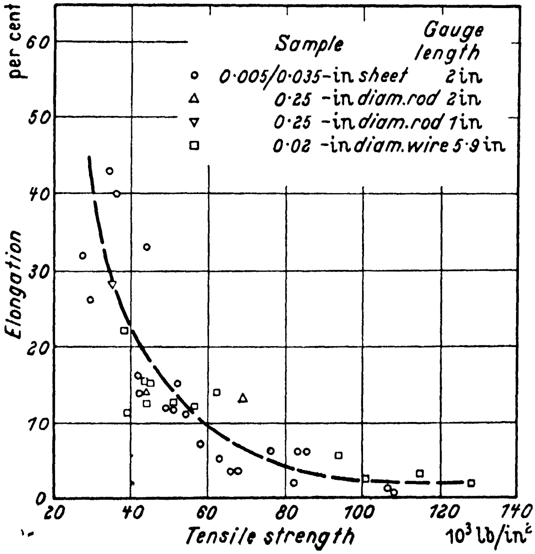

Figure 35. Correlation between strength and elongation in tensile tests for zirconium in various conditions (after F. W. BOULGER[4])

Table XII. Representative Properties of Iodide Zirconium Processed to Rod and Sheet and Tested in Various Conditions[21]

Material	*A*	*B*	*C*	*D*	*E*	*F*	*G*
Modulus of elasticity, 10^6 lb/in^2 . .	11·8	14·0	10·8	—	—	—	—
Proportional limit 0·01 per cent *offset*, 10^3 lb/in^2 . .	8·25	32·0	7·3	—	—	—	—
Yield strength, 0·1 per cent *offset*, 10^3 lb/in^2	13·5	61·0	12·0	—	—	—	—
Yield strength, 0·2 per cent *offset*, 10^3 lb/in^2	15·0	69·0	14·5	58·0	10·75	61·0	20·0
Ultimate strength, 10^3 lb/in^2 . .	34·5	86·0	39·5	82·0	29·0	84·0	44·0
Reduction in area, per cent . .	26	34	35	—	—	—	—
Elongation, per cent (*see note*) .	28	17	33	1·0 *to* 0·5	26	6	33
Rockwell hardness .	B25	B87	B42	—	—	—	—
	F70	F105	F83	—	—	—	—

Notes: *A*. 0·25-in diam. rod machined from as-deposited bars.
B. 0·125-in diam. rod, reduced from above by cold swaging 65 per cent.
C. Same as *B*, tested after annealing at 705° C *in vacuo*.
D. Crystal rod cold reduced 90 per cent to 0·025-in sheet.
E. Same as *D*, after vacuum annealing ½-hour at 725° C.
F. Rod vacuum melted in graphite, hot and cold rolled 90 per cent to 0·025-in sheet.
G. Same as *F*, after vacuum annealing ½-hour at 725° C.
Elongation values for rods based on four-diameter gauge lengths, those for sheet on 2-in gauge lengths.

Table XIII. Tensile Properties of Sheet and Wire Prepared from Iodide Zirconium*

Material	*Condition and reference*	*Elongation* per cent	*Yield strength* 10^3 lb/in^2	*Ultimate strength* 10^3 lb/in^2
0·005-in *sheet* . .	*Cold rolled*[1]	—	80·0	115·0
	Annealed 820° C	—	30·0	70·0
0·02-in *wire* . .	*Cold swaged*[8]	3	—	115·0
	Vacuum annealed:			
	3 h 400° C	2½	—	101·0
	3 h 500° C	12	—	56·0
	1 h 600° C	12½	—	51·0
	1 h 700° C	12½	—	44·0
	1 h 800° C	11	—	38·5
	1 h 900° C	15½	—	43·0
	½ h 1000° C	15	—	44·0
0·02-in *wire* . .	*Hard drawn*[19]	2	—	128·8
	Tempered 455° C	5½	—	93·5
	Annealed 790° C	14	—	61·0

* Yield strengths for 0·5 per cent deformation, elongation values for 5·9-in (15-cm) gauge length wire.

In the pure, soft condition, the strength of zirconium on a volume basis approximates to that of copper-base alloys. Zirconium has a strength : weight ratio better than normalized medium carbon steel but not as high as those of titanium, magnesium, or aluminium alloys. The tensile strength is increased by cold work,

Table XIV. Tensile Properties of ⅛-in *Iodide Zirconium Rod*[19]

Property	*As swaged* (75 per cent *reduced*)	*Tempered* ¼ h *at* 455° C	*Annealed* ¼ h *at* 790° C
Ultimate strength, 10^3 lb/in^2	88·3	81·6	35·9
Yield strength 0·2 per cent *offset*, 10^3 lb/in^2	69·7	52·2	15·9
Yield strength 0·1 per cent *offset*, 10^3 lb/in^2	63·3	48·3	13·8
Proportional limit 0·01 per cent *offset*, 10^3 lb/in^2	32·1	29·1	8·35
Reduction in area, per cent	40·6	26·0	32·2
Elongation in four diameters, per cent	18	20	31
Elongation in eight diameters, per cent	8½	12	25½

Table XV. Ranges for Tensile Properties of 0·005 *to* 0·035-in *Sheet Produced Commercially by Cold Rolling Rod from Iodide Composition*[21]

Condition of testing	*Specimen orientation compared to direction of rolling*	*Modulus of elasticity* 10^6 lb/in^2	*Prop. limit* 0·01 per cent *offset* 10^3 lb/in^2	*Yield strength* 0·2 per cent *offset* 10^3 lb/in^2	*Ultimate strength* 10^3 lb/in^2	*Elongation in* 2 in, per cent
As cold rolled	*Parallel*	11·3/13·5	41/47·5	68/93	85/107	1/8·6
(*Hard*)	*Transverse*	10/13·5	34/37·5	61/73	76/108	0·5/6
Cold rolled with intermediate anneals	*Parallel*	11·2/15·3	22/26	46/54	54/63	5/13
Ditto	*Transverse*	9/14·8	21/26	39/55	49/67	3·5/12
Half hard, tempered ½ h *at* 370° C *after each reduction of two B. and S. numbers*	*Parallel*	11·5/14·8	25/27	40/47	52/58	7/15
Ditto	*Transverse*	10/15·6	26/34	44/54	51/66	3·5/12
Cold rolled and annealed at 700° C	*Parallel*	10/14·6	11/12	16/24	36/42	16/40
Ditto	*Transverse*	7·2/16·4	6/16	15/30	27/42	14/32
Similar to above except sheet was given intermediate anneals.	*Parallel*	11/14·5	8·5/10	16/20	34/38	22/43

Note: Sheet specimens were 0·005 to 0·035-in thick and 0·5-in wide.

by oxygen, and presumably by certain impurities and deliberate alloying additions.

Tables XII, XIII and *XIV* give representative properties for iodide-process zirconium fabricated to sheet, rod and wire by various practices. *Table XIII* also shows the effect of tempering and annealing treatments on such metal.

Table XV gives the range in tensile properties to be expected from zirconium sheet produced by cold rolling and annealing iodide crystal rod. The composition of such metal is shown in *Table XVI.*

Table XVI. Typical Composition of Commercial Zirconium Produced by the Iodide Process[21]

(Illustrates the difficulty of analysis.)

Element	*Spectrographic value*, per cent	*Chemical analysis value*, per cent
Aluminium	0·01 *to* 0·02	*None detected*
Calcium	0·005 *to* 0·01	*ditto*
Copper	*Present*	*ditto*
Hafnium	2·58	—
Iron	0·005 *to* 0·01	0·21
Magnesium	0·005 *to* 0·10	0·30
Nickel	*Present*	0·21
Silicon	0·01 *to* 0·05	0·08
Titanium	0·0001 *to* 0·005	*None detected*

Table XVII gives tensile properties determined at the Massachusetts Institute of Technology[14, 15] on zirconium rods produced by different methods from iodide and magnesium-reduced metal. Remelting iodide zirconium in a graphite crucible increased its strength to a level comparable to that of Kroll metal.

The data are of particular interest because samples extruded experimentally had better ductility and higher strengths than normal for cold worked and tempered metal. Furthermore, these are probably the first experiments indicating that the rate of cooling from above the critical temperature affects the mechanical properties of zirconium. The tests indicated that water quenching from 1000° C raised the strength and lowered the ductility compared to the slowly cooled condition.

Table XVII. Tensile Properties of Zirconium Rods Produced by Different Methods

Material	*Processing treatment*	*Reduction in area* per cent	*Elongation* per cent	*Yield strength* (0·1 per cent *offset*) 10^3 lb/in^2	*Ultimate strength* 10^3 lb/in^2
Zirconium produced by decomposition of the iodide (*Rockwell B38 and F80*)	*As received*	40*	13·6	18·75	40·75
	Vacuum melted in graphite crucible, cast, extruded 11 *to* 1 *at* 800° C	39·7	23·7	—	64·75
	Melted in graphite crucible, cast, extruded 12 *to* 1 *at* 1060° C	46·2	21·5	35·25	56·5
	Crystal bar fragments packed in can, extruded 12 *to* 1 *at* 1060° C	49·4	24·5	30·25	55·5
	Chips from crystal bar packed in can, extruded at 1060° C	44·7	23·2	36·5	77·5
Magnesium - reduced zirconium (*Rockwell B84*)	*As received*	31·4	13·7	43·5	68·5
	1000° C in vacuo, *water quenched* (*duplicates did not agree closely*)	40·6 29·4	10·1 9·1	49·0 71·0	77·0 95·75
Magnesium - reduced zirconium (*Rockwell B84*)	*As-received metal, canned, extruded* 14 *to* 1 *at* 800° C	43·8	15·3	42·75	80·25
	Same as next above plus 1000° C in vacuo, *slowly cooled*	38·7	16·5	34·0	70·5
	As-received metal, canned, extruded 15 *to* 1 *at* 1060° C	43·7	19·9	47·75	79·5
	Same as next above plus 1000° C in vacuo, *water quenched*	37·5	9·6	59·75	89·7

* Offset used for proportional limit not stated. Specimens had a 0·25-in × 2·0-in gauge length, tested in duplicate. Magnesium-reduced zirconium was vacuum melted in a graphite crucible. This material probably contained significant quantities of iron, carbon and oxygen.

10.7. COMPRESSIBILITY

P. W. BRIDGMAN[5] determined the compressibility of zirconium

$$\text{at } 30^\circ\text{ C} \quad \Delta V/V_0 = 10{\cdot}97 \times 10^{-7}p - 7{\cdot}44 \times 10^{-12}p^2$$
$$\text{at } 70^\circ\text{ C} \quad \Delta V/V_0 = 11{\cdot}06 \times 10^{-7}p - 7{\cdot}80 \times 10^{-12}p^2$$

These equations apply to pressures of about 12,000 kg/cm² which are the units used by Bridgman in his book. P. W. BRIDGMAN[6] reported that when zirconium is compressed to 100,000 kg/cm² the volume decreases to 0·910 of the value under atmospheric pressure.

10.8. HARDNESS

Table XVIII. Typical Hardness Values for Zirconium Prepared in Various Ways and Tested in Different Conditions

Material	*Condition*	*Ref.*	*Measured hardness values (a)*	*Estimated BHN (b)*
Iodide zirconium	*As-deposited crystal rod*	21	B25 *to* 30	64 *to* 67
	Cold worked, amount unknown	1	B90 *to* 100	157 *to* 200
	Cold swaged, 75 per cent *R. of A.*	19	B87 *to* F106	148
	The same, tempered 455° C	19	B88 *to* F107	148
	The same, annealed 790° C	19	B30 *to* F75	67
	As-deposited crystal rod	14	B38	73
	Cold reduced 33 per cent	14	B79	128
	Cold reduced 56 per cent	14	B90	157
	Crystal rod remelted in graphite	14	B76	122
	Cold reduced 33 per cent	14	B89	154
	Cold reduced 56 per cent	14	B92	163
Magnesium - reduced zirconium	*Vacuum melted in graphite*	9	B68 *to* 76	107 *to* 122
	ditto	10	Brinell 200	167
	ditto	14	B84	140
	Cold reduced 33 per cent	14	B97	184
	Cold reduced 56 per cent	14	B101, C18	214
	Inert gas melted in water-cooled copper crucible	3	Brinell 142 *to* 152	125 *to* 132
Calcium-reduced zirconium	*Vacuum sintered*	11	Vickers 188	188
	Induction melted	11	Vickers 280	280

(*a*) 'B' and 'F' values are on Rockwell scales, 'Brinell' with 3000 kg load, 'Vickers' are diamond pyramid hardness values.

(*b*) Estimates based on *Wilson Chart 38* for converting Rockwell 'B' readings to Brinell 500 kg load.

Hardness values for zirconium specimens of various purities and conditions of processing are given in *Table XVIII.*

W. C. Lilliendahl and co-workers[12] state that the hardness of iodide zirconium is increased about 5 Vickers units for each 0·01 per cent oxygen it contains. The minimum hardness expected for crystal rod as-deposited is approximately 65 to 70 Brinell or Vickers or 25 to 30 on the Rockwell 'B' scale.

The hardness of magnesium-reduced zirconium after remelting is usually higher than that of iodide zirconium. Values as low as Rockwell 'B' 68 to 76 and 100 Brinell have been obtained[14]. The Brinell hardness of magnesium-reduced zirconium is reported by F. W. Boulger[4] as 100 for zero oxygen, 200 for 0·1, 250 for 0·2 and 300 for 0·3 per cent oxygen.

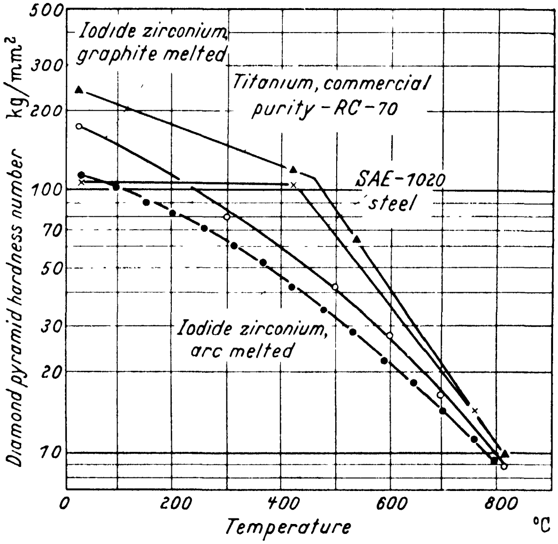

Figure 36. Effect of temperature on hardness of annealed zirconium, titanium and SAE–1020 steel sheet (after A. D. Schwope[22])

A. D. Schwope[22] compared the properties of zirconium with those of titanium and iron. The effects of temperature on the hardness of zirconium, titanium and SAE–1020 steel are shown in *Figure 36.* Two curves are shown for zirconium, one for arc melted iodide metal and the other for graphite melted metal which would be expected to contain about 0·20 per cent carbon. Schwope found that melting in graphite increased the room temperature Brinell hardness by 50 per cent over that of the arc melted zirconium.

F. B. Litton[13] reported that the calculated average hardness of 29 samples of iodide zirconium was Rockwell A 20·9 and Vickers

90·1. The maximum value was A 36·3; the minimum A 9·5; the arithmetical average A 20·9 and the standard deviation ±6·7 units. The maximum value of Vickers hardness was 140; the minimum 72, the average 90 and the standard deviation ±17 units. Litton concluded that it appeared to be impracticable to obtain zirconium softer than Rockwell A 9·5 and Vickers 72 by the iodide process.

F. B. Litton[13] also determined the effect of oxygen penetration on pure zirconium at 550, 750 and 950° C by measuring the hardness on polished cross sections. The results are shown in *Figure 59.*

A. D. Schwope and W. Chubb[24] in their report of investigations of the strength and hardness of zirconium alloys at elevated temperatures show a curve of the hot hardness of zirconium as in *Figure 37.* The zirconium samples were prepared by induction melting iodide zirconium in graphite crucibles and the final metal contained about 0·3 per cent carbon. See also 12.2. Reaction with Oxygen.

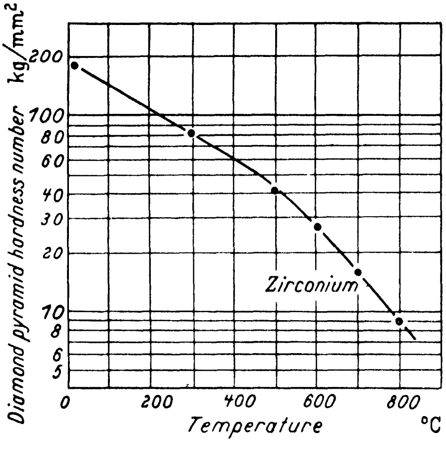

Figure 37. Hot hardness curve for zirconium (after A. D. Schwope *and* W. Chubb[24])

R. M. Treco[26, 27] measured the hardness of samples of iodide zirconium after absorption of known amounts of oxygen up to 2·5 atomic per cent. A plot of oxygen content/hardness was made and is shown in *Figure 38.* The increase in hardness is not linear, the first small addition having a greater effect than later additions. R. M. Treco[27] in his later paper points out that as little as 2·0 atomic per cent oxygen embrittles the zirconium to such an extent that cold working and machining are impossible. A plot of hardness/lattice strain was made by Treco and is shown in *Figure 39.* W. Munro and W. J. Fennell[16] also determined the hardness of zirconium (Kroll type) and produced results very similar to those of R. M. Treco[26].

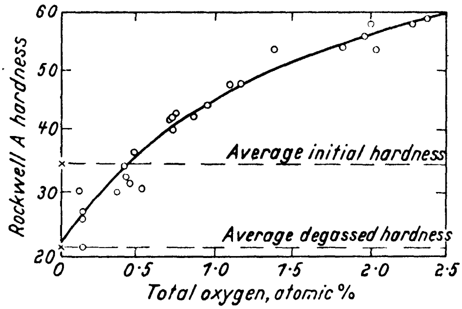

Figure 38. Effect of oxygen on hardness of iodide zirconium. Comparison of initial and degassed hardness as shown by the broken lines (*after* R. M. TRECO[26, 27])

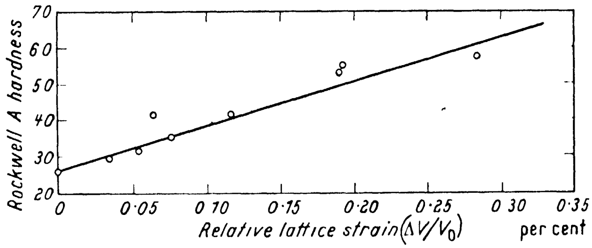

Figure 39. Hardness of zirconium in relation to relative lattice strain (*after* R. M. TRECO[27])

10.9. ERICHSEN CUPPING TEST

Erichsen cupping data in *Table XIX* indicate fairly good ductility for sheets fabricated by cold rolling and annealing.

Table XIX. Erichsen Cupping Test Data for Iodide Process Zirconium[8]

Condition	*Erichsen value*, mm
*As cold rolled**	2·69
Vacuum annealed 30 min, 480° C	2·95
Vacuum annealed 30 min, 530° C	4·00
Vacuum annealed 20 min, 580° C	4·04
Vacuum annealed 10 min, 680° C	4·23
Vacuum annealed 10 min, 900° C	4·21

* A 7·5-mm crystal rod was rolled at 650° C to 0·45 mm, pickled to 0·41 mm, and cold rolled to 0·3 mm sheet. Ball diameter not indicated, probably 8 mm.

Tests on Kroll sheet annealed in air also show good values as indicated in *Table XX*.

Table XX. Erichsen Cupping Test Data for Kroll Zirconium Sheet (Graphite Melted)

Condition	*Erichsen value*, mm
*Unannealed**	3·7
Air annealed at 650° C *for* ¾ min	10·3 (3·7 *on* 8-mm *ball*)
Air annealed at 650° C *for* 1¼ min	10·4 (4·2 *on* 8-mm *ball*)
Air annealed at 650° C *for* 2¼ min	9·8
Air annealed at 650° C *for* 4¼ min	9·7
Air annealed at 650° C *for* 8¼ min	10·0 (3·9 *on* 8-mm *ball*)

* 0·4-mm sheet, ball diameter 25 mm.

10.10. STRENGTH AT ELEVATED TEMPERATURES

F. W. Boulger[4] gives the results of short-term tensile properties of zirconium at temperatures up to 800° C in various atmospheres. The results are shown in *Table XXI.*

Table XXI. Short-term Tensile Properties of Zirconium at Elevated Temperatures in Various Atmospheres

Material	*Ref.*	*Atmosphere*	*Test temp.* °C	*Elongation* per cent	*R. of A.* per cent	*Ultimate tensile strength* 10^3 lb/in^2
Iodide, extruded	14	*Air*	20	23·7	39·7	65·0
Iodide, extruded	14	*Argon*	250	32·7	55·1	40·0
Iodide, extruded	14	*Argon*	500	39·7	68·0	28·5
Iodide crystal	25	*Helium*	500	—	—	24·0
		Nitrogen	500	—	—	15·0
Iodide crystal		*Helium*	700	—	—	10·0
		Nitrogen	700	—	—	7·0
Iodide, extruded	14	*Argon*	750	99·6	97·8	8·0
Iodide crystal	2	*Helium*	800	—	—	6·6
		Nitrogen	800	—	—	0·5

Note: The work reported by the Massachusetts Institute of Technology[14] was done on specimens prepared from iodide material, melted *in vacuo* in a graphite crucible, extruded at 800° C in a sheath with a reduction of 11·4 to 1.

Rapid absorption of nitrogen probably accounts for the lower hot strength of samples tested in that atmosphere.

Little information is available on the creep of pure zirconium. Boulger quotes preliminary results from tests made at 538° C (1000° F) in argon slightly above atmospheric pressure which gave the incomplete results shown in *Table XXII.*

Table XXII. Preliminary Creep Tests on Pure Zirconium

Material	*Stress* $\mathrm{lb/in^2}$	*Time* h	*Plastic deformation* in/in	*Comments*
U.S. Bureau of Mines	6892	1	0·001	
		13·8	0·01	*Good curve*
U.S. Bureau of Mines	7650	1	*Broke*	*Oxidized badly, no curve*
Iodide zirconium	3910	—	0·01	*Yielded during loading, no curve*

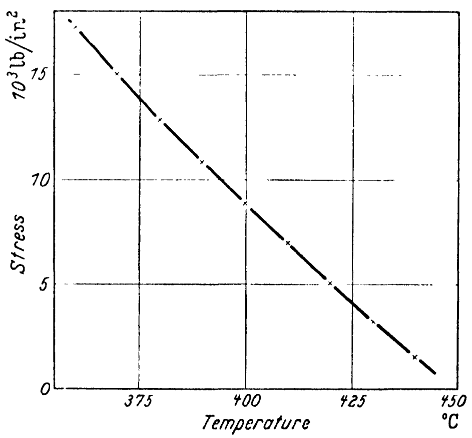

Figure 40. Stress/temperature curve for a creep rate of 1 × 10^{-6} per cent/hour *for zirconium* (*after* N. H. G. Daniels *and* J. Hutchings[7])

N. H. G. Daniels and J. Hutchings[7] made some tensile creep tests on samples of sheet produced from Kroll type zirconium. *Figure 40* indicates the stress and temperatures which would give a steady creep rate of 1 × 10^{-6} per cent per hour over the limited temperature range, 360 to 440° C. Further work on creep was done by W. Munro and W. J. Fennell[16]. For compression creep tests cast blocks of Kroll type zirconium were forged, swaged and machined to produce specimens. Tests were made at 350, 400, 450 and 500° C with creep stresses from 3 to 8 × 10^3 $\mathrm{lb/in^2}$. The results obtained, *Table XXIII*, confirmed the work of Daniels and Hutchings above.

It is reported[17] that zirconium maintained its strength rather better at high temperatures than rolled titanium of corresponding purity. A sample of swaged bar obtained from the U.S.A. and which was assumed to have been produced by the Kroll process (composition: Fe 0·065, Si 0·06, Ca 0·042, Ni 0·03 per cent) had a

Table XXIII. Summary of Compression Creep Results[16]

Machine	*Temp.* °C	*Stress* lb/in²	*Time* in hours *to strains of*							*Total time* h	*Total strain* per cent	*Creep rate* per cent × 10⁵/h *at* hours		
			0·1 per cent	0·2 per cent	0·5 per cent	1·0 per cent	2·0 per cent	3·0 per cent	4·0 per cent			500	1000	*Last* 100
4	350	8000	2	6	108	—	—	—	—	1684	0·72	0·1	0·04	—
5	350	8000	418	—	—	—	—	—	—	1361	0·148	0·1	—	—
3	400	6000	47	242	—	—	—	—	—	1535	0·39	0·2	0·1	0·1
3	400	7000	104	440	—	—	—	—	—	1031	0·31	0·2	0·2	0·2
6	400	7000	44	179	1155	—	—	—	—	1629	0·58	0·4	0·2	0·1
1	450	5000	24	84	328	960	—	—	—	1558	1·20	1·0	0·5	0·3
2	450	7000	2	8	45	143	417	844	1270	1797	4·60	2·7	2·2	1·6*
1	500	3000	7	34	210	680	—	—	—	683	1·00	1·0	—	1·0†

* Results corrected for interruption for 110 hours at 200 hours.
† Specimen tested in partial argon atmosphere.

stress for 1 per cent strain in 24 hours of about 2 ton/in² at 600° C, and 6 ton/in² at 400° C. Unworked cast zirconium supplied by the U.S. Bureau of Mines made by melting iodide zirconium in a graphite crucible was rather stronger, the corresponding stress at 600° C being 2·5 to 3 ton/in². It was found that oxygen appreciably raises the temperature at which the metal loses its strength. The samples tested contained about 0·12 per cent carbon.

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11

MECHANICAL PROPERTIES OF ZIRCONIUM ALLOYS AT ROOM AND ELEVATED TEMPERATURES

C. T. ANDERSON *et al.*[1], in their survey of zirconium alloys, investigated their suitability for high temperature applications. The report covers about twenty-five zirconium rich alloy systems. The alloying elements were: aluminium, beryllium, boron, carbon, calcium, chromium, cobalt, copper, iron, manganese, molybdenum, nickel, niobium, silicon, silver, tantalum, thorium, tin, titanium, tungsten and vanadium. Kroll sponge zirconium was melted in graphite crucibles *in vacuo* except in the case of volatile metal additions such as manganese, when helium was introduced after the outgassing period in order to minimize losses. The alloys tested were forged and annealed.

Further work at the U.S. Bureau of Mines by E. T. HAYES, A. H. ROBERSON and O. G. PAASCHE[2] was entirely devoted to the zirconium–titanium system and a more detailed study of the properties of the alloys was made. Alloys were prepared by both graphite melting and arc melting.

F. B. LITTON[3] studied the mechanical properties and the oxidation resistance of ten zirconium alloys. The ten alloying elements studied were: aluminium, copper, hafnium, molybdenum, niobium, nitrogen, oxygen, tantalum, titanium and tungsten. The oxidation resistance of the alloys was affected by the carbon contamination resulting from melting in graphite crucibles and this method of melting was discontinued. Arc melting with a tungsten electrode in gettered argon was used for most of the alloy production but codeposition of alloys by the van Arkel process was also tried as well as diffusion methods. It is presumed that iodide zirconium was employed in this work.

A. D. SCHWOPE and W. CHUBB[5] made small additions of several metals to zirconium and studied their effect on the strength of zirconium up to 800° C. The elements added were: aluminium, lead, molybdenum, niobium, tantalum, titanium, vanadium and zinc. The alloys were prepared from iodide zirconium by melting inductively in non-outgassed graphite crucibles. The alloys contained approximately 0·3 per cent carbon, some nitrogen and oxygen; they were melted in a pressure of less than 10 microns of mercury with the exception of the alloys of lead and zinc which were melted under purified argon. The ingots were forged in air at 1000° C and cold rolled, followed by vacuum annealing at 700° C. Duplicate tests were made in most cases and the results averaged. The results of the investigations may be summarized as follows:

Aluminium, chromium, molybdenum, nickel, niobium, nitrogen oxygen, titanium and tungsten all increased the strength at room temperature. Hafnium up to 8·2 per cent did not affect the tensile properties.

At elevated temperatures aluminium, molybdenum, niobium or tantalum additions improve the strength.

11.1. CREEP RESISTANCE

Very little information on the creep resistance of zirconium alloys has been published but A. D. SCHWOPE[4] reports that zirconium alloys are rapidly approaching commercial titanium alloys with respect to tensile strength at 500° C and are equal, if not superior, in creep strength at 500° C. Alloying elements which might be expected to improve the creep strength at 500° C are aluminium, tin and titanium. (See also section 10.10.)

11.2. MECHANICAL PROPERTIES OF ZIRCONIUM ALLOYS

11.2.1. *Zirconium–aluminium*

Table XXIV. Tensile Properties of Zirconium–Aluminium Alloys

Composition per cent			*Testing temperature*	*Yield strength* 0·2 per cent *offset* 10^3 lb/in^2	*Ultimate tensile strength* 10^3 lb/in^2	*Elongation* per cent 1 in	*Reduction in area* per cent	*Rockwell hardness* *B*
Aluminium	*Carbon*	*Iron*						
0·7	0·14	0·07	*Room*	59·4	97·6	16	27·02	92·5
1·4	0·11	0·07	*Room*	84·8	121·4	9	17·58	94·5
2·2	0·09	0·07	*Room*	96·3	120·5	7·5	10·14	101·5
0·7	0·14	0·07	650° C	11·29	28·22	—	33·0	—
1·4	0·11	0·07	650° C	14·74	36·47	27	32·0	—
2·2	0·09	0·07	650° C	24·6	54·53	26	20·0	—

All specimens tested were A.S.T.M. standard ¼-in diameter test bars.
Reprinted from U.S. Bureau of Mines *Report of Investigations 4658.*

The results of the determination of tensile properties at room temperature and 650° C of the forged alloys produced by C. T. ANDERSON *et al.*[1] are shown in *Table XXIV.*

The properties of zirconium–aluminium alloys prepared by various methods and in different states as determined by F. B. LITTON[3] are shown in *Table XXV.*

Table XXV. Tensile Properties of Zirconium–Aluminium Alloys at Room Temperature

Composition per cent *Aluminium*	*Yield strength* 0·05 per cent *offset* 10^3 lb/in^2	*Ultimate tensile strength* 10^3 lb/in^2	*Elongation* per cent 2 in	*Condition*
1 (a)	62·6	81·3	5·6	*Annealed at* 725° C
2 (a)	95·1	111·9	3·3	*Annealed at* 725° C
4 (a)	113·2	122·0	12·0	*Annealed at* 725° C
1 (b)	72·8	99·1	8·7	*As-rolled*
1·5 (b)	99·9	131·9	8·0	*As-rolled*
2 (c)	91·2	112·8	0·5	*Annealed at* 700° C

(a) Vacuum melted in graphite, rolled sheathed at 900° C.
(b) Arc melted, rolled in air at 600° C.
(c) Arc melted, rolled in air at 450° C.

A. D. SCHWOPE and W. CHUBB[5] found the tensile properties at 500° C as shown in *Table XXVI.* The three results given for induction melted zirconium, without intentional alloying additions, show a much wider disparity than is normally accepted in such work.

Table XXVI. Tensile Properties of Zirconium–Aluminium Alloys at 500° C

Composition *	*Yield strength* 0·2 per cent *offset* 10^3 lb/in^2	*Ultimate tensile strength* 10^3 lb/in^2	*Elongation* per cent 1 in	*Reduction in area* per cent
Induction melted zirconium .	11·2	21·5	45	55
Induction melted zirconium .	16·0	24·0	30	44
Induction melted zirconium .	9·0	15·0	71	63
Induction melted:				
Zr + 0·38 per cent Al .	18·0	30·0	31	34
Zr + 0·82 per cent Al .	22·4	34·7	49	57
Zr + 0·87 per cent Al .	25·0	38·0	30	37
Zr + 1·2 per cent Al .	23·5	37·5	34	41
Zr + 2·0 per cent Al .	32·0	46·1	25	38

* These alloys also contain approximately 0·3 per cent carbon.

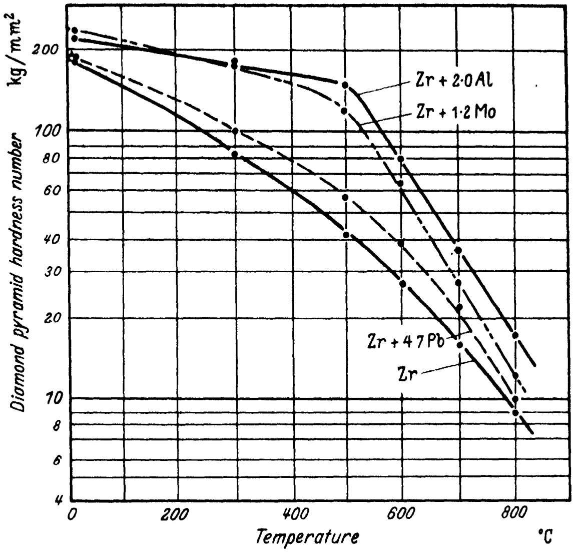

Figure 41. *Hot hardness curves for alloys of zirconium with aluminium, lead and molybdenum. Molybdenum does not maintain strength of zirconium above* 600° C, *while aluminium seems to be most effective above* 600° C (*after* A. D. SCHWOPE *and* W. CHUBB[5])

The hot hardness of the alloy containing 2 per cent aluminium is shown in *Figure 41*, as determined by Schwope and Chubb[5].

The limit of forgeability[1] at 850° C was 2 to 3 per cent aluminium.

11.2.2. *Zirconium–beryllium*

Alloys containing nominal 1 and 5 per cent beryllium were produced[1]. The 5 per cent alloy was too hard to cut and was abandoned.

The nominal 1 per cent alloy (containing Be 0·77 and C 0·09 per cent) showed considerable segregation.

11.2.3. *Zirconium–boron*

Alloys containing nominal 0·5 and 2·0 per cent boron were porous and unworkable[1]. The boron used in alloying was only 95 per cent pure and this may have contributed to failure.

11.2.4. *Zirconium–carbon*

The physical properties of zirconium containing 0·35 per cent carbon (this is the maximum that could be incorporated by melting in graphite crucibles[1]) are shown in *Table XXVII*.

C. T. ANDERSON *et al.*[1] noted that the tensile properties of zirconium sheet containing 0·10 to 0·15 per cent carbon did not vary appreciably from the strength of sheet containing 0·35 per cent

Table XXVII. Tensile Properties of Zirconium Sheet containing 0·35 per cent *Carbon at Room Temperature and* 650° C

Condition	*Testing temperature*	*Yield strength* 0·2 per cent *offset* 10^3 lb/in^2	*Ultimate tensile strength* 10^3 lb/in^2	*Elongation* per cent 1 in	*Reduction in area* per cent	*Rockwell hardness B*
Hot rolled at 850° C .	*Room*	34·9	63·1	15·0	—	83
Heated in air:						
1 h *at* 500° C (1) .	*Room*	35·3	60·6	14·0	—	82
1 h *at* 600° C .	*Room*	32·7	60·3	13·5	—	83
1 h *at* 700° C .	*Room*	34·2	60·8	14·4	—	82
1 h *at* 800° C .	*Room*	39·6	64·5	11·8	—	85
Hot swaged at 850° C (2)	*Room*	40·3	69·2	15·0	20·37	83
Hot swaged at 850° C .	650° C	4·62	14·32	36·0	57·2	—

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(1) U.S. Bur. Min. data, 0·62 in × 0·50 in standard A.S.T.M. sheet tensile specimens.
(2) Standard A.S.T.M. ¼-in round specimens.

Table XXVIII. Tensile Properties of Zirconium–Chromium Alloys

Composition per cent			*Testing temperature*	*Yield strength* 0·2 per cent *offset* 10^3 lb/in^2	*Ultimate tensile strength* 10^3 lb/in^2	*Elongation* per cent 1 in	*Reduction in area* per cent	*Rockwell hardness B*
Chromium	*Carbon*	*Iron*						
0·4	0·17	0·04	*Room*	43·2	67·9	18	35·2	85
0·9	0·14	0·06	*Room*	43·5	67·5	18·5	38	83
0·9	0·14	0·12	*Room*	42·8	76·8	21	29·5	87
0·9	0·08	0·06	*Room*	45·8	78·6	21	40	87
1·8	0·21	0·07	*Room*	54·4	75·4	6	10·1	87
3·6	0·14	0·05	*Room*	50·4	76·4	7	7·1	92
4·5	0·09	0·09	*Room*	59·5	85·8	8	16·9	93
6·0	0·08	0·09	*Room*	79·3	101·9	5	5·6	100
6·6	0·09	0·05	*Room*	74·6	98·7	5·5	9·8	98
9·8	0·08	0·07	*Room*	68·3	84·9	1·0	0	99
0·4	0·17	0·04	650° C	5·6	11·6	46	74·5	—
0·9	0·14	0·06	650° C	9·6	14·7	48·5	49·1	—
0·9	0·14	0·12	650° C	8·51	14·76	39	76	—
0·9	0·08	0·06	650° C	8·14	14·99	43	82	—
1·8	0·21	0·07	650° C	13·3	16·7	34	65·4	—
3·6	0·14	0·05	650° C	9·1	17·3	34	54·2	—
4·5	0·09	0·09	650° C	10·0	16·9	30	50	—
6·0	0·08	0·09	650° C	11·0	18·3	23	40	—
6·6	0·09	0·05	650° C	12·0	20·2	18	36	—
9·8	0·08	0·07	650° C	14·91	25·48	12	14·8	—

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carbon. It was concluded that the presence of 0·35 per cent carbon does not produce any deleterious effects upon the tensile properties of hot rolled sheet.

11.2.5. *Zirconium–cerium*

One alloy containing about 4 per cent cerium was prepared, but the alloy was segregated and too hard to cut[1].

11.2.6. *Zirconium–chromium*

The tensile properties of swaged zirconium–chromium alloys at room temperature and 650° C are shown in *Table XXVIII.*

Limit of forgeability[1] at 850° C: all alloys prepared up to 10 per cent chromium were forgeable.

11.2.7. *Zirconium–cobalt*

The tensile properties of swaged zirconium–cobalt alloys at room temperature and 650° C are shown in *Table XXIX.*

Table XXIX. Tensile Properties of Zirconium–Cobalt Alloys

Composition per cent *Cobalt*	*Testing temperature*	*Yield strength* 0·2 per cent *offset* 10^3 lb/in^2	*Ultimate tensile strength* 10^3 lb/in^2	*Elongation* per cent 1 in	*Reduction in area* per cent	*Rockwell hardness B*
0·6	*Room*	46·5	71·50	14·5	26·1	84
1·0	*Room*	47·2	70·70	9·5	13·1	85
2·9	*Room*	51·6	67·50	5	5	91
4·2	*Room*	59·1	72·30	1·5	1·6	98
0·6	650° C	4·3	9·9	73·5	79·2	—
1·0	650° C	6·5	14·0	61	78·2	—
—	650° C	10·3	20·0	50	71·1	—
2·9	650° C	6·8	15·1	47	55·6	—
4·2	650° C	—	25·1	23	26·6	—

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Limit of forgeability[1] at 850° C: 7 per cent.

11.2.8. *Zirconium–cobalt–chromium*

The tensile properties at room temperature and 650° C for the forgeable zirconium–cobalt–chromium ternary alloys are shown in *Table XXX.*

Limit of forgeability[1] at 850° C: all alloys studied were forgeable.

Table XXX. Tensile Properties of Zirconium–Cobalt–Chromium Alloys

Composition per cent				*Testing temperature*	*Yield strength* 0·2 per cent *offset* 10^3 lb/in^2	*Ultimate tensile strength* 10^3 lb/in^2	*Elongation* per cent 1 in	*Reduction in area* per cent	*Rockwell hardness B*
Cobalt	*Chromium*	*Carbon*	*Iron*						
0·2	0·9	0·17	0·05	*Room*	52·7	72·3	4·0	2·5	85
0·6	0·6	0·16	0·06	*Room*	56·7	81·8	13·5	25·5	87
0·4	1·8	0·15	0·09	*Room*	50·1	82·4	11·0	25·5	89
0·7	2·8	0·12	0·08	*Room*	63·6	89·2	8·0	22·1	92
0·4	4·8	0·11	0·06	*Room*	76·0	99·4	5·5	9·4	98
0·91	0·9	0·14	0·06	*Room*	54·6	83·5	8·5	13·8	90
0·97	2·8	0·13	0·07	*Room*	63·3	89·3	8·0	12·4	95
1·0	4·0	0·06	0·07	*Room*	76·2	90·6	9·0	12·5	106
1·8	0·9	0·11	0·09	*Room*	56·1	79·1	8·0	13·0	91
1·8	1·9	0·10	0·09	*Room*	64·1	83·7	6·0	5·6	95
1·5	3·5	0·06	0·07	*Room*	62·7	86·0	5·0	5·5	97
0·2	0·9	0·17	0·05	650° C	8·5	16·2	28	46	76
0·6	0·6	0·16	0·06	650° C	4·8	10·0	80	86	49
0·4	1·8	0·15	0·09	650° C	8·9	14·7	51	82	55
0·7	2·8	0·12	0·08	650° C	7·9	13·9	56	82	52
0·4	4·8	0·11	0·06	650° C	8·0	16·7	34	65	54
0·91	0·9	0·14	0·06	650° C	6·6	14·7	67	79	68
0·97	2·8	0·13	0·07	650° C	7·8	16·6	43	70	72
1·0	4·0	0·06	0·07	650° C	—	—	—	—	93
1·8	0·9	0·11	0·09	650° C	8·69	16·93	57	74	56
1·8	1·9	0·10	0·09	650° C	9·08	19·41	50	68	57
4·03	1·0	0·09	—	650° C	—	—	—	—	149
1·5	3·5	0·06	0·07	650° C	9·21	19·33	42	56	62

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11.2.9. *Zirconium–copper*

The tensile properties for forged zirconium–copper alloys at room temperature and 650° C as determined by C. T. ANDERSON *et al.*[1] are shown in *Table XXXI.*

Table XXXII shows the results obtained by F. B. LITTON[3].

11.2.10. *Zirconium–copper ternary alloys*

C. T. ANDERSON *et al.*[1] prepared ternary alloys containing: Zr 90, Cu 5 per cent, with 5 per cent Fe, Cr, Co or Ni. No tensile properties were determined.

Limit of forgeability[1] at 850° C: the alloys containing chromium, cobalt and nickel were readily swaged.

Table XXXI. Tensile Properties of Zirconium–Copper Alloys

Composition per cent			*Testing temperature*	*Yield strength* 0·2 per cent *offset* 10^3 lb/in^2	*Ultimate tensile strength* 10^3 lb/in^2	*Elongation* per cent 1 in	*Reduction in area* per cent	*Rockwell hardness B*
Copper	*Carbon*	*Iron*						
0·55	0·12	0·08	*Room*	47·3	78·6	19	29·86	85
1·0	0·12	0·07	*Room*	50·2	81·2	17	32·67	87
2·0	0·12	0·08	*Room*	49·7	82·4	18	28·43	90·5
2·9	0·11	0·10	*Room*	55·7	89·9	17	25·05	92·5
4·9	0·11	0·07	*Room*	49·2	83·1	12	10·14	90·5
10·5	0·05	0·04	*Room*	69·6	81·6	1	—	97
0·55	0·12	0·08	650° C	6·35	20·15	53	66	—
1·0	0·12	0·07	650° C	7·36	19·97	58	70	—
2·0	0·12	0·08	650° C	8·7	24·6	52	79	—
2·9	0·11	0·10	650° C	7·64	24·2	59	77	—
4·9	0·11	0·07	650° C	8·5	25·77	52	76	—
10·5	0·05	0·04	650° C	10·39	26·38	48	26	—

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Table XXXII. Tensile Properties of Zirconium–Copper Alloys at Room Temperature

Composition per cent *Copper*	*Yield strength* 0·05 per cent *offset* 10^3 lb/in^2	*Ultimate tensile strength* 10^3 lb/in^2	*Elongation* per cent 2 in	*Condition*
0·9	78·2	128·7	4·0	*As-rolled* 400° C
0·9	15·0	48·4	17·7	*Annealed at* 700° C
2·9	74·6	137·7	1·5	*As-rolled* 400° C
2·9	23·7	57·4	9·0	*Annealed at* 700° C

Table XXXIII. Tensile Properties of Zirconium–Hafnium Alloys at Room Temperature

Composition per cent *Hafnium*	*Yield strength* 0·05 per cent *offset* 10^3 lb/in^2	*Ultimate tensile strength* 10^3 lb/in^2	*Elongation* per cent 2 in	*Heat treatment**
0·10 (*Crystal bar*)	24·4	45·9	1·0	925° C *for* 1 h
0·12 (*Crystal bar*)	39·8	62·1	1·5	925° C *for* 1 h
0·16 (*Crystal bar*)	21·5	41·9	14·5	900° C *for* 2 h
0·50 (*Crystal bar*)	34·8	58·2	5·0	900° C *for* 2 h
2·34 (*Arc melt*)	15·7	35·1	26·5	700° C *for* 16 h
2·34 (*Arc melt*)	41·5	89·7	5·0	900° C *for* 16 h
2·88 (*Crystal bar*)	23·6	39·8	19·0	900° C *for* 2 h
6·20 (*Arc melt*)	21·3	49·1	12·0	700° C *for* 16 h
8·20 (*Crystal bar*)	24·6	50·5	3·5	925° C *for* 1 h

* Specimens wrapped in zirconium and sealed in welded cans back-filled with argon. Air cooled from heat treating temperature.

11.2.11. *Zirconium–hafnium*

F. B. LITTON[3] determined the tensile properties of zirconium–hafnium alloys shown in *Table XXXIII.*

11.2.12. *Zirconium–iron*

The tensile properties of zirconium–iron alloys at room temperature and 650° C as determined by C. T. ANDERSON *et al.*[1] are shown in *Table XXXIV.*

Limit of forgeability[1] at 850° C: alloys containing up to 9·0 per cent iron were swaged satisfactorily.

Table XXXIV. Tensile Properties of Zirconium–Iron Alloys at Room Temperature and 650° C

Composition per cent		*Testing temperature*	*Yield strength* 0·2 per cent *offset* 10^3 lb/in^2	*Ultimate tensile strength* 10^3 lb/in^2	*Elongation* per cent 1 in	*Reduction in area* per cent	*Rockwell hardness B*
Iron	*Carbon*						
0·029	0·140	*Room*	48·9	81·6	20	47·29	86
0·45	0·160	*Room*	51·9	72·1	16·5	28·66	85
0·66	0·23	*Room*	62·9	89·0	19	37·07	92
1·15	0·18	*Room*	46·1	78·8	15·5	29·86	87
1·73	0·15	*Room*	47·7	75·8	4	2·40	90·5
2·9	0·08	*Room*	55·4	92·9	7	7·88	96
5·16	0·15	*Room*	60·1	75·8	2·5	2·40	99·5
0·029	0·140	650° C	9·25	17·46	43	79	—
0·45	0·169	650° C	3·71	12·36	81	74	—
0·66	0·23	650° C	6·07	17·45	75	86	—
1·15	0·18	650° C	4·38	15·75	88	89	—
1·73	0·15	650° C	6·98	20·53	87	92	—
2·9	0·08	650° C	6·17	21·56	75	83	—
5·16	0·15	650° C	6·7	23·31	51	62	—

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11.2.13. *Zirconium–lead*

Table XXXV. Tensile Properties of Zirconium–Lead Alloy at 500° C

Composition per cent *Lead*	*Yield strength* 0·2 per cent *offset* 10^3 lb/in^2	*Ultimate tensile strength* 10^3 lb/in^2	*Elongation* per cent 1 in	*Reduction in area* per cent
4·7	21·2	31·0	31	39

A. D. Schwope and W. Chubb[5] prepared one zirconium–lead alloy containing 4·7 per cent lead and found the values given in *Table XXXV* for tensile properties at 500° C. The hot hardness curve for the alloy is shown in *Figure 41.*

11.2.14. *Zirconium–manganese*

The tensile properties at room temperature and 650° C of swaged bars of zirconium–manganese alloys are shown in *Table XXXVI.*

Limit of forgeability[1] at 850° C: satisfactory up to 12·5 per cent manganese.

Table XXXVI. Tensile Properties of Zirconium–Manganese Alloys

Composition per cent			*Testing temperature*	*Yield strength* 0·2 per cent *offset* 10^3 lb/in^2	*Ultimate tensile strength* 10^3 lb/in^2	*Elongation* per cent 1 in	*Reduction in area* per cent	*Rockwell hardness B*
Manganese	*Carbon*	*Iron*						
0·61	0·22	0·23	*Room*	62·6	93·4	2·5	1·59	93
1·31	0·19	0·07	*Room*	51·7	81·6	16	23·8	88
3·84	0·12	0·07	*Room*	62·6	86·9	2	1·59	95
5·12	0·14	0·05	*Room*	51·1	82·3	9	10·8	92
9·52	0·04	0·02	*Room*	56·2	86·5	3	6·36	96
12·48	0·07	0·04	*Room*	67·1	93·9	13	35·2	99
0·61	0·22	0·23	650° C	8·71	19·18	48	35·8	—
1·31	0·19	0·07	650° C	10·74	20·41	34	32·6	—
3·84	0·12	0·07	650° C	9·68	22·71	13	43·6	—
5·12	0·14	0·05	650° C	6·60	21·70	29	54·5	—
9·52	0·04	0·02	650° C	12·52	26·97	20	61·2	—

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11.2.15. *Zirconium–molybdenum*

The tensile properties at room temperature and 650° C of swaged zirconium–molybdenum alloys as determined by C. T. Anderson *et al.*[1] are shown in *Table XXXVII.*

F. B. Litton[3] found the values shown in *Table XXXVIII* which include the effect of annealing.

A. D. Schwope and W. Chubb[5] determined the properties at 500° C as shown in *Table XXXIX.* This table also includes the properties of zirconium–molybdenum–titanium and zirconium–molybdenum–niobium alloys.

Hot hardness values for the 1·2 per cent molybdenum alloy are shown in *Figure 41. Figure 42* shows the hot hardness of the ternary alloys.

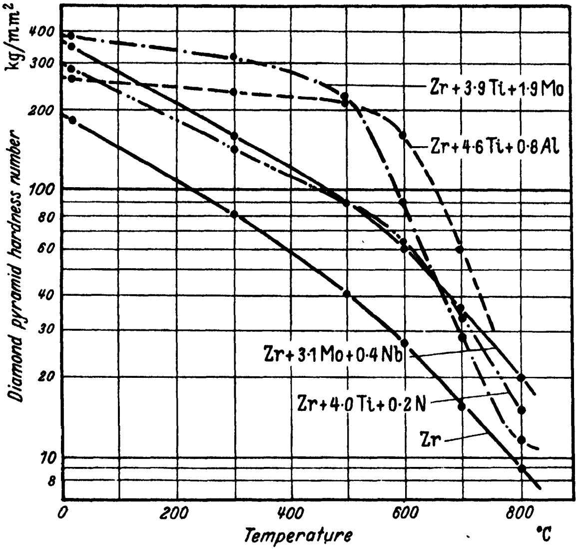

Figure 42. Hot hardness curves of ternary alloys of zirconium. The Zr–Ti–Mo *alloy loses hardness and strength above* 500° C, *while the* Zr–Ti–Al *alloy has highest hardness above* 500° C (*after* A. D. SCHWOPE *and* W. CHUBB[5])

Limit of forgeability[1] at 850° C: all alloys investigated up to 10 per cent molybdenum forged satisfactorily.

Table XXXVII. Tensile Properties of Zirconium–Molybdenum Alloys

Composition per cent			*Testing temperature*	*Yield strength* 0·2 per cent *offset* 10^3 lb/in^2	*Ultimate tensile strength* 10^3 lb/in^2	*Elongation* per cent 1 in	*Reduction in area* per cent	*Rockwell hardness B*
Molybdenum	*Carbon*	*Iron*						
0·4	0·17	0·16	*Room*	71·5	100·4	17	41·4	98
0·9	0·21	0·07	*Room*	82·0	113·0	15	31·5	100
2·3	0·38	0·03	*Room*	84·8	127·0	1	0·79	106
2·9	0·25	0·14	*Room*	—	129·7	2	0	114
3·3	0·31	0·12	*Room*	—	121·0	2	0	116
7·8	0·12	0·08	*Room*	130·6	138·8	7·5	24·4	105
10·0	0·13	0·04	*Room*	136·3	145·0	7·0	12·8	104
0·9	0·21	0·07	650° C	12·06	20·91	38·0	66·0	—
2·3	0·38	0·03	650° C	11·33	25·55	27·0	38·0	—
2·9	0·25	0·14	650° C	11·87	30·78	54·0	84·0	—
3·3	0·31	0·12	650° C	11·29	34·43	69·0	77·0	—
7·8	0·12	0·08	650° C	14·75	43·18	44·0	18·5	—

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Table XXXVIII. Tensile Properties of Zirconium–Molybdenum Alloys at Room Temperature

Composition per cent *Molybdenum*	*Yield strength* 0·05 per cent *offset* 10^3 lb/in^2	*Ultimate tensile strength* 10^3 lb/in^2	*Elongation* per cent 2 in	*Condition*
0·4	89·8	129·7	5·2	*As-rolled* 400° C
0·4	26·8	58·2	20·0	*Annealed at* 700° C
0·9	83·7	126·2	0·2	*As-rolled* 400° C
0·9	28·4	68·6	15·5	*Annealed at* 700° C
1·0	86·8	131·4	*Nil*	*As-rolled* 825° C
5·0	115·2	144·0	*Nil*	*As-rolled* 825° C

Table XXXIX. Tensile Properties of Zirconium-Molybdenum, Zirconium–Molybdenum–Titanium, Zirconium–Molybdenum–Niobium Alloys at 500° C

Composition per cent				*Yield strength* 0·2 per cent *offset* 10^3 lb/in^2	*Ultimate tensile strength* 10^3 lb/in^2	*Elongation* per cent 1 in	*Reduction in area* per cent
Molybdenum	*Carbon*	*Niobium*	*Titanium*				
0·82	0·3	—	—	14·5	24·3	52	62
0·90	0·3	—	—	29·9	42·5	27	60
0·90	0·3	—	—	30·0	43·5	21	54
1·2	0·3	—	—	35·8	48·0	44	58
3·1	0·3	0·4	—	32·0	39·0	12	16
1·9	0·3	—	3·9	37·6	52·5	30	57

11.2.16. *Zirconium–nickel*

The tensile properties at room temperature and 650° C of swaged bars of zirconium–nickel alloys as determined by C. T. ANDERSON *et al.*[1] are shown in *Table XL.*

A. D. SCHWOPE and W. CHUBB[5] determined the tensile properties of the 1·8 per cent nickel alloy at 500° C as shown in *Table XLI.*

This alloy also contains approximately 0·3 per cent carbon. Its hot hardness is shown in *Figure 43.*

Limit of forgeability[1] at 850° C: alloys up to 7·8 per cent nickel were forged satisfactorily.

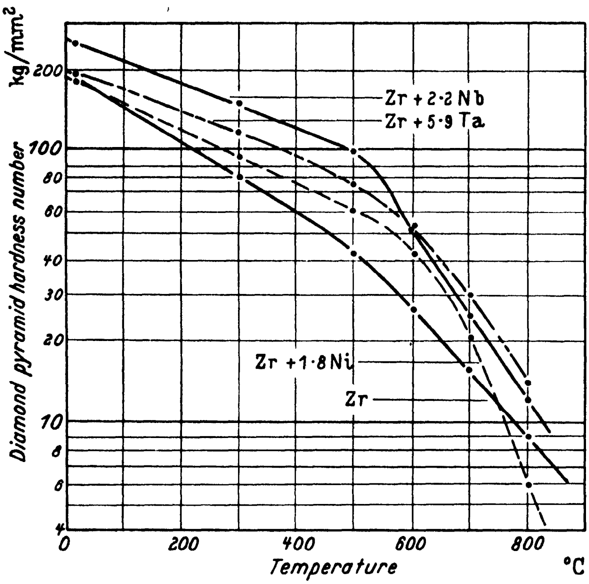

Figure 43. Hardness / temperature curves for alloys of zirconium with niobium, tantalum, and nickel. Tantalum is most effective above 600° C, while the effect of niobium falls off at that temperature (after A. D. SCHWOPE *and* W. CHUBB[5])

Table XL. Tensile Properties of Zirconium–Nickel Alloys

Composition per cent			*Testing temperature*	*Yield strength* 0·2 per cent *offset* 10^3 lb/in^2	*Ultimate tensile strength* 10^3 lb/in^2	*Elongation* per cent 1 in	*Reduction in area* per cent	*Rockwell hardness* *B*
Nickel	*Carbon*	*Iron*						
0·5	0·16	0·04	*Room*	42·9	73·5	17	34·3	84
1·0	0·18	0·04	*Room*	50·5	76·3	14	32·7	86
1·9	0·13	0·05	*Room*	50·4	74·0	9	13·9	87
2·7	0·07	0·04	*Room*	58·8	78·5	—	0	104
4·0	0·15	0·04	*Room*	54·0	77·2	4	7·05	89
5·0	0·12	0·05	*Room*	62·0	81·5	4	3·28	92
6·0	0·10	0·05	*Room*	75·8	87·2	1	—	96
7·8	0·08	0·21	*Room*	50·7	63·4	1	1·61	97
0·5	0·16	0·04	650° C	3·5	10·3	72	72	—
1·0	0·18	0·04	650° C	3·8	11·5	100	77	—
1·9	0·13	0·05	650° C	3·5	11·7	88	79	—
2·7	0·07	0·04	650° C	9·0	19·5	30	44	—
4·0	0·15	0·04	650° C	7·2	15·9	69	85	—
5·0	0·12	0·05	650° C	8·6	16·4	84	86	—
6·0	0·10	0·05	650° C	7·9	17·1	79	83	—
7·8	0·08	0·21	650° C	9·4	17·9	57	71	—

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Table XLI. Tensile Properties of Zirconium–Nickel Alloy at 500° C

Composition per cent *Nickel*	*Yield strength* 0·2 per cent *offset* 10^3 lb/in^2	*Ultimate tensile strength* 10^3 lb/in^2	*Elongation* per cent 1 in	*Reduction in area* per cent
1·8	7·8	14·4	82	64

11.2.17. *Zirconium–niobium*

C. T. ANDERSON *et al.*[1] determined the tensile properties of zirconium–niobium alloys at room temperature and 650° C as shown in *Table XLII.*

F. B. LITTON[3] explored a wider range and obtained the values shown in *Table XLIII.*

Table XLII. Tensile Properties of Zirconium–Niobium Alloys

Composition per cent			*Testing temperature*	*Yield strength* 0·2 per cent *offset* 10^3 lb/in^2	*Ultimate tensile strength* 10^3 lb/in^2	*Elongation* per cent 1 in	*Reduction in area* per cent	*Rockwell hardness*	
Niobium	*Carbon*	*Iron*						*B*	*C*
0·6	0·13	0·05	*Room*	54·6	83·7	19·0	36·66	89·0	—
5·1	0·07	0·03	*Room*	79·8	104·7	14·0	40·45	111·0	38·0
12·9	0·14	0·08	*Room*	—	150·3	1·0	0·80	113·0	43·0
0·6	0·13	0·05	650° C	9·32	17·8	60·0	83·8	—	—
5·1	0·07	0·03	650° C	7·91	21·63	51·0	84·1	—	—
12·9	0·14	0·08	650° C	10·02	28·39	68·0	81·1	—	—

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Table XLIII. Tensile Properties of Zirconium–Niobium Alloys at Room Temperature

Composition per cent *Niobium*	*Yield strength* 0·05 per cent *offset* 10^3 lb/in^2	*Ultimate tensile strength* 10^3 lb/in^2	*Elongation* per cent 2 in	*Condition*
2·5	63·3	87·5	9·0	*Annealed at* 725° C
7·5	93·7	107·0	1·0	*Annealed at* 725° C
12·5	81·5	102·2	2·0	*Annealed at* 725° C
17·5	78·7	91·2	1·0	*Annealed at* 725° C
22·5	67·5	72·5	—	*Annealed at* 725° C
27·5	57·8	74·3	1·0	*Annealed at* 725° C

A. D. Schwope and W. Chubb[5] determined the tensile properties of niobium alloys at 500° C as shown in *Table XLIV.*

Table XLIV. Tensile Properties of Zirconium–Niobium Alloys at 500° C

Composition per cent *Niobium*	*Yield strength* 0·2 per cent *offset* 10^3 lb/in^2	*Ultimate tensile strength* 10^3 lb/in^2	*Elongation* per cent 1 in	*Reduction in area* per cent
1·6	19·2	26·9	59	77
2·2	35·0	43·0	9	15

The hot hardness for the 2·2 per cent niobium alloy is shown in *Figure 43.*

Limit of forgeability[6] at 850° C: despite high hardness all alloys investigated up to 12·9 per cent forged satisfactorily.

11.2.18. *Zirconium–silicon*

The tensile properties of zirconium–silicon alloys at room temperature and 650° C were determined by C. T. Anderson *et al.*[1] and are shown in *Table XLV.*

Table XLV. Tensile Properties of Zirconium–Silicon Alloys

Composition per cent			*Testing temperature*	*Yield strength* 0·2 per cent *offset* 10^3 lb/in^2	*Ultimate tensile strength* 10^3 lb/in^2	*Elongation* per cent 1 in	*Reduction in area* per cent	*Rockwell hardness*	
Silicon	*Carbon*	*Iron*						*B*	*C*
0·53	0·10	0·13	*Room*	57·6	92·3	16·0	26·9	94	—
0·57	0·11	0·09	*Room*	68·7	96·0	12·0	19·8	96	—
2·06	0·08	0·07	*Room*	68·3	105·4	6·0	4·0	99	—
2·84	0·07	0·09	*Room*	78·6	121·4	3·5	3·2	103	28
0·53	0·10	0·13	650° C	5·81	17·15	59	69·2	—	—
0·57	0·11	0·09	650° C	7·99	13·55	44	57·2	—	—
2·06	0·08	0·07	650° C	9·07	23·98	40	55·3	—	—
2·84	0·07	0·09	650° C	12·65	23·23	39	55·2	—	—

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Limit of forgeability[1] at 850° C: alloys up to 2·85 per cent silicon were swaged satisfactorily.

11.2.19. *Zirconium–silver*

The tensile properties of zirconium–silver alloys at room temperature and 650° C were determined by C. T. ANDERSON *et al.*[1] and are shown in *Table XLVI.*

Limit of forgeability[1] at 850° C: all alloys investigated up to 7·74 per cent silver forged satisfactorily.

Table XLVI. Tensile Properties of Zirconium–Silver Alloys

Composition per cent *Silver*	*Testing temperature*	*Yield strength* 0·2 per cent *offset* 10^3 lb/in^2	*Ultimate tensile strength* 10^3 lb/in^2	*Elongation* per cent 1 in	*Reduction in area* per cent	*Rockwell hardness*	
						B	*C*
0·3	*Room*	42·90	68·10	22·0	40·7	104	25
5·9	*Room*	41·20	74·70	20·0	38·4	86	—
7·74	*Room*	59·70	92·80	16·3	31·3	94	—
0·3	650° C	12·80	17·75	—	—	—	—
5·9	650° C	12·42	26·82	40·0	58·0	—	—
7·74	650° C	12·92	30·75	61·7	71·0	—	—

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11.2.20. *Zirconium–tantalum*

C. T. ANDERSON *et al.*[1] determined the tensile properties of forged zirconium–tantalum alloys at room temperature and 650° C as shown in *Table XLVII.*

Table XLVII. Tensile Properties of Zirconium–Tantalum Alloys

Composition per cent			*Testing temperature*	*Yield strength* 0·2 per cent *offset* 10^3 lb/in^2	*Ultimate tensile strength* 10^3 lb/in^2	*Elongation* per cent 1 in	*Reduction in area* per cent	*Rockwell hardness B*
Tantalum	*Carbon*	*Iron*						
1·2	0·14	0·08	*Room*	51·3	82·8	20·5	40·68	90
5·3	0·14	0·08	*Room*	73·0	110·2	17	35·67	99
9·7	0·15	0·07	*Room*	92·2	124·8	9	15·31	101·5
14·1	0·26	0·07	*Room*	84·4	118·8	19·5	33·87	101·5
1·2	0·14	0·08	650° C	9·68	21·77	53	79·5	—
5·3	0·14	0·08	650° C	17·21	33·40	36	70·4	—
9·7	0·15	0·07	650° C	16·42	34·90	35	73	—
14·1	0·26	0·07	650° C	16·45	36·90	20	34	—

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F. B. LITTON[3] determined the tensile properties of the alloys in various conditions as shown in *Table XLVIII.*

Table XLVIII. Tensile Properties of Zirconium–Tantalum Alloys at Room Temperature

Composition per cent *Tantalum*	*Yield strength* 0·05 per cent *offset* 10³ lb/in²	*Ultimate tensile strength* 10³ lb/in²	*Elongation* per cent 2 in	*Condition*
0·5 (a)	13·0	41·7	24·0	*Annealed at* 700° C
1·0 (a)	13·0	43·7	19·0	*Annealed at* 700° C
2·5	35·7	64·8	17·0	*Annealed at* 725° C
2·5	59·5	90·5	3·0	*Cold reduced* 80 per cent
3·0 (a)	21·8	54·7	15·2	*Annealed at* 700° C
7·5	50·2	76·6	17·5	*Annealed at* 725° C
7·5	59·4	96·0	3·5	*Cold reduced* 80 per cent
12·5	41·0	111·9	2·5	*Cold reduced* 80 per cent
17·5	92·2	138·8	0·8	*Heat treated* (b)
22·5	93·6	111·4	4·0	*As-rolled*
27·5	100·2	105·7	3·0	*As-rolled*

(a) Arc melted. Rolled at 400° C. Other alloys in this series were melted *in vacuo* in graphite crucibles. Rolled sheathed at 900° C.
(b) Quenched from 1000° C. Aged 2 h at 500° C.

A. D. SCHWOPE and W. CHUBB[5] found the tensile properties of tantalum alloys at 500° C as shown in *Table XLIX.*

Table XLIX. Tensile Properties of Zirconium–Tantalum Alloys at 500° C

Composition per cent* *Tantalum*	*Yield strength* 0·2 per cent *offset* 10³ lb/in²	*Ultimate tensile strength* 10³ lb/in²	*Elongation* per cent 1 in	*Reduction in area* per cent
3·0	21·5	28·0	21	32
5·9	23·0	32·0	36	53
6·4	27·0	32·8	24	46

* These alloys also contain approximately 0·3 per cent carbon.

The hot hardness for the 5·9 per cent tantalum alloy is shown in *Figure 43.*

Limit of forgeability[1] at 850° C: alloys containing up to 20 per cent tantalum swaged satisfactorily.

11.2.21. *Zirconium–thorium*

C. T. ANDERSON *et al.*[1] produced alloys containing 0·4 and 5·4 per cent thorium. The tensile properties of the alloys at room temperature and 650° C are shown in *Table L.*

Table L. Tensile Properties of Zirconium–Thorium Alloys

Composition per cent			*Testing tempera-ture*	*Yield strength* 0·2 per cent *offset* 10^3 lb/in^2	*Ultimate tensile strength* 10^3 lb/in^2	*Elon-gation* per cent 1 in	*Reduc-tion in area* per cent	*Rock-well hard-ness B*
Thorium	*Carbon*	*Iron*						
0·4	0·11	0·34	*Room*	72·7	76·0	20·5	37·3	86·0
5·4	0·13	0·07	*Room*	54·4	82·5	18·5	32·8	90·0
0·4	0·11	0·34	650° C	5·82	16·50	63·0	75·6	—
5·4	0·13	0·07	650° C	10·18	25·26	49·0	71·3	—

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Limit of forgeability[1] at 850° C: both the 0·4 and 5·4 per cent thorium alloys swaged satisfactorily.

11.2.22. *Zirconium–tin*

C. T. ANDERSON *et al.*[1] determined the tensile properties of a few zirconium–tin alloys at room temperature and 650° C as shown in *Table LI.*

Table LI. Tensile Properties of Zirconium–Tin Alloys

Composition per cent			*Testing tempera-ture*	*Yield strength* 0·2 per cent *offset* 10^3 lb/in^2	*Ultimate tensile strength* 10^3 lb/in^2	*Elon-gation* per cent 1 in	*Reduc-tion in area* per cent	*Rock-well hard-ness B*
Tin	*Carbon*	*Iron*						
0·69	0·10	0·05	*Room*	42·6	71·7	20	34·5	83
5·56	0·11	0·05	*Room*	64·6	100·0	9	13·1	93
0·69	0·10	0·05	650° C	5·46	13·96	63	29·6	—
5·56	0·11	0·05	650° C	17·80	34·55	24	59·8	—

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Limit of forgeability[1] at 850° C: alloys up to 12·15 per cent tin swaged satisfactorily.

11.2.23. *Zirconium–titanium*

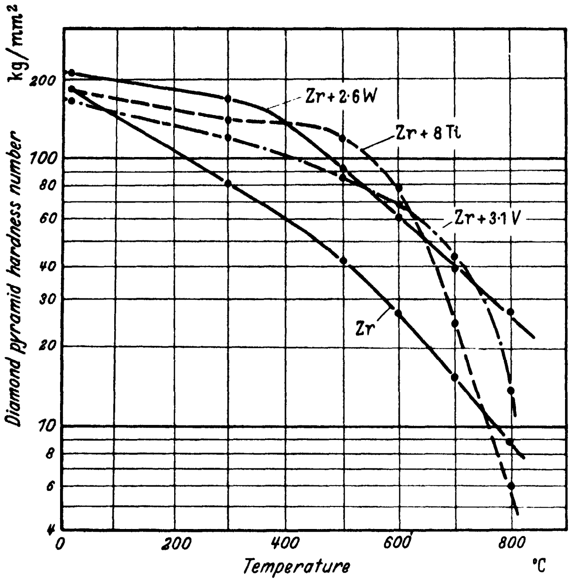

Figure 44. In these hot hardness curves for alloys of zirconium with tungsten, titanium, and vanadium, the curve for the tungsten alloy must be disregarded for comparison. The carbides present in this alloy increase hardness but do not correspondingly increase strength (after A. D. SCHWOPE *and* W. CHUBB[5])

Table LII. Tensile Properties of Swaged Zirconium–Titanium Alloys

Composition per cent			*Testing temperature*	*Yield strength* 0·2 per cent *offset* 10^3 lb/in²	*Ultimate tensile strength* 10^3 lb/in²	*Elongation* per cent 1 in	*Reduction in area* per cent	*Rockwell hardness*	
Titanium	*Carbon*	*Iron*						*B*	*C*
1·0	0·11	0·24	*Room*	59·7	90·2	16	37·1	92	—
2·0	0·20	0·19	*Room*	48·5	83·6	14	26·8	90	—
2·8	0·21	0·23	*Room*	57·8	87·4	14	28·0	92	—
4·8	0·30	0·34	*Room*	66·4	95·4	9	18·4	97	—
7·0	0·17	0·20	*Room*	76·2	100·7	14	28·5	99	—
8·4	0·16	0·08	*Room*	85·2	97·3	15	35·5	106	29
13·8	0·33	0·05	*Room*	87·7	102·7	4	9·2	111	37
24·3	0·11	0·04	*Room*	103·1	112·3	7	29·8	111	39
34·0	0·42	0·13	*Room*	139·1	162·3	2·5	3·2	112	39
44·8	0·15	0·05	*Room*	130·7	151·5	3	3·2	110	35
58·5	1·30	0·12	*Room*	111·3	123·2	2	1·6	95	—
2·8	0·21	0·23	650° C	8·4	16·6	—	75	—	—
3·8	0·30	0·34	650° C	12·9	23·3	—	82·7	—	—
7·0	0·17	0·20	650° C	17·3	24·7	—	77	—	—
8·4	0·16	0·08	650° C	8·01	13·66	67	76·2	—	—
13·8	0·33	0·05	650° C	8·95	11·68	—	—	—	—

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C. T. ANDERSON *et al.*[1] determined the tensile properties of swaged zirconium–titanium alloys at room temperature and 650° C as shown in *Table LII.*

The properties of the zirconium–titanium alloys, rolled at 850° C, in various conditions as determined by E. T. HAYES *et al.*[2] are shown in *Table LIII.*

Table LIII. Tensile Properties of Hot Rolled Zirconium–Titanium Alloys; the Effect of Heat Treatment

Composition per cent *Titanium*	*Ultimate tensile strength* 10^3 lb/in^2	*Yield strength* 0·2 per cent *offset* 10^3 lb/in^2	*Elongation* per cent 2 in	*Rockwell hardness*	
				B	*C*
0	63·2	41·5	15·0	86	—
12·1	75·0	47·7	15·0	86	—
18·4	89·2	73·5	14·0	94	—
20·3	149·5	—	3·0	—	28
30·6	155·4	131·0	3·4	—	34
34·1	157·4	137·2	1·5	—	36
46·6	133·2	120·8	1·0	—	27
59·5	129·2	—	3·0	—	27
69·4	125·5	—	1·5	—	22
76·7	102·0	—	2·5	—	19
86·1	102·8	97·0	1·5	—	25
100	95·4	83·5	15·5	95	—
950° C for 2 hours, water quench					
0	74·2	57·0	13·7	89	—
12·1	73·1	43·4	13·5	80	—
18·4	122·0	114·3	5·0	—	29
20·3	135·1	126·0	0·5	—	—
30·6	157·2	124·0	5·5	—	36
34·1	158·0	127·0	4·5	—	33
59·5	149·0	121·0	3·0	—	34
69·4	139·8	115·8	4·0	—	28
76·7	110·6	98·7	3·5	—	—
950° C for 2 hours, furnace cooled					
0	59·5	37·0	22·0	—	—
12·1	73·5	52·4	17·4	—	—
18·4	102·2	89·8	13·5	—	—
20·3	115·0	92·0	15·0	—	—
30·6	123·1	114·5	8·5	—	—
34·1	124·0	115·0	4·5	—	—
59·5	102·4	—	8·5	—	—
69·4	94·5	86·3	13·0	—	—
76·7	91·5	85·5	5·7	—	—
100	63·5	60	25·0	—	—

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F. B. LITTON[3] also determined the tensile properties of zirconium–titanium alloys over the whole range for various conditions as shown in *Table LIV.*

Table LIV. Tensile Properties of Zirconium–Titanium Alloys at Room Temperature

Composition per cent *Titanium*	*Yield strength* 0·05 per cent *offset* 10^3 lb/in^2	*Ultimate tensile strength* 10^3 lb/in^2	*Elongation* per cent 2 in	*Condition*
3·2	42·5	85·4	17·3	*Annealed at* 700° C
3·2	83·5	134·6	7·2	*As rolled* 400° C
15·0	74·2	90·8	1·5	*Annealed at* 725° C
35·0	110·0	138·8	2·7	*Annealed at* 725° C
35·0	97·6	148·4	5·0	20 per cent *cold reduced*
50·0	113·2	140·4	1·5	*Annealed at* 725° C
50·0	89·4	132·4	1·0	20 per cent *cold reduced*
65·0	115·0	125·0	1·2	*Annealed at* 725° C
65·0	114·6	138·9	0·5	20 per cent *cold reduced*
85·0	78·0	101·4	1·0	*Air cooled* 900° C

A. D. SCHWOPE and W. CHUBB[5] determined the tensile properties of the alloys at 500° C as shown in *Table LV.*

Table LV. Tensile Properties of Zirconium–Titanium, Zirconium–Titanium–Aluminium, and Zirconium–Titanium–Nitrogen Alloys at 500° C

Composition per cent*			*Yield strength* 0·2 per cent *offset* 10^3 lb/in^2	*Ultimate tensile strength* 10^3 lb/in^2	*Elongation* per cent 1 in	*Reduction in area* per cent
Titanium	*Aluminium*	*Nitrogen*				
1·6	—	—	14·2	28·6	31	48
6·4	—	—	29·8	42·4	19	28
8·0	—	—	29·0	45·0	30	43
10·4	—	—	41·2	58·3	33	44
4·6	0·8	—	32·0	46·8	23	34
4·0	—	0·2	34·0	49·0	18	24

* These alloys also contain approximately 0·3 per cent carbon.

The hot hardness of the 8 per cent titanium alloy is shown in *Figure 44.*

Limit of forgeability[1] at 850° C: all zirconium–titanium alloys forged satisfactorily.

11.2.24. *Zirconium–titanium ternary alloys*

A. D. Schwope and W. Chubb[5] also determined the tensile properties at 500° C of some zirconium–titanium ternary alloys containing aluminium or nitrogen. The results are shown in *Table LV.* The hot hardness curves of these alloys are shown in *Figure 42.*

11.2.25. *Zirconium–tungsten*

C. T. Anderson *et al.*[1] determined the tensile properties at room temperature and 650° C of a few zirconium–tungsten alloys as shown in *Table LVI.*

Table LVI. Tensile Properties of Zirconium–Tungsten Alloys

Composition per cent			*Testing tempera-ture*	*Yield strength* 0·2 per cent *offset* 10^3 lb/in^2	*Ultimate tensile strength* 10^3 lb/in^2	*Elon-gation* per cent 1 in	*Reduc-tion in area* per cent	*Rockwell hardness*	
Tung-sten	*Carbon*	*Iron*						*B*	*C*
*1·0	0·24	0·04	*Room*	26·40	84·60	15·0	34·3	90	—
1·3	0·28	0·03	*Room*	58·70	83·50	8·0	19·2	95	—
2·5	0·40	0·16	*Room*	67·00	93·80	2·5	4·7	95	—
4·2	0·20	0·16	*Room*	69·00	106·30	10·0	18·9	98	—
6·9	0·24	0·10	*Room*	61·40	94·10	5·5	7·1	95	—
9·9	0·17	0·09	*Room*	91·30	109·50	2·0	1·6	102	25
*1·0	0·24	0·04	650° C	10·98	18·68	40	72·3	—	—
1·3	0·28	0·03	650° C	22·65	25·18	16	56·0	—	—
2·5	0·40	0·16	650° C	10·48	22·21	20	48·4	—	—
4·2	0·20	0·16	650° C	11·28	21·76	59	83·6	—	—
6·9	0·24	0·10	650° C	11·22	21·95	40	63·7	—	—
9·9	0·17	0·09	650° C	12·16	25·60	39	40·0	—	—

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* Nominal analysis.

F. B. Litton[3] determined the tensile properties of zirconium with small additions of tungsten under various conditions, as shown in *Table LVII.*

A. D. Schwope and W. Chubb[5] determined the properties of a few zirconium–tungsten alloys at 500° C as shown in *Table LVIII.* The hot hardness of the 2·6 per cent tungsten alloy is shown in *Figure 44.*

Limit of forgeability[1] at 850° C: all alloys containing up to 9·9 per cent tungsten swaged satisfactorily.

Table LVII. Tensile Properties of Zirconium–Tungsten Alloys at Room Temperature

Composition per cent *Tungsten*	*Yield strength* 0·05 per cent *offset* 10^3 lb/in^2	*Ultimate tensile strength* 10^3 lb/in^2	*Elongation* per cent 2 in	*Condition*
0·3	23·9	58·0	18·0	*Annealed at* 700° C
0·5	32·6	67·7	17·3	*Annealed at* 700° C
0·5	89·5	127·4	5·3	*As rolled* 400° C
1·0	82·1	110·2	7·3	*As rolled* 825° C

Table LVIII. Tensile Properties of Zirconium–Tungsten Alloys at 500° C

*Composition** per cent *Tungsten*	*Yield strength* 0·2 per cent *offset* 10^3 lb/in^2	*Ultimate tensile strength* 10^3 lb/in^2	*Elongation* per cent 1 in	*Reduction in area* per cent
0·44	16·7	22·0	47	65
0·45	10·4	16·0	26	56
2·6	13·3	19·1	50	56

* These alloys also contain approximately 0·3 per cent carbon.

11.2.26. *Zirconium–vanadium*

The tensile properties of zirconium–vanadium alloys at room temperature and 650° C were investigated by C. T. ANDERSON *et al.*[1] The results are shown in *Table LIX.*

Table LIX. Tensile Properties of Zirconium–Vanadium Alloys

Composition per cent			*Testing temperature*	*Yield strength* 0·2 per cent *offset* 10^3 lb/in^2	*Ultimate tensile strength* 10^3 lb/in^2	*Elongation* per cent 1 in	*Reduction in area* per cent	*Rockwell hardness B*
Vanadium	*Carbon*	*Iron*						
0·8	0·12	0·08	*Room*	74·50	107·6	11·5	16·0	98
1·8	0·17	0·08	*Room*	82·5	122·2	10	10·1	102
3·5	0·16	0·21	*Room*	75·3	123·4	8	3·7	101
4·7	0·32	0·07	*Room*	72·6	83·2	2	0·8	101
0·8	0·12	0·08	650° C	9·59	21·66	41	75	—
1·8	0·17	0·08	650° C	10·45	26·23	43	75	—
3·5	0·16	0·21	650° C	11·43	26·6	43	75	—
4·7	0·32	0·07	650° C	14·72	32·92	25	34	—

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The vanadium used in the preparation of the alloys was only 94 to 95 per cent pure and undoubtedly contained oxygen.

A. D. SCHWOPE and W. CHUBB[5] determined the tensile properties of zirconium–vanadium alloys at 500° C as shown in *Table LX.*

Table LX. Tensile Properties of Zirconium–Vanadium Alloys at 500° C

Composition per cent* *Vanadium*	*Yield strength* 0·2 per cent *offset* 10^3 lb/in^2	*Ultimate tensile strength* 10^3 lb/in^2	*Elongation* per cent 1 in	*Reduction in area* per cent
3·1	27·7	34·6	40	60
3·2	21·6	35·0	44	73

* These alloys also contain approximately 0·3 per cent carbon.

The hot hardness of the 3·1 per cent vanadium alloy is shown in *Figure 44.*

Limit of forgeability[1] at 850° C: alloys containing up to 4·7 per cent vanadium forged satisfactorily.

11.2.27. *Zirconium–zinc*

A. D. SCHWOPE and W. CHUBB[5] examined a zirconium–zinc alloy containing 0·40 per cent zinc and found the properties shown in *Table LXI.*

Table LXI. Tensile Properties of Zirconium–Zinc Alloy at 500° C

*Composition** per cent *Zinc*	*Yield strength* 0·2 per cent *offset* 10^3 lb/in^2	*Ultimate tensile strength* 10^3 lb/in^2	*Elongation* per cent 1 in	*Reduction in area* per cent
0·40	12·0	23·2	47	46

* This alloy also contained approximately 0·3 per cent carbon.

11.2.28. *Zirconium alloys with oxygen and nitrogen*

F. B. LITTON[3] determined the tensile properties of zirconium alloys containing oxygen and nitrogen. The specimens were produced by arc melting iodide zirconium with a 'hardener' addition to vary the composition.

The alloys contained up to 0·3 per cent oxygen and 0·15 per cent nitrogen, as determined by the hydrochloric acid and Kjeldahl

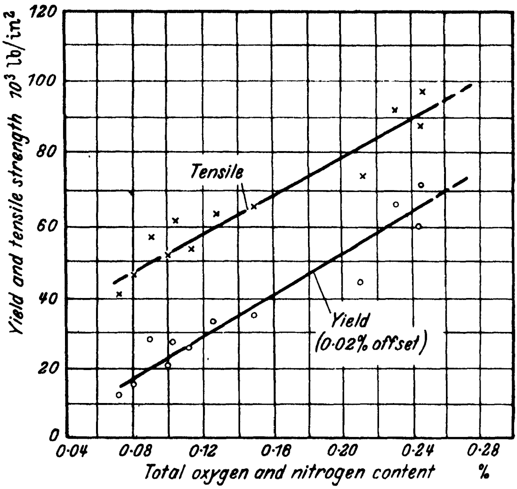

Figure 45. Effect of oxygen and nitrogen combined on the tensile and yield strengths of samples annealed at 700° C (*after* F. B. LITTON[3])

methods. Tensile data were obtained on specimens annealed at 700° C.

In *Figure 45* the tensile and yield strengths of the alloys are plotted against the combined oxygen and nitrogen contents. The results

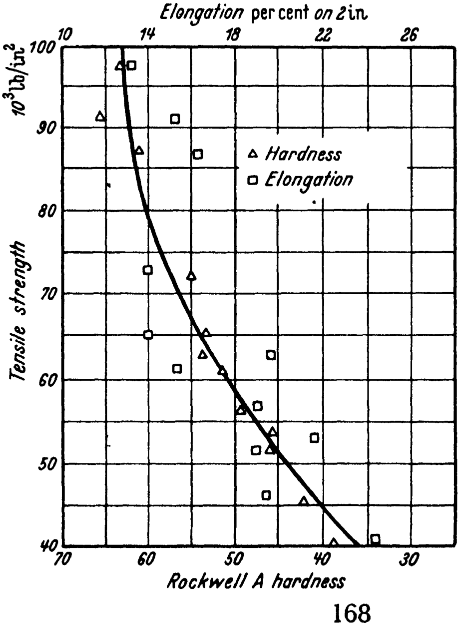

Figure 46. Tensile/hardness relationships on zirconium – oxygen – nitrogen alloys represented in Figure 45 (*after* F. B. LITTON[3])

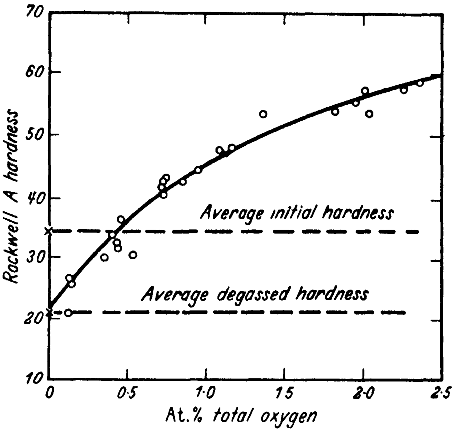

Figure 47. Effect of oxygen on hardness of iodide zirconium. Comparison of initial and degassed hardness as shown by the broken lines (after R. M. TRECO[6])

are rather scattered but they serve to demonstrate that alloys containing limited quantities of oxygen and nitrogen have high strength and good elongation values in the annealed condition.

The highest strength alloy containing 0·102 per cent oxygen and 0·145 per cent nitrogen had 71,600 yield and 97,800 lb/in^2 tensile strengths and 13·1 per cent elongation.

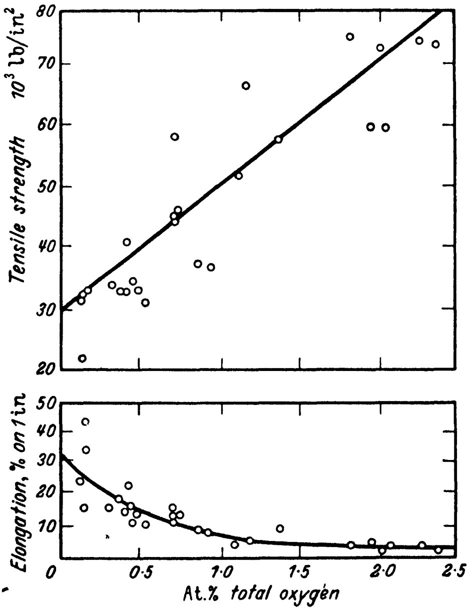

Figure 48. Effect of oxygen on ultimate tensile strength and elongation of rectangular test specimens of iodide zirconium (after R. M. TRECO[6])

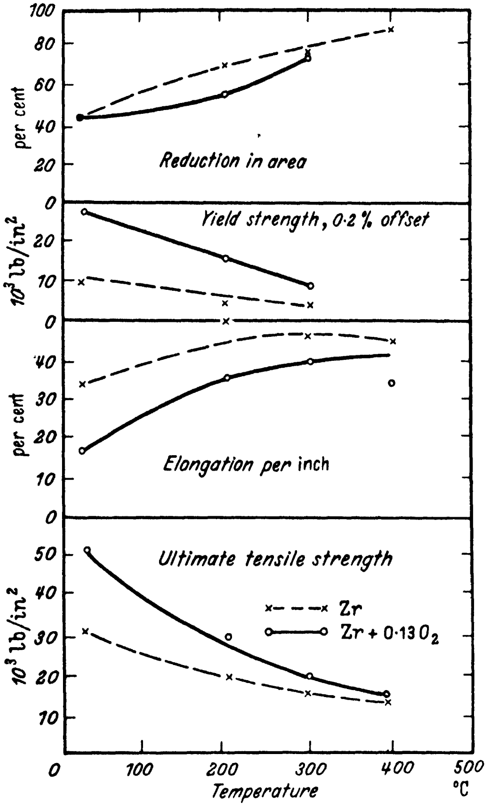

Figure 49. Elevated temperature tensile properties (after R. M. Treco[6])
$c = Q/(\pi Dt)^{\frac{1}{2}}$
where D = *diffusion constant* (cm²/sec), c = *concentration* (cm³ *of oxygen*/cm³ *of zirconium*), t = *time* (sec) *and* Q = *ratio of diffused oxygen to surface area* (cm³/cm²)

Figure 46 shows the relationship between tensile strength, hardness and elongation of the alloys plotted in *Figure 45.*

R. M. Treco[6] investigated the physical and mechanical properties of dilute alloys of oxygen (up to 2·359 atomic per cent) in iodide zirconium. The alloys were prepared by the controlled addition of oxygen to the metal in a high vacuum system.

A marked strengthening effect was observed as a result of the oxygen additions. It was shown also that the strength at elevated temperatures (up to 400° C) was increased by the addition of oxygen. *Figure 47* shows the effect of oxygen on hardness of iodide zirconium. The effect on the ultimate tensile strength and elongation is shown in *Figure 48,* while the tensile properties at elevated temperatures are shown in *Figure 49.* The microstructure of the alloys was similar to that of the pure metal. No structural features related to the added oxygen were detected or expected in view of the high solubility of oxygen in zirconium. A microstructure of an alloy containing 0·13 per cent oxygen showed the mixed structure typical of metal which has been cycled through the alpha–beta transformation.

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12

REACTIONS OF ZIRCONIUM WITH THE COMMON GASES

ZIRCONIUM is extremely stable at room temperature to reactions with the common gases, but at temperatures of a few hundred degrees centigrade it reacts readily with oxygen, nitrogen and hydrogen.

Oxidation resistance at elevated temperatures is poor despite factors which usually indicate good resistance. These factors are: (*a*) the high melting point of the metal, (*b*) the high melting point of the oxide, (*c*) the stability of the oxide, and (*d*) the volume ratio of oxide to metal is greater than unity indicating a continuous oxide film.

The unfavourable factors are: (*a*) the metal reacts to form nitrides, hydrides and carbides, (*b*) the oxide is soluble in the metal at elevated temperatures, and (*c*) the oxide, ZrO_2, undergoes crystal structure transformation at high temperatures.

E. A. GULBRANSEN and R. F. ANDREW[19] calculated the equilibrium constants of the reactions of zirconium with oxygen, nitrogen, carbon monoxide, carbon dioxide and water vapour from thermodynamic data:

1. $Zr(s) + O_2(g) \rightleftharpoons ZrO_2(s)$
2. $Zr(s) + \frac{1}{2}N_2(g) \rightleftharpoons ZrN(s)$
3. $3Zr(s) + 2CO(g) \rightleftharpoons ZrO_2(s) + 2ZrC(s)$
4. $2Zr(s) + CO_2(g) \rightleftharpoons ZrO_2(s) + ZrC(s)$
5. $Zr(s) + 2CO_2(g) \rightleftharpoons ZrO_2(s) + 2CO(g)$
6. $Zr(s) + 2H_2O(g) \rightleftharpoons ZrO_2(s) + 2H_2(g)$

The letters (*s*) and (*g*) refer to the solid and gaseous states respectively. The results of the calculations are shown in *Figure 50* in which the logarithm of the gas pressure or pressure ratios is plotted against the temperature.

The results show the following: (*1*) zirconium oxide, nitride and carbide are stable at all temperatures up to at least 1500° C and from a thermodynamic point of view zirconium will remove oxygen, nitrogen, carbon monoxide and carbon dioxide at the lowest pressures used in modern vacuum technology, (*2*) the reactions of

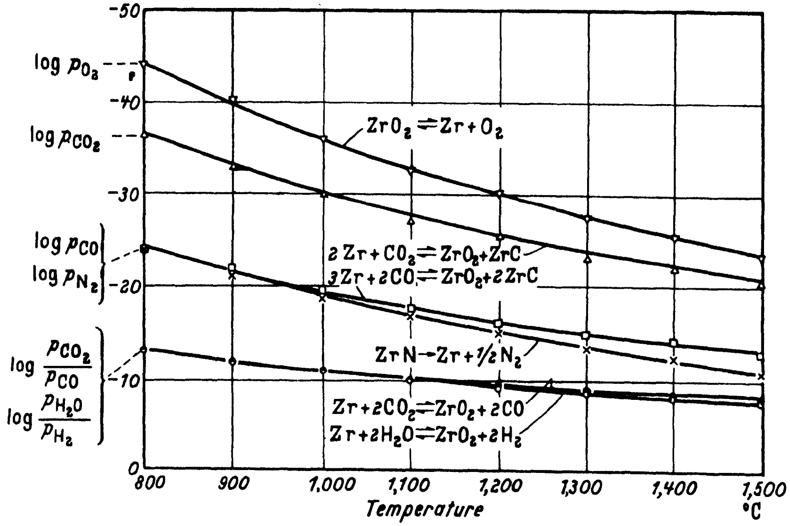

Figure 50. Equilibrium calculations on zirconium reactions (after E. A. GULBRANSEN *and* R. F. ANDREW[19])

water and carbon dioxide to form zirconium oxide, and hydrogen and carbon monoxide respectively are possible below 1100° C in vacua of the order of 10^{-7} mm of mercury.

At temperatures above 200° C zirconium combines readily with the halogens to form volatile tetrahalides[5].

With the common gases except hydrogen, with which the reaction is appreciable at 300° C, little significant attack occurs below 400° C. Above this temperature zirconium reacts with oxygen, nitrogen, carbon monoxide, carbon dioxide and water vapour, the rate increasing rapidly with rise in temperature. It is probable that only the inert gases are stable to zirconium at high temperatures.

Finely divided zirconium is pyrophoric and under certain conditions the dust forms an explosive mixture with air.

12.1. REACTION WITH HYDROGEN

Hydrogen is readily absorbed by zirconium in quantities which decrease with increasing temperature at constant pressure. According to D. P. SMITH[41] the reaction occurs in much the same way as with palladium. At room temperature the occlusion corresponds to a composition approaching ZrH_2 whereas with palladium it approximates to $PdH_{0.7}$.

M. N. A. HALL, S. L. MARTIN and A. L. REES[23] investigated the solubility of hydrogen in zirconium, including the effect of the presence of oxygen in the metal on the hydrogen absorption. Zirconium in various forms was used, including compact ductile iodide metal and wire from the same source; powders were also examined. The compact metal contained 0·4 per cent oxygen and a hafnium content of about 1·0 per cent. The saturation solubility at atmospheric pressure is about 240 cm^3 of hydrogen per gramme of zirconium at 20° C. Corresponding values at 400, 800 and 1100° C were approximately 235, 160 and 40 cm^3/g respectively.

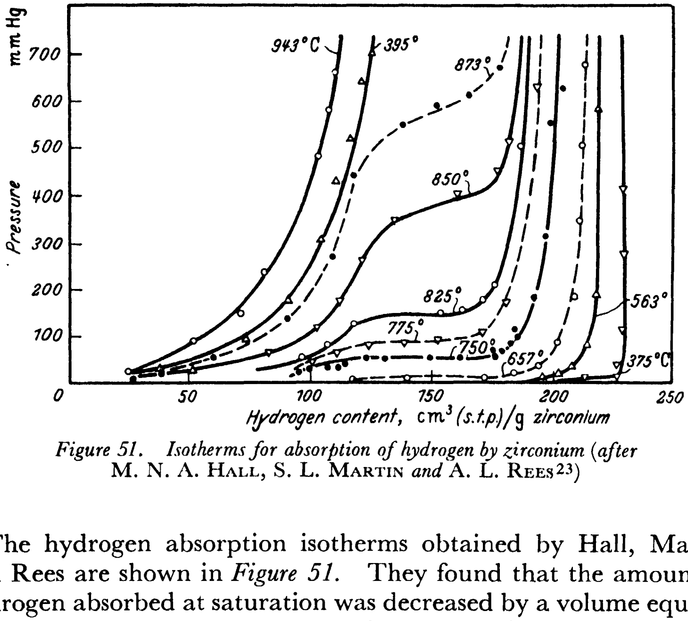

Figure 51. Isotherms for absorption of hydrogen by zirconium (after M. N. A. HALL, S. L. MARTIN *and* A. L. REES[23])

The hydrogen absorption isotherms obtained by Hall, Martin and Rees are shown in *Figure 51.* They found that the amount of hydrogen absorbed at saturation was decreased by a volume equivalent to that of the oxygen present. More recently C. F. BEVINGTON, S. L. MARTIN and D. H. MATHEWS[4a] showed that the effect of oxygen, nitrogen and carbon atoms in solid solution in zirconium on the absorption of hydrogen increases in the order of their atomic radii as does their effect on the lattice expansion. It was suggested by the authors that these atoms, known to occupy the octahedral interstitial positions, render definite proportions of the tetrahedral positions unavailable to the hydrogen atoms.

J. H. DE BOER and J. D. FAST[9] had found absorption was relatively rapid at 300 to 400° C in disagreement with other workers who claimed that the reaction did not take place below 500° C. Hall confirmed the results of de Boer and Fast and found appreciable absorption at room temperature. The variance in the results is due to the surface condition of the zirconium. M. N. A. HALL *et al.*[23] prepared their samples by heating to 1050° C in a low pressure of hydrogen and degassing before cooling to the required temperature. This treatment ensured that all oxygen was absorbed into the metal lattice and the surface was free from contamination. Failure to remove the oxide by this treatment retards or inhibits the absorption.

D. P. SMITH[41] discusses the available information on zirconium–hydrogen systems. He considers the evidence of Hall *et al.* and of A. SIEVERTS and E. ROELL[39] (for the existence of two phases in the system) more convincing than the report of G. HÄGG[22] of five solid phases.

J. FITZWILLIAM, A. R. KAUFMANN and C. F. SQUIRE[18] found that the adsorption of hydrogen by zirconium stabilizes the high temperature beta form of zirconium so that it may be undercooled without transition. It was also noted that hydrogen appears to form a solid solution with zirconium in amounts up to about 5 atomic per cent, while with higher concentrations the structure of the metal was changed from hexagonal to tetragonal face centred.

According to J. H. DE BOER and J. D. FAST[9] and G. HÄGG[22] zirconium, while transforming from the alpha to the beta form, absorbs hydrogen and liberates it during cooling through the allotropic transformation. The higher solubility of hydrogen in beta zirconium has been confirmed by C. F. SQUIRE and A. R. KAUFMANN[43] who also found the solubility to be 1·36 mole of atomic hydrogen to one mole of zirconium[44].

The absorption of hydrogen by zirconium is exothermic and causes large increases in volume. J. FITZWILLIAM *et al.*[18] reported a volume increase of 8·2 per cent for a sample containing 80 cm^3 of hydrogen per gramme of zirconium, and A. SIEVERTS *et al.*[40] found an expansion of 15·4 per cent accompanied by the absorption of 235 cm^3/g.

E. A. GULBRANSEN and R. F. ANDREW[19] studied the kinetics of the reactions of iodide zirconium with oxygen, nitrogen and hydrogen, as a function of time, temperature and pressure. The specimens were prepared by abrading under purified kerosene. The reaction was sensitive to the presence of surface films and, in addition, it was noted that the range 275 to 300° C was critical. While little reaction occurred at 280° C, at 300° C there was a rapid reaction. The effect is shown in *Figure 52*. The effect of pressure at 300° C is shown in *Figure 53*. The results show that the reaction

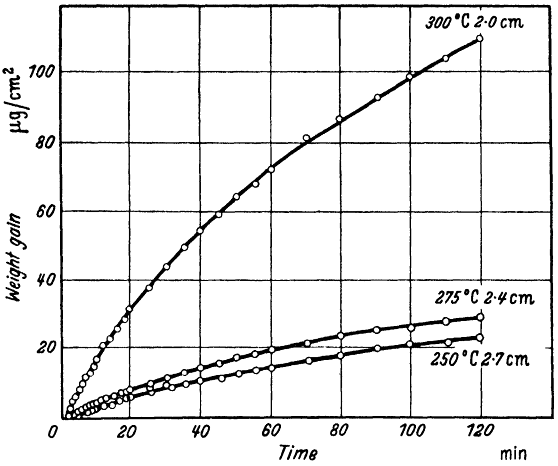

Figure 52. Reaction of zirconium with hydrogen: effect of temperature (after E. A. GULBRANSEN *and* R. F. ANDREW[19])

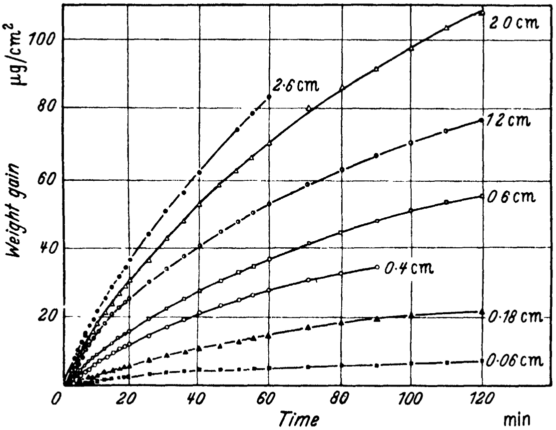

Figure 53. Reaction of zirconium with hydrogen at 300° C*: effect of pressure (after* E. A. GULBRANSEN *and* R. F. ANDREW[19])

is pressure dependent. Plotting the initial reaction rate against the square root of the pressure, a straight line was obtained from which it was deduced that no surface film is formed and that the rate controlling factor is the diffusion of hydrogen atoms into the metal. It was also shown that the hydride is stable in vacua of the order of 10^{-6} mm of mercury up to 400° C.

E. A. GULBRANSEN and R. F. ANDREW[20] compared the reactions of zirconium, titanium, niobium and tantalum with hydrogen at elevated temperatures and found the order of increasing reactivity at 300° C and 2·1 cm of hydrogen to be niobium, zirconium and titanium (tantalum not mentioned).

The reactions of zirconium with oxygen, nitrogen, hydrogen and water vapour at low pressure were studied by W. G. GULDNER and L. A. WOOTEN[21]. The zirconium was in the form of metal powder, which was bonded with colloidal silicic acid and applied to a molybdenum anode which was heated to 1300° C in a vacuum to remove gases and surface oxide before testing. Hydrogen was unique among the gases studied in that the reaction with zirconium is reversible, the gas being completely liberated at approximately 800° C. The optimum temperature for absorption of hydrogen was found to be 300° C. At this temperature the total amount of gas absorbed was in excess of 17 micron-litres hydrogen per mg zirconium.

E. T. HAYES *et al.*[25] studied the reactions which took place when zirconium sheet was heated in several gases, including hydrogen, at atmospheric pressures. The zirconium sheet was produced from Kroll zirconium sponge which had been melted in a graphite crucible. The carbon content was 0·2 per cent and the oxygen 0·07 to 0·08 per cent. The ingot was forged and then sandblasted and pickled to remove the oxide before rolling. The specimens were thoroughly degreased before testing. The sheets were not activated

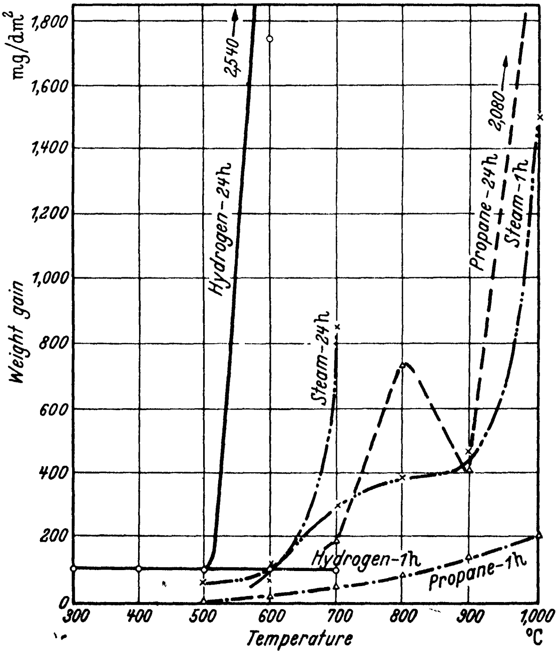

Figure 54. Weight gain of zirconium sheet heated in hydrogen, steam and propane (after E. T. HAYES *et al.*[25])

by heating to about 1000° C *in vacuo* as it was desired to simulate conditions that would be consistent with the normal use of zirconium metal. Within the range 300 to 700° C the weight gains remained virtually constant in one-hour tests, but 24-hour tests showed a sharp rise in weight increase just above 500° C. The results are shown graphically in *Figure 54* with those for steam and propane.

Metallographic examination revealed that fine intergranular areas of hydride are found below 300° C, even in specimens without activated surfaces. Hydrogen penetrated the metal completely, forming intergranular second-phase areas that widened with increasing hydrogen content. Rapid absorption did not occur below 500° C at atmospheric pressure; samples treated at 700° C showed a marked increase in the amount of second phase, while at 800° C the field was almost completely hydride. Most of the second phase was removed by heating the specimen in a vacuum at 700° C, thus confirming that the phase was due to hydride.

Hayes *et al.* found that hydride formation embrittles the zirconium and it can be crushed readily. Heating the hydrided specimen at 700° C *in vacuo* restored the ductility of the metal.

12.1.1. *Effect of hydrogen on alpha–beta transformation*

The transition temperature of zirconium is lowered to 960° K by the solution of hydrogen.

The heat of solution of hydrogen in zirconium was determined[16] at a hydrogen content of 0·4 atomic per cent. It was found to be 19·7 ± 1 kg cal/mole in α-zirconium (under 865° C) and 33·0 ± 1 kg cal/mole in β-zirconium (above 865° C). These values are of the same order of magnitude as the heat of formation of the compound ZrH_2, which amounts to 40·5 kg cal per mole[42].

The heat of solution of molecular and atomic hydrogen in zirconium is quoted by F. W. BOULGER[5] without reference as −17,500 cal/mole and −59,800 cal/g atom respectively.

12.1.2. *Hydrogen embrittlement of zirconium*

Zirconium and zirconium–tin alloys have been found to be susceptible to embrittlement on the notch impact test when subjected to certain heat treatment conditions. W. C. MUDGE[36] reported that embrittlement resulted from a pre-age at a temperature above 315° C followed by either a slow cool or a quench directly to an isothermal heat treatment in the temperature range 95 to 225° C. The type of metal, tin content, and melting procedure did not affect the embrittlement. Hydrogen was considered to be responsible and may be the cause of noticeable reductions in impact strength when present in amounts of 10 p.p.m. or greater. The particular precipitated compound of hydrogen responsible for embrittlement has not yet been identified.

12.2. REACTION WITH OXYGEN

Oxygen reacts readily with zirconium at rates controlled by the temperature, purity, particle size and surface condition of the metal. Zirconium powder absorbs oxygen at temperatures as low as 180° C and rapidly at 450 to 800° C[28] as indicated in *Figure 55.*

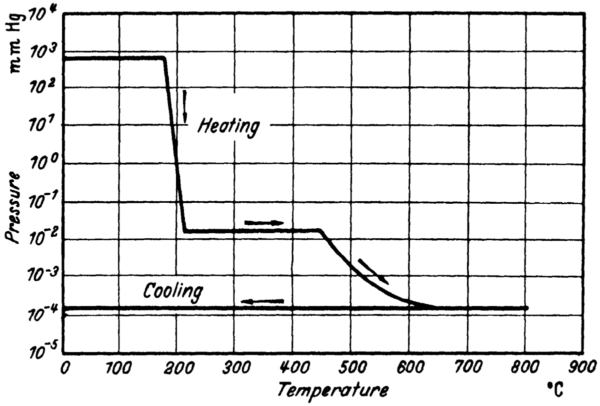

Figure 55. Absorption of oxygen by zirconium on heating (after S. HUKAGAWA *and* J. NAMBO[28])

The protective film formed at lower temperatures dissolves at around 450° C thus permitting further absorption of oxygen.

J. J. POLLING and A. CHARLESBY[36b] found that the effect of an anodic oxide film on the absorption of atmospheric gases by heated zirconium depends on the thickness of the film. A thin anodic film of less than the limiting thickness will eventually tend to the same state as a thermally produced film, its structure and composition will alter and it will become blue-grey and cease to grow. It will not prevent the absorption of gas by zirconium.

A thick anodic film, however, shows no tendency to change its character, the only effect of heating being to evaporate volatile impurities from the film. The oxide film formed by anodizing at potentials up to 130 V or higher affords complete protection from oxygen absorption for periods of several hundred hours at temperatures up to 300° C.

At temperatures up to 600° C the protective effect of the anodic film is very small except where the period of heating is very short. For oxide films up to 10^4 Å in thickness the weight increase on

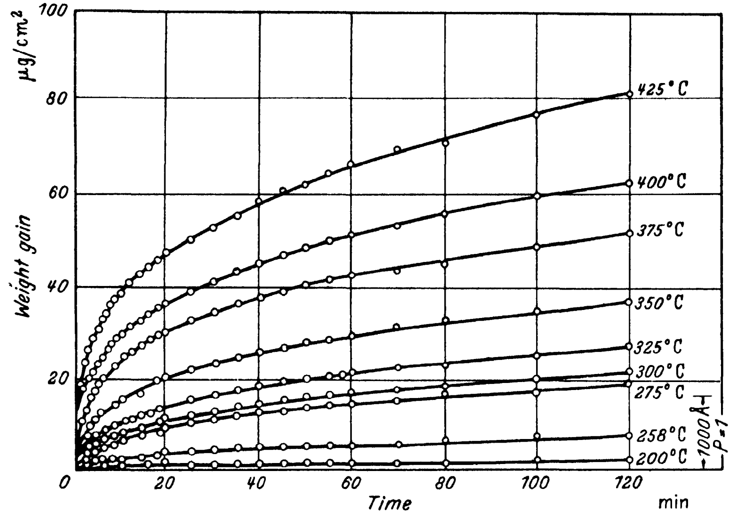

Figure 56. Reaction of zirconium with oxygen at 7·6 cm *pressure: effect of temperature* 200 *to* 425° C (*after* E. A. Gulbransen *and* R. F. Andrew[19])

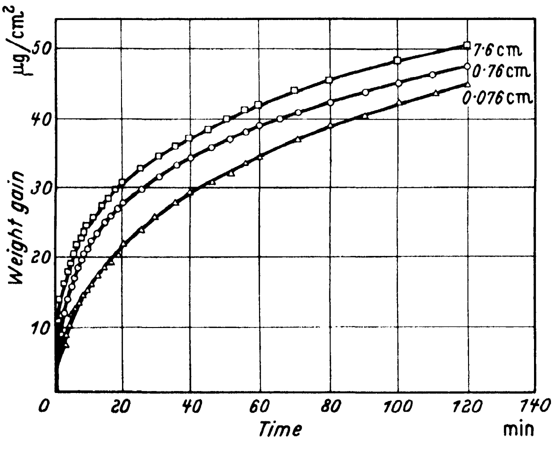

Figure 57. Reaction of zirconium with oxygen at 375° C*: effect of pressure* (*after* E. A. Gulbransen *and* R. F. Andrew[19])

heating in air appears to be due to surface oxidation alone and not to solution of atmospheric gases in the metal.

The minimum temperature for oxygen absorption by massive zirconium has been reported as 700° C[16] and 850° C[15]. E. A. Gulbransen and R. F. Andrew[19] reported an appreciable rate of oxidation at 200° C. The effect of temperature in the range

200 to 425° C at an oxygen pressure of 7·6 cm is shown in *Figure 56* and the effect of pressure at a temperature of 375° C is shown in *Figure 57*. The divergence in the above results is probably due to the state of the surface of the zirconium under investigation. A fast rate of reaction is observed in the early stages; this gradually decreases as the film thickens, as the oxide at these low temperatures has protective properties. At the right of the curves in *Figure 56* is shown the weight gain corresponding to a thickness of 1000 Å. A comparison of the 200° C curve with the 425° C curve after two hours of reaction shows a film thickness of 150 Å at 200° C and a thickness of 5000 Å at 425° C.

Gulbransen and Andrew found that no simple rate law fitted their data over a wide temperature range. However, a modification of the parabolic rate law predicts the general shape of the time curve. An analysis of the parabolic rate law plots, for long periods of reaction time, shows straight lines. Using the transition state theory of gas–metal reaction, an energy of activation of 18,200 cal/mole and an entropy of activation of $-25{\cdot}6$ cal/mole/C° were calculated.

D. CUBICCIOTTI[7] studied the oxidation of zirconium in the temperature range 600 to 900° C which includes the condition where the oxygen is reacting with the metal and the oxide is dissolving into the metal phase. The results obtained by Cubicciotti do not entirely agree with those of Gulbransen and Andrew. The latter took precautions in the preparation of their samples to present a clean surface. Cubicciotti found that the oxidation curves were parabolic at all temperatures tested except 920° C where a small deviation towards a linear relationship was observed. The calculated activation energy was 32,000 cal/mole.

W. G. GULDNER and L. A. WOOTEN[21] studied the rate of clean-up of gases and the minimum and optimum temperatures for their absorption on zirconium powder coated on molybdenum anodes. It was found after out-gassing and activating by heating to 1000° C or over *in vacuo* that zirconium would take up approximately one atomic per cent of oxygen at room temperature and oxidation was appreciable at 400° C. Pure zirconium sheet did not show any evidence of the zirconium dioxide structure after taking up 38·3 atomic per cent of oxygen. Similar results have been reported by other workers. J. D. FAST[16] and J. H. DE BOER[11] found zirconium dissolved large quantities of oxygen in true solid solution. Samples containing 40 and 60 atomic per cent oxygen were prepared which still had only a single hexagonal lattice according to x-ray examination.

D. Cubicciotti[8], whose work is described in Chapter 14, reported that the solubility of oxygen in zirconium near its melting point was 55 atomic per cent.

Fast found the pressure of oxygen in equilibrium with a saturated solution of oxygen in zirconium was less than 8×10^{-5} mm of mercury at 1480° C indicating that it is impossible to remove oxygen from zirconium by vacuum heating. He also reported that the oxygen had great mobility in the zirconium lattice at high temperatures.

It has been shown[10] that dissolved oxygen behaves as a negative ion at high temperatures when under the influence of an electric field of about one V/cm; the oxygen moves towards the anode. The oxygen atoms (or ions) can therefore move from interstice to interstice through the lattice. D. B. Alnutt and C. L. Scheer[1] repeated this experiment at 900° C and found that a sample taken from the cathodic end of the wire showed enhanced ductility.

A process for the removal of dissolved oxygen from zirconium has been described by W. C. Lilliendahl and E. D. Gregory[30]. The method was based upon the theory that the diffusion process could be reversed by the application of a strong reducing agent, such as liquid calcium, in contact with the heated metal.

Samples of iodide zirconium crystal bar were oxidized and homogenized by vacuum treatment at 1300° C. The bars were 0·125 in in diameter and samples were heated in molten calcium for one hour in an atmosphere of argon (99·7 per cent). The results of the treatment are shown in *Table LXII.*

Table LXII. Oxygen Content of Zirconium before and after Calcium Soaking at 1000° C

Weight per cent *oxygen, original*	*Weight* per cent *oxygen, after treating*	Per cent *total oxygen removed*	*Hardness*, original*	*Hardness*, after treating*
1·32	0·50	62·0	319	220
1·04	0·69	33·6	270	254
0·95	0·47	50·0	290	203

* Hardness figures are Vickers Pyramid Numbers.

Further samples containing less oxygen were treated in molten calcium for varying times at 1000 and 1300° C and yielded the results shown in *Table LXIII.*

The process is complicated by the fact that calcium contains

Table LXIII. Oxygen Removal from Zirconium by Molten Calcium Treatment

Treatment			*Oxygen content* wt per cent		*Fraction removed*
Sample No.	*Temperature* °C	*Time* h	*Original*	*Final*	
1	1000	5	0·06	0·02	0·67
2	1000	5	0·06	0·02	0·67
3	1000	5	0·28	0·02	0·93
4	1000	5	0·46	0·15	0·67
5	1300	1	0·07	0·02	0·71
6	1300	1	0·14	0·02	0·86
7	1300	1	0·20	0·02	0·90
8	1300	1	0·37	0·08	0·78
9	1300	4	0·02	0·02	0·00
10	1300	4	0·34	0·02	0·94
11	1300	4	0·45	0·07	0·85

nitrogen as an impurity and care is necessary to ensure that while the oxygen is passing from the zirconium to the calcium, the nitrogen is not passing from the calcium to the zirconium.

The reaction between zirconium oxide and calcium proceeds moderately fast at temperatures in the range 1000 to 1300° C, while the reaction between calcium nitride and zirconium proceeds slowly at temperatures below 1000° C but is rapid at 1300° C. It is therefore possible to remove oxygen without contaminating the zirconium with nitrogen by treating at temperatures not in excess of 1000° C. It is also possible first to remove the nitrogen from the calcium by treatment with zirconium at 1300° C and then employing the denitrided calcium to purify zirconium. Treatment with calcium vapour was also successfully employed, this method having the advantage that it avoids the complications due to the adverse nitrogen reaction.

Table LXIV. Gain in Weight and Hardness of Zirconium heated in Oxygen

Temperature °C	*Gain in weight* mg/dm²	*Hardness*	
		Rockwell	*Knoop*
500	19	*B* 90	279
600	38	85	279
700	75	87	323
*			
800	222	89	668
900	310	92	882

* This line indicates recommended heating limits for working in air.

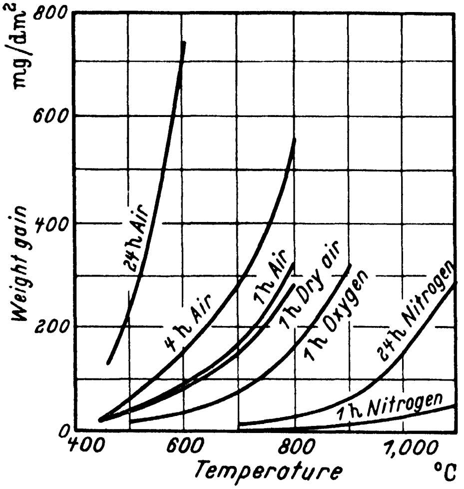

Figure 58. *Weight gain in U.S. Bureau of Mines zirconium heated in oxygen, nitrogen and air (after* E. T. Hayes *and* A. H. Roberson[26])

The gain in weight of degreased zirconium sheet specimens (prepared from Kroll sponge which had been melted in a graphite crucible and contained 0·12 per cent carbon) heated for one hour in dry oxygen at temperatures from 500 to 900° C was measured by E. T. Hayes and A. H. Roberson[26]. The changes in weight and hardness are shown in *Table LXIV*.

Figure 58 shows the comparison of weight gained when zirconium is heated in oxygen, nitrogen and air.

Metallographic examination of the specimens revealed no evidence of oxygen diffusing into the body of the metal until a temperature of 800° C was reached. The beginning of this diffusion is characterized by the appearance of small, rodlike markings on the grains near the surface of the specimen. At 900° C a bright solid solution zone near the surface overlaps an area in which the oxide occurs in the grain boundaries as well as within the grains. Samples heated to 1000° C ignited spontaneously, while powdered zirconium ignited at 200° C.

The order of increasing reactivity for the metals titanium, zirconium, tantalum and niobium to oxygen at 350° C was determined by E. A. Gulbransen and R. F. Andrew[20] to be in the order given.

12.2.1. *Oxygen penetration*

In order to determine the extent of oxygen penetration in pure iodide zirconium F. B. Litton[31] heated dulpicate cold swaged rods in still air at 500, 750 and 950° C for a period of two hours. The extent

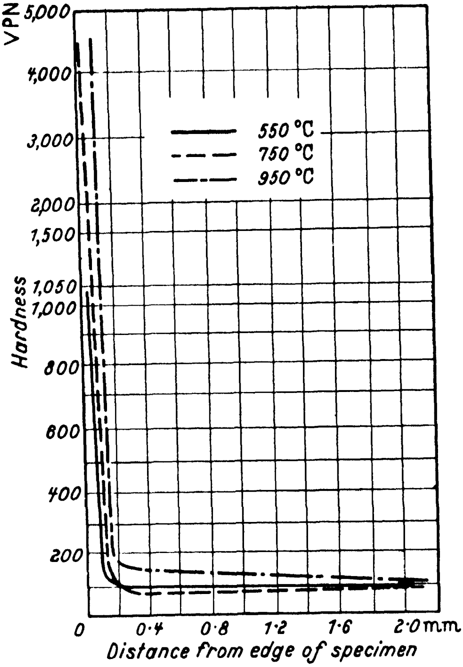

Figure 59. Extent of oxygen penetration in pure iodide zirconium (*after* F. B. LITTON[31])

of penetration was determined on polished cross sections by measuring Vickers hardness, using 1200-g load, for 20 sec, at various distances from the edge of the specimens. The results are plotted in *Figure 59.*

12.2.2. *Nature of the oxide film*

The stable oxide, ZrO_2, exists in three crystallographic forms, cubic[6], tetragonal[38], and monoclinic[24].

An electron diffraction study of the oxide film formed on zirconium at temperatures between 300 and 600° C has revealed to J. E. HICKMAN and E. A. GULBRANSEN[27] that the monoclinic form of ZrO_2 was present in every case. The heat of formation of ZrO_2 is 259 kg cal[12].

According to A. CHARLESBY[5a] when an oxide layer is formed on zirconium metal by making it the anode in an electrolytic cell the oxide form is amorphous, with some crystallites of the cubic modification with lattice parameter equal to 5·103 Å. On heating to 700° C a new modification is obtained which does not correspond to any of the above structures.

12.2.3. *Effect on alpha–beta transformation*

In a private communication to F. W. BOULGER[5], Scheer stated that the alpha–beta transformation temperature is raised to as high as 1150° C by oxygen absorption but J. H. DE BOER and J. D. FAST[12] state that they found the transition occurred over a wide range up to 1800° K after the absorption of 10 atomic per cent of oxygen.

12.2.4. *Lattice constants*

J. D. FAST[16] quotes the following lattice constants of solid solutions of oxygen in zirconium (see also Chapter 11):

Pure zirconium	$a = 3{\cdot}22$ Å	$c = 5{\cdot}13$ Å
90 at. per cent zirconium plus 10 at. per cent oxygen	$a = 3{\cdot}23$ Å	$c = 5{\cdot}15$ Å
80 at. per cent zirconium plus 20 at. per cent oxygen	$a = 3{\cdot}23$ Å	$c = 5{\cdot}17$ Å
70 at. per cent zirconium plus 30 at. per cent oxygen	$a = 3{\cdot}23$ Å	$c = 5{\cdot}19$ Å

12.2.5. *Oxidation resistance of zirconium alloys*

Table LXV. Oxidation Resistance of Zirconium Alloys (after C. T. ANDERSON, E. T. HAYES, A. H. ROBERSON *and* W. J. KROLL[2])

Alloying addition	*Limit of addition* per cent	*Heat resistance** *at* 650° C
Al	10	*C*
Be	5	*C*
B	5	*C*
Ce	5	*C*
Cr	10	*B*
Co	46	*B*
Co–Cr	4 Co, 5 Cr	*C*
Cu	15	*B*
Cu *ternary* (Co, Cr, Fe, Ni *or* Al)	5	*A*
Fe	60	*A*
Mn	25	*C*
Mo	10	*C*
Ni	10	*A*
Nb	12	*C*
Si	5	*C*
Ag	10	*C*
Ta	30	*C*
Th	5	*C*
Sn	10	*C*
Ti	90	*C*
W	10	*C*
V	10	*C*
Zr	—	*B*

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* *A*—weight gain less than 600 mg/dm²/day (mdd)
B—weight gain 600 to 1500 mdd
C—alloy disintegrated in less than 24 hours.

Resistance to oxidation is reduced by aluminium, calcium, titanium, silicon, molybdenum and most alloying additions. Iron, nickel and silver appear to improve resistance.

C. T. ANDERSON *et al.*[2] examined a number of alloys for resistance to oxidation when heated in air at 650° C and prepared a table showing their results for the most resistant alloys of each series. These are shown in *Table LXV.*

Anderson *et al.* noted that the most resistant alloys were those with the poorest yield strength at elevated temperatures.

The oxidation or heat resistance of several zirconium alloys was also determined by F. B. LITTON[32] and the results are shown in *Table LXVI.*

Table LXVI. Oxidation Resistance of Zirconium Alloys (after F. B. LITTON[32])

Intended composition per cent	*Weight gain* mg/dm²	
	* *Induction melt* 6 h *at* 750° C	*Arc melt* 2 h *at* 750° C
100 Zr	3300	415
5 Ti, 95 Zr	*Disintegrated*	—
1 Al, 99 Zr	*Disintegrated*	—
4 Al, 96 Zr	—	550
5 Al, 95 Zr	413	—
5 Ta, 95 Zr	1450	314
5 Nb, 95 Zr	*Disintegrated*	—
5 W, 95 Zr	2600	209
5 Mo, 95 Zr	*Disintegrated*	957
5 Ni, 95 Zr	1690	181
7·5 Ni, 92·5 Zr	3120	—
5 Cr, 95 Zr	3198	—
5 V, 95 Zr	*Disintegrated*	—
5 Pt, 95 Zr	*Disintegrated*	—
5 Be, 95 Zr	1660	—
5 Si, 95 Zr	*Disintegrated*	—
50 Ti, 50 Zr	*Disintegrated* †	—
1 Al, 50 Ti, 49 Zr	*Disintegrated* ‡	*Disintegrated* ‡

* Graphite crucibles
† Alloy disintegrated in about 45 min
‡ Alloy disintegrated in about 10 min.

The effect of carbon contamination is clearly shown by this table and it would have been interesting to have obtained the result for the arc melted 5 per cent aluminium alloy which, when graphite melted, produced by far the best alloy in the carbon-contaminated series.

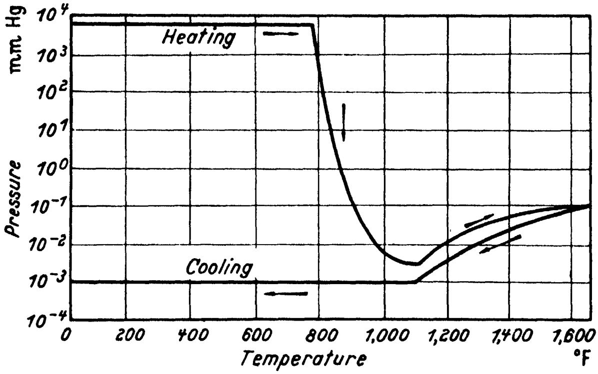

Figure 60. Absorp- of nitrogen by zirconium on heating (after S. Hukagawa *and* J. Nambo[28])

12.3. Reaction with Nitrogen

No reaction occurs between nitrogen and zirconium at low pressure and room temperature. At 400° C the reaction proceeds slowly and at 800° C it is rapid. These results were obtained by W. G. Guldner and L. A. Wooten[21] using activated zirconium powder bonded to molybdenum. The absorption was said to be complete at 600° C by S. Hukagawa and J. Nambo[28] using zirconium powder. The rates of absorption as determined by Hukagawa and Nambo and shown in *Figure 60* are slower for nitrogen than for oxygen.

J. D. Fast[16] and R. I. Jaffee[29] both found that nitrogen in amounts up to 20 atomic per cent forms a solid solution with zirconium. If more nitrogen is absorbed the cubic nitride, ZrN, is formed in addition to the saturated hexagonal solution. Nitrogen atoms, like those of oxygen, are absorbed in the interstices of the metal lattice but have less mobility.

As with oxygen the gas pressure with which the saturated solutions of nitrogen are in equilibrium is too low for direct measurement; even at 1500° C it is less than 10^{-8} atmospheres and for unsaturated metal it is much lower still. The result is that zirconium at elevated temperatures is capable of absorbing all but minute quantities of gases provided there is a surplus of metal. Likewise, it is impossible to free zirconium from dissolved nitrogen by vacuum heat treatment.

J. D. Fast[17] gives the most favourable temperature for the absorption of oxygen and nitrogen by zirconium as 1000 to 1600° C.

The reaction of nitrogen with zirconium at 7·6 cm pressure in the temperature range 400 to 825° C was studied by E. A. Gulbransen and R. F. Andrew[19]. Iodide zirconium was used for the tests, the samples being abraded under purified kerosene. Some reaction

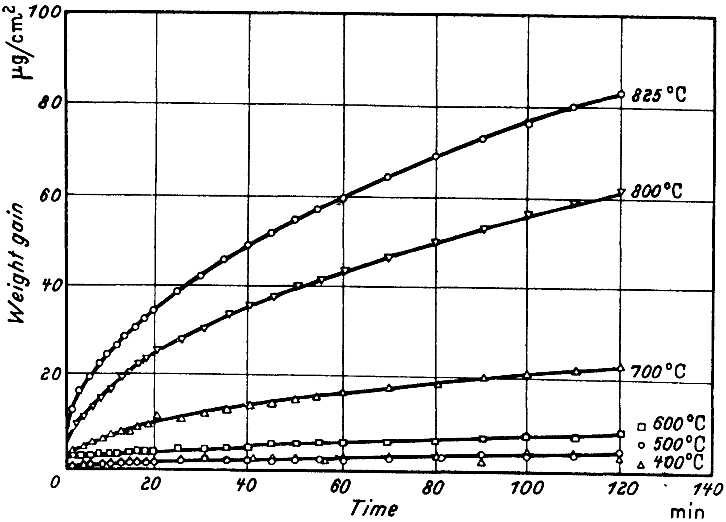

Figure 61. Reaction of zirconium with pure nitrogen at 7·6 cm *pressure: effect of temperature (after* E. A. GULBRANSEN *and* R. F. ANDREW[19])

occurred at 400 to 600° C and from 700 to 825° C it increased rapidly, as shown in *Figure 61.* The rate of reaction was much slower than with oxygen and hydrogen and is sensitive to traces of these gases in the nitrogen. The shape of the curves in *Figure 61* approximates to the parabolic rate law. An activation energy of 39,200 cal/mole was calculated from the results. The reaction of nitrogen with zirconium is insensitive to pressure.

The nitride produced at 750° C was found to be stable up to at least 900° C at 10^{-6} mm of mercury. A. DRAVNIEKS[13] used iodide zirconium (Hf 2·5 to 3·0, O_2 0·03, Fe 0·04 and N_2 0·01 per cent; no details of the preparation of the samples are given) to measure the rate of reaction at 862 to 1043° C by the pressure-drop method. The initial rate obeyed the parabolic law and was independent of pressure. The calculated activation energy was 52,000 cal/mole, a result considerably greater than that determined by Gulbransen and Andrew on the temperature range 400 to 825° C. It was noted that lengthening the duration of the reaction to 70 hours caused some pressure dependence to appear, and the rate law deviated towards the linear.

The reaction of zirconium and nitrogen at low pressures was investigated by W. G. GULDNER and L. A. WOOTEN[21] using zirconium powder bonded to molybdenum and activated before testing by heating to 1300° C in a vacuum. It was reported that the reaction starts slowly at 400° C and at 800° C it is very rapid.

A sample which had absorbed 13 atomic per cent nitrogen was heated to 1300° C without nitrogen being liberated; the sample showed evidence of compound formation, the compound being identified as zirconium nitride; this is not in agreement with Fast who reported solid solutions up to 20 atomic per cent.

Degreased graphite melted Kroll zirconium specimens were heated in nitrogen and the effect studied by E. T. HAYES and A. H. ROBERSON[26]. *Table LXVII* shows the weight gain and hardness of the specimens after exposure to dry nitrogen in the temperature range 700 to 1200° C.

Table LXVII. Gain in Weight and Hardness of Zirconium Metal Heated in Nitrogen

Temperature °C	*Weight gain* mg/dm^2		*Hardness, Rockwell*		*Hardness, Knoop*	
	1 h	24 h	1 h	24 h	1 h	24 h
700	4·7	16	*B*86	*B*92	246	494
800	7·2	28*	88	94	379	940
900	15	65	85	100	698	842
1000	27	149	83	*C*19	502	829
1100	65	304	86	22	486	698
1200	102	572	89	23	736	736

* This line indicates recommended heating limits for heating in air.

These results are plotted in *Figure 58* which compares the weight gain when zirconium is heated in oxygen, nitrogen and air. Heating for periods of one hour produces a small but linear increase while the longer heating period produces a more rapid absorption of nitrogen above 800° C.

Metallographic examination showed that the nitride skin formed at the lower temperatures was thin and adherent; no evidence of nitride penetration was observed in specimens heated at less than 1000° C. Penetration was denoted by coarsening of the grain boundaries at the metal/nitride interface. At 1100° C the penetration was obvious, extending completely through the 1·6-mm specimen which had been heated for 24 hours. Heating for one hour at 1200° C produced a very similar result.

X-Ray analysis of specimens taken from the centre of the samples heated up to 1200° C failed to show the presence of zirconium nitride or an expanded lattice. There were indications of lattice expansion in the 'case' or skin formed at 1000 and 1100° C. The case formed at 1200° C showed a body centred cubic pattern with lattice parameter $a = 4{\cdot}55$ Å. A second phase near the bottom of the case was an expanded alpha zirconium lattice with an axial ratio of 1·599 compared to a normal c/a value of 1·588 listed by C. S. BARRETT[3] and showed that some nitrogen is being retained in the alpha zirconium.

E. A. GULBRANSEN and R. F. ANDREW[20] reported that the order of increasing reactivity for the reaction at 700° C between nitrogen and the metals tested was zirconium, niobium, tantalum and titanium.

The removal of oxygen from zirconium by treatment with molten calcium which was examined by W. C. LILLIENDAHL and E. D. GREGORY[30] has been described in Section 12.2. Nitrogen is not removed from the zirconium, and if present as an impurity in the calcium, will not pass from the calcium to the zirconium unless the treatment temperature exceeds 1000° C.

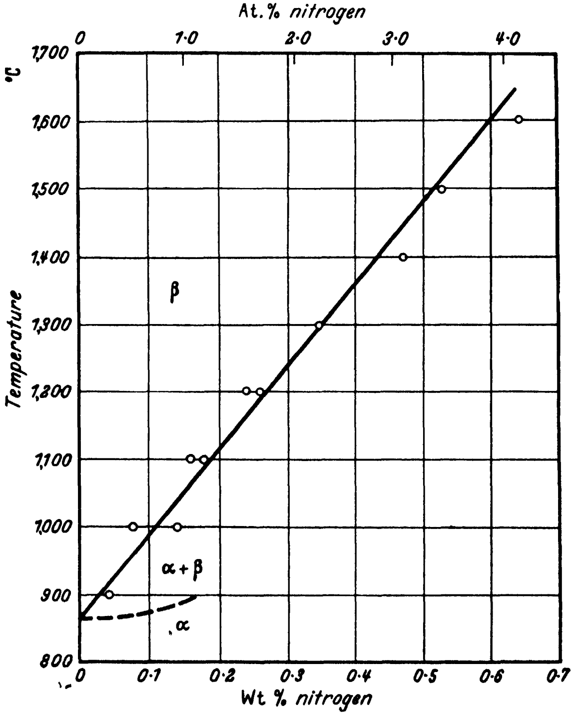

Figure 62. Solubility limits of nitrogen in beta zirconium (after M. W. MALLETT *et al.*[33])

The diffusion and solubility of nitrogen in beta zirconium in the temperature range 900 to 1600° C at atmospheric pressure were studied by M. W. MALLETT *et al.*[33] Outgassed iodide zirconium crystal bars were machined to produce cylindrical specimens.

Diffusion-rate calculations based on a solution of the usual diffusion equation gave a diffusion coefficient

$$D_\beta = 3 \times 10^{-2}\ e^{-33{,}600/RT}\ \mathrm{cm^2/sec}$$

The energy of activation of diffusion 33,600 cal/mole has a probable error of 1600 cal/mole. The limiting solubilities of nitrogen in beta zirconium were determined from the diffusion data and are shown in *Figure 62.*

F. N. RHINES[37] showed that a binary diffusion system consists of one-phase layers with the layer of highest content of diffusing matter on the surface. The nitrogen–zirconium system consisted of a beta solid solution core surrounded by a thin alpha layer, and this in turn was surrounded by a thin gamma layer of zirconium nitride.

12.3.1. *Effect of nitrogen on alpha–beta transformation*

Nitrogen, like oxygen, raises the transformation temperature, and J. H. DE BOER and J. D. FAST[12] reported a transition range up to 1500° K for an absorption of 8·5 atomic per cent of nitrogen.

The heat of formation of ZrN is 82,300 cal/mole[42].

12.3.2. *Lattice constants*

According to K. BECKER and F. EBERT[4] the structure of ZrN is cubic and the lattice parameter is 4·63 Å, compared to 4·567 determined by P. DUWEZ and F. ODELL[14]. The lattice constants of the solid solution of nitrogen in zirconium, at 90 atomic per cent zirconium and 10 atomic per cent nitrogen are $a = 3{\cdot}25$ Å and $c = 5{\cdot}21$ Å compared to pure zirconium which has $a = 3{\cdot}22$ Å and $c = 5{\cdot}13$ Å. (See also Chapter 11.)

12.4. REACTION WITH CARBON MONOXIDE AND CARBON DIOXIDE

The reaction of carbon monoxide and carbon dioxide with zirconium in the micron pressure range was investigated by W. G. GULDNER and L. A. WOOTEN[21]. The zirconium was in the form of powder bonded to molybdenum and heated to 1300° C *in vacuo* to activate the surface. Absorption of carbon dioxide occurred at 400° C and at 800° C it was rapid. In one case working in the pressure range of 10^{-1} to 10^{-3} mm, 28·5 micron-litres of carbon

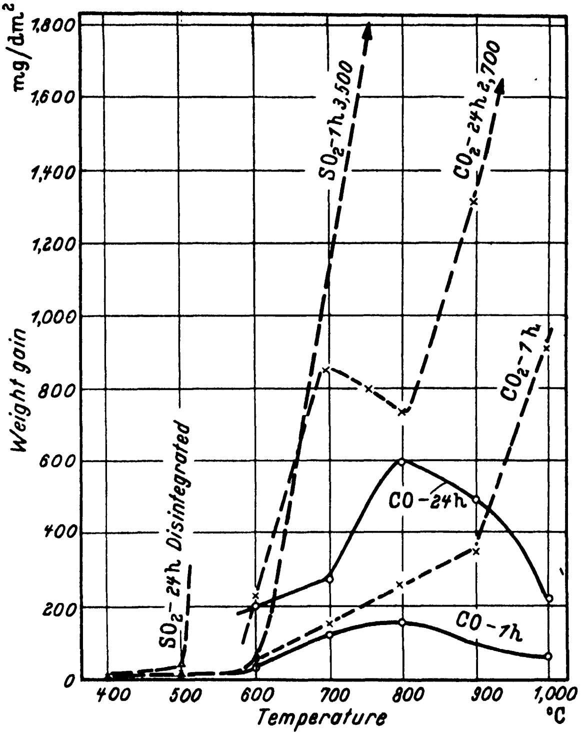

Figure 63. Weight gain of zirconium sheet heated in carbon monoxide, carbon dioxide, and sulphur dioxide (*after* E. T. HAYES *et al.*[25])

dioxide/mg zirconium were absorbed without reaching saturation although the rate of reaction had decreased greatly. When this sample was heated to 1300° C in a vacuum no gas was evolved. Both zirconium oxide, ZrO_2, and zirconium carbide, ZrC, were shown to be present in the sample, the oxide being distributed throughout the

Table LXVIII. Weight Gains of Zirconium Sheet Heated in Carbon Dioxide

Temperature °C	*Weight gain* mg/dm²	
	1 h	24 h
600	37	220
700	150	864
750	—	790
800	265	740
900	365	1325
1000	900	2700

metal and the carbide on the surface. The structures of zirconium nitride and carbide are isomorphous, and their cell constants are nearly equal, so it is difficult to differentiate between the two.

Guldner and Wooten found that the reaction between carbon monoxide and zirconium was very similar to that with the dioxide.

E. T. HAYES, A. H. ROBERSON and R. H. ROBERTSON[25] heated degreased graphite melted Kroll zirconium in carbon dioxide, carbon monoxide, and other atmospheres. Weight gains for various temperatures are shown in *Table LXVIII* and illustrated graphically with the results of other gaseous reactions in *Figure 63.* A sudden acceleration in the rate of reaction was noted at 1000° C; this was attributed to activation of the metal surface due to the diffusion of the products of reaction into the interior.

Carbon deposits were found on the zirconium heated from 600 to 1000° C in both carbon monoxide and carbon dioxide atmospheres, and there was no evidence of carbide formation in the body of the specimen. Carbide formation would be expected at higher temperatures.

Tensile tests on zirconium which had been treated with carbon monoxide at temperatures from 600 to 1000° C indicated that a maximum strength was reached after treatment at 800° C as shown in *Table LXIX.*

Table LXIX. Tensile Properties of Zirconium heated in Carbon Monoxide

Treatment temperature °C	*Yield strength* 0·2 per cent *offset* 10^3 lb/in^2		*Ultimate strength* 10^3 lb/in^2		*Elongation* per cent *on* 2 in	
	1 h	24 h	1 h	24 h	1 h	24 h
Untreated	38·8		69·7		21·0	
700	36·3	38·9	60·6	60·1	17·0	—
800	41·7	58·0	69·1	80·3	14·2	7·2
900	—	56·6	62·6	62·5	9·5	—

Specimens exposed at the higher temperatures contained carbide lines which could be differentiated from the rounded carbide present in the original metal.

12.5. REACTION WITH WATER VAPOUR

The reaction of water vapour with zirconium at low pressures was studied by W. G. GULDNER and L. A. WOOTEN[21] using zirconium

Table LXX. Weight Gain of Zirconium heated in Steam

Temperature °C	*Weight gain* mg/dm²	
	1 h	24 h
500	—	72
600	73	107
700	284	860
800	385	—
900	464	—
1000	1496	—

powder bonded to molybdenum and activated by heating to 1300° C in a vacuum. In the range 200 to 350° C water vapour is absorbed at about the same rate as oxygen. On raising the temperature hydrogen is liberated. When the metal is treated with water vapour at 700 to 800° C, free hydrogen is produced.

The effect of steam on degreased graphite melted Kroll zirconium at temperatures from 500 to 1000° C was determined by E. T. HAYES, A. H. ROBERSON and R. H. ROBERTSON[25]. Weight-gain data are shown in *Table LXX* and *Figure 54*, Section 12.1.

A sharp gain at 1000° C is explained on the basis of the allotropic transformation from alpha to beta zirconium, the transition temperature (862° C for pure zirconium) having been raised by the addition of the oxygen. A loose white oxide deposit was formed on the specimens treated with steam in contrast to the compact blue-black film formed by heating in oxygen.

The reaction with water vapour was more severe than with carbon dioxide, carbon monoxide, propane or nitrogen. The reaction with air was less than that with water vapour at 800° C but much more intense than that with water vapour at 900° C. Sulphur dioxide was more vigorous in its reaction than water vapour.

12.6. REACTION WITH AIR

The results which have been discussed show that zirconium reacts with all the main constituents of the atmosphere at elevated temperatures.

It has been reported[34] that iodide zirconium samples, when heated in air at 200° C, attained a fairly constant weight after 167 hours. At higher temperatures the weight gains were much greater and continued for periods up to 3000 hours. S. MCLAIN[35] reported that zirconium sheet, 0·002-in thick, gradually darkened, gained

Table LXXI. Gain in Weight and Hardness of Zirconium Metal Heated in Air

Temp. °C	*Weight gain* mg/dm²			*Hardness, Rockwell B*			*Hardness, Knoop*		
	1 h	4 h	24 h	1 h	4 h	24 h	1 h	4 h	24 h
425	7·6	11·4	36	88	88	87	227	224	227
500	36	63	159 *	81	81	80	296	298	352
600	95	179	3740	80	81	79	278	374	†
700	169	286	515	81	70	80‡	486	†	†
800	326	565	5930	80	†	†	†	†	†
900	6500	†	†	†	†	†	†	†	†
Dry air									
500	35			83			363		
600	63			84			232		
700	160 *			83			525		
800	287			86			900		
900	2170			—			—		

* This line indicates recommended heating limits for working in air
† Indeterminate because of heavy oxide
‡ Base metal after flaking off oxide.

weight and became brittle when heated at 300 to 600° C in air. A specimen heated at 600° C for four days gained 10 per cent in weight and became very brittle.

E. T. Hayes and A. H. Roberson[26] heated degreased graphite melted Kroll zirconium in air with a relative humidity of approximately 25 per cent at room temperature as well as with dry air. The gain in weight and hardness of the zirconium after treatment are shown in *Table LXXI* and the results are shown graphically with those from oxygen and nitrogen in *Figure 58.*

No evidence was found of oxygen or nitrogen penetration into the body of the metal in samples heated below 700° C. Short term exposures of less than one hour at 800° C did not show penetration but specimens exposed for one hour and longer showed the intergranular rods and coarsened grain boundaries found in the oxygen series. Diffusion was rapid at 900° C and it is assumed that the sudden vulnerability to oxygen penetration can be ascribed to the change in volume associated with the allotropic transformation.

The coatings produced were bluish-black and strongly adherent up to 600° C. White spots of oxide accompanied by scaling appeared at this temperature and increased steadily until the specimen was almost completely white after 24 hours at 700° C, four hours at 800° C or a few minutes at 900° C. The surface of specimens heated at 800 and 900° C had an 'off-white with a yellow cast' appearance, but x-ray and chemical analyses failed to show the presence of nitride. The specimen heated for one hour at 900° C in moist air increased in dimensions by 15 to 18 per cent; similar specimens heated in dry air increased by 8 to 10 per cent.

Hayes and Roberson observed the character of the oxide formed by heating nitride surfaces in air, and the effect of limited amounts of water vapour, and considered that both nitrogen and water vapour contribute to the production of the voluminous deposits formed at high temperatures in air. The nature of the decomposition products formed when zirconium nitride is heated in air indicates that nitrogen had more effect than 30 per cent relative humidity in producing spalling. These authors also considered that the metal undergoes simultaneous attack by both oxygen and nitrogen when heated in air, the nitride subsequently reacting with oxygen to form the voluminous white oxide.

Suggested upper limits of time and temperature for heating the metal in air are as follows: 24 hours at 500° C, four hours at 700° C and not more than a few minutes above 800° C.

Kroll graphite melted zirconium is usually considered to be less resistant to attack by hot air than iodide crystal bar metal. F. W. Boulger[5] in *Figure 64* compares the results obtained with the two types of metal. He suggests that the differences may be no greater than experimental errors.

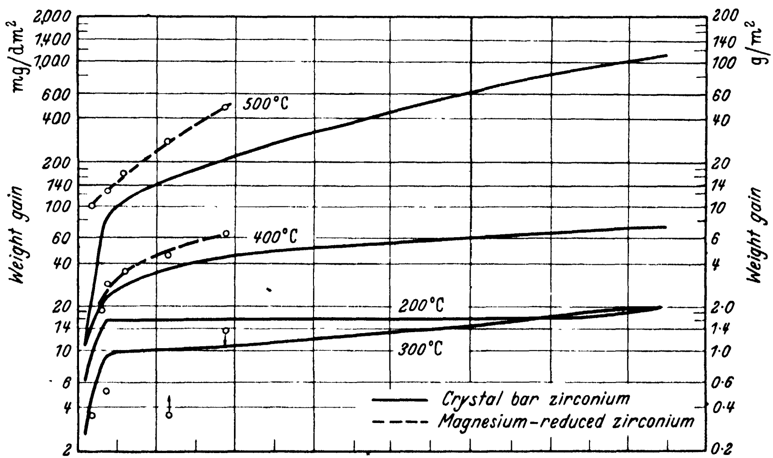

Figure 64. Weight gained by zirconium samples heated in air at various temperatures (*after* F. W. Boulger[5])

A relatively higher scaling rate of zirconium in air as compared with that of zirconium in oxygen or nitrogen is reported by C. A. PHALNIKAR and W. M. BALDWIN[36a]. Both oxygen and nitrogen enter into the scaling reaction. Given sufficient time zirconium forms a double-layered scale: an outer white or buff scale (monoclinic ZrO_2) that predominates at temperatures below 1050° C and an inner black scale (monoclinic and tetragonal ZrO_2, and cubic ZrN) that occupies the greater thickness at temperatures above 1050° C. The outer white layer does not form immediately, but requires time to nucleate. This time is as high as 100 hours near 400° C and less than 5 minutes at 1300° C. The appearance of the white scale layer coincides with an enormous increase in scaling rate at low temperatures, but not at high temperatures.

Phalnikar and Baldwin also report extraordinary dimensional changes during scaling. Increases in dimensions in the rolling plane trebled the original sample area in some cases. The phenomenon did not set in immediately on heating, but also required a definite time to commence. These times were, in general, much greater than those required to nucleate the white outer scale layer, except in the temperature range 850 to 1050° C where the two times coincided.

12.7. REACTION WITH SULPHUR DIOXIDE

The reaction of sulphur dioxide with degreased graphite melted Kroll zirconium was studied by E. T. HAYES, A. H. ROBERSON and R. H. ROBERTSON[25]. A slight reaction occurred at 500° C but at 600° C the reaction was very vigorous. The weight gains are shown in *Table LXXII.*

Table LXXII. Weight Gain of Zirconium heated in Sulphur Dioxide

Temperature °C	*Weight gain* mg/dm^2	
	1 h	24 h
400	—	1·1
500	20	40
600	4000	*Decomposed*
700	5500	*Decomposed*

In contrast to the other zirconium–gas systems investigated a well-defined critical temperature was established between 500 and 600° C. Samples heated at 600° C decomposed rapidly to a voluminous oxide powder containing both tetragonal and monoclinic oxides of zirconium. Free sulphur was deposited in the cool parts of the apparatus.

12.8. REACTION WITH AMMONIA

Ammonia reacts with zirconium at temperatures near 1000° C to form Zr_3N_2 but there is little or no reaction at lower temperatures[29].

12.9. REACTION WITH THE HALOGENS

Zirconium reacts readily with all the halogens at moderate temperatures (200 to 400° C) to form volatile tetrahalides[29].

Under certain conditions, the less volatile dihalides, which offer some protection to attack, may be formed. This is particularly true in the reaction with iodine over the stated temperature range. At temperatures above 500 to 600° C the di-iodide is sufficiently volatile to prevent the formation of an effective protective film.

The reactivity of the halogens towards zirconium decreases with increasing atomic number, hence the iodides are the least stable of the zirconium halides.

12.10. REACTION WITH PROPANE

E. T. HAYES, A. H. ROBERSON and R. H. ROBERTSON[25] heated Kroll graphite melted zirconium metal in propane at temperatures between 500 and 1000° C. *Table LXXIII* and *Figure 54* (shown in Section 12.1.) show the weight gains for the specimens used in the test. Weight gains up to 800° C are due to hydrogen absorption, with the drop around 900° C caused by the decomposition of the hydride. Above 900° C the increase in weight is due to both hydride and carbide formation.

Table LXXIII. Weight Gains of Zirconium Sheet heated in Propane

Temperature °C	*Weight gain* mg/dm^2	
	1 h	24 h
500	15	—
600	39	—
700	50	193
800	85	760
900	143	420
1000	205	2080

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13

CHEMICAL AND CORROSION RESISTING PROPERTIES

13.1. CORROSION BY LIQUIDS

THE corrosion resistance of zirconium is affected by its purity and the type of surface film present, but generally its resistance is very good. Its resistance to corrosion by alkalis is noteworthy, being better than that of tantalum, titanium or 18–8 stainless steel. The resistance of zirconium to acid corrosion is extremely good except for hydrofluoric acid, very concentrated sulphuric and phosphoric acids.

Resistance to hydrochloric acid is only bettered by tantalum and the precious metals.

Little attack occurs with sulphuric acid solutions below 70 per cent concentration but, above this, attack increases rapidly with rising concentration. The resistance to nitric acid is excellent, likewise organic acids have little effect. Behaviour in *aqua regia* is erratic, indicative of borderline passivity. An important factor may be purity as it has been reported that graphite melted metal dissolves readily but iodide crystal bar dissolves either slowly or not at all.

Preliminary tests indicate that zirconium has excellent resistance to marine corrosion.

During recent years many reports have been published on the corrosion resistance of zirconium. H. W. GILLETT[5] and W. M. RAYNOR[14] compared the corrosion resistance of zirconium and tantalum. E. A. GEE *et al.*[4] and L. B. GOLDEN *et al.*[7] investigated the corrosion resistance in many media. H. H. UHLIG's *Corrosion Handbook*[17] also contains data on corrosion resistance. R. I. JAFFEE and I. E. CAMPBELL[11] have amassed much data on the corrosion resistance of zirconium.

E. J. BRUMBAUGH[2] describes the effect of oxygen, nitrogen, carbon and hafnium on the corrosion resistance of zirconium in acids and gases. D. F. TAYLOR[16] compared the relative resistances of tantalum, niobium, zirconium and titanium to the common mineral acids. W. L. WILLIAMS[19] describes the effect of sea-water on titanium and zirconium at normal temperatures.

W. M. RAYNOR[15] refers to the excellent corrosion resistance of zirconium to hot concentrated caustic solutions as well as to acids.

W. H. WAGGAMAN and E. A. GEE[18] state that zirconium appears equal to tantalum in corrosion resistance to concentrated mineral

Table LXXIX. U.S. Bureau of Mines Data on the Corrosion of Graphite Melted Sponge Zirconium in Hydrochloric Acid—6-day *Tests*

Acid concentration wt per cent	*Corrosion rate* mil/year					
	Air-saturated			*Non-aerated*		
	35° C	60° C	100° C	35° C	60° C	100° C
1	—	—	—	0·02	0·04	0·03
5	—	0·06	0·09	<0·01	0·07	0·01
10	—	0·41	0·10	0·06	0·10	0·06
15	—	0·37	0·58	0·08	0·11	0·06
20	—	0·52	0·69	0·07	0·10	0·05
37	—	—	—	3·02	39·0*	—

* Sealed in glass tube under pressure.
1 mil=0·001 in

Table LXXX. U.S. Bureau of Mines Data on the Corrosion of Graphite Melted Sponge Zirconium in Sulphuric Acid—6-day *Tests*

Acid concentration wt per cent	*Corrosion rate* mil/year			
	Air-saturated			*Nitrogen-saturated*
	35° C	60° C	100° C	35° C
10	0·05	—	—	0·11
20	0·08	—	—	0·17
30	0·34	—	—	0·15
40	0·41	—	—	0·12
50	0·37	—	0·51	0·09
60	0·42	—	0·60	0·08
70	0·34	0·53	0·76	0·07
75	1·11	3·7	21·6	—
80	56·3	210	—	0·41
82·5	242	5500*	—	11·6
85	865	3060†	—	303·0
90	1620	—	—	—
96·5	752	1707	—	—
104·5	98·5	—	—	—

* 1-day test † 2-day test

acids and has the advantage of being lighter in weight, more plentiful in nature and cheaper to produce. G. E. Evans[3] discusses the possibilities of titanium, zirconium and beryllium as constructional materials for nuclear reactors.

The most recent work on the corrosion resistance of zirconium is by L. B. Golden[6]. He refers to most of the earlier work on the corrosion resistance of zirconium and describes his own investigations with induction graphite melted zirconium and arc melted metal using zirconium with 2 to 2·5 per cent and less than 0·1 per cent hafnium.

The resistance to specific agents in laboratory tests by various investigators are shown in *Tables LXXIX* to *LXXXVII*[11]. It will be noticed that most of these apply to graphite melted zirconium sponge. *Table LXXXVII* is included to give a comparison with iodide crystal bar metal but as the conditions of the tests are not given it is wrong to attempt an accurate comparison.

Table LXXXI. U.S. Bureau of Mines Data on the Corrosion of Graphite Melted Sponge Zirconium in Nitric Acid—6-day *Tests*

Acid concentration wt per cent	*Average corrosion rate* mil/year*				
	Room	35° C	60° C	100° C	*Boiling*
10 . . .	—	0·01	—	—	—
20 . . .	—	0·01	—	—	—
30 . . .	—	0·02	—	—	—
40 . . .	—	—	—	—	—
50 . . .	—	0·87	—	1·68	—
60 . . .	—	0·83	0·01	—	—
69·5 . . .	—	0·69	—	—	—
70·4 . . .	—	—	0·03	—	0·33
95 (*white fuming*) .	0·02	—	—	—	—
92 + 6·5 per cent NO_2 (*red fuming*)	0·05†	—	—	—	—

* In aerated solutions where applicable.

† 30-day test gave value of +0·61 mil/year.

The effect of oxygen, nitrogen, carbon and hafnium on the corrosion resistance of zirconium has been studied by E. J. Brumbaugh[2]. The tests were conducted under quiescent conditions, *i.e.* without stirring or aeration of solutions and at a temperature of 35° C. All samples were prepared from iodide crystal bar. Alloys were prepared by adding master alloys of oxygen or nitrogen and zirconium, or lampblack, to the zirconium melt.

Table LXXXII. U.S. Bureau of Mines Data on the Corrosion of Graphite Melted Sponge Zirconium in Mixed Sulphuric and Nitric Acids—6-day *Tests*

Acid concentration wt per cent		*Average corrosion rate* mil/year		
		Aerated	*Non-aerated*	
H_2SO_4	HNO_3	35° C	35° C	60° C
1	99	—	—	0·00
2·5	92·5	—	—	0·00
5	95	—	—	0·00
10	90	—	—	0·00
20	80	—	—	25·2
25	75	—	—	50·0
30	70	—	—	49·0
35	65	—	—	55·2
40	60	—	0·00	9·05
45	55	—	0·71	8·10
50	50	0·0	0·63	28·6
55	45	—	6·20	19·3
60	40	—	70·4	280
65	35	—	245	695
70	30	—	614	—
75	25	458	261	—
80	20	—	256	—
85	15	448	397	—
90	10	447	420	—
95	5	—	620	—
97·5	2·5	—	1930	—
99	1	—	2780	—
100	0	—	925	—

Table LXXXIII. U.S. Bureau of Mines Data on the Corrosion of Graphite Melted Sponge Zirconium in Phosphoric Acid—6-day *Tests*

Acid concentration wt per cent	*Average corrosion rate* mil/year *aerated solutions*			*Acid concentration* wt per cent	*Average corrosion rate* mil/year *aerated solutions*		
	35° C	60° C	100° C		35° C	60° C	100° C
5	—	—	0·03	60	0·49	0·46	3·84
10	0·05	—	0·21	65	—	—	7·37
20	0·23	—	0·63	70	0·53	—	9.27
30	0·37	—	0·86	75	—	0·74	18·0
40	0·44	—	1·16	80	0·56	—	24·8
50	0·49	0·46	1·68	85	0·05	1·56	43·3
55	—	—	2·38				

Table LXXXIV. U.S. Bureau of Mines Data on the Corrosion of Graphite Melted Sponge Zirconium in Organic Acids—6-day *Tests in Aerated Solutions*

Acid concentration wt per cent	*Average corrosion rate* mil/year								
	Acetic acid		*Formic acid*				*Citric acid*		
	60° C	100° C	35° C	60° C	100° C	*Boiling*	35° C	60° C	100° C
1	—	—	—	—	—	—	—	—	—
5	—	0·00	—	—	—	—	—	—	—
10	—	—	0·04	0·00	0·02	0·00	0·00	0·04	0·00
25	—	0·00	0·05	0·00	0·02	0·09	0·00	0·09	0·00
50	—	0·03	0·03*	0·00‡	0·00	0·19	0·23	0·06	0·06‖
75	0·00	0·03	—	—	—	—	—	—	—
85	—	—	—	—	—	—	—	—	—
90	—	—	0·12†	0·04§	0·05	0·16	—	—	—
99·5	—	0·00	—	—	—	—	—	—	—

Acid concentration wt per cent	*Oxalic acid*			*Lactic acid*				*Tartaric acid*		
	35° C	60° C	100° C	35° C	60° C	100° C	*Boiling*	35° C	60° C	100° C
1	0·13	0·20	0·25	—	—	—	—	—	—	—
5	0·29	0·30	0·28	—	—	—	—	—	—	—
10	0·48	0·66	0·51	0·00	0·00	—	0·01	0·00	0·00	0·04
25	—	0·24	0·29	0·03	0·02	0·00	—	0·00	0·00	0·05
50	—	—	—	0·00	0·00	0·07¶	0·00	—	0·00	—
75	—	—	—	—	0·00	—	—	—	—	—
85	—	—	—	0·00	—	—	0·04	—	—	—
90	—	—	—	—	—	—	—	—	—	—
99·5	—	—	—	—	—	—	—	—	—	—

* 0·017 non-aerated
† 0·24 non-aerated
‡ 0·07 non-aerated
§ 0·00 non-aerated
‖ Boiling
¶ Non-aerated

The specimens were carefully degreased and immersed in the corrosive media for a period of two weeks. *Table LXXXVIII* shows the composition of the samples tested and *Table LXXXIX* shows the corrosion results[2].

The results are expressed in both mg/dm²/day and mil/year. The results, with few exceptions, are in agreement with those of other investigators[4, 9, 10, 16].

Brumbaugh reports that only a slight difference in corrosion resistance was detected between arc melted iodide zirconium (specimen No. *1*) and cold rolled iodide metal (specimens *2* and *3*) and concluded that arc melting in argon did not affect the corrosion

Table LXXXV. U.S. Bureau of Mines Data on the Corrosion of Graphite Melted Sponge Zirconium in Inorganic Salt Solutions—6-day *Tests in Aerated Solutions*

Average corrosion rate mil/year

Salt solution wt per cent	$FeCl_3$			$HgCl_2$			$CuCl_2$			$CaCl_2$			$AlCl_3$			$ZnCl_3$		
	35° C	60° C	100° C	35° C	60° C	100° C	35° C	60° C	100° C	35° C	60° C	100° C	35° C	60° C	100° C	35° C	60° C	100° C
1	0·10	0·19	0·35	0·00	—	0·00	0·19	0·91	17·5	—	—	—	—	—	—	—	—	—
2·5	0·30	0·44	2·27	—	—	—	5·42	41·8	149·0	—	—	—	—	—	—	—	—	—
5	1·04	0·67	30·7	0·07	0·00	0·00	4·65	18·2	167·0	0·06	0·03	0·01	0·00	0·01	0·02	0·01	0·08	0·04
7·5	—	—	—	—	—	—	16·1	—	—	—	—	—	—	—	—	—	—	—
10	3·90	5·42	14·5†	—	0·00	0·00	19·2	—	—	0·00	0·00	0·00	0·00	0·00	0·00	—	—	—
12·5	—	—	—	—	—	—	397	—	—	—	—	—	—	—	—	—	—	—
15	14·0	27·0	(*)	—	—	—	670	—	—	—	—	—	—	—	—	—	—	—
17·5	—	319	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
20	27·2	462	—	—	—	—	(*)	—	—	—	—	—	—	—	—	0·05	0·00	0·00
25	498	—	—	—	—	—	—	—	—	—	—	0·02	0·00	0·00	0·24	—	—	—
30	(*)	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
42	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Saturated	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

Salt solution wt per cent	$MgCl_2$			$BaCl_2$			$SnCl_4$			$MnCl_2$			$NiCl_2$			$FeCl_3 + 10\%$ NaCl			NaCl†		
	35° C	60° C	100° C	35° C	60° C	100° C	35° C	60° C	100° C	35° C	60° C	100° C	35° C	60° C	100° C	35° C	60° C	100° C	35° C	60° C	100° C
1	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
2·5	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
5	0·02	0·00	0·00	0·02	0·02	0·05	0·09	0·1	0·00	0·05	0·00	0·05	0·01	0·00	0·12	5·98	2·34	1·33	0·00	0·03	—
7·5	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
10	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	0·06
12·5	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
15	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
17·5	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
20	0·15	0·00	0·08	0·04	0·00	0·07	—	—	—	0·05	0·00	0·09	0·04	0·00	0·00	—	—	—	—	—	—
25	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
30	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
42	—	—	0·00	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Saturated	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	0·00	0·02	0·02

* Completely embrittled.

† 10 per cent boiling—433 mil/year.

Table LXXXVI. Corrosion Resistance of Graphite Melted Zirconium in Various Media

Reagent	*Corrosion resistance*
H_2SO_3	*Excellent* at room temperature*
Aqua regia	*Iodide metal not attacked; graphite melted sponge rapidly attacked*
NaOH *solution* 10 *to* 50 per cent.	*Excellent at room temperature to* 100° C
NaOH *fused*	*Excellent*
Water-saturated chlorine	*Poor at room temperature*
Chlorine-saturated water	
Na_3PO_4 5 *to* 20 per cent	*Excellent at room temperature*
Acetic anhydride	*Excellent at* 139·6° C
NH_4OH 28 per cent	*Excellent at room temperature to* 100° C
Chromic acid 30 per cent	*Excellent at* 20 *to* 100° C
Hydrogen peroxide 10 per cent	*Excellent at* 50° C
KOH 10 *to* 40 per cent	*Excellent at room temperature to* 100° C
KOH *fused*	*Slight attack*
KNO_3 *fused*	*Poor*
Mercuric chloride	*Excellent*
Aluminium sulphate	*Excellent*
Ammonium sulphate	*Excellent*

* Excellent = less than 0·5 mil/year

Table LXXXVII. Corrosion Data on Crystal Bar Zirconium in Various Media— 14-day *Tests Except where Noted*

Media	*Concentration*	*Average corrosion rate* mil/year	
		20° C	100° C
HCl	5 per cent	*No attack*	*No attack*
	Concentrated	0·1	0·2
H_2SO_4	10 per cent	0·2	0·7
	Concentrated	—	*Attacked*
HNO_3	10 per cent	0·01	0·03
	Concentrated	0·01	0·05
Aqua regia	—	*Slow attack*	*Attacked*
HF	—	*Rapid attack*	—
H_3PO_4	10 per cent	0·02	0·05
	Concentrated	0·04	*Attacked*
NaOH*	10 per cent	*No attack* †	0·02 †
"	50 per cent	—	0·17 †
KOH	10 per cent	0·02	*No attack*
NH_4OH	28 per cent	0·03	*Gained weight*
Chlorine water	—	*Attacked*	*Embrittled*
$FeCl_3$ *solution*	—	*Attacked*	*Embrittled*
NaCl	20 per cent	—	*Slight tarnish* ‡

* In fused NaOH—no attack † 4 days ‡ 5 days

Table LXXXVIII. Oxygen, Nitrogen, and Carbon Analyses of Zirconium used in Corrosion Tests

Specimen No.	*Intended composition or physical treatment*	*Actual composition** per cent		
		Oxygen	*Nitrogen*	*Carbon*
1	*Arc melted* . .	0·263	0·011	0·170†
2	*Cold rolled* . .	0·416	0·007	0·000
3	*Cold rolled* . .	0·289	0·006	0·000
4	0·1 per cent *oxygen* .	0·286	0·008	0·022
5	0·3 per cent *oxygen* .	0·660	0·014	0·000
6	0·05 per cent *nitrogen* .	0·123	0·062	0·044
7	0·28 per cent *nitrogen* .	0·371	0·219	0·000
8	0·1 per cent *carbon* .	0·122	0·009	0·000
9	0·3 per cent *carbon* .	0·234	0·009	0·077
10	*Standard*‡ . .	0·071	0·000	0·022

* Determined by analysis.

‡ Contained 2 to 3 per cent hafnium. All other specimens contained less than 0·1 per cent hafnium.

† This is probably incorrect, see text.

resistance of crystal bar. The oxygen content of all three specimens is very high and oddly enough the arc melted sample is the lowest of the three values, suggesting that Brumbaugh encountered the usual difficulty in obtaining reliable oxygen data.

The carbon value of 0·17 per cent for sample No. *1* is undoubtedly erroneous (a private communication from the Foote Mineral Company states that a tungsten electrode was used and while the value of 0·17 per cent carbon was reported, the sample showed considerable segregation), as Brumbaugh reported little difference in corrosion between this sample and Nos. *2* and *3*, which are carbon-free, whereas other samples, *e.g.* No. *9* (0·077 per cent carbon), did show the deleterious action of the presence of carbon.

The presence of more than one of the added elements in any specimen tended to obscure the effect of single contaminants, but Brumbaugh considered that there was sufficient evidence to indicate the relative effects of increasing the amounts of the elements. He concluded that the addition of small amounts of oxygen, nitrogen or carbon, to zirconium resulted in only slight lowering of the corrosion resistance of the metal to most media. With hydrochloric acid, however, the effect was quite pronounced.

Brumbaugh does not indicate what he means by small amounts of impurities but as far as carbon is concerned it must be about 0·05 per cent and this must be a critical value in view of the rapid corrosion of sample No. *9* with 0·077 per cent carbon.

Table LXXXIX. Effect of Oxygen, Nitrogen, Carbon and Hafnium on the Corrosion Resistance of Zirconium

Solution	*No. 6 low-hafnium zirconium*		*No. 9 low-hafnium zirconium*		*No. 10 standard-hafnium zirconium*		*No. 7 low-hafnium zirconium*		*No. 4 low-hafnium zirconium*		*No. 5 low-hafnium zirconium*	
	Corrosion		*Corrosion*		*Corrosion*		*Corrosion*		*Corrosion*		*Corrosion*	
	mg/dm^2/day	mil/year	mg/dm^2/day	mil/year	mg/dm^2/day	mil/year	mg/dm^2/day	mil/year	mg/dm^2/day	mil/year	mg/dm^2/day	mil/year
Sulphuric acid, concentrated .	*Soluble*	—	*Soluble*	—	*Soluble*	—	*Soluble*	—	*Soluble*	—	*Soluble*	—
Sulphuric acid, 10 per cent .	*Gained* 0·4	—	*Gained* 0·4	—	0·5	0·11	0·17	0·036	*Gained* 0·1	—	0·78	0·18
Hydrochloric acid, concentrated .	94	21	1069	240	107	24	1339	300	83	17	54	12
Hydrochloric acid, 10 per cent .	*Gained* 0·5	—	*Gained* 0·4	—	0·28	0·061	0·44	0·097	0·056	0·013	1·2	0·26
Nitric acid, concentrated . .	*Gained* 0·4	—	*Gained* 0·3	—	11	2·5	0·055	0·012	0·22	0·05	0·17	0·036
Nitric acid, 10 per cent. .	*Gained* 0·2	—	*Gained* 0·1	—	0·22	0·05	*No change*	—	*Gained* 0·2	—	*No change*	—
Sodium hydroxide, 50 per cent.	*Gained* 0·1	—	*Gained* 0·4	—	0·44	0·1	0·28	0·061	0·11	0·025	0·33	0·074
Sodium hydroxide, 10 per cent.	*Gained* 1·0	—	*Gained* 0·5	—	0·22	0·05	*Gained* 0·6	—	*No change*	—	0·22	0·05
Sodium chloride, 20 per cent .	*Gained* 0·8	—	*Gained* 0·5	—	0·11	0·025	*Gained* 0·5	—	*Gained* 0·1	—	0·44	0·1
Hydrochloric acid–nitric acid 1 : 1	*Slowly attacked*	—	*Slowly attacked*	—	*Slowly attacked*	—	*Slowly attacked*	—	*Slowly attacked*	—	*Slowly attacked*	—
Hydrochloric acid–sulphuric acid 1 : 1.	0·21	0·046	0·07	0·016	0·22	0·05	*Gained* 1·9	—	0·99	0·22	1·2	0·25
Sulphuric acid–nitric acid 1 : 1 .	705	0·16	670	150	1113	250	45·2	100	554	120	262	58
Nitric acid, fuming . .	*Gained* 12·1	—	*Gained* 10·3	—	*Gained* 59·7	—	*Gained* 5·6	—	*Gained* 3·9	—	*Gained* 59·5	—
Ammonia, 29·6 per cent* .	0·11	0·025	*Gained* 0·5	—	*Gained* 0·4	—	*Gained* 0·2	—	0·39	0·09	*Gained* 0·1	—

* At room temperature

Nitrogen increases attack more than equal amounts of oxygen or carbon, and oxygen appears to be the least harmful addition of the three.

L. B. GOLDEN[6] investigated the corrosion resistance of samples prepared by induction graphite melting and arc melting using zirconium containing 2 to 2·5 per cent hafnium and less than 0·1 per cent hafnium, referring to these metals by the misleading titles of 'normal' and 'high purity' metal respectively.

Induction graphite melted zirconium showed excellent resistance in all but the highest concentrations. It is almost completely resistant to attack by organic acids and by inorganic chloride solutions, but is embrittled by the ferric and cupric chloride solutions.

Arc melted zirconium which contained about 0·02 per cent carbon compared to about 0·2 per cent in the graphite melted metal was almost completely resistant to concentrated hydrochloric acid under pressure. Golden indicated an important point when he stated that the presence of ferric chloride or nitric acid had a very adverse effect on the corrosion resistance of zirconium to hydrochloric acid.

Golden's work on the zirconium alloys indicated that there was little hope of producing an alloy with a better corrosion resistance than *pure* zirconium but as this was difficult to produce, alloying additions might be employed to counteract the effect of some impurities. A typical example is the addition of niobium to zirconium containing carbon. A 3·7 per cent addition of niobium to induction graphite melted zirconium produced an alloy which practically withstood the action of concentrated hydrochloric acid under pressure. It is reported that an addition of 1·08 per cent tantalum failed to achieve the same purpose.

Alloying additions of tantalum, molybdenum, manganese and aluminium to zirconium produced metals which had good resistance to the attack of hydrochloric acid under pressure but, in general, increasing amounts of the alloying constituent caused a decrease in corrosion resistance of the alloys. However, it was found possible to increase greatly the corrosion resistance of other metals by large additions of zirconium, *e.g.* a titanium alloy containing 13·8 per cent zirconium prepared by graphite melting showed a 70-fold improvement in corrosion resistance in 5 per cent hydrochloric acid at 100° C. Zirconium additions to titanium also improved the resistance to sulphuric acid and phosphoric acid.

13.2. Corrosion Resistance of Zirconium and Zirconium Alloys in Concentrated Hydrochloric Acid at Elevated Temperatures

L. B. Golden *et al.*[8] described the results obtained with zirconium, zirconium alloys and tantalum exposed to the corrosive action of concentrated hydrochloric acid in sealed glass tubes at elevated temperatures and pressures.

The results of the tests with various samples of zirconium are shown in *Table XC*. The zirconium used was supplied by the U.S. Bureau of Mines, Albany, Oregon, and was presumably produced from Kroll zirconium sponge. Golden describes three types of zirconium used in the tests: (*i*) ordinary purity metal induction melted in graphite, (*ii*) high purity metal induction melted in graphite, and (*iii*) high purity metal arc melted in water-cooled copper crucibles with a tantalum-tipped electrode.

Two high purity zirconium alloys were also supplied, these contained 1·08 per cent tantalum and 3·07 per cent niobium respectively. These alloys were produced by melting the elemental metals in graphite crucibles by induction heating.

The terms 'ordinary' and 'high purity' refer to the hafnium content, as previously explained. Ordinary purity zirconium contains 2 to 2·5 per cent hafnium and the high purity metal contains less than 0·1 per cent hafnium.

A series of 103 binary alloys was also examined; these were produced by arc melting (tantalum electrode) pressed compacts of the metal powders in helium in water-cooled crucibles.

Table XC. Hydrochloric Acid Embrittlement of Zirconium Metal
(Specimen configuration: ½ in × 2 in × 0·040 in)

Sample	*Principal impurity*	Wt per cent	*Average corrosion rate* mil/year	
			60° C	100° C
Arc melted	C	0·022	0·30	0·13
Arc melted	C	0·024	0·09	0·08
Arc melted	C	0·022	0·17	0·11
Induction melted	C	0·195	164*	386*
Induction melted	C	0·223	14·0*	55·2*
Induction melted	C	0·103	68·8*	199*
Induction melted	Ta	1·08	8·15	—†
Induction melted	Nb	3·70	0·64	2·47
Powder metallurgy	Ta	99·9	0·03	0·06

* Badly embrittled † Embrittled and disintegrated

The results of the investigations were summarized as follows:

Corrosion rates for ordinary purity zirconium induction melted in graphite were determined in various concentrations of non-aerated and static hydrochloric acid at atmospheric pressure. Embrittlement occurred in one lot of the metal in a 6-day test in concentrated (37 per cent) hydrochloric acid, but not in a second lot exposed for 30 days. This has been attributed to differences in the purity of the separate lots of metal. Samples of high purity arc melted metal were almost completely resistant under these conditions. High purity zirconium induction melted in graphite was evenly etched but showed no signs of embrittlement.

Arc melted zirconium and commercial tantalum were almost completely resistant to concentrated hydrochloric acid under pressure at elevated temperatures, and neither showed signs of embrittlement. A zirconium–niobium alloy (induction melted) exhibited only shallow surface embrittlement in acid at 100° C. Ordinary purity induction melted (graphite crucible) zirconium was completely embrittled and disintegrated at 60° C.

Forty-six of a total of 103 arc melted binary zirconium alloys containing tantalum, molybdenum, silver, manganese, aluminium and chromium were resistant (*i.e.* corrosion rates were less than 4 mil/year) to concentrated hydrochloric acid at 60° C under pressure. After testing alloys containing tantalum, molybdenum, manganese and aluminium at 100° C, 22 of the 46 alloys tested were still resistant and showed few or no signs of embrittlement. In general, increasing amounts of the alloying constituent caused a decrease in the corrosion resistance of the alloys.

The results obtained with the zirconium alloys at high temperatures and pressures are shown in *Tables XCI* and *XCII.*

Tests were also made with arc melted and graphite melted zirconium in concentrated hydrochloric acid at room temperature. The tests, which were continued for 30 days, showed corrosion rates for the arc melted metal of less than 0·01 mil/year whereas the graphite melted metal was attacked at a rate of 0·38 to 0·49 mil/year, the attack being preferential on the insoluble carbide particles.

13.3. CORROSION BY WATER AT ELEVATED TEMPERATURES

F. W. BOULGER[1] in dealing with the corrosion in air and water, suggests that liquid or gaseous media might be used as coolants in nuclear power piles, thus explaining the interest in these particular corrosion agents. He indicates that the corrosion data in this particular field consist of a series of isolated observations on materials of undisclosed prior history and purity, and since corrosion tests are notoriously influenced by slight variations in purity, sample preparation and testing conditions, the observations should be considered qualitatively.

Table XCI. Corrosion Resistance of Arc Melted Zirconium Alloys in Hydrochloric Acid

(Tests at 60° C, 3 atmospheres; specimen configuration: 1 in × 0·5 in × 0·040 in)

Alloying element	Wt per cent	*Corrosion rate* mil/year	*Observations*
Ag	1	0·53	No visible signs of corrosion
Ag	1	0·26	
Ag	3	1·32	
Ag	3	0·48	
Ag	5	1·22	
Ag	5	6·80	
Ag	10	2·98	
Ag	10	5·20	
Ni	1	0·64	
Ni	1	0·53	
Al	1	0·21	
Al	1	0·16	
Al	2	0·16	Covered with very thin varicoloured film
Al	2	0·32	
Al	3	21·3	Dulled (tarnished); no signs of embrittlement
Al	3	2·17	
Si	1	3·62	Small, irregular shaped, shallow patches of embrittled metal
Si	1	2·45	
Si	2	11·5	
Si	2	14·0	
Si	3	9·03	
Si	3	7·97	
Ni	3	12·4	
Ni	3	11·1	
Ni	5	68·5	
Ni	5	70·2	
Ni	8	93·0*	
Ni	8	116*	
W	1	55·2	Covered with thin film of embrittled metal with patches of more deeply embrittled metal
W	1	47·6	
W	5	41·9	
W	5	40·2	
W	10	52·3	
W	10	70·6	
Mo	1	0·32	No visible signs of corrosion
Mo	1	0·32	
Mo	3	1·01	Dulled (tarnished); no signs of embrittlement
Mo	3	0·64	
Mo	5	1·06	
Mo	5	0·95	
Mo	10	2·82	
Mo	10	1·38	
Sb	1	0·26	No visible signs of corrosion
Sb	3	1·96	
Sb	3	1·54	
Sb	5	13·8	
Sb	5	11·9	
Fe	1	1·11	
Fe	1	1·22	
Fe	3	5·88	
Fe	3	9·00	
Fe	5	35·7	Areas on one side where shallow embrittlement was present
Fe	5	40·1	No visible signs of corrosion
Cu	1	1·06	
Cu	1	1·33	
Cu	3	96·3	
Cu	3	136	Darkened areas on one side; no embrittlement
Cu	5	12·2*	No visible signs of corrosion
Cu	5	21·2*	
Cu	7	44·7*	Large areas of dulled metal on one side
Cu	7	37·5*	
Cu	10	68·6*	Surfaces slightly dulled
Cu	10	80·6*	
Mn	1	0·26	No visible signs of corrosion
Mn	1	0·32	
Mn	3	0·00	
Mn	3	0·37	
Mn	5	1·59	
Mn	5	1·27	
Mn	10	2·45	
Mn	10	4·15	
Co	1	4·30	No visible signs of corrosion
Co	1	24·0	
Co	3	38·3	Small, shallow areas of embrittlement
Co	3	50·2	
Co	5	195	Definite signs of embrittlement over entire surface
Co	5	292	
Co	7	274	Badly embrittled
Co	7	538	
Ta	5	0·00	No visible signs of corrosion
Ta	5	0·11	
Ta	10	0·00	
Ta	10	0·00	
Ta	15	0·21	
Ta	15	0·32	
Ce	1	0·58	
Ce	1	0·26	
Ce	2	5·30	
Ce	2	3·97	
Ce	3	41·1	Signs of general embrittlement
Ce	3	—	Completely disintegrated
Cr	1	0·32	No visible signs of corrosion
Cr	1	0·32	
Cr	2	0·26	
Cr	2	0·42	
Cr	5	3·55	
Cr	5	2·12	
Cr	8	25·2	Embrittlement in the form of evenly distributed flakes on the surface
Cr	8	20·2	
Be	1	15·6	Embrittlement cracks in which powdery, embrittled metal was present
Be	1	9·40	
Be	2	35·7	
Be	2	18·2	

* Run at room temperature and atmospheric pressure because of excessive gas evolution.

Table XCII. Corrosion Resistance of Arc Melted Zirconium Alloys in Hydrochloric Acid

(Tests at 100° C, 11 atmospheres; specimen configuration: 1 in × 0·5 in × 0·040 in)

Alloying element	Wt per cent	*Corrosion rate* mil/year	*Observations*
Ag	1	3·40	Badly embrittled; easily broken in the hand
Ag	1	4·19	
Ag	3	—	Completely embrittled and disintegrated
Ag	3	—	
Ag	5	54·7	Badly embrittled and easily broken in the hand
Ag	5	42·3	
Ag	10	105	
Ag	10	203	
Ni	1	0·42	No visible signs of corrosion
Ni	1	0·37	
Al	1	0·53	Surfaces covered with a varicoloured film
Al	1	0·37	
Al	2	1·05	
Al	2	1·48	
Al	3	29·6	Evenly corroded to a grey-black, pickled finish; no signs of embrittlement
Al	3	17·8	
Si	1	3·51	No visible signs of corrosion
Si	1	3·05	
Mo	1	0·21	
Mo	1	0·53	
Mo	5	0·11	Surfaces covered with a grey-black film
Mo	5	3·40	
Mo	10	6·35	Surfaces covered with very thin, iridescent, varicoloured film
Mo	10	4·61	
Sb	3	285	Badly embrittled and easily broken in the hand
Sb	3	92·0	
Fe	1	1·59	No visible signs of corrosion
Fe	1	1·11	
Cu	1	4·13	
Cu	1	4·30	
Mn	1	0·53	
Mn	1	0·69	
Mn	3	0·53	
Mn	3	0·70	Sample snapped in two on bending by hand (embrittled)
Mn	5	1·59	No visible signs of corrosion
Mn	5	1·70	No visible signs of corrosion
Mn	10	1·43	
Mn	10	3·35	
Ta	5	0·42	
Ta	5	3·77	Surfaces covered with a grey film (some evidence of embrittlement)
Ta	10	0·32	Surfaces covered with a grey-black film
Ta	10	0·85	No visible signs of corrosion but some evidence of embrittlement
Ta	15	0·26	Surfaces coloured a smoky amber
Ta	15	0·42	
Ce	1	0·53	No visible signs of corrosion
Ce	1	0·48	

Iodide crystal bar specimens tested in distilled water at 100° C showed that beyond a slight gain in weight produced in the first 24 hours no further change occurred even after 1357 hours.

Samples heated in a steel autoclave with distilled water at 180° C showed no appreciable weight change in 129 hours except for the small initial gain. Later tests indicated that crystal bar zirconium maintained a fairly constant weight during 1613 hours exposure in water at 250° C while a companion sample of Kroll metal gained three to four times as much weight in only 213 hours. (Presumably the Kroll metal was graphite melted, as it appears to be the custom to compare as-deposited crystal bar with graphite melted sponge, instead of employing the more accurate comparison of applying the same melting treatment to crystal bar and sponge before comparing their properties.)

Static tests in autoclaves at 260° C and 700 lb/in^2 pressure, using test solutions of distilled water having a pH of 6·0 to 6·5, indicate that zirconium, suffering only minor changes in weight, is better than aluminium alloys and beryllium.

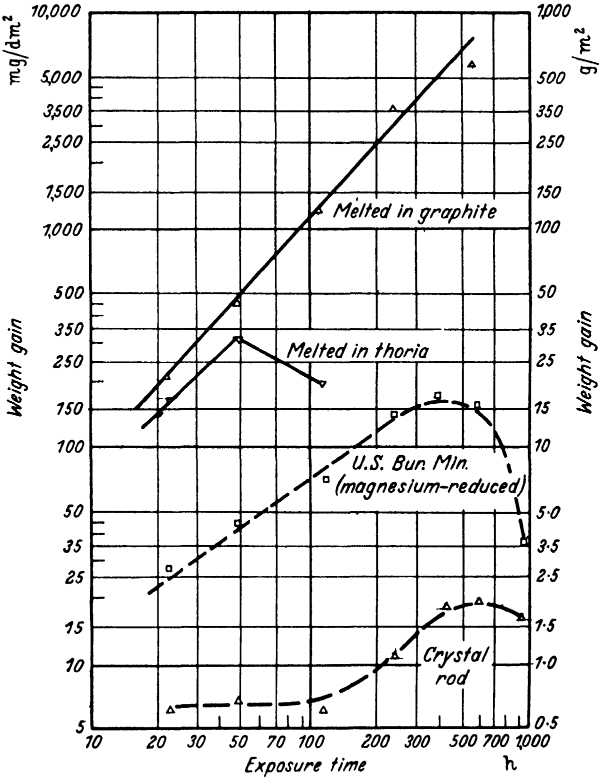

Figure 65. Corrosion data for static tests in distilled water at 300° C *on iodide and Kroll zirconium* (*after* F. W. Boulger[1])

More comprehensive tests have been made with distilled water in autoclaves at 300° C using various forms of zirconium[1]. The results are shown in *Figure 65.* The specimens were prepared by polishing with *0000* emery paper before testing, and the tests were made in triplicate. It is noticeable that the worst specimen was graphite melted iodide zirconium which confirms the point made above that it is wrong to compare metals produced by different processes which have received different treatments in the later stages of processing.

The samples of iodide metal melted in thoria crucibles, presumably by induction heating, also corroded rapidly and were cracked and distorted after 250 hours exposure. The U.S. Bureau of Mines specimen, which was in the form of a 'flat rectangle', was presumably produced from graphite melted Kroll sponge, this specimen gained weight slowly for 419 hours with the formation of an oxide coating which then came off in the water and the weight decreased until the tests were stopped after 925 hours.

The sample of crystal bar zirconium was the most satisfactory but it was uncertain if the sample had reached a constant weight at the end of the tests. The wide disparity in the results obtained for the graphite melted iodide and Kroll zirconium samples is surprising.

Very variable results have been reported for the corrosion resistance of iodide zirconium in water at elevated temperatures, and it has been so difficult to specify the purity of the zirconium for this work that it has been necessary to test each batch of zirconium in the autoclave before acceptance.

Iodide zirconium has very good resistance to distilled water, saturated with oxygen or hydrogen at 26° C in tests made at 315° C.

Dynamic corrosion tests made with iodide and Kroll zirconium in water for 163 hours at 250° C and 1250 lb/in^2 showed that iodide zirconium was more resistant than the Kroll metal. The water was moving at the rate of 43 ft/sec.

In a 500-hours erosion-corrosion test a zirconium specimen showed less corrosion than samples of 18–8 stainless steel, niobium,

Table XCIII. Resistance of Oxygen–Zirconium and Nitrogen–Zirconium Alloys to Water at 315° C

Oxygen series		*Nitrogen series*	
Oxygen content per cent	*Weight gain* mg/dm^2	*Nitrogen content* per cent	*Weight gain* mg/dm^2
0·041	153	0·013	600
0·044	129	0·061	313
0·059	150	0·079	227
0·073	121	0·080	474
0·105	131	0·091	1575
0·445	143	0·093	252
1·002	127	0·136	484
		0·144	318
Average	136·3	0·156	313
		0·408	248
		Average	480·4

beryllium, carbon steel and aluminium; the corrosion increasing in the order of the metals given.

F. B. Litton[13] compared the corrosion resistance of a number of zirconium alloys with that of zirconium. The alloys were tested in an autoclave at 315° C for two weeks. *Table XCIII* shows the results of tests with zirconium containing oxygen and nitrogen, and shows clearly that while the presence of oxygen has little effect, presence of nitrogen is very detrimental.

Zirconium alloys containing aluminium, tantalum and niobium were also tested by Litton under the same conditions, in an autoclave. The results in *Table XCIV* show that small concentrations of aluminium decreased the resistance to corrosion while tantalum and niobium had little effect.

Table XCIV. Resistance of Zirconium Containing Aluminium, Tantalum or Niobium to Water at 315° C

Aluminium series		*Tantalum series*		*Niobium series*	
Aluminium content per cent	*Weight gain** mg/dm^2	*Tantalum content* per cent	*Weight gain* mg/dm^2	*Niobium content* per cent	*Weight gain** mg/dm^2
Zr *base*	14·6	—	—	—	—
0·05 Al–Zr	203·5	0·25 Ta–Zr	16·3†	0·5 Nb–Zr	9·5
0·10 Al–Zr	394·0	1·5 Ta–Zr	*Weight loss* †	1·5 Nb–Zr	9·2
0·20 Al–Zr	696·0	7·0 Ta–Zr	51·1†	30·0 Nb–Zr	72·6
0·30 Al–Zr	*Severely attacked*	—	—	—	—

* 1-week test period † 2-week test period

13.4. CORROSION BY LIQUID METALS

F. W. Boulger[1] refers briefly to the work that has been done to determine the corrosion resistance of zirconium to low melting point metals and alloys.

When zirconium was heated at 600° C in contact with gallium the elements reacted completely to form a soft, friable, crystalline mass. The test period was from 2 to 12 days and the metals were in an inert atmosphere of argon. Other workers reported general attack by gallium at temperatures as low as 450° C.

A sample of zirconium (purity not indicated) showed a negligible gain in weight after being heated in liquid sodium–potassium for six days at 600° C. The container was made of nickel and the sodium–potassium which was probably the 50–50 alloy was of questionable purity.

The data given in the *Liquid-Metals Handbook*[12] and reproduced in *Table XCV* are based on information from several reports. The resistance to attack is rated as good, limited and poor for rates of attack of <1, >1 and <10, and >10 mil/year.

Table XCV. Corrosion of Zirconium by Liquid Metals

Liquid metal		Na, K Na–K	Li	Mg	Zn	Cd	Hg	Al	Ga
Melting point °C		- 12·3 *to* 98·3	186	651	419·5	321	- 38·8	660	29·8
Zirconium	800° C	*U*	*L*	*U*	*U*	*U*	*U*	*U*	*U*
	600° C	*G*	*L*	∨*P*	*U*	*U*	*P*	*U*	*P*
	300° C	*G*	*G*	*U*	*U*	*U*	*P*	*U*	*L*

Liquid metal		In	Tl	Sn	Pb	Bi–Pb	Bi-Pb–Sn	Sb	Bi
Melting point °C		156·4	303	231·9	327	125	97	630·5	271·3
Zirconium	800° C	*U*	*U*	*U*	*L*	*U*	*U*	*U*	*P*
	600° C	*U*	*U*	*U*	*L*	*L*	*L*	*U*	*P*
	300° C	*U*	*U*	*G*	∨*G*	*G*	*G*	*U*	*U*

U = Unknown *G* = Good *L* = Limited *P* = Poor

∨ + *U*, *G*, *L* or *P* = degree of resistance at the melting point.

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14

ALLOYS OF ZIRCONIUM

14.1. THEORETICAL CONSIDERATIONS

THE factors affecting the constitution of zirconium alloys were examined by P. C. L. PFEIL[59]. W. HUME-ROTHERY[37] has shown that if the atomic sizes of two elements, as defined by their interatomic distances in the crystals of the elements, differ by more than a critical amount of 14 to 15 per cent of the atomic size of the solvent, substitutional solid solution formation is restricted. The 'size factor' is then said to be unfavourable. Even if the size factor is favourable, *i.e.* within the ±15 per cent range, other effects may restrict the extent of solid solution formation; for example, if the two elements concerned have markedly different electrochemical characteristics, there will be a tendency to form intermediate phases at the expense of solid solutions.

In certain alloy systems comprised chiefly of elements of relatively low valency it has been established that, other things being equal, solutes of low valency tend to dissolve more of a higher valency element than the reverse. A deficit of electrons seems to lead to instability whereas, in the absence of Brillouin zone effects, an increase in the number of electrons leads to a relatively small increase in the average Fermi energy which is countered by an increase in the stability of the structure caused by increasing the number of cohesive electrons. The effect is termed the 'relative valency effect.' It is reasonable to postulate that for elements of higher valency, such as may be so for zirconium, a deficit of electrons will be much less serious than for elements of lower valency.

Where metals and intermetallic compounds crystallize in complex structures it has often been found that there is a Brillouin zone which can just accommodate all the valency electrons to give a decrease in the average Fermi energy. In the alloys with copper and silver as solvents the limits of solid solubility of many elements occur where the Fermi surface first touches the bounding planes comprising the first Brillouin zone. The form of the Brillouin zone has also been shown to be of importance in the alloying behaviour of certain other elements such as magnesium.

The above principles were deduced from a study of numerous alloy systems with copper, silver and gold as solvents, and with suitable modifications they have been shown to apply to several other solutes, particularly aluminium and magnesium. Before applying these principles to zirconium it is necessary to consider the electronic nature, crystal structure, and electrochemical characteristics of the metal.

14.2. APPLICATION OF ALLOYING THEORY TO ZIRCONIUM

The range of favourable size factors for solid solution formation is shown in *Figure 66*[59].

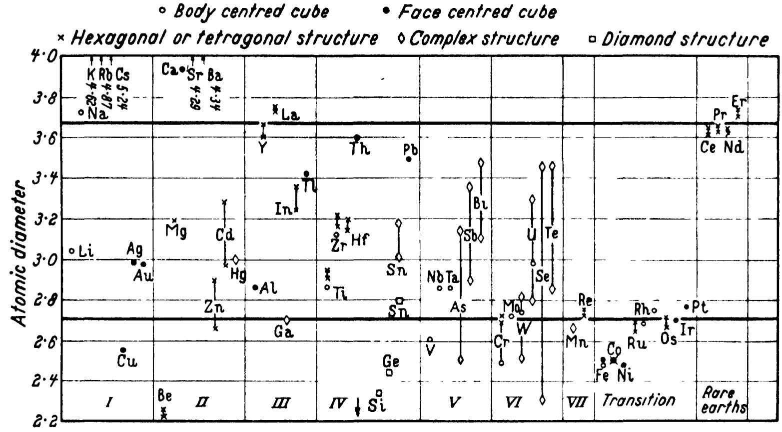


Figure 66. Range of favourable size factors for solid solution in zirconium (after P. C. L. PFEIL[59])

In the close packed hexagonal structure the effective atomic size as defined by the interatomic distance, is conventionally taken as the mean of the distance of the two sets of neighbours in those cases where the difference is small. The atomic size for alpha zirconium is therefore 3·2 Å. In the beta structure it is 3·13 Å though this value refers to 867° C. The volumes per atom in the alpha and beta structures at the same temperature being very similar, it is convenient in discussion to take the atomic size of zirconium as being the same in the two modifications. The range where favourable size factors exist will be taken as 3·19 Å ± 15 per cent, *i.e.* 2·71 to 3·67 Å. It is possible that even slight differences in the size factor with respect to the two modifications may be of significance in borderline cases.

Zirconium differs from most other metals the alloying behaviour of which has been examined in that the zirconium ion is much smaller than the atom. This factor is conveniently expressed by saying that the 'degree of fullness' of zirconium is appreciably less than that of the more familiar metals, and it may be of particular importance in alloys composed of metals of markedly different degrees of fullness.

14.2.1. *Comparison of atomic volumes of alpha and beta zirconium*

The mean volume per atom of the close packed hexagonal modification at room temperature is 23·04 kX^3, whereas the body centred cubic allotrope has a mean volume per atom of 25·52 kX^3, taking the lattice parameter at 867° C. The actual axial ratio of 1·589 compared with 1·633, the ideal for closest packing, increases the volume per atom to a value approaching that of the less closely packed body centred cubic structure.

For a proper comparison between the atomic volumes of alpha and beta zirconium they should be compared at the same temperature. Various experimenters[43, 69, 73] have reported widely different values for the thermal expansion of alpha zirconium. The most recent values have been determined by R. B. RUSSELL[64] by x-ray methods. Pfeil states that if Russell's values be adopted then the atomic volume of alpha zirconium is 23·7 kX^3 at 862° C which is close to 23·5 kX^3 for beta zirconium at 867° C. The atomic volumes of alpha and beta zirconium are therefore similar when compared at the same temperature.

14.2.2. *Variation of magnetic susceptibility, electrical resistivity and specific heat with temperature*

P. C. L. PFEIL[59] states that the variation of the physical properties of zirconium is of importance to the theory of zirconium alloys because clues may be obtained to the variation of the number of valency electrons with temperature. The variation of magnetic susceptibility (*Figure 33*), electrical resistivity (*Figure 31*) and specific heat (*Figure 30*) with temperature was measured by C. F. SQUIRE and A. R. KAUFMANN[73], on zirconium containing 0·11 per cent of iron. The presence of this impurity enforces some reserve on any conclusions drawn about the behaviour of pure zirconium.

The paramagnetic susceptibility increases linearly with temperature in the range 50 to 1000° K (*Figure 33*). The susceptibility then increases more rapidly up to 1140° K, the allotropic transformation temperature. In the body centred cubic phase the susceptibility decreases slowly with temperature in the range investigated. There are insufficient points at or near the transition temperature to decide whether there is a discontinuity or not.

The electrical resistivity (*Figure 31*) increases linearly with temperature up to about 600° K after which the increase is much less rapid. The electrical resistivity of the beta phase is less than that of alpha at the same temperature, but in the temperature range investigated its rate of increase with temperature seems to be greater.

Figure 30 shows that the specific heat at constant pressure, C_p, reaches the Dulong and Petit value at about 600° K and continues to increase up to 7·3 cal/g-atom at 1100° K.

These results give no definite indication of any large change in valency in passing from alpha to beta zirconium. A possible explanation of the evidence in terms of the variation of Brillouin zone overlaps is suggested later.

14.2.3. *Electrochemical nature*

Since zirconium is strongly electropositive, many of the elements which on size factor grounds might form extensive solid solutions will tend to form stable intermetallic compounds instead. This is the behaviour to be expected with electronegative and weakly electropositive elements so that the number of elements which will form extensive solid solutions is greatly reduced.

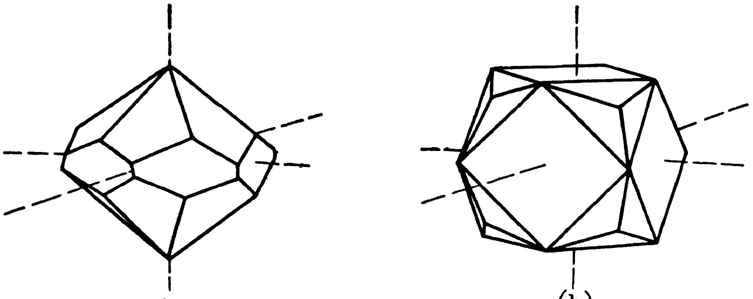
14.2.4. *Probable valency*

Zirconium has only four electrons outside the krypton-like core, so that it is difficult to see how the effective valency in the solid state can be greater than four; it may be less than four if a proportion of these electrons remain core electrons, *i.e.* if in the solid state zirconium is incompletely ionized.

Chemically, zirconium behaves as a quadrivalent element but divalent and trivalent compounds have been prepared[70] though these are relatively unstable. This evidence suggests that zirconium will probably behave as a quadrivalent element in the solid state.

There are indications which suggest that there is no appreciable change in the number of valency electrons between alpha and beta zirconium. First, the atomic volumes of alpha and beta zirconium are very similar. Secondly, there does not appear to be any discontinuity in the paramagnetic susceptibility greater than that which could be accounted for as due to the change in crystal structure at the transition from alpha to beta form.

It is not thought that the resistivity/temperature and susceptibility/temperature relationships of zirconium in the alpha range

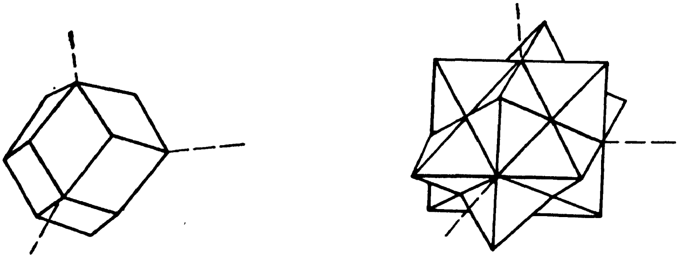


(a)

An outer Brillouin zone of close packed hexagonal structure (*after* R. L. BERRY *et al.*[6])

(b)

An outer zone for the body centred cubic structure (*after* R. L. BERRY *et al.*[6])

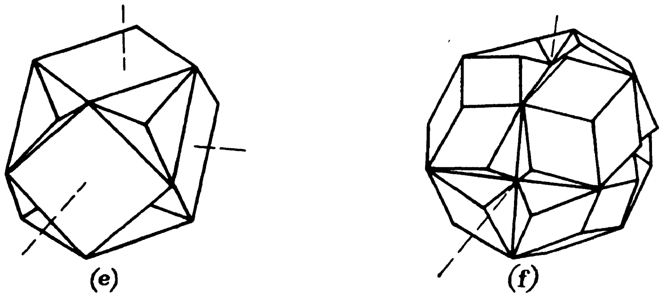


(c)

First zone (*after* J. F. NICHOLAS[53])

(d)

Second zone (*after* J. F. NICHOLAS[53])



(e)

Third zone (*after* J. F. NICHOLAS[53])

(f)

Fourth zone (*after* J. F. NICHOLAS[53])

Figure 67. Brillouin zone characteristics of alpha and beta zirconium

necessarily indicate that the effective valency of alpha zirconium changes with temperature.

14.2.5. *Brillouin zone characteristics of alpha and beta zirconium*

Although it is not clear that the Fermi energy term is the most important factor governing the relative stabilities of alternative structures in many important zirconium alloy systems, nevertheless, Brillouin zone considerations may be of significance. P. C. L. Pfeil[59] considers it is advisable to give considerable attention to the characteristics of the relevant Brillouin zones, to see which of the experimental observations on zirconium (and titanium) alloy systems can be interpreted on Brillouin zone and other previously recognized alloying factors.

Unless zirconium has a valency in the region of unity, it is the outer Brillouin zones which are of chief interest with regard to its alloying behaviour. The forms of the outer Brillouin zones of close packed hexagonal metals have been calculated by R. L. Berry, M. B. Waldron and G. V. Raynor[6] for titanium which has a closely similar axial ratio. The results have been confirmed by Pfeil and a closely similar situation shown to hold for zirconium. There are several possible zones outside the well-known inner ones bounded by $(1\bar{1}00)$, (0002) or by $(1\bar{1}00)$, (0002) and $(1\bar{1}01)$ planes but these culminate in the well-marked zone formed by a combination of $(10\bar{1}2)$ and $(11\bar{2}0)$ planes illustrated by *Figure 67* (a). In titanium this zone can contain 5·15 electrons per atom though the inscribed sphere to it can only hold 3·59 electrons per atom. For an axial ratio of 1·589, which is approximately that of alpha zirconium, the volume of this inscribed sphere becomes 3·60 electrons per atom. Berry *et al.* state that any overlap across the $(10\bar{1}2)$ faces would take place into a zone bounded by $(10\bar{1}3)$ and $(11\bar{2}0)$ planes, the inscribed sphere of which corresponds to 5·81 electrons per atom.

If alpha zirconium possesses four valency electrons per atom then it is likely that overlap will exist over the $(10\bar{1}2)$ faces but since the Fermi surface will probably be far from symmetrical it is not possible to make any estimate of the magnitude of the overlap. Some solid solubility may be shown by elements of valency less than four though a considerable reduction in the number of valency electrons might seriously weaken the cohesive forces holding the structure together. If the Brillouin zone at 4 electrons per atom shows an overlap across the $(10\bar{1}2)$ faces into the next zone then a reduction of the electron:atom ratio until the overlap is removed would give a larger decrease in the average Fermi energy than further reduction of the number of valency electrons by alloying. A change in the overlap of electrons across the $(10\bar{1}2)$ faces of the Brillouin zone may lead to a change in the axial ratio of the structure in accordance with the theory of H. Jones[39].

The accommodation of extra electrons in a Brillouin zone of this type with initially four electrons per atom will increase the overlap if one is already present or possibly give rise to an overlap if one is not in existence. In any case the average Fermi energy will increase, possibly at a rate greater than that given by the normal parabolic law.

The outer Brillouin zones for the body centred cubic structure have been discussed by F. Seitz[68], R. L. Berry, M. B. Waldron and G. V. Raynor[6] and by J. F. Nicholas[53]. The second zone given by Seitz does not appear to be significant since it involves planes of the type (111) for which the structure factor is zero in the body centred cubic lattice. According to Berry *et al.* the next outer zone surrounding the first zone bounded by (110) planes, is that formed by a combination of (200) and (211) planes to give the zone illustrated in *Figure 67* (b). The volume of this outer zone corresponds with seven electrons per atom and the inscribed sphere to it touches the (200) faces at an electron concentration of 4·189 per atom.

Nicholas has pointed out that a second zone can be formed by extending the (110) planes to give a volume which can contain four electrons per atom [*Figure 67* (c) and (d)]. (Here it may be noted that certain workers define the volume of an outer zone as the volume between the planes forming that zone and the planes forming the preceding zone, but here it is more convenient to use the alternative definition of the volume of the outer zones as including the whole volume enclosed by the planes forming the outer zone.) The volume of the inscribed sphere to the zone formed by extending the (110) planes corresponds to 2·72 electrons per atom.

The next zone described by Nicholas, which is illustrated by *Figure 67* (e), is formed from (200) and (110) planes, and its volume corresponds to six electrons per atom. The (110) planes make deep re-entrants to the same position as those where the inscribed sphere first touched the bounding faces of the preceding zone. The volume of the inscribed sphere corresponds to the same number of electrons as that for the previous zone, *i.e.* 2·72 electrons per atom. The metallurgical significance of this third zone is doubtful, because there is no obvious reason why in Nicholas's second zone overlap should not first take over those parts of the (110) faces which also form the re-entrants of the third zone, since they are closer to the origin of *k*-space.

The fourth zone described by Nicholas is formed from planes of the types (110) and (211). This zone has a volume corresponding to eight electrons per atom and the inscribed sphere first touches the bounding surfaces at 4·19 electrons per atom [*Figure 67* (f)].

These zones fulfil a condition that the volumes of the zones increase in the ratio 1:2:3:4. This condition is claimed to be a necessary characteristic of Brillouin zones[68], but its application to the electron energies in metals and alloys is uncertain. In non-cubic structures particularly, it is difficult to advance a plausible argument for the requirement. Nicholas criticizes the zone put forward by Berry, Waldron and Raynor on the ground that the volume suggested corresponds to seven electrons per atom, which is not an integral multiple of the number of electrons corresponding to the volume of the first zone of two per atom.

Whatever is the true position with regard to the details of the Brillouin zones, it seems probable that the existence of the (200) planes having a perpendicular distance from the origin of *k*-space equivalent to an electron:atom ratio of 4·189, will be of significance in the metallurgy of quadrivalent, body centred cubic metals. These elements can be expected to be tolerant of an increase in their average electron:atom ratio because an increase of the electron:atom ratio from 4·0 to approximately 4·19 is likely to cause a smaller than normal increase, or possibly a decrease, in the average Fermi energy. Further solubility may be possible before the electronic energy rises to prohibitive values.

The characteristics of the Brillouin zones of alpha and beta zirconium if they each have four electrons per atom are compared by P. C. L. PFEIL[59]. It seems that a small increase in the average number of electrons per atom could be accommodated better by the beta structure than by the alpha structure. The forecast of the probable effects of a small decrease in the average number of electrons is less certain but probably the alpha structure will be favoured, especially if with four electrons per atom there is an actual overlap across the $(10\bar{1}2)$ faces. Unfortunately, it is not readily possible to calculate the probable magnitude of the effects.

14.3. BINARY SYSTEMS

The published literature relating to zirconium alloys indicates that the purposes of the investigators were varied. Some workers produced and studied the properties of a number of zirconium rich alloys paying particular attention to their mechanical and corrosion resisting properties. Others produced a few alloys which they considered might have properties suitable for particular applications. Little attempt was made to determine constitutional diagrams until recently when extensive work has resulted in a number of the more important diagrams being established.

In view of the effect of impurities such as oxygen, nitrogen and carbon on zirconium it is desirable when considering the results of investigations to note the purity of the metal employed as well as the conditions used for the production of the alloys.

14.3.1. *Group I elements*

(a) *Zirconium–hydrogen*—Hydrogen dissolves readily in zirconium, the quantity dissolved depending on the temperature of the metal (see Section 12.1.). The transformation temperature of the metal is lowered by the absorbed hydrogen[38] so that the metal may be greatly undercooled without transition[71]. Zirconium hydride is stable *in vacuo* up to a temperature of about 440° C[29].

The crystal structure of zirconium hydride is a function of the hydrogen content[28]. Starting initially as hexagonal with constants $a = 3{\cdot}25$ Å and $c = 5{\cdot}17$ Å, it changes progressively to face centred cubic, close packed hexagonal, face centred cubic, and finally to face centred tetragonal of dimensions $a = 4{\cdot}964$ Å and $c = 4{\cdot}440$ Å which is the richest hydrogen phase.

(b) *Zirconium–copper*—This system like several others was studied by the Armour Research Foundation[3]. Most of the alloys investigated were prepared by melting zirconium and the alloying metal in a purified helium atmosphere in an arc furnace with a tungsten electrode. High purity crystal bar or iodide zirconium was used with the highest purity metals available. The charges were remelted four to eight times to ensure homogeneity.

Metallographic examination of specimens quenched after isothermal annealing was the principal means used to determine the diagrams.

In the presentation of the diagrams, Armour Research Foundation kept to the following rules regarding the intermediate phases:

(1) Solid lines are used when the composition of the phase is felt to be firmly established.
(2) Dashed lines are used when some displacement of the phase from the composition is deemed possible.
(3) The phase formula is followed by a question mark when there is another simple stoichiometric formula that might alternatively be selected.

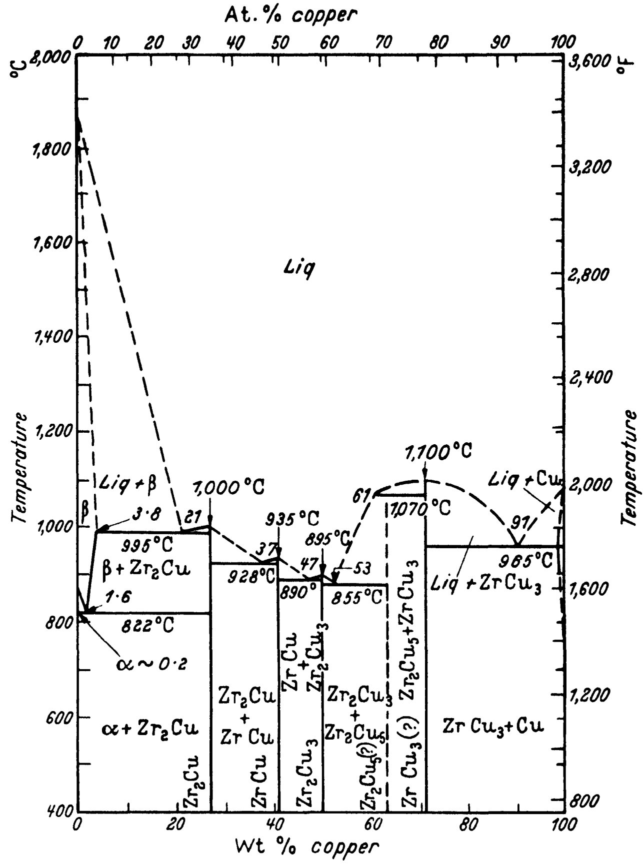


Figure 68. Zirconium–copper system (after C. E. LUNDIN *et al.*[46])

Some of the systems studied by the Armour Research Foundation have been published in the technical journals, such cases are noted as they occur.

The zirconium–copper system determined by C. E. LUNDIN *et al.*[46] is shown in *Figure 68. Figure 69* shows the zirconium rich portion.

There is general agreement between Lundin *et al.* and E. RAUB and M. ENGEL[61], authors of the latest and until now most complete investigation, on the nature of the system between $ZrCu_3$ and copper. Melting points of the intermediate phase $ZrCu_3$ and the eutectic $ZrCu_3$–Cu compare favourably.

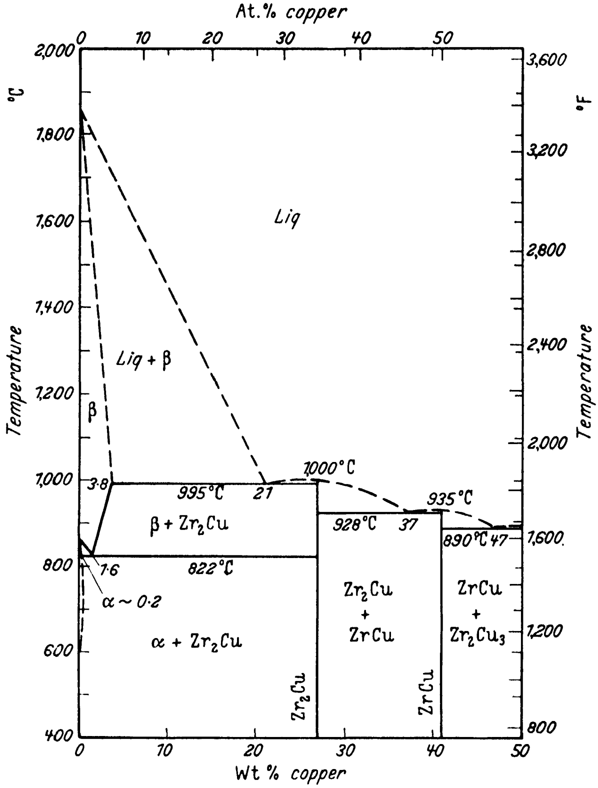


Figure 69. Partial diagram of zirconium–copper system (after C. E. LUNDIN *et al.*[46])

In the area on the zirconium side of $ZrCu_3$, Raub and Engel reported only a eutectic between $ZrCu_3$ and an unidentified zirconium rich phase. Lundin shows the existence of three intermediate phases ZrCu, $ZrCu_3$ and Zr_2Cu_5, the last named being peritectically formed, and three eutectics in this same region.

The principal features of the zirconium–copper system may be summarized as follows:

(*i*) The maximum solubility of copper in beta zirconium is 3·8 per cent at the eutectic temperature. The solubility of copper in alpha zirconium is less than 0·18 per cent at all temperatures. A eutectoid reaction occurs at 1·6 per cent copper and 822 ± 10° C.

(*ii*) A eutectic exists at 21 per cent copper and 995 ± 10° C, between zirconium and Zr_2Cu (25·83 per cent copper).

(*iii*) An intermediate phase is formed at about 27 per cent copper and 1000 ± 10° C, which probably corresponds to the formula Zr_2Cu (25·83 per cent copper).

(*iv*) A eutectic occurs at 37 per cent copper and 928 ± 10° C between Zr_2Cu and ZrCu (41·06 per cent copper).

(*v*) An intermetallic compound forms at 41 per cent copper and 935 ± 10° C, corresponding to the formula ZrCu (41·06 per cent copper).

(*vi*) A eutectic between ZrCu and Zr_2Cu_3 (51·09 per cent copper) exists at 47 per cent copper and 890 ± 10° C.

(*vii*) An intermetallic compound forms at 50 per cent copper and 895 ± 10° C, corresponding to the formula Zr_2Cu_3 (51·09 per cent copper).

(*viii*) A eutectic between Zr_2Cu_3 and Zr_2Cu_5 (tentative, 63·52 per cent copper) occurs at 53 per cent copper and 885 ± 10° C.

(*ix*) The intermediate phase designated Zr_2Cu_5 is formed peritectically by a reaction between the melt containing 61 per cent copper and $ZrCu_3$ (tentative, 67·63 per cent copper) at 1070 ± 10° C.

(*x*) An intermediate phase exists at about 71·5 per cent copper and melts at 1100 ± 10° C. The formula $ZrCu_3$ (67·63 per cent copper) has been tentatively accepted for this phase on a basis of previous literature.

(*xi*) A eutectic between $ZrCu_3$ and copper exists at 91 per cent copper and 965 ± 10° C.

(*xii*) The solubility of zirconium in copper is very limited. Previous investigators, although in disagreement on exact values, agree that the solubility is less than 1 per cent zirconium.

The allotropic transformation temperature ($\alpha \rightleftharpoons \beta$) is decreased from 862 to 822° C by increasing amounts of copper. Thus, a eutectoid reaction, $\beta \rightleftharpoons \alpha + Zr_2Cu$, occurs at a composition of about 1·6 per cent copper.

The phase Zr_2Cu has the face centred tetragonal type of structure with parameters $c = 3{\cdot}716$ Å, $a = 4{\cdot}536$ Å, $c/a = 0{\cdot}819$.

(c) *Zirconium–silver*—The presence of the compound AgZr in silver rich alloys was noted by E. RAUB and M. ENGEL[61]. Micrographic and x-ray work place the maximum solid solubility of zirconium in silver at less than 0·1 weight per cent at 900° C. The silver rich part of the diagram obtained by Raub and Engel is shown in *Figure 70.*

The microstructure of zirconium rich alloys containing up to 7·74 weight per cent silver was reported by C. T. ANDERSON *et al.*[2]

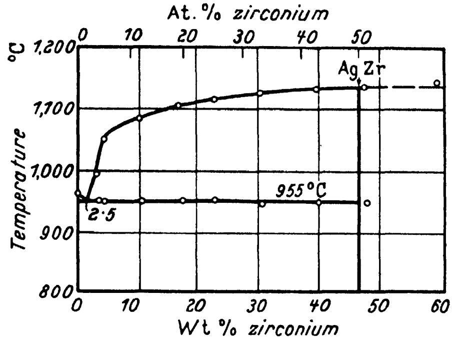


Figure 70. Silver–zirconium equilibrium diagram (after E. Raub *and* M. Engel[61])

to be a single-phase solid solution with a Widmanstätten pattern of acicular needles which decreased in size somewhat as the silver content was increased.

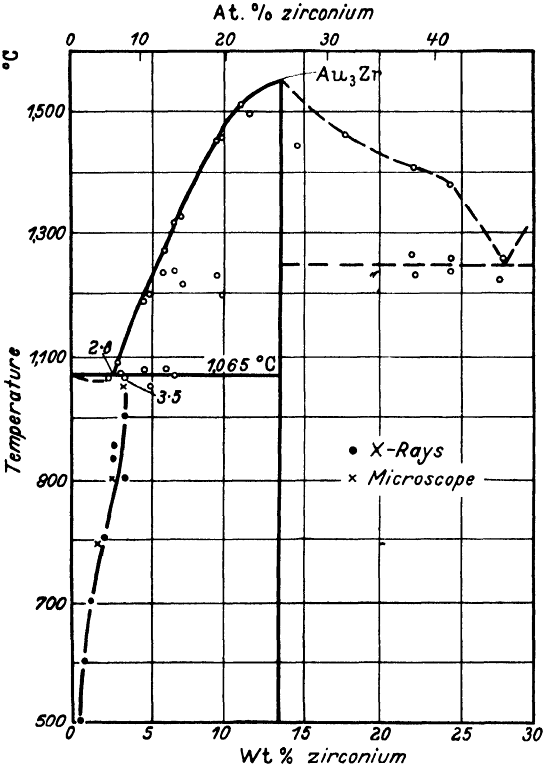


Figure 71. Gold–zirconium system (after E. Raub *and* M. Engel[61])

All the alloys mentioned in the report were prepared by melting Kroll sponge and the alloying metal in a graphite crucible in a helium atmosphere.

(d) *Zirconium–gold*—According to E. RAUB and M. ENGEL[61] the solubility of zirconium in gold increases with temperature up to a maximum of approximately 7·5 atomic per cent at 1065° C. Some reaction with the crucible occurred at the higher temperatures. The increase in lattice parameter is less than that to be expected from Vegard's law. There is an intermediate phase, Au_3Zr. No data are available on the zirconium rich alloys. The gold rich portion of the diagram determined by Raub and Engel is shown in *Figure 71.*

(e) *Zirconium alloys with alkali metals*—No data are available.

14.3.2. *Group II elements*

(a) *Zirconium–beryllium*—Preliminary powder metallurgy investigations by H. H. HAUSNER and H. S. KALISH[32] indicate the existence of several compounds and of a low melting point eutectic at the zirconium rich end. A hypothetical phase diagram proposed by Hausner and Kalish is shown in *Figure 72.* C. T. ANDERSON *et al.*[2] prepared a 0·77 weight per cent and a nominal 5·0 weight per cent alloy. The latter alloy was too hard to cut and was abandoned as unsuitable for further study. The 0·77 weight per cent alloy when worked showed considerable segregation. Some areas showed normal zirconium structure with a minor amount of second phase, whereas other areas showed a large proportion of a eutectic-like second phase. Work at the Atomic Energy Research Establishment[60] has confirmed the existence of a eutectic in zirconium rich alloys. The eutectic temperature is 980 ± 20° C and it occurs at a composition of 5·5 to 6·0 weight per cent beryllium.

(b) *Zirconium–magnesium*—Magnesium rich alloys containing less than 1 per cent zirconium have achieved considerable commercial importance (see Section 2.2.4).

It appears to be impossible to introduce more than about 0·7 per cent zirconium into magnesium. G. A. MELLOR[48] found the equilibrium conditions were difficult to establish but the solid solubility at 500° C was estimated to be 0·4 to 0·5 per cent zirconium.

H. NOWOTNY, R. WORMNES and A. MOHRNHEIM[58] claim to have made alloys over the entire composition range, but attempts by the Armour Research Foundation[3] to produce the alloys by the same method were completely without success.

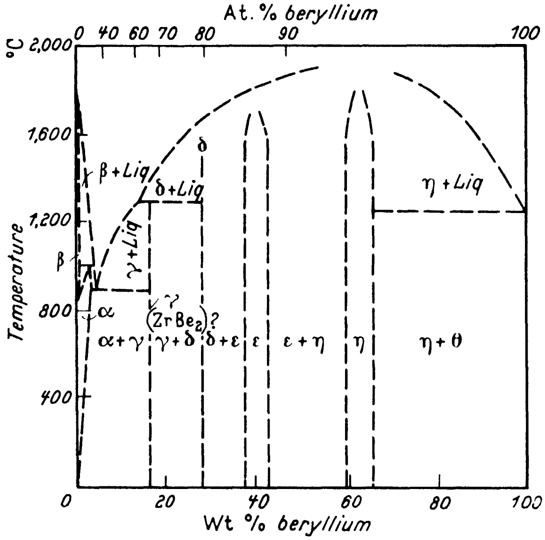


Figure 72. Hypothetical zirconium–beryllium diagram (*after* H. H. Hausner *and* H. S. Kalish[32])

W. J. Kroll, in a private communication to the Armour Research Foundation[3], has told of the many attempts made at the U.S. Bureau of Mines to produce zirconium–magnesium alloys without success. Similar experiences have been noted with other systems in which the melting point of the second component is higher than the boiling point of magnesium and all attempts to produce alloys of beryllium with magnesium have proved useless.

Armour Research Foundation[3] made many experiments to produce the alloys, using six different methods, including: induction melting (claimed by Nowotny *et al.* to be successful), gradual additions of zirconium to a magnesium bath, diffusion of the solid metals, powder metallurgy methods and special arc melting methods. This investigation confirmed the approximate extent of alloying at the magnesium end of the system claimed by previous workers. There was an indication that zirconium takes some magnesium into solid solution but little control could be exercised over the production of the alloys, which were often badly segregated.

J. H. Schaum and H. C. Burnett[67] developed the magnesium rich side of the magnesium–zirconium diagram shown in *Figure 73* which is similar to those developed by F. von Sauerwald[66] and Mellor. The intersection of the liquidus and peritectic lines was located between the values reported by these two previous investigators. The peritectic reaction and the solidus were observed at higher temperatures than in the other two diagrams. Location

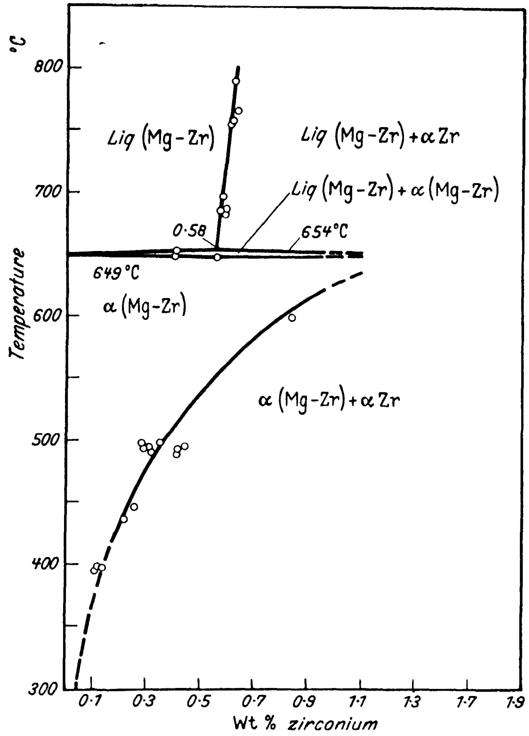


Figure 73. Partial diagram of magnesium–zirconium system (after J. H. SCHAUM *and* H. C. BURNETT[67])

of the solidus at high temperatures was handicapped by the vapour pressure of magnesium and the reactivity of zirconium. Heat treatment below 400° C apparently had no effect on the soluble zirconium constituent of the alloys. Schaum and Burnett developed an improved chemical analysis technique to distinguish accurately between the soluble and insoluble zirconium. The separation depends upon the difference in solubility of the two forms in hydrochloric acid solution.

14.3.3. *Group III elements*

(a) *Zirconium–boron*—The existence of Zr_3B_4 has been noted by M. HANSEN[31]. A boride of the composition ZrB_2 was found by P. M. MCKENNA[49]. C. T. ANDERSON *et al.*[2] produced, with difficulty, a few alloys using a low grade, 95 per cent, boron. The alloys contained long, needle-like grains, considered to be zirconium boride and which were easily distinguished from the rounded carbides. R. KIESSLING[41] investigated the zirconium–boron system by x-ray methods. Iodide zirconium and 99 per cent boron were melted in a high frequency vacuum induction furnace (crucible material not mentioned). Small amounts of boron were dissolved by the α-zirconium lattice, the solubility limit of boron in zirconium being about one atomic per cent boron. Only one intermediate phase was found, this had the composition ZrB_2 and had a narrow homogeneity range. Powder photographs showed that ZrB_2 had a hexagonal cell with unit dimensions $a = 3{\cdot}169$ Å, $c = 3{\cdot}530$ Å, $c/a = 1{\cdot}11$.

A study was made of the structure of various metallic borides including that of zirconium by J. T. NORTON *et al.*[54]. All the borides were found to correspond to the formula MeB_2 and have isomorphous crystal structure with the metal atoms arranged in a simple hexagonal lattice having an axial ratio slightly greater than unity. The unit cell was found to contain one molecule of MeB_2 corresponding to the alternate layers of metal and boron atoms, parallel to the basal plane of the lattice. The borides had well developed metallic properties.

F. W. GLASER and W. IVANICK[26] found that the isomorphous diborides of zirconium and titanium form a continuous series of solid solutions. (See also Section 18.3.)

(b) *Zirconium–aluminium*—The binary system zirconium–aluminium was investigated by the Armour Research Foundation[3]. The technique described for the zirconium–copper system was used. The zirconium–aluminium phase diagram is shown in *Figure 74*. Considering them generally in the order of increasing aluminium content, the principal features of the zirconium–aluminium system may be summarized as follows:

(*i*) Zirconium forms a eutectic with Zr_5Al_3 (15·07 per cent aluminium) at 11 per cent aluminium and 1350 ± 10° C.

(*ii*) The maximum solubility of aluminium in beta zirconium is 9·5 per cent at the eutectic temperature.

(*iii*) The intermediate phase Zr_2Al (12·88 per cent aluminium) is formed in the solid state at 1250 ± 50° C by the peritectoid reaction

$$\beta + Zr_5Al_3 \rightleftharpoons Zr_2Al$$

(*iv*) The intermediate phase Zr_3Al (8·80 per cent aluminium) is formed at 975 ± 25° C by the peritectoid reaction

$$\beta + Zr_2Al \rightleftharpoons Zr_3Al$$

(*v*) Aluminium additions raise the $\alpha \rightarrow \beta$ transformation temperature to 940 ± 10° C. At this temperature, the peritectoid reaction

$$\beta + Zr_3Al \rightarrow$$

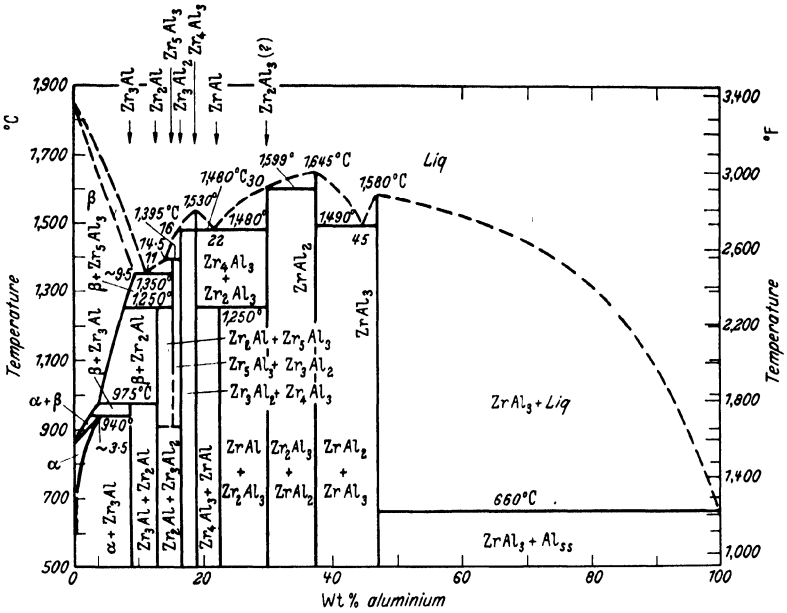


Figure 74. The zirconium–aluminium system (after Armour Research Foundation[3])

occurs, yielding an alpha solid solution containing about 3·5 per cent aluminium.

(*vi*) The solubility of aluminium in alpha zirconium decreases with falling temperature from 3·5 per cent aluminium at 940° C to 1 per cent at 800° C, and 0·5 per cent at 700° C.

(*vii*) Zr_5Al_3 (15·07 per cent aluminium) is formed by the peritectic reaction between Zr_3Al_2 (16·46 per cent aluminium) and a melt containing about 15 per cent aluminium at 1395 ± 10° C. Zr_5Al_3 breaks down at lower temperatures, probably eutectoidally.

(*viii*) Zr_3Al_2 (16·46 per cent aluminium) is formed by the peritectic reaction between Zr_4Al_3 (18·15 per cent aluminium) and a melt containing about 16 per cent aluminium at 1480 ± 20° C.

(*ix*) Zr_4Al_3 (18·15 per cent aluminium) melts with an open maximum at 1530 ± 20° C.

(*x*) A eutectic occurs at 22 per cent aluminium between Zr_4Al_3 and Zr_2Al_3 (tentative, 30·72 per cent aluminium) at 1480 ± 20° C.

(*xi*) ZrAl (22·82 per cent aluminium) is formed in the solid state at 1250 ± 50° C by the peritectoid reaction

$$Zr_4Al_3 + Zr_2Al_3 \rightarrow ZrAl$$

(*xii*) Zr_2Al_3 (tentative, 30·72 per cent aluminium) is formed at 1595 ± 25° C by a peritectic reaction between $ZrAl_2$ (37·16 per cent aluminium) and the melt containing about 30 per cent aluminium.

(*xiii*) $ZrAl_2$ (37·16 per cent aluminium) melts with an open maximum at 1645 ± 25° C.

(*xiv*) A eutectic between $ZrAl_2$ and $ZrAl_3$ (47·00 per cent aluminium) occurs at 45 per cent aluminium and 1490 ± 20° C.

(*xv*) $ZrAl_3$ (47·00 per cent aluminium) melts with an open maximum at 1580 ± 25° C.

(*xvi*) At all aluminium contents higher than 47 per cent, only two phases exist: $ZrAl_3$ and aluminium.

The phase $ZrAl_2$ has the orthorhombic structure with lattice parameter $a = 10{\cdot}40$ Å, $b = 7{\cdot}21$ Å, $c = 4{\cdot}97$ Å while $ZrAl_3$ is tetragonal with parameters $c = 16{\cdot}90$ Å, $a = 4{\cdot}306$ Å, $c/a = 3{\cdot}92$.

Al_3Zr, Al_2Zr and Al_4Zr_3 have all been mentioned by M. HANSEN[31]. G. BRAUER[8] found that $ZrAl_3$ was tetragonal with $a = 4{\cdot}00$ Å and $c = 17{\cdot}31$ Å.

The solid solubility of zirconium in aluminium was found to be less than 0·13 weight per cent by W. L. FINK and L. A. WILLEY[24] who investigated the constitution of the aluminium rich alloys.

F. B. LITTON and S. C. OGBURN[45] state that the solubility of aluminium in beta zirconium is greater than 3 per cent whereas in the alpha modification it is less than 0·5 per cent.

C. T. ANDERSON and his colleagues[2] examined zirconium–aluminium alloys up to 4·8 weight per cent aluminium and reported all were single-phase solid solution alloys.

(c) *Zirconium with other elements of Group III*—The only information available is that there is a compound $ZrGa_3$. C. J. SMITHELLS[72] quotes it as being tetragonal with parameters $a = 5{\cdot}6$ Å and $c = 8{\cdot}71$ Å, isomorphous with both $TiAl_3$ and $TiGa_3$.

14.3.4. *Group IV elements*

(a) *Zirconium–carbon*—The stable zirconium carbide[5] ZrC has a cubic structure of the NaCl type.

A second carbide ZrC_2 was suspected by O. RUFF and R. WALLSTEIN[63] but according to M. HANSEN[31] this was probably a mixture of ZrC and C.

H. NOWOTNY and R. KIEFFER[57] reported the parameter as 4·669 Å. W. G. BURGERS and J. L. M. BASART[10] reported 4·6965 Å but the most recent value is that of P. DUWEZ and F. ODELL[21] who found it to be 4·685 Å.

The U.S. Bureau of Mines[2] have reported that despite several remeltings of zirconium in graphite crucibles the carbon did not exceed 0·35 per cent.

J. T. Norton and A. L. Mowry[55] found that the binary carbide systems TiC–ZrC, ZrC–NbC and ZrC–TaC formed continuous series of solid solutions. The binary carbide system ZrC–VC shows very small solubility; the limits at 2100° C being 5 per cent at the zirconium rich end and 1 per cent at the vanadium rich end.

H. J. Goldschmidt[27] gives a hypothetical zirconium–carbon system as shown in *Figure 75.* (See also Section 18.2.)

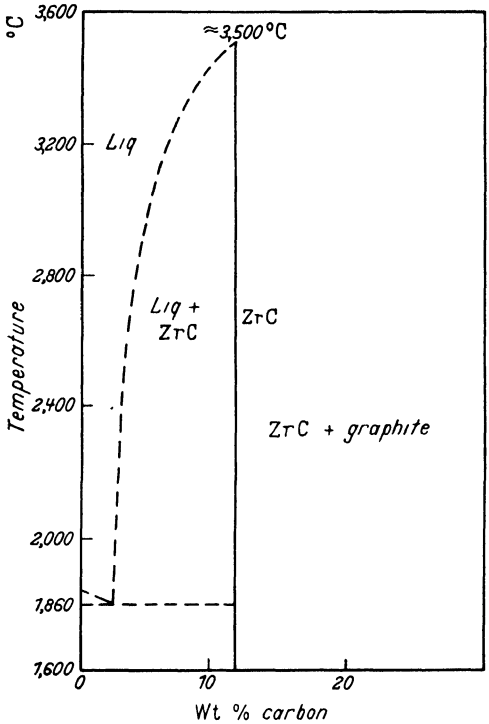


Figure 75. Hypothetical zirconium–carbon system (after H. J. Goldschmidt[27])

(b) *Zirconium–silicon*—The phase diagram of the zirconium–silicon system was determined with particular emphasis on the zirconium rich portion by C. E. Lundin, D. J. McPherson and M. Hansen[47]. This work was a part of the main investigation on zirconium alloy systems undertaken by the Armour Research Foundation. The technique employed was as for zirconium–copper.

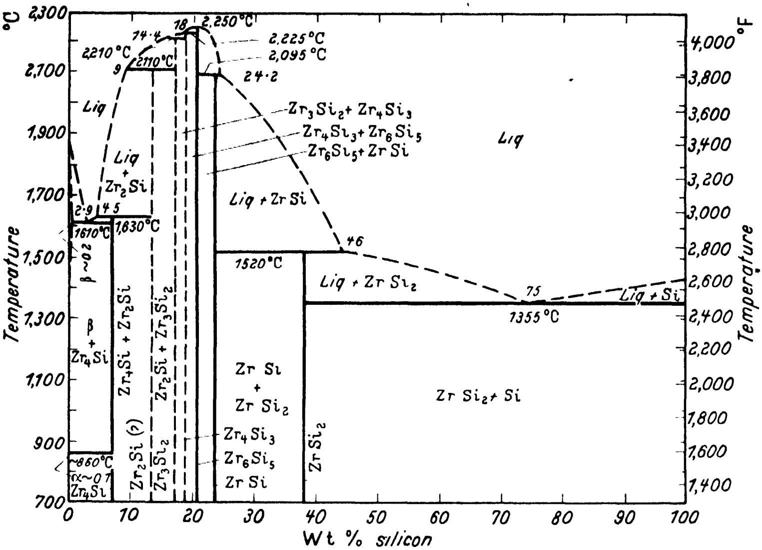


Figure 76. Zirconium–silicon system (after C. E. Lundin *et al.* [47])

The zirconium–silicon system is shown in *Figure 76* and a partial diagram covering the zirconium rich portion is shown in *Figure 77.*

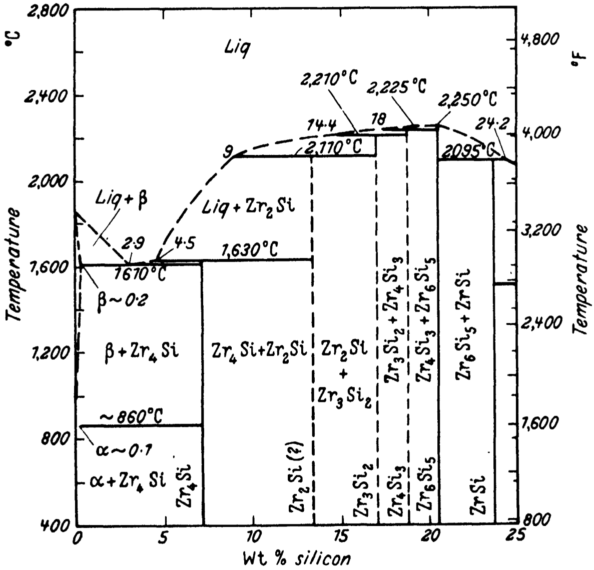


Figure 77. Partial diagram of zirconium–silicon system (after C. E. Lundin *et al.* [47])

A summary of the major features of the diagram, on a weight per cent basis, in the sequence of increasing silicon content, is as follows:

(*i*) The maximum solubility of silicon in beta zirconium is less than 0·2 per cent at 1610° C. The maximum solubility of silicon in alpha zirconium is less than 0·1 per cent at 860° C.

(*ii*) Zirconium forms a eutectic with Zr_4Si at 2·9 per cent silicon and 1610 ± 15° C.

(*iii*) The intermediate phase Zr_4Si (7·14 per cent silicon) is formed by peritectic reaction between Zr_2Si (tentative, 13·33 per cent silicon) and the melt containing 4·5 per cent silicon at 1630 ± 15° C.

(*iv*) The phase Zr_2Si (tentative) is formed by the peritectic reaction between Zr_3Si_2 (17·02 per cent silicon) and the melt containing 9 per cent silicon at 2110 ± 25° C.

(*v*) The phase Zr_3Si_2 is formed by the peritectic reaction between Zr_4Si_3 (18·74 per cent silicon) and the melt containing 14·4 per cent silicon at 2210 ± 25° C.

(*vi*) The intermediate phase Zr_4Si_3 is formed by the peritectic reaction between Zr_6Si_5 (20·40 per cent silicon) and the melt containing 18 per cent silicon at 2225 ± 25° C.

(*vii*) The intermediate phase Zr_6Si_5 is formed at 20 per cent silicon and melts with an open maximum at 2250 ± 25° C.

(*viii*) The phase ZrSi (23·53 per cent silicon) is formed by a peritectic reaction between Zr_6Si_5 and the melt containing 24·2 per cent silicon at 2095 ± 25° C.

(*ix*) The phase $ZrSi_2$ (38·09 per cent silicon) is formed by a peritectic reaction between ZrSi and the melt containing 46 per cent silicon at 1520 ± 15° C.

(*x*) A eutectic exists between $ZrSi_2$ and silicon at 75 per cent silicon and 1355 ± 15° C.

(*xi*) The solubility of zirconium in silicon is considerably less than 5 per cent, but no attempt was made to determine the value precisely.

The phase ZrSi has the hexagonal structure with lattice parameters $c = 12{\cdot}77$ Å, $a = 7{\cdot}01$ Å, $c/a = 1{\cdot}823$.

Examination of the zirconium rich alloy revealed that the effect of silicon additions on the allotropic transformation of zirconium could not be determined because of the extremely small solubility of this element in both zirconium modifications. The solubility of silicon in beta zirconium is less than 0·2 per cent even at high temperatures. The maximum solubility of silicon in alpha zirconium is less than 0·1 per cent. The low solubility of silicon in both alpha and beta zirconium is confirmed by F. B. Litton and S. C. Ogburn[45] who stated that it was less than 0·23 per cent. The U.S. Bureau of Mines[9] also investigated alloys containing 0·05 to 2·9 per cent silicon. The alloys were quenched from 1000° C and the investigators did not mention the presence of a second phase from which P. C. L. Pfeil[60] infers that there is appreciable solubility of silicon in beta zirconium. (See also Section 18.4.)

(c) *Zirconium–germanium*—The only information abstracted is that there is a compound $ZrGe_2$ isomorphous with $ZrSi_2$ (orthorhombic). The lattice parameters taken from C. J. Smithells[72] are $a = 3{\cdot}80$ Å, $b = 15{\cdot}01$ Å, $c = 3{\cdot}76$ Å.

(d) *Zirconium–tin*—The system zirconium–tin was investigated by D. J. McPherson and M. Hansen[50] as a part of the Armour Research Foundation investigations on the zirconium binary alloys.

A slight modification had to be made in the technique which was used successfully to prepare most of the other alloys and which is

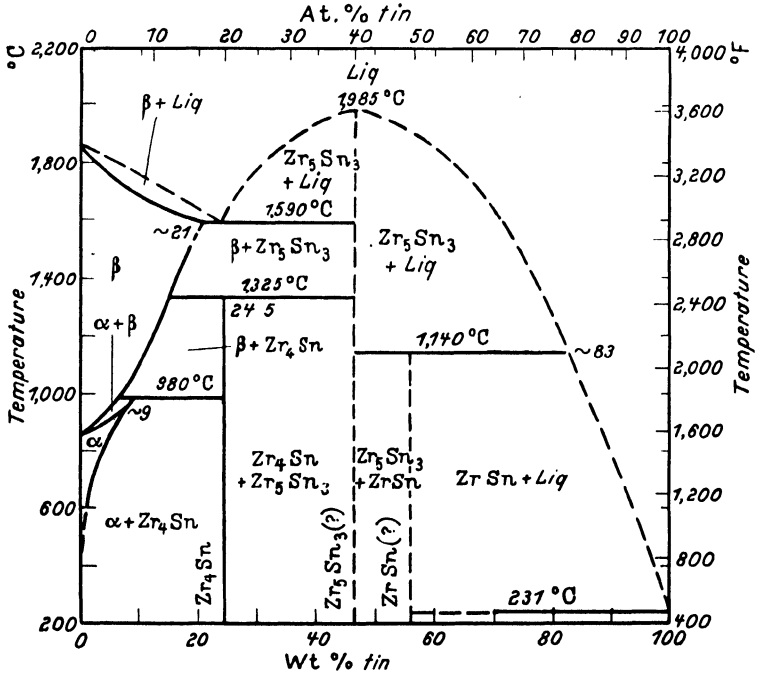


Figure 78. The zirconium–tin system (after D. J. McPherson *and* M. Hansen[50])

described briefly for zirconium–copper. The alloys up to 35 per cent tin were melted without much difficulty in the arc furnace but richer tin alloys gave high tin losses when melted in this manner. When the metals were compacted into slugs before melting the losses of tin were minimized.

The zirconium–tin system is shown in *Figure 78* and the zirconium rich end in *Figure 79.*

The principal features of the zirconium–tin system may be summarized as follows:

(*i*) Three intermediate phases exist: these are Zr_4Sn (24·55 per cent tin) which is formed by the peritectoid reaction

$$\beta + Zr_5Sn_3 \rightarrow Zr_4Sn$$

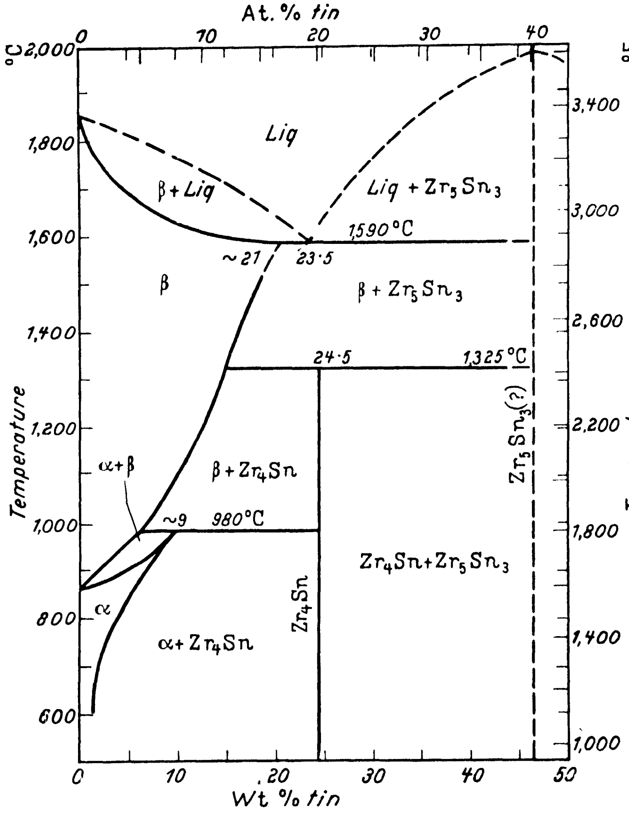


Figure 79. Partial diagram of zirconium–tin system (after D. J. McPherson *and* M. Hansen[50])

at 1325 ±20° C; Zr_5Sn_3 (tentative 43·84 per cent tin), which melts with an open maximum at 1985 ± 25° C; and ZrSn (tentative, 56·55 per cent tin), formed by a peritectic reaction between Zr_5Sn_3 and a melt containing about 83 per cent tin at 1140 ± 15° C.

(*ii*) Zirconium and Zr_5Sn_3 give rise to a eutectic at 23·5 per cent tin and 1590 ± 15° C.

(*iii*) The solubility of tin in beta zirconium is approximately 21 per cent at the eutectic temperature, 15 per cent at 1325° C, and 6·5 per cent at 980° C.

(*iv*) Tin raises the $\alpha \rightleftharpoons \beta$ transformation temperature of zirconium, which at 980 ±20° C results in the peritectoid reaction

$$\beta + Zr_4Sn \rightarrow \alpha$$

(*v*) The solubility of tin in alpha zirconium decreases from 9 per cent at 980° C to about 1·5 per cent at 600° C.

(*vi*) Tin displays no appreciable solid solubility for zirconium. The eutectic or peritectic (undetermined) between tin and ZrSn lies at a higher tin content than 99·5 per cent, and not more than 1 C° above or below the melting point of tin.

The phases Zr_4Sn and ZrSn had a tetragonal and orthorhombic structure respectively with lattice parameters $c = 11{\cdot}10$ Å, $a = 6{\cdot}90$ Å and $c/a = 1{\cdot}63$ for Zr_4Sn and $a = 7{\cdot}433$ Å, $b = 5{\cdot}822$ Å and $c = 5{\cdot}157$ Å for ZrSn.

(e) *Zirconium–lead*—No published information.

(f) *Zirconium–titanium*—The transition-point diagram determined by J. D. FAST[22] indicated that the two metals are completely miscible in all proportions in both the alpha and beta forms.

The zirconium–titanium system was investigated over the whole range by E. T. HAYES, A. H. ROBERSON and O. G. PAASCHE of the U.S. Bureau of Mines[33]. The alloys were prepared from Kroll sponge zirconium by arc melting and by melting in graphite crucibles. The equilibrium diagram obtained, *Figure 80*, shows the following features.

The solidus temperature shows a minimum melting point of 1610° C at 53 weight per cent or 66 atomic per cent titanium. The liquidus line was not determined accurately and accordingly is shown as a dotted line.

Zirconium and titanium form a continuous series of solid solutions in both the alpha and beta forms with the transformation temperature depressed to a minimum at 35 weight per cent (50 atomic per cent) zirconium.

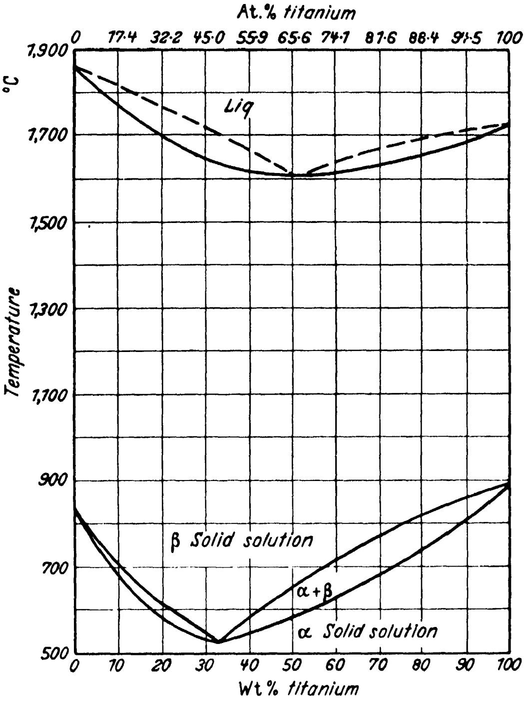


Figure 80. The zirconium – titanium system (after E. T. HAYES *et al.*[33] *Reprinted from U.S. Bureau of Mines* Report of Investigations, 4826.)

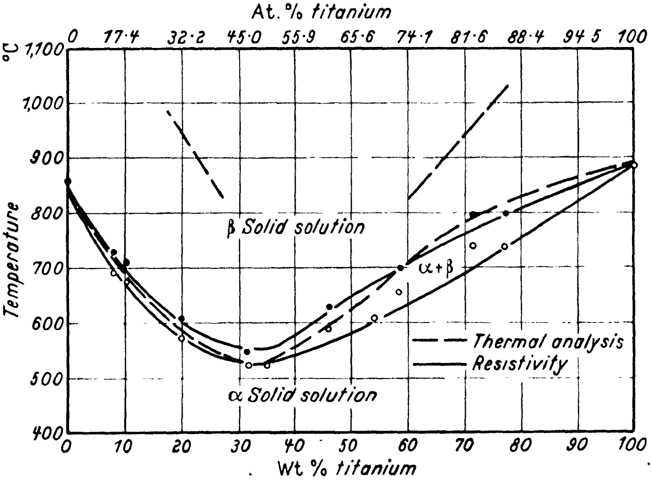


Figure 81. Alpha–beta transition based on resistivity at temperature, cooling curves (after E. T. HAYES *et al.*[33] *Reprinted from U.S. Bureau of Mines* Report of Investigations, 4826.)

The minimum in the transformation temperature is unique in binary metal phase diagrams and further serves to identify zirconium and titanium as unusual metals.

The transition-point diagram determined by Hayes *et al.* is shown in *Figure 81*, it is similar to that of J. D. Fast[22] with the exception that the α + β field is considerably narrower.

P. Duwez[19] found that the high temperature beta solid solution transforms, at least partially, into alpha solid solution at rates of cooling as high as 8000 C°/sec. The transformation temperature/composition diagram shows a minimum of 490° C compared to about 550° C found by Fast and Hayes.

The lattice parameters of zirconium–titanium alloys in the alpha condition have been determined by both J. D. Fast[22] and P. Duwez[19] and are shown in *Figure 82.* Fair agreement is obtained for the *a* parameters but the *c* values show poor agreement. The lattice parameters of beta retained by rapid cooling of the 30 to 70 atomic per cent titanium alloys are linear with composition and extrapolate to 3·27 and 3·59 Å for titanium and zirconium respectively.

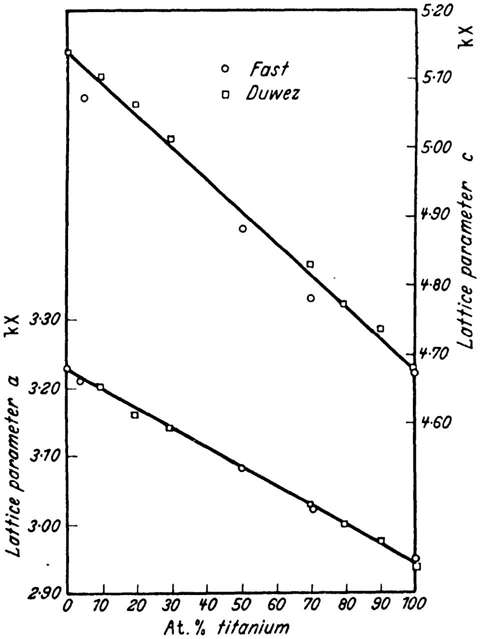


Figure 82. Lattice parameters of alpha zirconium–titanium alloys (after J. D. Fast[22] *and* P. Duwez[19])

(g) *Zirconium–hafnium*—The existence of a continuous series of solid solutions is probable, according to M. HANSEN[31], based on the experiments of J. H. DE BOER and J. D. FAST[14], and of A. E. VAN ARKEL[76]. F. B. LITTON and S. C. OGBURN[45] found no change greater than experimental variations in the mechanical properties of zirconium–hafnium alloys containing 0·1 to 8·2 weight per cent hafnium.

R. B. RUSSELL[65] quotes the lattice parameters at room temperature for zirconium–hafnium alloys as follows:

Hafnium per cent		*Parameters*	
Weight	Atomic	*a* Å	*c* Å
100	100	3·1946	5·0510
99·0	98·5	3·1947	5·0524
98	96·5	3·1992	5·0602
76	61·8	3·2108	5·0944
2·4	1·2	3·2309	5·1457
0	0	3·231	5·144
0·01	0·005	3·2312	5·1477

(h) *Zirconium–thorium*—C. T. ANDERSON and his colleagues at the U.S. Bureau of Mines[2] prepared zirconium–thorium alloys containing 0·4 and 5·4 per cent thorium. Examination of the cast ingots showed that the microstructure of both alloys was a single-phase solid solution with the usual Widmanstätten structure of large acicular grains indicating that the beta phase was not retained at room temperature.

O. N. CARLSON[11] investigated the thorium–zirconium system and proposed the phase diagram *Figure 83.* The alloys were produced by several methods, the most satisfactory being the reduction of the mixed fluorides of thorium and zirconium with calcium, followed by melting the master alloy with Kroll sponge zirconium in a graphite crucible heated by induction. The zirconium rich alloys show an extensive solid solubility of thorium in beta zirconium and only a relatively small one in alpha zirconium. The beta/(alpha + beta) phase boundary is depressed to about 650° C with 14·4 atomic per cent thorium, where there is a eutectoid decomposition of the beta solid solution into a mixture of alpha zirconium and face centred cubic thorium. There is some evidence that the maximum solid solubility of thorium in alpha zirconium is less than 5 weight per cent (2·2 atomic per cent). The lattice constants of a 9 weight per

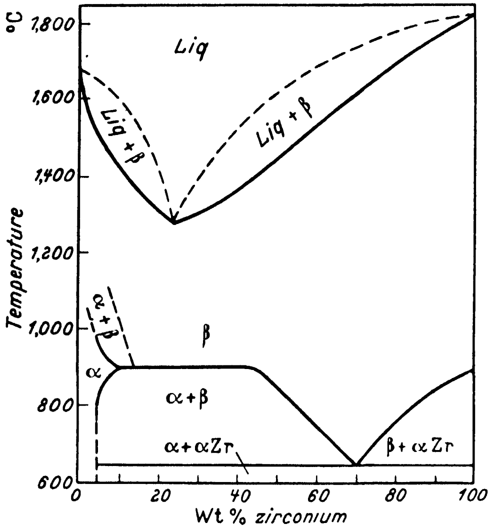


Figure 83. The zirconium–thorium system (after O. N. CARLSON[11])

cent thorium alloy were, within experimental error, those of zirconium itself, although on quenching a 20 weight per cent thorium alloy from 900° C appreciably larger lattice constants were obtained, which may indicate that supersaturated solid solutions of thorium can be formed in alpha zirconium. Carlson interprets his results on the hypothesis that there is a high temperature allotropic modification of thorium. The maximum solid solubility of zirconium in the face centred cubic form of thorium appears to be between 5 and 6·5 weight per cent.

(i) *Zirconium–uranium*—Uranium is included in this section because when alloyed with zirconium, it appears to behave like a Group IV element.

According to O. N. CARLSON[11], Kaufmann reported in 1944 that the melting point of uranium was raised by additions of zirconium, 20 atomic per cent of zirconium causing a rise from 1133 to 1225° C. With higher zirconium contents Kaufmann suggested that a peritectic reaction probably occurred at a temperature of 1250° C. Extensive solid solubility of zirconium in gamma uranium was indicated by the homogeneous structures obtained by quenching 10 and 20 atomic per cent alloys from 925° C. On quenching the 49 and 60 atomic per cent zirconium alloys from 700 and 1000° C, a body centred cubic structure was obtained, whereas quenching from 600° C gave rise to a body centred tetragonal phase.

The same writer states that according to work at the Iowa State College by Peterson, gamma uranium and beta zirconium form a continuous series of solid solutions. There is one eutectoid with 10 per cent zirconium at 688° C and possibly another at a lower temperature.

Preliminary investigations at the Associated Electrical Industries Research Laboratories, Aldermaston[60], have also revealed a continuous series of solid solutions between gamma uranium and beta zirconium at high temperatures. The solid solubility of uranium in alpha zirconium appears to be less than 5 atomic per cent while a 70 atomic per cent zirconium alloy remains homogeneous body centred cubic on annealing at 610° C, after preliminary high temperature treatment. The maximum solubility in alpha zirconium appears to be less than 5 atomic per cent at 600° C.

14.3.5. *Group V elements*

(a) *Zirconium–nitrogen*—M. HANSEN[31] mentions a compound, ZrN, which is cubic NaCl type, with a parameter of 4·63 Å. J. D. FAST[23] found that zirconium will absorb up to 20 atomic per cent nitrogen without x-ray evidence of an actual compound being formed. As with the solution of oxygen, the transformation temperature was raised. The lattice parameters of a 10 atomic per cent nitrogen alloy are reported as $a = 3{\cdot}25$ Å, $c = 5{\cdot}21$ Å in comparison with 3·223 and 5·123 Å respectively for the pure metal. Unlike the case with oxygen, both parameters are affected, but as with oxygen the axial ratio is increased. P. DUWEZ and F. ODELL[21] studied the binary systems of the nitrides and carbides of several metals including zirconium. The binary nitride system ZrN–NbN forms a continuous series of solid solutions while in the system ZrN–VN the solution of ZrN in VN is less than 1 per cent and the solubility of VN in ZrN is approximately 5 per cent. Titanium carbide, TiC, forms a continuous series of solid solutions with ZrN, and the system VC–ZrN shows very limited solubility. In the system NbC–ZrN no reactions took place at a firing temperature of 2450° C. (See also Sections 11.2.28., 12.3. and 18.1.)

(b) *Zirconium alloys with arsenic, antimony and bismuth*—No information available except that zirconium dissolves in bismuth (see Section 13.4).

(c) *Zirconium–vanadium*—H. J. WALLBAUM[79] has identified a compound, ZrV_2, which crystallizes with the hexagonal $MgZn_2$ type of structure. The parameters are $a = 5{\cdot}277$ Å, $c = 8{\cdot}647$ Å. C. T. ANDERSON *et al.* at the U.S. Bureau of Mines[2] prepared alloys from

94 to 95 per cent vanadium and sponge zirconium containing from 0·8 to 7·0 per cent vanadium. The 0·8 per cent alloy was single phase, but a 1·8 per cent alloy contained a eutectic that occupied 20 per cent of the field. A 4·7 per cent alloy was almost entirely eutectic while the 7 per cent alloy was composed of small eutectic grains with scattered clusters of a white second phase.

(d) *Zirconium–niobium*—Zirconium–niobium alloys containing up to 12·9 per cent niobium were prepared by C. T. ANDERSON *et al.* at the U.S. Bureau of Mines[2]. A 0·6 per cent niobium alloy was composed mainly of the Widmanstätten structure, normally found when pure zirconium is cooled rapidly from the beta field, with a small amount of a second phase. P. C. L. PFEIL[60] considers that the second phase is retained beta.

The cast 5·1 per cent alloy was made up of large grains filled with fine needles arranged in a Widmanstätten pattern; in the swaged alloy small spheroids of a second phase were scattered throughout the grains. The cast 12·9 per cent alloy was composed of very large grains filled with finely foliated fernlike patterns and the alloy appeared to be single-phase.

F. B. LITTON[44] prepared alloys of zirconium and niobium by melting *in vacuo* in graphite crucibles. Additions of niobium ranged from 2·5 to 27·5 per cent. No microstructures were reported for the niobium alloys.

P. C. L. PFEIL[60] suggested that the values obtained by Litton for the yield strength of his alloys at 649° C, *i.e.* 9320,7910 and 10,020 lb/in^2 for 0·6, 5·0 and 12·75 per cent niobium, were explicable on the hypothesis that niobium decreases the alpha–beta transformation temperature of zirconium. The alloy containing 5·0 atomic per cent niobium appeared to contain substantial quantities of beta phase at 649° C, equivalent to the presence of 15·0 atomic per cent titanium in zirconium at the same temperature. Niobium would appear to depress the transformation temperature more rapidly than titanium.

(e) *Zirconium-tantalum*—C. T. ANDERSON *et al.* at the U.S. Bureau of Mines[2] prepared zirconium–tantalum alloys ranging from 1·2 to 30·3 per cent tantalum by melting Kroll sponge and tantalum clippings *in vacuo* in a graphite crucible. The carbon content rose from 0·14 to 0·44 per cent with the tantalum additions. The 1·2 per cent alloy had a microstructure very similar to that of pure zirconium. The 5·3 per cent alloy was similar but the beta phase grain boundaries were better delineated. The 9·7 per cent alloy appeared to have been solid solution at the casting temperature and two-phase in the solid state. The alloy with 14·1 per cent contained about 20 per cent of a second phase, concentrated along the grain boundaries, and this phase occupied the whole field with the 20·8 per cent tantalum addition. Anderson *et al.* believed the new phase was a eutectic but P. C. L. PFEIL[60] considered this unlikely to be correct because a reduction in hardness, noted by Anderson *et al.*, indicates that the beta phase may have been retained down to room temperature in the 20·8 per cent alloy. The 30·3 per cent alloy consisted of a background of eutectic plus about 10 per cent of a bright constituent in the form of large dendrites. Pfeil considers it is possible that this alloy really consists of a matrix of beta phase together with dendrites of either an intermediate phase or of a tantalum rich solid solution.

The tensile properties of the alloys containing up to 14 per cent tantalum at both room temperature and at 649° C were determined at the U.S. Bureau of Mines[2]. P. C. L. PFEIL[60] suggested that the results (51,300, 73,000, 92,200, 84,400 lb/in^2 yield strength at room temperature and 9680, 17,210, 16,420, 16,450 lb/in^2 at 649° C for alloys containing 0·6, 2·8, 5·2 and 7·7 atomic per cent tantalum respectively) are consistent with the view that tantalum tends to stabilize the beta phase.

F. B. LITTON[44] prepared alloys containing up to 27·5 per cent tantalum by melting in graphite crucibles. A photomicrograph of a 12·5 per cent alloy appears to be substantially homogeneous. P. C. L. PFEIL[60] comments that the microstructure may represent beta retained (though not necessarily stabilized) down to room temperature. Pfeil also considered that the available data suggested that niobium and tantalum, compared on an atomic per cent basis, were similar in their effectiveness in depressing the transformation point.

J. H. KEELER[40] found that zirconium containing 2·7 atomic per cent tantalum transformed between 807 and 852° C indicating that tantalum lowers the transformation range.

14.3.6. *Group VI elements*

(a) *Zirconium–oxygen*—Oxygen can dissolve to a wide extent in zirconium. According to J. H. DE BOER and J. D. FAST[15] the alpha–beta transition of oxygen-containing zirconium occurs over a wide temperature range up to 1800° K after absorption of 10 atomic per cent oxygen. J. D. FAST[23] has reported the lattice parameters of zirconium–oxygen alloys containing up to 30 atomic per cent oxygen. The *a* parameter is unaffected, but the *c* parameter is increased from 5·123 to 5·191 Å.

D. CUBICCIOTTI[13] prepared oxidized samples of zirconium by heating iodide zirconium wire in known amounts of 99·8 per cent oxygen and calculating the oxygen content from the weight gains. The samples were homogenized by further heating in a vacuum.

The samples were melted by passage of an electric current *in vacuo* and the melting point observed as brightness temperature with a Leeds and Northrupp optical pyrometer. Samples with more than 30 per cent oxygen were melted in a heated tungsten spiral.

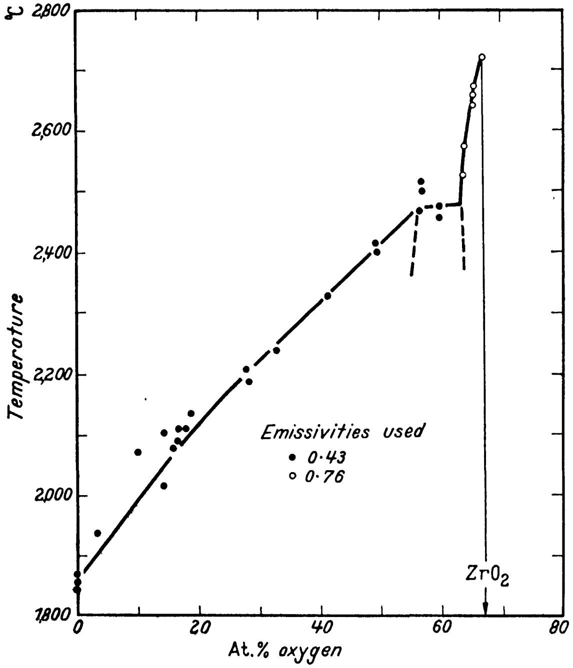


Figure 84. *Solidus curve for zirconium–oxygen system (after* D. CUBICCIOTTI[13])

A solidus curve of the system was determined and is shown in *Figure 84*. The results show that near the melting point, oxygen dissolves to the extent of 55 atomic per cent in solid zirconium, while zirconium dissolves in the solid zirconium oxide to form a 15 mole per cent solution.

No evidence was found for compounds other than ZrO_2.

R. M. TRECO[75] more recently investigated the effect of oxygen additions on the lattice constants of zirconium. Samples were prepared containing up to 2·5 atomic per cent oxygen by the controlled addition of oxygen to the heated metal in a high vacuum system.

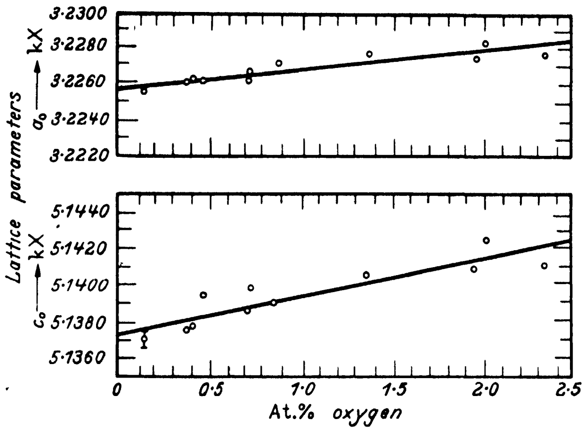


Figure 85. Change of lattice parameters of zirconium due to added oxygen (after R. M. TRECO[75])

The results are shown in *Table XCVI* and plotted in *Figure 85.* The figures show a linear expansion of the lattice with increasing oxygen content and within the range investigated there was no apparent effect on the axial ratio which remained constant.

R. M. TRECO[74] determined the effect of dissolved oxygen on the thermal conductivity of zirconium and found it decreased by about 10 per cent for each atomic per cent of oxygen absorbed. Likewise resistivity was affected by oxygen absorption as shown by *Figure 86.*

Treco noted that the presence of oxygen did not appear to affect

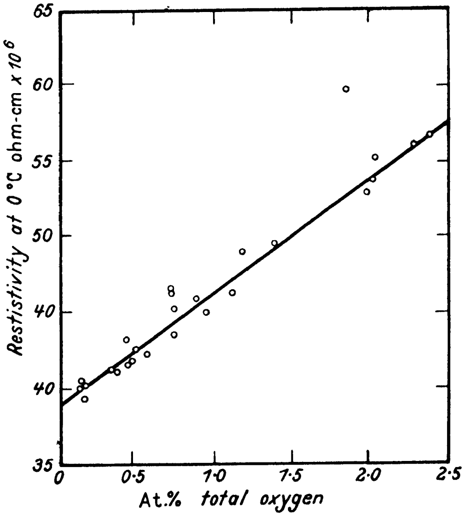


Figure 86. Effect of absorption of oxygen on electrical resistivity of iodide zirconium (after R. M. TRECO[74])

the recrystallization of zirconium after cold working followed by heat treatment.

A detailed investigation of diffusion of oxygen in zirconium was not made by Treco but he did determine an approximate diffusion constant at 1280° C by determining the homogeneity of a sample of metal to which a known amount of oxygen was added and noting the time required for complete diffusion through a known volume. The relationship between these quantities is represented by the equation[4]

$$c = Q/(Dt)^{\frac{1}{2}}$$

where D = diffusion constant, cm^2/sec
c = concentration, cm^3 oxygen/cm^3 zirconium
t = time, sec
Q = ratio of diffused oxygen to surface area.

From this equation R. M. TRECO[74] obtained a diffusion constant equal to $5{\cdot}25 \times 10^{-6}$ cm^2/sec.

Table XCVI. Lattice Constants of Zirconium–Oxygen Alloys at 25° C

Oxygen Weight per cent	*Oxygen* Atomic per cent		a_0 kX	c_0 kX	c/a	*Volume of unit cell* kX^3	*Relative strain* $\times 10^6$
	Added	*Corrected**					
0·026	0	0·147	3·22562†	5·13709†	1·59259†	46·2884†	0
0·064	0·166	0·364	3·22611	5·13743	1·59245	46·3054	368
0·074	0·222	0·420	3·22634	5·13746	1·59235	46·3129	531
0·083	0·376	0·471	3·22624	5·13926	1·59296	46·3245	781
0·125	0·536	0·708	3·22619	5·13858	1·59277	46·3191	664
0·128	0·756	0·725	3·22662	5·13994	1·59298	46·3424	1181
0·153	0·708	0·866	3·22711	5·13877	1·59238	46·3468	1266
0·244	1·27	1·38	3·22760	5·14046	1·59266	46·3765	1904
0·350	1·91	1·96	3·22749	5·14093	1·59286	46·3772	1919
0·361	2·11	2·02	3·22845	5·14246	1·59246	46·4186	2813
0·422	2·32	2·36	3·22765	5·14096	1·59279	46·3819	—

* Added oxygen corrected for initial oxygen.
† Final digits uncertain.

The lattice parameters for oxygen-free zirconium were determined as:

$$a = 3{\cdot}2258_0 \pm 0{\cdot}00064 \text{ kX units}$$
$$c = 5{\cdot}1373_2 \pm 0{\cdot}00105 \text{ kX units}$$
$$c/a = 1{\cdot}5926$$

from the following equations developed by R. M. TRECO[74]:

$$a = 3{\cdot}22580 + 0{\cdot}0010184 \times (\text{atomic per cent oxygen})$$
$$\text{std deviation} = \pm 0{\cdot}00095$$

$$c = 5{\cdot}13732 + 0{\cdot}0019967 \times (\text{atomic per cent oxygen})$$
$$\text{std deviation} = \pm 0{\cdot}00156$$

It was considered by Treco that his results might be used as a means of determining oxygen in zirconium.

R. M. Treco[75] also determined the effect of dissolved oxygen on the hardness of zirconium and the result was identical with that obtained in his earlier work.

The effect of oxygen absorption on the density of zirconium was determined by R. M. Treco[75]. The results are shown in *Table XCVII.*

Table XCVII. Effect of Oxygen on Density of Zirconium

Oxygen Atomic per cent	*Density* g/cm³	*Source*
0	6·541	J. H. de Boer and J. D. Fast[16]
2	6·555	,, ,, ,, ,,
10	6·601	,, ,, ,, ,,
0	6·507*	R. M. Treco[75]
0·147	6·509	,, ,,
1·961	6·517	,, ,,

* By unit-cell volume extrapolation.

Table XCVIII. Density and Composition of Several Types of Zirconium

Material	*Iodide crystal bar. Low hafnium*	*Magnesium-reduced purified sponge. Low hafnium*	*Iodide crystal bar. High hafnium*	*Magnesium-reduced graphite melted. High hafnium*
Atomic per cent *zirconium*	99·325	99·050	98·423	95·428
Atomic per cent *oxygen*	0·147	0·566	0·130	1·450
Atomic per cent *carbon*	0·468	0·226	0·084	1·493
Atomic per cent *hafnium*	0·014	0·040	1·239	1·310
Atomic per cent *iron*	0·046	0·117	0·119	0·114
Atomic per cent *titanium*	*	*	*	0·058
Atomic per cent *aluminium*	*	*	*	0·146
Atomic per cent *lead*	*	*	0·005	*
Archimedes density at 25° C (g/cm³)	6·518	6·492	6·578	6·634
X-Ray density at 25° C (g/cm³) *corrected for composition*	6·509	6·497	6·574	6·605
X-Ray density at 25° C (g/cm³) *not corrected for composition*	6·504	6·489	6·497	6·502
a_0 kX	3·2256	3·2279	3·2267	3·2264
c_0 kX	5·1371	5·1415	5·1388	5·1356

* Not detected.

Table XCVIII shows the purity of various types of zirconium which R. M. Treco[75] examined. The lattice constants were determined and the densities calculated. (See also Sections 11.2.28. and 12.2.)

(b) *Zirconium–sulphur*—There is a compound[77] ZrS_2 which is hexagonal and isomorphous with CdI_2. The lattice parameters are $a = 3{\cdot}68$ Å, $c = 5{\cdot}85$ Å.

(c) *Zirconium–chromium*—R. F. Domagala, D. J. McPherson and M. Hansen[17] of the Armour Research Foundation investigated zirconium–chromium alloys prepared by melting iodide zirconium with 99·9 per cent chromium in an arc melting furnace.

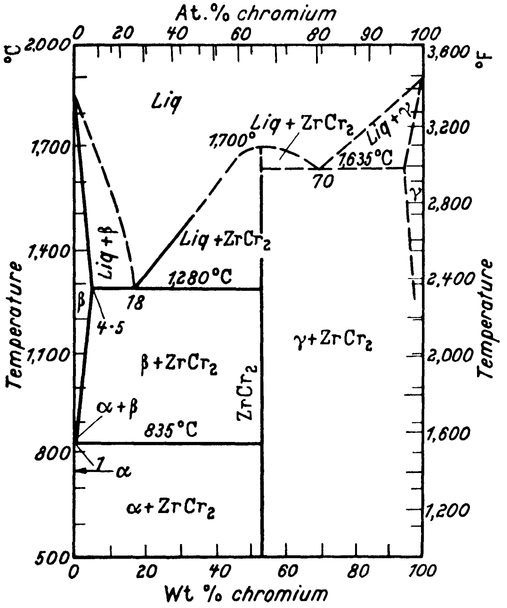


Figure 87. The zirconium – chromium system (after R. F. Domagala *et al.*[17])

The diagram for the zirconium–chromium system determined by Domagala *et al.* is shown in *Figure 87.* The principal features of the diagram include:

(*i*) The limit of solubility of chromium in β-zirconium is 4·5 per cent.

(*ii*) A eutectic occurs between β-zirconium and $ZrCr_2$ at 18 per cent chromium and 1280 ± 10° C.

(*iii*) A single intermediate phase exists in the system, at 53 per cent chromium, corresponding to the formula $ZrCr_2$. This phase melts with an open maximum at 1700 ± 25° C.

(*iv*) A eutectoid decomposition of β into α-zirconium plus $ZrCr_2$ occurs at 835 ± 10° C and 1 ±0·25 per cent chromium.

(*v*) The solubility of chromium in α-zirconium is less than 0·28 per cent at all temperature levels.

(*vi*) A eutectic occurs between $ZrCr_2$ and chromium rich solid solution at 70 per cent chromium and 1635 ± 15° C.

(*vii*) The maximum solubility of zirconium in chromium is less than 3 per cent.

The phase $ZrCr_2$ has the hexagonal ($MgZn_2$ type) structure with lattice parameter $c = 8{\cdot}262$ Å, $a = 5{\cdot}079$ Å, $c/a = 1{\cdot}627$.

W. ROSTOKER[62] noted that whereas Domagala *et al.* had found an as-cast alloy having the composition of $ZrCr_2$ to be isomorphous with $MgZn_2$ (*C*14 hexagonal lattice, 12 atoms per unit cell) E. T. HAYES, A. H. ROBERSON and M. H. DAVIES[35] reported it was isomorphous with $MgCu_2$ (*C*15 cubic lattice, 24 atoms per unit cell). It appeared that this difference might be explained by a temperature modification and it was successfully demonstrated by Rostoker that a transition from the $MgZn_2$ structure at lower temperatures to the $MgCu_2$ structure did occur at some temperature between 900 and 994° C.

R. F. DOMAGALA *et al.*[17] discuss the phase diagrams of the zirconium–chromium system which have been published by E. T. HAYES *et al.*[35] and by M. K. MCQUILLAN[51]. The former authors extended their investigation from zirconium to $ZrCr_2$ while McQuillan presented the entire diagram. The general features of these two diagrams may be summarized as follows:

(*1*) Hayes *et al.*:

(*i*) Zr–$ZrCr_2$ eutectic at 18 per cent chromium and 1380° C.
(*ii*) Maximum solubility of chromium in β-zirconium, 6·2 per cent at 1380° C.
(*iii*) Eutectoid $\beta \rightarrow \alpha + ZrCr_2$ at 1·8 per cent chromium and 805° C.
(*iv*) Negligible solubility of chromium in α-zirconium.
(*v*) Intermediate phase $ZrCr_2$ melting at 1525° C. Crystal structure: cubic $MgCu_2$ type, $a = 7{\cdot}21$ Å.

(*2*) McQuillan:

(*i*) Single intermediate phase at 48 per cent chromium, formed by the peritectic reaction $Liq + \beta \rightarrow C$ at 1650° C (C = compound).
(*ii*) Solubility of chromium in β-zirconium decreasing sharply from about 48 per cent at 1650° C to about 5 per cent at 1350° C, then gradually to about 2 per cent at 835° C.

(*iii*) Eutectoid: β → α + *C* at 2 per cent chromium and 835° C.
(*iv*) Very limited solubility of chromium in α-zirconium.
(*v*) Eutectic between the intermediate phase and chromium solid solution at 70 per cent chromium and about 1545° C.
(*vi*) Solubility of zirconium in chromium less than 2·6 per cent at the eutectic temperature.

Comparing the features established in this work with the literature it may be seen that Hayes *et al.* and Domagala *et al.* are in agreement on the general constitution of the zirconium rich region, whereas McQuillan has determined a greatly different set of phase relationships. The work of Domagala, however, agrees with that of McQuillan that the intermediate phase and the chromium rich solid solution form a eutectic. To a certain extent, differences in the results may be attributable to the use of different zirconium stock in the three programmes. Hayes *et al.* and McQuillan used magnesium-reduced zirconium metal while Domagala's work is based on alloys prepared with higher purity iodide crystal bar.

(d) *Zirconium–molybdenum*—R. F. Domagala, D. J. McPherson and M. Hansen[18] of the Armour Research Foundation investigated the system zirconium–molybdenum. The technique varied somewhat from the standard procedure which has been described for copper. The electrode tip was made of molybdenum to preclude

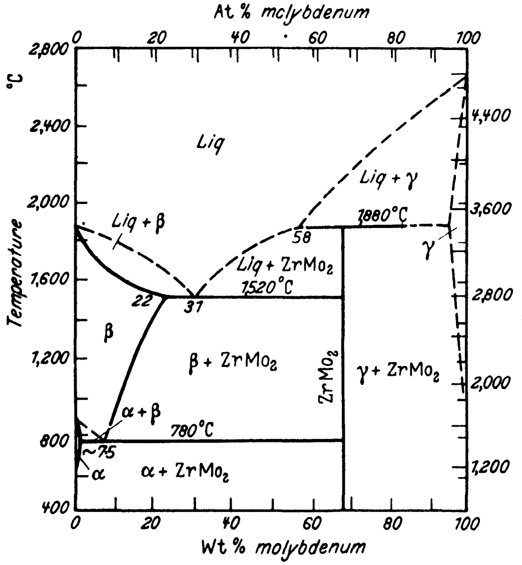


Figure 88. Zirconium–molybdenum system (after R. F. Domagala *et al.*[18])

any possibility of contamination. Iodide zirconium of nominal purity 99·8 per cent was used with molybdenum of 99·9 per cent purity.

The phase diagram determined by Domagala *et al.* is shown in *Figure 88.* The most important features of this system include:

(*i*) Only one intermediate phase, $ZrMo_2$ (ideally 67·78 per cent molybdenum), exists. It is formed by the peritectic reaction: *Liq* (58 per cent molybdenum) + molybdenum rich solid solution → $ZrMo_2$ at 1880 ± 20° C.

(*ii*) A eutectic between β solid solution and $ZrMo_2$ exists at 31 ± 1 per cent molybdenum and 1520 ± 15° C.

(*iii*) The limit of solubility of molybdenum in β-zirconium is about 22 per cent at the eutectic temperature.

(*iv*) A sluggish eutectoid decomposition of $\beta \rightarrow \alpha + ZrMo_2$ occurs at 7·5 ± 1 per cent molybdenum and 780 ± 5° C.

(*v*) The limit of solubility of molybdenum in α-zirconium is less than 0·18 per cent at all temperatures.

(*vi*) Less than 10 per cent zirconium is soluble in molybdenum.

The phase $ZrMo_2$ has the cubic (ZrW_2 type) of structure with lattice parameter $a = 7{\cdot}59$ Å.

P. DUWEZ and P. B. JORDAN[20] proved that $ZrMo_3$ did not exist and they identified a face centred cubic phase as $ZrMo_2$ with the *C*15 ($MgCu_2$) structure. The lattice parameter of the phase was 7·58 Å; this is in agreement with the value of 7·59 Å obtained by Domagala.

C. T. ANDERSON *et al.* of the U.S. Bureau of Mines[2] prepared zirconium–molybdenum alloys containing up to 10 per cent molybdenum from Kroll sponge zirconium and scrap molybdenum (99·9 per cent). Microstructure, forgeability, heat resistance and tensile properties were studied.

(e) *Zirconium–tungsten*—R. F. DOMAGALA, D. J. MCPHERSON and M. HANSEN[18] of the Armour Research Foundation investigated the system zirconium–tungsten. The technique varied slightly from that employed for the zirconium–copper work which has been described.

An arc furnace was employed and the tungsten electrode was used as usual but, due to the large difference between the melting points of tungsten and zirconium, master alloys were first prepared and used as alloying additions. Iodide zirconium of 99·8 per cent nominal purity was used with tungsten of 99·9 per cent purity.

The zirconium–tungsten phase diagram is shown in *Figure 89.*

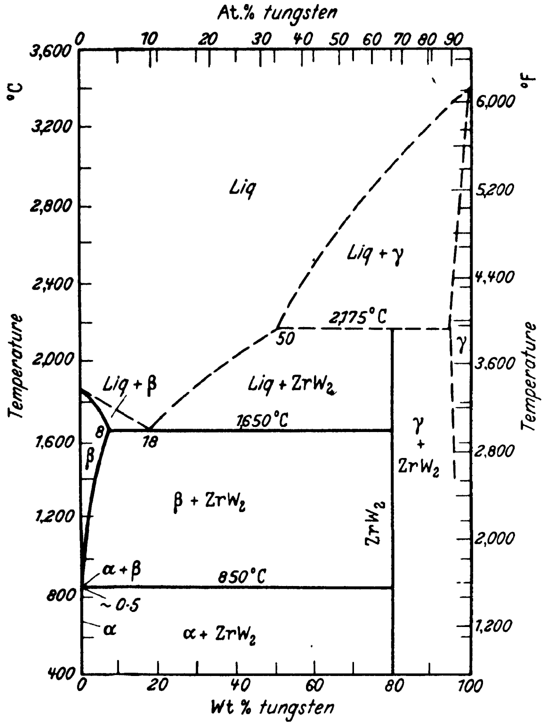


Figure 89. Zirconium–tungsten system (after R. F. DOMAGALA *et al.*[18])

The system is similar to the zirconium–molybdenum system and shows the following features:

(*i*) A single intermediate phase, ZrW_2 (ideally 80·13 per cent tungsten), exists. It is formed by the reaction: *Liq* (50 per cent tungsten) + tungsten rich solid solution → ZrW_2 at 2175 ± 25° C.

(*ii*) A eutectic between β solid solution and ZrW_2 occurs at 1650 ± 15° C and 18 per cent tungsten.

(*iii*) The limit of solubility of tungsten in β-zirconium is about 8 per cent at the eutectic temperature.

(*iv*) β decomposes into $\alpha + ZrW_2$ eutectoidally at about 0·5 per cent tungsten and 850 ± 15° C.

(*v*) The solubility of tungsten in α-zirconium is less than 0·5 per cent at all temperatures.

(*vi*) Less than 10 per cent zirconium is soluble in tungsten.

G. A. GEACH and G. F. SLATTERY[25] substantially confirmed the results obtained by Domagala *et al.*

X-Ray patterns were not made to check the structure of the compound ZrW_2 and the work of A. CLAASSEN and W. G. BURGERS[12] was accepted by DOMAGALA *et al.*[18]. Claassen and Burgers identified the compound ZrW_2 and stated it had a face centred cubic structure with a lattice parameter of 7·61 Å.

C. T. ANDERSON *et al.* of the U.S. Bureau of Mines[2] prepared zirconium–tungsten alloys containing up to 9·9 per cent tungsten and examined their microstructure, forgeability, heat resistance and tensile properties.

14.3.7. *Groups VII and VIII elements*

(a) *Zirconium–manganese*—A compound $ZrMn_2$ has been detected by H. J. WALLBAUM[80, 81]. It is hexagonal, isomorphous with $MgZn_2$, and has lattice parameters $a = 5{\cdot}029$ Å and $c = 8{\cdot}223$ Å with an axial ratio $c/a = 1{\cdot}635$.

The alloys prepared by Anderson *et al.* contained up to 25 weight per cent manganese. P. C. L. PFEIL[60] commenting on Anderson's results states that the alloy containing 0·61 weight per cent manganese was single phase showing an acicular pattern but the 1·31 weight per cent alloy showed in addition another structural feature with the appearance described as being that of a eutectoid. This structure occupied the entire field of the 3·92 weight per cent alloy and is described now as a eutectic. It is most probably a eutectoid structure. From the microstructural description the 5·12 weight per cent alloy consists of this structure cross-hatched by long, thin needles intersecting at 120°. These needles may possibly be of an intermetallic compound precipitating out of the beta phase as it cools. The needles were observed in no other alloy. With 7·5 weight per cent manganese the eutectoid material was surrounded by a network with the appearance of a eutectic. The proportions of the eutectic material steadily increased in the 2·5, 12·5 and 14·1 weight per cent alloys. The 25 weight per cent alloy contained very hard particles of a new phase embedded in the matrix of eutectic.

(b) *Zirconium–iron*—E. T. HAYES, A. H. ROBERSON and W. O'BRIEN[36] investigating the zirconium–iron system developed the diagram for the zirconium rich alloys shown in *Figure 90.* Phase diagrams of this system have been published before, the emphasis being on the iron rich section. R. VOGEL and W. TONN[78] developed a complete diagram but since most of their alloys were melted in alumina crucibles the higher zirconium alloys must have been contaminated due to the reduction of the alumina by the

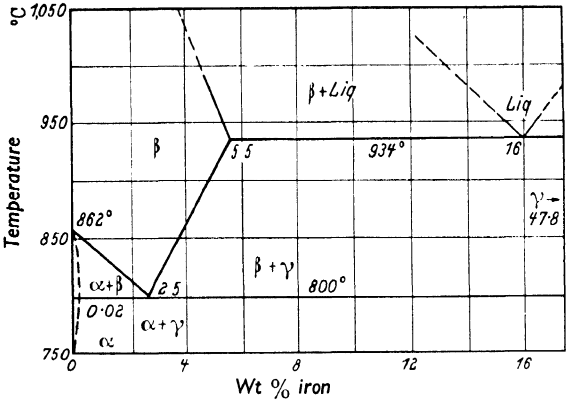


Figure 90. *Partial diagram of zirconium–iron system* (*after* E. T. Hayes *et al.*[36])

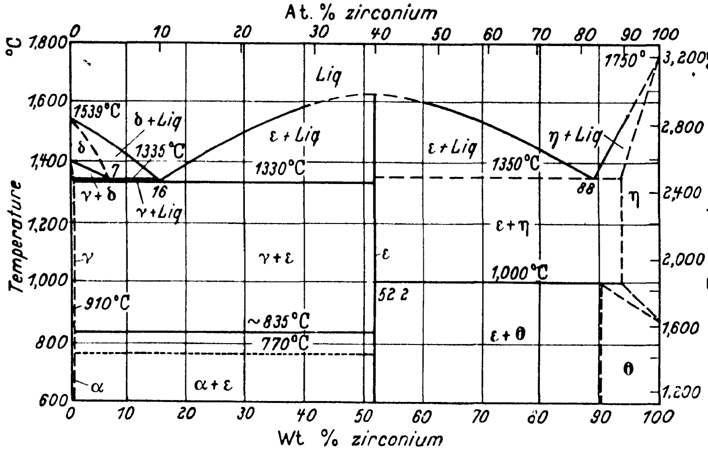


Figure 91. *The zirconium–iron system* (*after* H. J. Wallbaum[80, 81; 52])

zirconium. T. E. Allibone and C. Sykes[1] studied alloys containing less than 30 per cent zirconium.

H. J. Wallbaum[80, 81] prepared a few high zirconium alloys by melting in alumina. A diagram based on the work of this investigator has been developed[52], and is shown in *Figure 91.*

E. T. Hayes *et al.*[36] prepared their alloys from Kroll sponge by melting in graphite crucibles. This was preferred to arc melting with tungsten electrodes because the carbon pick-up, from 0·05 to 0·96 per cent, was considered to be less objectionable than the pick-up of 0·1 to 0·3 per cent tungsten, since the carbide was formed as a discrete and easily recognizable phase.

R. Vogel and W. Tonn[78] gave a compound, Zr_2Fe_3, while Wallbaum gave it as $ZrFe_2$. Both give the iron rich eutectic at 18 per cent zirconium and 1335° C. Hayes *et al.* give the eutectic at 16 per cent iron and melting at 934° C, a result which is confirmed by those who have operated the Kroll process for the production of zirconium, as the 'tears' or nodules formed on the walls of the iron distillation pot when the temperature exceeds 935° C have a consistent iron content of 16 per cent and melt at a temperature below 950° C.

Hayes *et al.* first considered the intermetallic compound to be Zr_2Fe_3 but later decided it was $ZrFe_2$. X-Ray diffraction showed the phase to be face centred cubic with a parameter $a = 7{\cdot}040$ Å. No confirmation was obtained of the results of Wallbaum, which showed two phases of different composition, one isomorphous with $MgCu_2$ and the other with $MgNi_2$.

The solid solubility of iron in alpha zirconium was found by Hayes *et al.* to be between 0·013 and 0·02 per cent. The 0·09 per cent alloy gave a eutectoid arrest at 800° C; therefore the solid solubility of iron in alpha zirconium at 800° C must be less than this amount. Examination of a series of fairly rapidly cooled alloys indicated that the eutectoid composition was 2·5 per cent iron. The eutectoid temperature was found to be 800° C by thermal analysis.

It was not found possible to retain the beta phase by quenching even with the maximum amount of iron in solid solution (5·5 per cent).

The lattice parameter of the alpha phase remained constant, suggesting that supersaturated solid solutions of iron in alpha zirconium were not formed. Specimens quenched from the beta phase field had a characteristic Widmanstätten structure. The alpha phase originally present in alloys quenched from the two-phase (alpha and beta) field could be recognized even in small amounts, because of its rounded appearance.

(c) *Zirconium–cobalt*—The zirconium–cobalt system has been investigated by U. Hashimoto[30], W. Köster and W. Mulfinger[42] and H. J. Wallbaum[80]. A eutectic is formed with 12 per cent zirconium at 1460° C between a cobalt rich solid solution containing 2 per cent zirconium and a high melting point compound $ZrCo_4$.

Another compound, $ZrCo_2$, has the cubic $MgCu_2$ type of crystal structure with a lattice parameter of 6·887 Å. The evidence regarding the effect of zirconium on the allotropic transformation temperature of cobalt is contradictory.

Zirconium alloys containing up to 46 per cent cobalt were prepared by C. T. **Anderson** *et al.* at the U.S. Bureau of Mines[2]. The alloys were prepared by melting Kroll zirconium sponge and cobalt rondelles in graphite crucibles in a vacuum. The carbon content of the alloys varied from 0·05 to 0·42 per cent and the iron from 0·05 to 0·48 per cent. The microstructure of the alloys was examined and it was found that small additions of cobalt produced a Widmanstätten pattern of bright needle-like grains with a small amount of second phase between the grains. Above 2 per cent cobalt the second phase was agglomerated into irregularly shaped areas surrounded by bright solid solution grains containing a fine pearlitic pattern. This pearlitic pattern reached a maximum at about 3 per cent cobalt. At 5 per cent the second phase formed a connecting network surrounding bright zirconium grains and less of the intergranular pearlitic structure was evident. The second phase comprised about 60 per cent of the field in the 13 per cent specimen and the pearlitic structure disappeared from the solid solution grains.

P. C. L. **Pfeil**[60] comments that it is difficult to be sure of the nature of the pearlitic materal but it is possible that a eutectoid reaction with decomposition of a solid solution based on beta zirconium is involved. The 19·4 per cent cobalt alloy contains two phases and has the appearance of bright dendrites in a slightly darker background. The alloy was resistant to attack by the usual etching reagent and the difference in hardness between the two phases was small. P. C. L. **Pfeil**[60] considered it was probable that this alloy contained two intermetallic compounds. The 25 per cent alloy was similar except for the presence of small clusters of needles in the matrix phase.

The 45 per cent alloy contained approximately equal amounts of bright angular phase and coarse eutectic. The Knoop hardness of the lower cobalt alloys was 82 in the solid solution arrest and 253 in the second phase. These hardnesses became 104 and 290 respectively in the 10·1 per cent alloy.

The major phase of the 25 per cent alloy had a hardness of 435, and this would confirm the suggestion that a different intermediate phase is present in this alloy.

(d) *Zirconium–nickel*—A tentative equilibrium diagram has been developed by M. **Hansen**[31] based upon the experimental work of T. E. **Allibone** and C. **Sykes**[1] and of other workers. Two compounds are shown: $ZrNi_3$ and $ZrNi_4$, the latter being formed peritectically. Also shown are eutectics with 16 and 60 weight per cent zirconium. The x-ray work of H. J. WALLBAUM[80] gives the structure of $ZrNi_3$ as face centred cubic. C. T. ANDERSON *et al.*[2] at the U.S. Bureau of Mines prepared alloys containing up to 8 per cent nickel by melting Kroll zirconium sponge and nickel in graphite crucibles *in vacuo.* The carbon content varied between 0·07 and 0·18 per cent, the iron content was 0·04 to 0·05 per cent except in the 7·8 and 8·0 per cent alloys when the iron was 0·21 and 0·42 per cent respectively. According to the U.S. Bureau of Mines report, small amounts of nickel produced a fine intergranular constituent surrounding transformed beta zirconium. In the 8 per cent nickel alloy, which was the upper limit investigated, the amount of intergranular constituent was up to 40 per cent. Fine laminations in the constituent were shown by the higher alloy contents. It is suggested at the Bureau that a eutectic is involved, and the results quoted are consistent with this possibility. The microstructure of the 0·47 per cent nickel alloy in the as-cast state shown by F. B. LITTON[44] also favours this possibility.

F. B. LITTON and S. C. OGBURN[45] state the solubilities of nickel in both alpha and beta zirconium are less than 0·47 per cent presumably basing their statement on the fact that the as-cast microstructure of this alloy contains a second phase. P. C. L. PFEIL[60] suggests that if this is all the evidence upon which the statement is based then it may be in error for similar reasons to those suggested to be applicable to the zirconium–silicon system.

The latest work on the zirconium–nickel alloy system has been done by E. T. HAYES, A. H. ROBERSON and O. G. PAASCHE[34]. The investigation covered composition ranges up to 40 per cent nickel, the alloys being prepared by arc melting pure nickel and

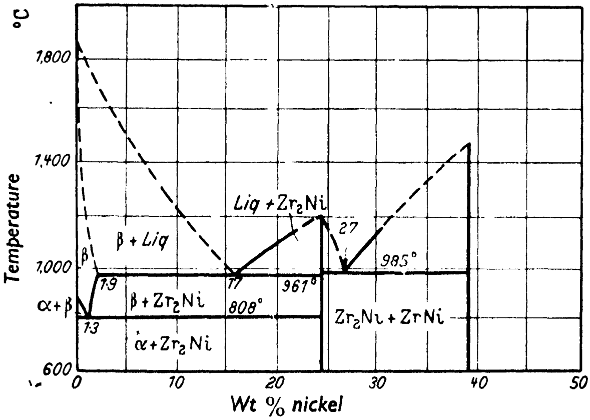


Figure 92. Partial diagram of zirconium–nickel system (after E. T. HAYES *et al.*[34]*)*

Kroll zirconium. The Kroll metal had a typical analysis of: O_2 0·08, Fe 0·06, N_2 0·01, C 0·02 per cent and other impurities such as Pb, Ti, Si, Ni and Al less than 0·001 per cent each. The constitution diagram developed by Hayes *et al.* is shown in *Figure 92.*

The results of quenching and slow cooling selected alloys from various temperature levels are depicted in the detailed diagram of the beta field shown in *Figure 93.* The following salient features were established:

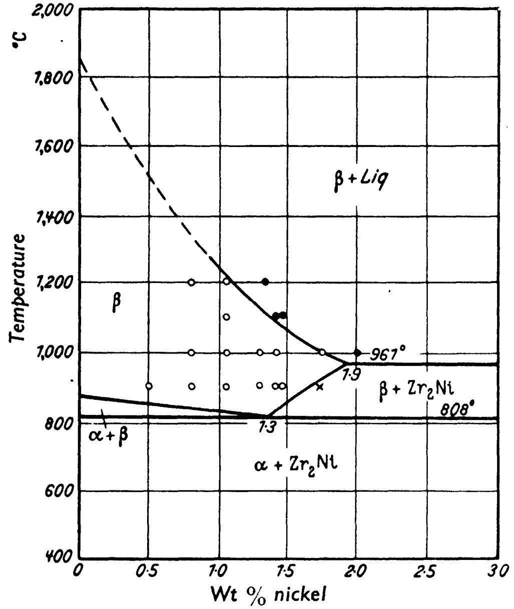


Figure 93. Beta field of zirconium – nickel system (after E. T. HAYES *et al.*[34])

(*i*) Negligible solubility of nickel in zirconium at room temperature.

(*ii*) Eutectoidal decomposition of the beta solid solution at 1·3 per cent nickel and 808° C.

(*iii*) The maximum solubility of nickel in beta zirconium is about 1·9 per cent at the eutectic temperature (961° C).

(*iv*) Presence of an intermediate phase at 24·4 per cent nickel. This phase, believed to be Zr_2Ni, has a melting point near 1200° C.

(*v*) A eutectic reaction occurs between beta zirconium and the intermediate phase Zr_2Ni at 17 per cent nickel and 961° C.

(*vi*) A second intermediate phase was located at 39·2 per cent nickel and tentatively identified as ZrNi. This compound melted at approximately 1470° C.

(*vii*) Between the two intermediate compounds a eutectic was located at 27 per cent nickel and 985° C.

(e) *Zirconium alloys with ruthenium, rhodium and palladium*—The only piece of evidence concerning these three systems appears to be the recognition of a compound $ZrRu_2$ by H. J. WALLBAUM[79]. This compound is isomorphous with the hexagonal $MgZn_2$, and has parameters of $a = 5{\cdot}131$ Å, $c = 8{\cdot}490$ Å.

(f) *Zirconium alloys with osmium, iridium and platinum*—The compounds formed by osmium and iridium are isomorphous[79] with $MgZn_2$. That formed with platinum[56] is isomorphous with $TiNi_3$ (hexagonal). The lattice parameters are shown in *Table XCIX*.

Table XCIX. Crystal Structures of Zirconium Compounds with Metals of the Platinum Group

Compound	*Isomorphous with*	*a*	*c*
$ZrOs_2$	$MgZn_2$	5·179	8·509
$ZrIr_2$	$MgZn_2$	—	—
$ZrPt_3$	$TiNi_3$	5·633	9·21

It is of interest to note that $ZrPt_3$ is not isomorphous with $TiPt_3$ which is cubic.

P. C. L. PFEIL[60] comments that so far as data are available, the systems of the platinum group of metals resemble the corresponding systems with iron, cobalt, and nickel. It is possible that the suggested explanation[7] why the Laves phases $TiNi_2$, $ZrNi_2$ *etc* do not occur also applies to $ZrPt_2$, and if this is so the behaviour of platinum and nickel in this range of alloy compositions would appear to be similar.

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15

MELTING PRACTICES

THE production of bars of zirconium metal by the iodide process has been described and also the production of sponge metal by the Kroll process; both these forms have limited or little use in commerce and require further processing to convert them to useful forms such as sheet and wire.

While it is true that the crystal bar produced by the iodide method can be cold worked by drawing and rolling into wire and sheet, it is not always satisfactory to do this as the large crystals tend to overlap one another and form imperfections in the finished product. Even the thickest filaments or crystal bars are still much too small to consider as a basis for the production of sheet and it is therefore necessary to melt the crystal bar and produce ingots suitable for forming. The same conclusion obviously applies to the spongy metal which usually contains small amounts of impurities such as residual magnesium chloride and magnesium which have not been completely removed during the vacuum treatment, but which are eliminated during the process of melting to produce ingot.

Molten zirconium is an extremely reactive metal not only towards the common gases but also to most of the ceramic materials which are normally used in the form of crucibles to contain molten metals. Such oxides as silica, alumina, magnesia and beryllia are reduced by molten zirconium and if these oxides or allied materials are used for crucible production the zirconium is embrittled by the absorption of oxide. Thoria is probably the least attacked of the normal refractory materials but this is expensive and not entirely satisfactory. Therefore, when melting zirconium two important conditions must be satisfied if the ingot metal is to be ductile, (*a*) the furnace atmosphere must be free from oxygen, nitrogen and other common gases and (*b*) the crucible should be capable of withstanding the action of molten zirconium. Unfortunately, while it is possible to satisfy the first condition, it is difficult to satisfy the second without introducing other difficulties, and the present position is that while there are methods which may be used to melt zirconium, none of these is entirely satisfactory, particularly when applied to alloy production.

In describing the various methods which have been used to melt zirconium it has been thought best to follow the order in which they were developed.

15.1. THE SPLIT GRAPHITE TUBE RESISTOR FURNACE

The application of this furnace to the melting of zirconium was first proposed by W. J. KROLL and his associates[7] at the U.S. Bureau of Mines, Albany, Oregon. W. J. KROLL *et al.*[8] were also responsible for the development of the furnace from the less efficient graphite tube resistors used by Tammann and others.

Before proceeding to describe the split graphite tube resistor furnace it is important to return to the subject of crucible material because it has been mentioned that there is no likely crucible material which is not attacked by molten zirconium. In making melting tests with graphite crucibles, W. J. KROLL[6] found, much to his surprise, that graphite was not unduly attacked, and that the maximum contamination by carbon appeared to be about 0·33 per cent. With reasonable care values of the order of 0·15 per cent have since been consistently obtained. Time and temperature are important factors in determining the degree of contamination and the usual practice is to arrange to cast automatically by having a small hole in the bottom of the graphite crucible which is plugged with zirconium metal before use. The heating cycle is arranged so that a few moments after melting the zirconium in the crucible, the plug melts and the molten zirconium drains into a tapered graphite mould placed directly beneath the crucible. This arrangement gives a simple method for melting and casting in a vacuum.

The novel feature of the furnace was the use of a slotted graphite tube so that the current passed up one leg and down the other with both electrode clamps at the bottom of the tube. In this arrangement the electrical resistance is almost four times that of a similar tube with top and bottom clamps and the heat loss through the clamps is only half as great because the connections are made at only one end. Furthermore, both clamps may be rigidly fixed permitting the tube to expand freely upwards. Heat insulation is simple since there are no side connections and it is a simple matter to fit heat baffles round the tube. The furnace can be designed for single phase or multiphase current by cutting the necessary slots in the tube, and the arrangement can easily be fitted into a vacuum container with the current and water-cooling connections fitted to a rigid base supporting the tube while the main body of the furnace can be raised exposing the furnace parts for maintenance. Such a furnace designed[15] on the Kroll principle is shown in *Figure 94.*

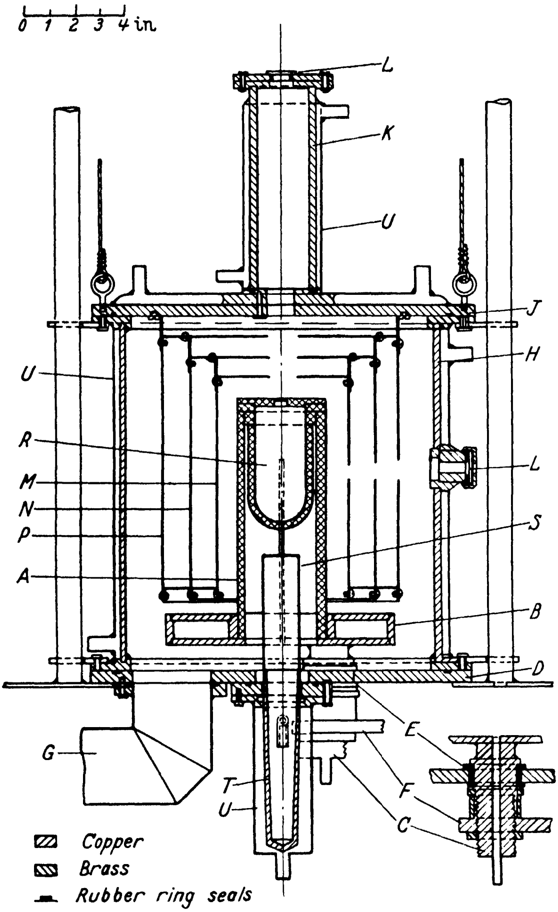

Figure 94. Sectional elevation of the graphite resistor furnace (after J. A. Rees *and* R. J. L. Eborall[15])

A Graphite resistor, B 'C' *segments, C Electrical conductors, D Baseplate, E Neoprene, F Bus bars, G Vacuum orifice, H Casing, J Top plate, K Extension, L Silica window, M Molybdenum screen, N Nickel screen, P Stainless steel screen, R Graphite melting pot, S Alumina guard tube, T Mould, U Water jacket*

The split or slotted graphite tube, in this instance 9-in long, 3½-in outside diameter, and having 1-cm thick wall, is shown as item *A* in the figure. The slot extends to within 2 in from the top. Each side of the split tube is supported in a C-shaped water-cooled copper segment, *B*, and electrical contact is made by copper plating the bottom end of the tube and soft soldering each half to its respective segment. Equally satisfactory contact can be made by forcing copper wedges tightly between the graphite tube and the segment. Two hollow electrical conductors, *C*, which also act as the cooling-water leads are brazed to each segment. These conductors pass through the baseplate, *D*, to which they are attached and from which they are insulated by neoprene washers and rings, which also effect a vacuum seal. The vacuum-tight furnace cover is made from a cylindrical metal casing, *H*, with a top plate, *J*, both being water-cooled and the whole easily raised from the baseplate. Three metal radiation screens, *M*, *N* and *P*, are attached to the cover; these are made of molybdenum, nickel and stainless steel respectively.

No refractory materials are used in the construction of the furnace as such materials absorb gases and moisture which make it difficult to obtain satisfactory vacuum conditions in reasonable pumping times. The progress of the heating may be observed through the window, *L*. The furnace is evacuated through the orifice *G*; oil or mercury diffusion pumps being used backed by a rotary mechanical pump.

To obtain optimum operating conditions liquid air and phosphorus pentoxide traps are used, between the furnace and the diffusion pump, and between the diffusion and rotary pumps respectively to remove condensable vapours.

The power required to operate the furnace is obtained from a transformer with nine primary tappings so that about 5 to 22 kW are available at secondary voltages between 4 and 8 V. Connection is made to the conductors *C*, by copper bus bars and flexible copper leads.

In the actual melting process the zirconium sponge which is recovered from the reduction crucible is cut into pieces, which are small enough to feed to a die in which the sponge is pressed into cylindrical briquettes, suitable for charging into the graphite crucible. The crucible is prepared by degassing at a temperature of about 2000° C and a small amount of metal is melted in the crucible. The metal is allowed to drain through the hole when sufficient is retained to form a seal. Zirconium very readily wets the graphite, and the crucibles after use are lined with a bright metallic coating of zirconium. The graphite crucible is placed in the split tube and the furnace sealed and evacuated before raising the temperature. The metal is not melted immediately; the temperature is held at about 1000° C for a short period to degas the metal before the final melting. The degassing period is important as it removes the last traces of magnesium and magnesium chloride as well as hydrogen. It is good practice to use a water-cooled condenser to collect the products of distillation which would otherwise be dispersed throughout the furnace. The distillate is hygroscopic and if exposed to the atmosphere absorbs water which is difficult to remove by pumping.

When the metal is degassed as indicated by the vacuum instruments the temperature is raised rapidly and it is possible to observe when the metal is molten by inspection through the window. By slightly increasing the power the zirconium plug is melted and the metal cast instantly. The vacuum must be maintained until the ingot is cold.

Zirconium produced by melting in a graphite crucible is satisfactory except in one detail—the carbon content—and unfortunately the presence of carbon considerably reduces the corrosion resistance of the metal. The corrosion resistance of the zirconium depends on the degree of carbon contamination and on the corroding medium, and while for most purposes zirconium melted with care in a graphite crucible is perfectly satisfactory, the best properties can only be obtained from low carbon metal. The presence of carbon up to about 0·2 per cent does not affect the working of the metal unduly, and ductile sheet and other forms of the metal are produced without difficulty.

The use of the split graphite tube resistor provides a means of producing zirconium and its alloys as homogeneous ingots. The control required is a minimum, and a reasonably skilful operator has no difficulty in producing metal that is only slightly contaminated with carbon. Little maintenance is required and the split tube has a very long life.

15.2. INDUCTION MELTING

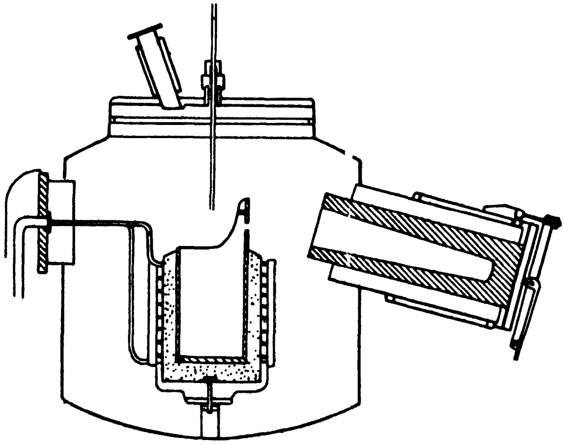

Figure 95. 100-kW *vacuum induction furnace used in melting titanium and zirconium. The diagram shows the shell with its loading hatches and the seals through which water-cooled high frequency leads enter the furnace (after National Lead Co.*[12])

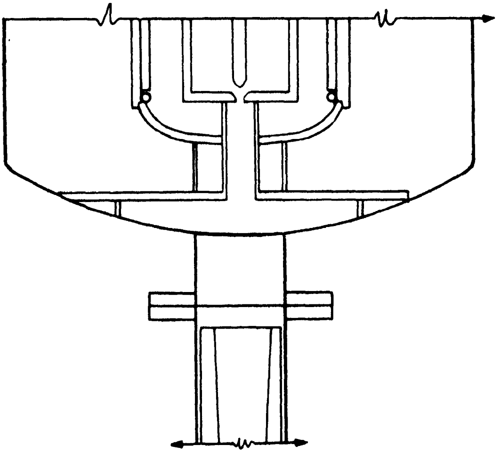

Figure 96. Tilting type furnace was redesigned, as shown here, to allow bottom pouring down into a vertically aligned ingot mould rather than pouring over lip of crucible (after National Lead Co.[12])

High frequency induction furnaces can be used to melt zirconium using graphite crucibles in which the heat is generated by induction. The melting of both zirconium and titanium on a production scale as practised by the Titanium Alloy Manufacturing Division of the National Lead Company of America has been described[12]. Zirconium was melted in graphite crucibles with bottom-pour and ingots up to nearly 40 lb weight were cast with carbon contamination from 0·17 to 0·24 per cent and Brinell hardness ranging from 170 to 229. The arrangement of a 100-kW vacuum induction furnace which was used to melt zirconium and titanium is shown in *Figures 95* and *96*. *Figure 95* shows the shell with its loading hatches and the slots through which water-cooled high frequency leads enter the furnace. *Figure 96* illustrates the arrangement to permit bottom pouring into a vertically aligned ingot mould rather than pouring by tilting. A graphite stopper rod is shown which was actuated through the furnace cover using a modified Wilson seal.

15.3. ARC MELTING FURNACES

The most successful method for melting high melting point reactive metals without contamination is the electric arc technique, operating in an atmosphere of pure argon or helium with a water-cooled copper crucible. This method was used originally in 1903 by von Bolton to melt tantalum and appears to have excited little interest until W. J. KROLL[5] resurrected it in 1940. The method was subsequently developed by the Battelle Memorial Institute where it was

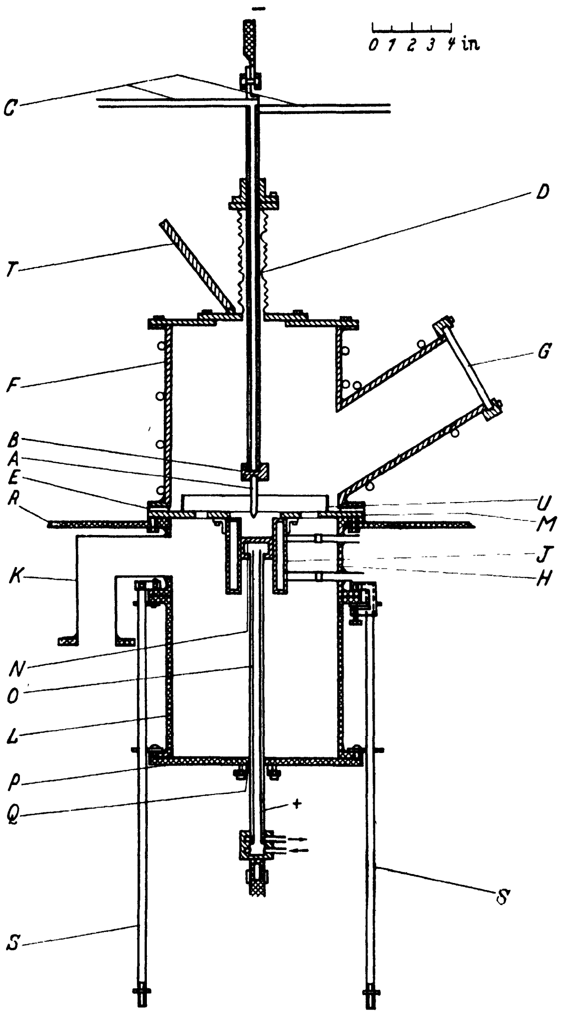

Figure 97. Diagram of arc melting furnace (after J. A. REES *and* R. J. L. EBORALL[15])

A Tungsten electrode, B Copper electrode holder, C Handlebars, D Metal bellows, E Tufnol *insulating ring, F Copper furnace bell with brass flanges and lid, G Silica windows, H Fixed section (steel), J Copper mould walls, K Vacuum pipe, L Free section (steel), M Brass hearth plate, N Copper mould base, O Copper tubes, P Steel baseplate, Q Wilson seal, R Steel table top, S Guide rods, T Hinged clamp rod, U Radiation shield*

used to melt titanium and its alloys on a small scale[17]. More recently the method has been developed to full scale production melting of titanium and its alloys, and ingots weighing more than a ton have been made.

The basis of the electric furnace technique for melting titanium and zirconium is to strike an electric arc from an electrode, usually made of tungsten, on to the metal which is contained in a water-cooled copper crucible, and the molten pool of metal is chilled before it can react with the crucible. In this manner an ingot is built up progressively by feeding the metal into the arc and cooling the pool of molten metal almost as rapidly as it is formed. The only molten metal present at any instant is that portion of the metal which is within the field of the arc. While it is possible by this method to build up ingots of metal free from crucible contamination, it is impossible to ensure homogeneity as the sponge tends to vary slightly in composition. The production of alloys introduces further complications as it is necessary to add the alloying ingredients in the exact proportions required throughout the whole process, thus ensuring that every pool of metal is of the same composition.

Before proceeding to describe the various modifications which have been introduced to improve the arc melting technique, it is desirable to describe in detail a simple arrangement such as is used by investigators in laboratory work[15]. The furnace is shown in *Figure 97*. The electrode assembly comprises a replaceable tungsten electrode, *A*, which is brazed on to a copper disc (it is better to form a thread on the end of the tungsten electrode and fix by screwing) fitted to the electrode holder, *B*, which carries the cooling water as well as the current. A metal bellows, *D*, is fitted to the upper part of the electrode holder and to the cover of the furnace, thus providing a flexible seal. Convoluted rubber tubing may be used instead of the metal bellows, is simpler to fix and gives even greater flexibility. Another method used on larger furnaces is to use a Wilson seal which is very satisfactory but as it permits only vertical movement it is necessary to move the arc by means of a magnet manipulated from outside the furnace. The water connections are made in the electrode holder above the bellows. The lower part of the furnace casing may be lowered and within this is fitted the crucible. The furnace shown has been designed to permit lowering of the ingot as it is built up and so the electrode level is constant instead of requiring to be raised continuously.

The copper crucible is in two water-cooled parts, the walls, *J*, and a movable base, *N*, which is a sliding fit between the walls. The base is cooled and supported by two concentric tubes, *O*, which pass through a Wilson seal in the baseplate, *P*.

The power required to operate this furnace, with a ¼-in electrode and capable of producing small ingots of a few pounds, is obtained from a direct current welding generator with a variable 0 to 400 A current range. The mould is made positive and the tungsten electrode negative and the bell is insulated from the base by a *Tufnol* ring, *E*.

When preparing to melt, it is desirable to be able to strike the arc without actually touching the zirconium with the electrode. By this means contamination may be reduced. The result may be achieved by wrapping a strip of magnesium ribbon round the electrode; the ribbon touches the metal and strikes an arc, the magnesium being volatilized. Another method is to superimpose on the electrode a high frequency current, such as is used for argon- or heli-arc welding, by this means the arc can be struck without the electrode touching the zirconium; in argon the arc strikes across about 0·5 in. The latter method is preferred as it permits the arc to be re-struck during melting operations without the risk of the electrode becoming united to the ingot due to the tip contacting the cooling pool of metal.

The system is evacuated through the pipe, *K*, by means of a rotary mechanical pump with a phosphorus pentoxide trap between the furnace and the pump. The usual procedure when preparing to melt is to evacuate and refill with argon and then evacuate again and finally fill with argon. The argon is usually maintained under a slight flow which may need to be increased if the chloride content is appreciable. A mixture of argon and helium is claimed to give better results than argon alone. Helium gives the maximum power for a given arc length while argon stabilizes the arc. If argon is used without helium higher voltage is required. In small scale operations the residual impurities in the argon, mainly nitrogen and some moisture, are removed by 'gettering' with a piece of scrap zirconium which is melted on the copper base, and pushed aside by the electrode before proceeding to melt the ingot. With very small melts, several charges can be prepared in dishes cut out of the copper base; one of these contains the zirconium for 'gettering' and by moving the electrode the other charges are melted in turn and thus six or even more samples can be prepared in one operation.

An improved type of arc melting furnace is shown in *Figure 98*. The arrangement shows the water-cooled electrode with a double O-ring vacuum seal. This arrangement permits only vertical movement of the electrode tip but a magnetic field is induced inside the crucible by means of a large permanent magnet or coils operated from just outside the water-cooled jacket.

The magnetic field is used to move the arc over the surface of the melt and may be controlled manually or mechanically. By means of this device and by reducing the cooling to a minimum it is possible to melt up to the wall of the crucible. A high frequency current

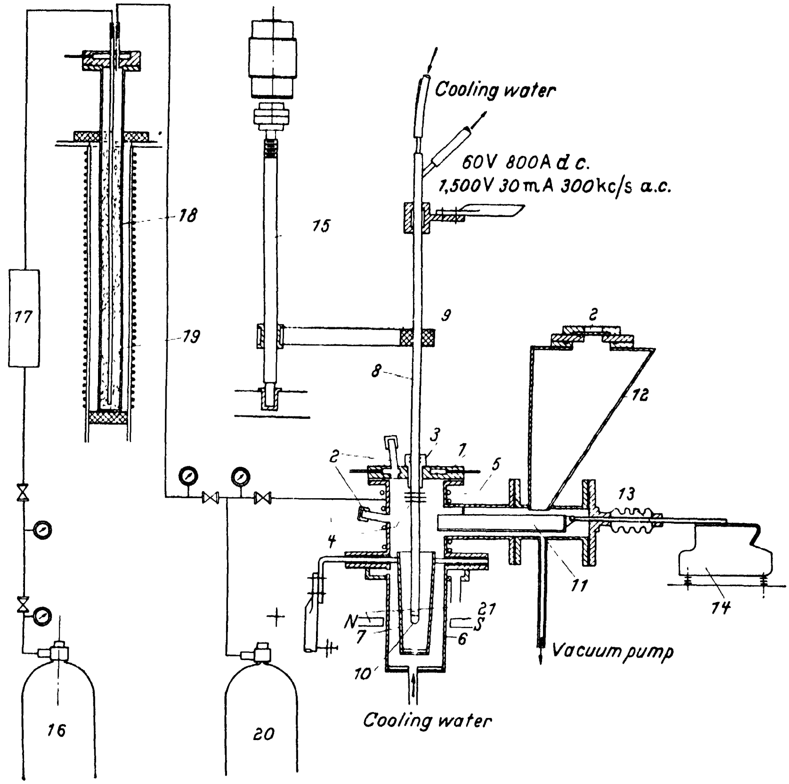

Figure 98. Tungsten electrode arc furnace

1 Water-cooled furnace head, 2 Sight glass, 3 Permali *high frequency insulating bush with double O-ring seal, 4 Radiation shields attached to 3, 5 Upper furnace casing cooled by external coils, 6 Water-cooled jacket for melting crucible, 7 Copper crucible, 8 Water-cooled electrode, 9* Tufnol *insulation, 10 Tungsten tip, 11 Spring-suspended feed tray, 12 Feed hopper, 13 Convoluted rubber seal for 14, 14 Vibrator with variable control, 15 Electrode feed drive, 16 Argon gas supply, 17 Phosphorus pentoxide drying chamber, 18 Argon purification furnace, 19 Zirconium turnings, 20 Purified argon storage cylinder, 21 Magnetic arc control*

from a modified argon arc welding set is superimposed on the main arc current and operated to strike the arc either at the commencement of operations or at any time during the run. This arrangement has been found to be almost indispensable.

A feed hopper is shown with a *Syntron* feeding device sealed from the atmosphere by means of a convoluted rubber tube.

Melting operations may be performed *in vacuo*, sufficient vapour being present to maintain the arc. Vacuum melting can assure complete elimination of volatile impurities.

15.4. ARGON PURIFICATION

In larger operations the practice is to purify the argon by one of several methods before feeding it to the furnace. These methods are generally based on the removal of the impurities which may be nitrogen, oxygen, or water vapour, by contact with a hot reactive metal such as magnesium, titanium, zirconium, calcium, sodium or alloys of these metals. The production of pure argon is a difficult matter and great care is required to ensure the complete removal of the impurities. Purity of the argon is difficult to determine but oxygen and nitrogen can be detected by melting a small button of zirconium or titanium in the gas and noting the extent of discoloration after cooling.

An argon purification apparatus is included in the arrangement shown in *Figure 98.* The argon is passed over heated zirconium scrap contained in a *Nimonic 90* tube. The purification is carried out under a pressure of 150 lb/in^2 at 900° C. This method has many advantages including improved purification and absence of large gas-holders.

15.5. TUNGSTEN CONTAMINATION

While the use of the electric arc in conjunction with a water-cooled copper crucible permits melting zirconium without crucible contamination, there is another source of contamination to be considered. The furnace which has been described employs a tungsten electrode and it is found in practice that the zirconium ingot often contains tungsten. The tungsten is usually found in small discrete particles in the finished ingot and causes failure of the metal when worked. Tungsten contamination is mainly the result of spattering while melting sponge and there is much less likelihood of contamination when crystal bar or fully de-chlorinated sponge is melted by this method. Nevertheless, it is still almost impossible to produce large ingots of metal free from tungsten if tungsten electrodes are used.

15.6. PREPARATION OF SPONGE TO REDUCE SPATTERING

It had been observed that the spattering during melting increased as the magnesium chloride content of the sponge increased; for example, from the same reduction batch the finer portion of the sponge metal spattered more than the coarser which contained less chloride. It was suggested that the spattering was due to the water of hydration combined with the magnesium chloride, entrapped in the sponge, being released with explosive violence when the sponge was fed into the intense heat of the arc.

The metal which is splashed on to the tungsten tip is believed to form a low melting point alloy which drops off into the arc and is cooled before alloying with the main charge.

Leaching titanium sponge metal with water followed by drying at 120° C gave little reduction in the spattering but produced softer ingots[9]. The spattering in this case was presumably due to hydrogen absorbed during the leaching. Methanol used for leaching produces more satisfactory results[2, 16] but the best method is to ensure that the magnesium chloride is reduced to a low level by the salts separation treatment after reduction. However, it is possible by after-treatment of the crushed sponge at about 1000° C in a vacuum, to reduce considerably the magnesium chloride content of sponge metal but long treatment periods are necessary and the cost of such treatment is high.

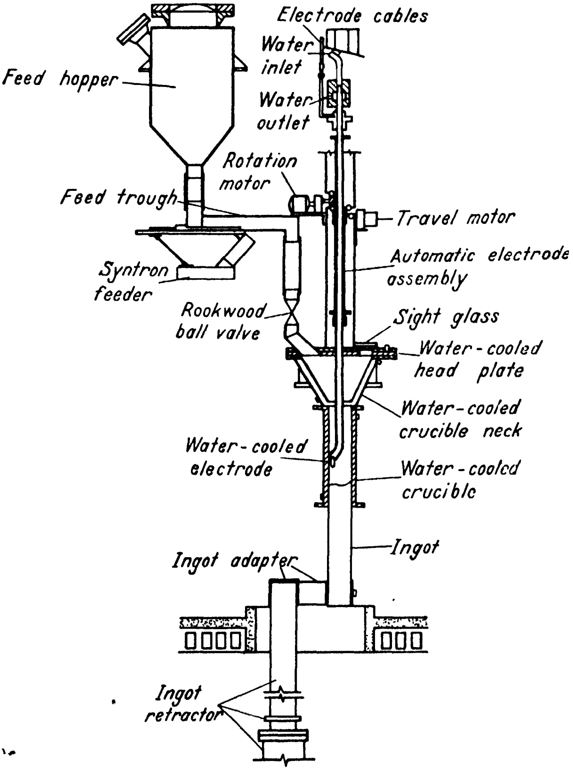

Figure 99. Schematic diagram of automatic arc melting, continuous casting furnace showing essential furnace and control details and the manner in which the ingot is withdrawn from the unit (after S. F. RADTKE *et al.*[14])

Despite the difficulties which have been indicated, large scale melting with a non-consumable electrode is possible and the du Pont Company developed a continuous casting arc furnace with a direct current arc for the melting of titanium[14]. A feature of the furnace is the use of a rotating electrode to cover the surface of the large ingot. This furnace could be used to melt similar reactive metals such as zirconium. The arrangement is shown in *Figure 99.*

15.7. ALTERNATIVE ELECTRODE MATERIALS

While it is possible to produce zirconium with a relatively low chloride content which can be melted reasonably quickly in the arc, it still requires skill on the part of the operator to minimize tungsten contamination, particularly when operating for long periods when it is difficult to avoid overheating the electrode.

Considerable investigation has been done to find an electrode material more suitable than tungsten. Some improvement is obtained by using thoriated tungsten electrodes; these give a more stable arc and resist breakdown at high temperatures better. Graphite has been used but is not very successful and carbon is absorbed by the zirconium; however, it was observed that after using a graphite electrode for three melts of titanium the electrode became partially coated with titanium and the carbon pick-up dropped to a comparatively low value. Deliberate coating of the graphite electrode with titanium by dipping in molten metal confirmed that carbon contamination could be controlled[9]. Results with zirconium-coated graphite are shown in *Table C.*

Table C. Melting Zirconium Metal in the Arc Furnace using a Zirconium-Coated Graphite Tip*

Current A	*Melting rate* lb/h	*Weight of ingot* lb	*Carbon in ingot* per cent	*Condition of tip*
400 *to* 600	—	½	0·31	*Uncoated*
400 *to* 600	2·0	5¾	0·03	*Coated*
400 *to* 600	1·7	5½	0·03 *to* 0·02	*Coated*

* U.S. Bureau of Mines sponge zirconium used.

Examination of a titanium-coated graphite electrode showed there were three distinct layers on the coating; the layer immediately adjacent to the graphite was titanium carbide and the next two layers consisted of titanium carbide dendrites in varying amounts in a matrix of titanium containing carbon in solution.

The good results obtained by coating graphite with zirconium are subject to doubt because other investigators found 0·1 per cent carbon in the ingots produced by this method[4].

Zirconium carbide electrodes produced by impregnating zirconium carbide with zirconium gave a satisfactory arc but again contamination was about 0·1 per cent carbon.

Zirconium metal would be the ideal electrode material but tests show that despite a copious supply of cooling water the tip melts rapidly.

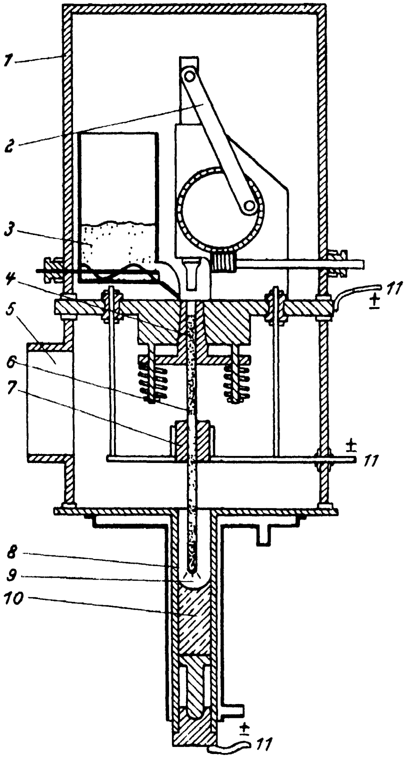

Figure 100. Furnace for melting and casting molybdenum using consumable electrodes (after R. M. PARKE *and* J. L. HAM[13])

1 Vacuum case, 2 Piston drive, 3 Powder supply and feed, 4 Nozzle, 5 To vacuum pumps, 6 Sintering zone, 7 Contact, 8 Water-cooled copper mould, 9 Arc, 10 Cast metal, 11 Electrical connections

15.8. CONSUMABLE ELECTRODE

One of the earliest recorded applications of consumable electrodes in a metallurgical operation was in 1910. In an attempt to volatilize aluminium from zirconium–aluminium, two opposing electrodes of the alloy were melted in the arc formed by passing a current between them in a vacuum furnace[19]. Later, the same worker melted consumable electrodes of tungsten[20]. The first commercial application of this type of melting was made about 1937 for the production of high quality alloy steels[1]. A furnace for the commercial production of molybdenum ingots using consumable electrodes in a vacuum and incorporating a water-cooled copper crucible was developed by the Climax Molybdenum Company[13]. The arrangement of this furnace is shown in *Figure 100* and it is particularly interesting to note that the electrode is produced continuously during the melting operation. The molybdenum powder is fed from a hopper and pressed in a die designed on the principle of a collet, so that when a predetermined pressure is built up on the powder compact, the die opens and releases the compact which is pressed downwards forcing the whole electrode to move. The upper part of the electrode is made up of compacts pressed against each other but on the lower section the compacts are sintered together to form a continuous electrode, which is melted in the arc in the lower part of the furnace. This furnace has been developed to the stage where the production of 1000-lb ingots is a routine operation and it is claimed that zirconium and titanium can be melted satisfactorily operating in an atmosphere of argon or helium. The difficulty in applying this furnace to zirconium or titanium is the necessity to crush the sponge metal into pieces small enough to feed to the die and give strong briquettes. Zirconium sponge can be crushed but not too readily and crushing may introduce oxygen, while fine crushing would greatly increase this hazard. Nevertheless, this type of furnace has definite advantages in the production of ingots of high melting point, reactive metals.

An arc furnace with a consumable electrode has been developed specially for the melting of zirconium[4]. This furnace was designed and operated at the U.S. Bureau of Mines, Albany, Oregon, where so much of the zirconium development work has been done. There zirconium was melted in graphite crucibles heated by a split graphite tube resistor and then, in order to avoid carbon contamination, tungsten electrodes were used for arc melting. It was found that carbon contamination was replaced by tungsten contamination, which although small as a percentage of the ingot was present in areas of high concentration that produced flaws in the rolled sheet. It was concluded that the difficulty could best be solved by using a consumable electrode of zirconium. Electrodes were made by pressing pieces of zirconium (up to 1 in) into briquettes which were sheathed in steel cases, forged and rolled to square bars. These rods were threaded for attachment to the electrode holder and used

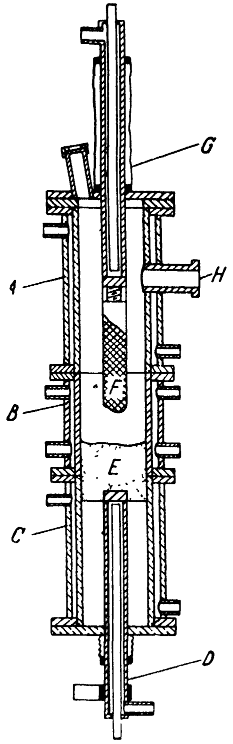

Figure 101

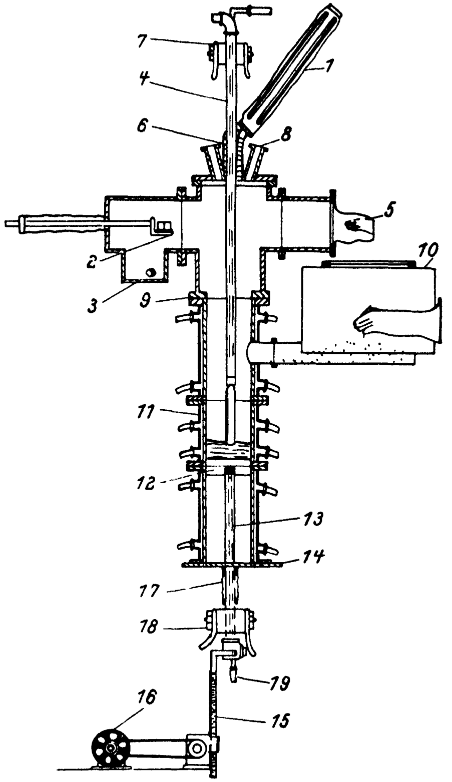

Figure 102

Figure 101. Arc furnace (*after* H. L. GILBERT *et al.*[4])

A Feeding section, B Melting section, C Extraction chamber, D Retractor, E Zirconium starter plug, F Zirconium electrode, G Electrode holder, H Attachment flange for feed box

Figure 102. A 4-in *diameter arc production furnace* (*after* H. L. GILBERT *et al.*[4])

1 Rubber container for new electrodes, 2 Stub removing wrench, 3 Well for stubs, 4 Electrode holder, 5 Electrode charging glove, 6 Bicycle inner tube, 7 Power lugs, 8 Eyepiece, 9 Electrical insulation, 10 Feed box, 11 Melting chamber, 12 Zirconium starter plug, 13 Ingot extractor, 14 Base, 15 Geared retractor, 16 Variable speed motor, 17 Bicycle inner tube, 18 Power lug, 19 Water cooling on extractor

in the small arc furnace shown in *Figure 101.* Before proceeding with the arcing the furnace was evacuated to a pressure of less than 1 mm of mercury and back-filled with argon. Little success was obtained as the arc was erratic, and satisfactory melting could not be achieved. The use of a high voltage, high frequency current superimposed on the d.c. input facilitated starting the arc but did not improve its stability and it was concluded that the vapour pressure of zirconium was insufficient to support a stable arc. It was

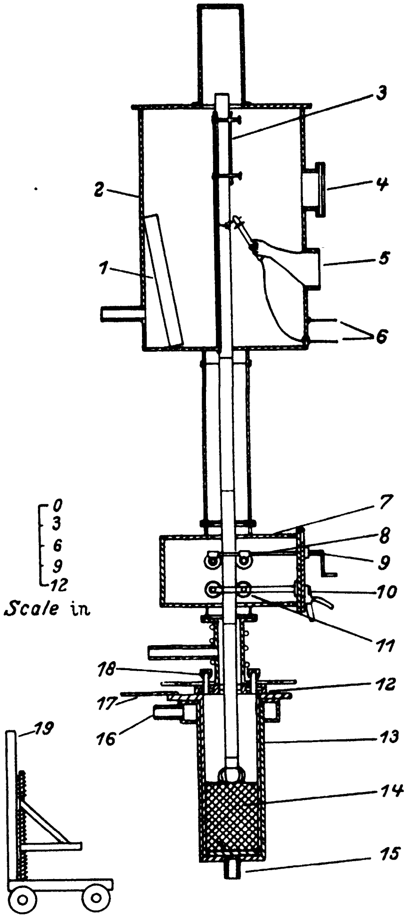

Figure 103. General design of arc furnace (after W. W. STEPHENS *et al.*[18])

1 Electrode supply, 2 Vacuum-tight tank, 3 Aligning guides, 4 Viewing port, 5 Rubber glove for bar joining, 6 Welding power leads, 7 Drive box, 8 Mechanically driven rolls, 9 Crank for electrode drive, 10 Main power to electrode, 11 Power application rolls, 12 Electrical insulation ring, 13 Water jacket, 14 Zirconium ingot in melting cup, 15 Water inlet, 16 Water outlet, 17 Main power to melting cup, 18 Eyepiece, 19 Cart for removing melting cup assembly

observed that stability of the arc varied with different batches of sponge, and with sponge containing rather more magnesium than normal, stability was good. This suggested that magnesium might be a useful addition and when tested it was found that the addition of small amounts of magnesium to the sponge prior to pressing produced an electrode which melted quietly and steadily. During melting a small spherical zone of ionized magnesium vapour was formed between the electrode and the molten pool of zirconium. It was found possible to feed zirconium pieces into the pool of molten metal and ingots were produced containing equal weights of electrode zirconium and feed zirconium. The residual magnesium in the ingot was less than 0·005 per cent with additions to the electrode varying from 0·02 to 0·45 per cent.

The next step was the production of a furnace capable of more continuous operation and the 4-in diameter (ingot size) furnace shown in *Figure 102* was built. This design permits the introduction of electrodes as required, by means of the rubber tube *1*. Each electrode is melted down to a stub which can be unscrewed and the new electrode attached by the operator inserting his hand in the rubber glove *5*. As before, the melting takes place in an argon atmosphere and magnesium is incorporated in the zirconium electrodes. The arc is extremely stable up to distances of 2 in and no perforation of the crucible occurred despite the electrode being within $\frac{1}{8}$-in of the wall. Forty-pound ingots are melted in 50 minutes using 20 lb of electrode and 20 lb of feed. Seven d.c. generators are used to supply the power at 1800 A with 20 V across the arc. Actual melting requires about 1 kW per hour of power per pound of ingot.

The latest development of the consumable-electrode arc melting furnace at the U.S. Bureau of Mines is described by W. W. STEPHENS, H. L. GILBERT and R. A. BEALL[18] and shown in *Figure 103*. The main development has been in the method of preparing the electrodes. Sponge zirconium is pressed into bars which are joined by arc welding *in situ* as the melting proceeds.

Magnesium wire is pressed into the zirconium sponge at the rate of 0·02 to 0·04 per cent by weight. The furnace operates in a mixture of 80 per cent helium and 20 per cent argon, this mixture permitting a higher voltage arc than pure argon and a steadier arc than pure helium. Ingots of 200-lb weight have been produced with a power requirement of less than 0·5 kWh/lb.

15.9. FEEDING DEVICES FOR ALLOY PRODUCTION

Arc furnace melted ingots are composed of a large number of superimposed melts, and when melting alloys it is necessary to ensure that the feed is of uniform composition. Various devices have been employed to obtain the required condition. One of these, used in titanium alloy production[17], is illustrated in *Figure 104*.

The total charge is divided up into a number of small batches of equal composition each of which is placed in a feeder bucket and as the melting proceeds the chain conveyor is operated at a controlled rate to discharge the mixture in the buckets into the screw feed. To be reasonably successful the batches should not be greater than the quantity of metal in the molten pool and the smaller the batches the

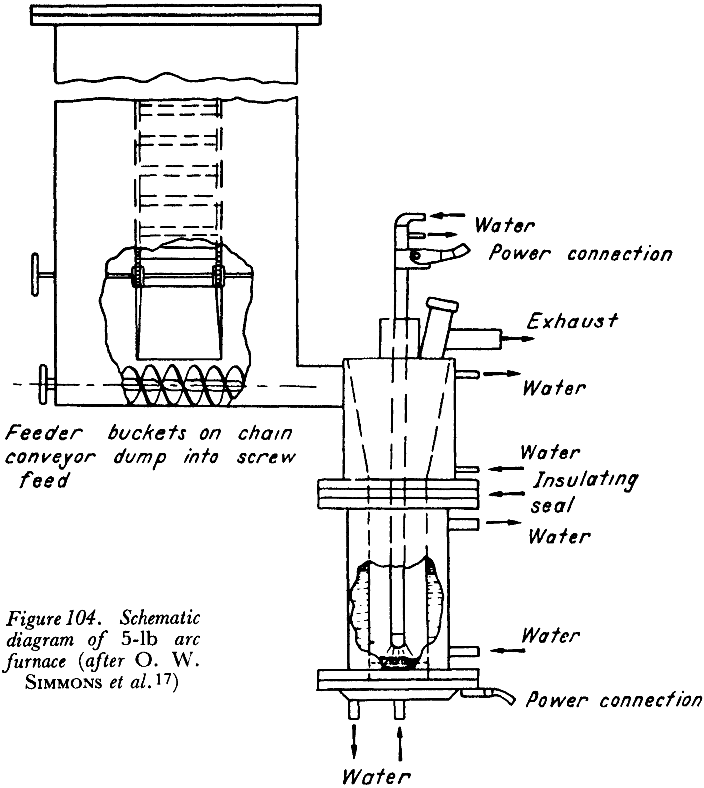

Figure 104. Schematic diagram of 5-lb *arc furnace* (*after* O. W. Simmons *et al.*[17])

nearer will the final alloy approach homogeneity. It is patent that the size of the ingredients is important if segregation during conveying is to be avoided.

When consumable electrodes are used alloying ingredients are added from a feeding device at a controlled rate matched to the rate of melting. In this case a simple vibrator type conveyor can be employed. W. W. Stephens *et al.*[18] produced alloys by inserting wires of the alloying elements into the pressed consumable electrodes. It was claimed that with the addition of 2·5 per cent the usual distribution range in the finished ingots was 2·2 to 2·8 per cent.

15.10. POSSIBLE DEVELOPMENTS IN MELTING TECHNIQUE

None of the methods used for melting zirconium and its alloys can be considered as being entirely satisfactory. The use of graphite crucibles introduces carbon which is deleterious. Arc melting with tungsten electrodes solves one problem and introduces another. Undoubtedly the best method is the consumable electrode technique which is capable of development but there is still the fundamental problem of all arc melting techniques to be solved—the assured production of homogeneous ingots. Despite claims for success of the various techniques for melting reactive metals it would appear that a method of ingot production which would permit the whole charge to be melted simultaneously without contamination would be very welcome. Nevertheless the latest developments in the arc melting of titanium alloys are yielding homogeneous ingots up to two tons in weight. It would appear that heterogeneity troubles disappear when large ingots of 18 inches diameter or more are produced, particularly as the depth of molten metal is somewhat more than the diameter. Double melting is becoming used as a means of ensuring perfect homogeneity.

Investigations to find crucible materials suitable for titanium and zirconium melting have been renewed. At the Battelle Memorial Institute[3] small melts of titanium were prepared in crucibles made from various refractory materials including tungsten, molybdenum, plain and coated graphite, carbides, beryllia, alumina, thoria, magnesia, calcium titanate, calcium zirconate, titanium nitride, zirconium nitride, cerium sulphide, borides and silicides. It was found that none of these materials was appreciably better than graphite.

15.11. FLOAT MELTING

Entirely novel methods have recently been proposed for the melting of reactive metals such as titanium and zirconium. One method was suggested by workers with the Westinghouse Electric Corporation[21] and described as a method of heating and melting metals without a crucible, by suspension in space within an electro-

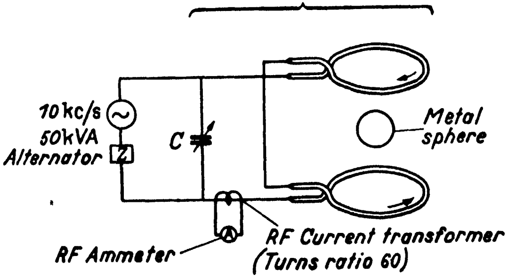

Figure 105. Schematic circuit diagram of levitation experiment (after D. M. WROUGHTON *et al.*[21])

Figure 106. Levitation of the molten metal by the coil system of Figure 105 (after D. M. WROUGHTON *et al.*[21])

magnetic field. The required field is generated by applying high frequency alternating current to two coaxial coils connected in series opposition. The circuit used is shown in *Figure 105. Figure 106* shows the levitation of the molten metal and the typical 'top' shape obtained when the metal melts.

Stable levitation and heating of various metals in the solid state was obtained between the coils in the vicinity of the common axis in both air and vacuum. Weights levitated ranged up to 500 g, smaller weights of aluminium, tin and brass were melted in air and continued in levitation while in the liquid state. Attempts to maintain levitation *in vacuo* on samples of molten silver, titanium and zirconium failed, but one sample of aluminium weighing 10 g was melted and maintained in a state of levitation for about one minute. There is no difficulty in levitating and heating metals but when melting occurs the metals tend to drain downwards and drip away. This tendency is reduced by the oxide skin formed when melting takes place in air, but in a vacuum no such skin is formed and it is possible, but by no means certain, that it will be impracticable to maintain the molten metals in a state of levitation without the aid of an oxide skin.

It is calculated that several pounds of a metal could be stably levitated with a 50 kVA 10 kc/s alternator.

'Float melting', as the new technique is termed, offers advantages if it can be developed. In the case of alloys the whole charge could be melted and thoroughly mixed electromagnetically before casting.

15.12. DRIP MELTING

Another melting technique which has original features is described[11] as 'Drip Melting' and is intended for use with metals such as titanium and zirconium. The principle of this method of melting is to feed a bar of metal vertically into an induction coil so that the end is melted continuously and drains into a copper mould. The most satisfactory results were obtained with a 20 kW spark gap oscillator operating at 150 kc/s. The detailed arrangement is shown in *Figure 107.* The metal rod is suspended inside a quartz tube which is evacuated to a low pressure. The induction coil surrounding the tube is moved upwards and the end of the rod heats rapidly, melts and drops off into the copper mould. The coil is moved at the same rate as the metal melts and drains away. Provided that the diameter of the mould is not much greater than that of the bar, sound ingots are obtained despite the intermittent nature of casting. Zirconium, titanium and beryllium in the form of 1-in diameter rods have all been melted and a rate of melting of about 100 g/min obtained.

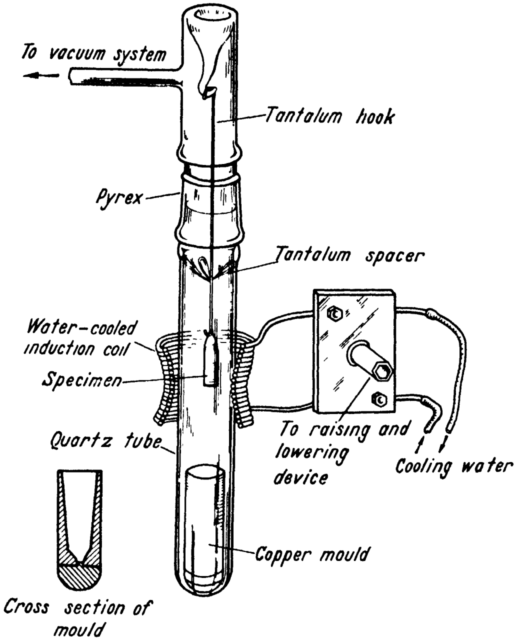

Figure 107. Arrangement of drip melting apparatus which has been used to melt small quantities of zirconium and zirconium alloys without contamination (after T. T. MAGEL *et al.*[11])

To illustrate how successfully this technique can be applied to zirconium one specimen was remelted six times without an appreciable increase in oxygen and nitrogen. Alloys were produced by drilling holes in the bar and filling these with the alloying elements.

As the preliminary experiments had been so successful the next step was to test the method on a larger scale. A 2-in diameter bar was melted by means of a 100 kW generator operating at 3 kc/s, at a rate of 2 to 3 lb/min, but the melting was not successful because invariably the molten metal drained from the end of the bar before the entire cross section was melted. The remaining solid metal would not melt, presumably because the flow of eddy currents was impaired and later when the next portion of the bar melted the unmelted section dropped off. All attempts to rectify the trouble failed and it was decided to investigate an alternative procedure which was called 'Auto-Crucible Melting'.

15.13. Auto-Crucible Melting

Induction heating is used again but instead of melting the end of a bar of metal, which is fed into the induction zone, a pool of molten

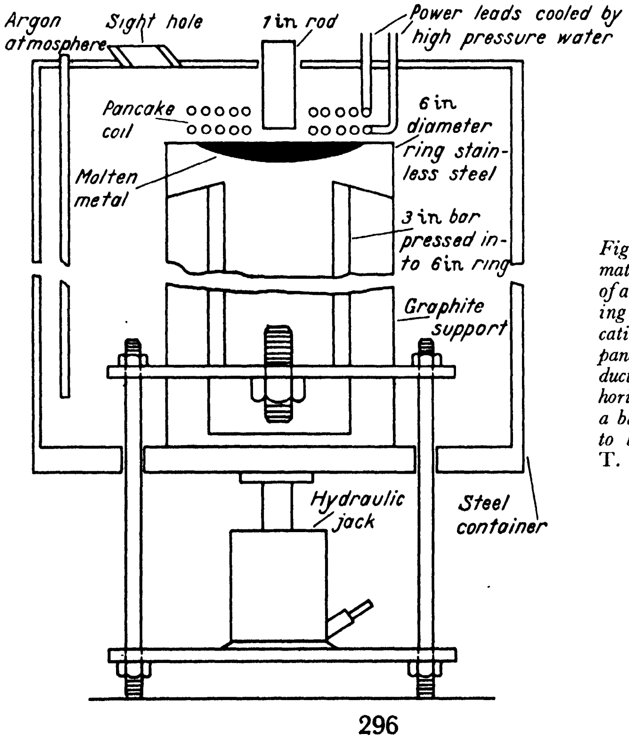

Figure 108. Schematic arrangement of auto-crucible melting apparatus, indicating position of pancake-shaped induction coil near flat horizontal surface of a block of the metal to be melted (after T. T. Magel *et al.*[11])

metal is formed in the top of a flat piece of metal. A pancake-shaped induction coil is used and the eddy currents heat the metal which is placed directly under the coil. The arrangement is shown in *Figure 108*. When the pool of molten metal is formed a bar of the same metal may be fed through the middle of the coil and melted by the heat of the pool. The eddy currents tend to push the liquid metal into a mound in the middle, and arcing may occur. The pool of melt is about the same area as the coil and is ½ to 1-in deep. The molten metal is actually stirred by the action of the eddy currents which ensure homogeneity in alloy production. Thirty to fifty per cent of the power output of the generator goes into the metal. With a block of zirconium placed ¼ to ⅜-in below the coil a 4½-in diameter pool of molten metal can be maintained using a 20 kW 10 kc/s generator. The detailed arrangement of the

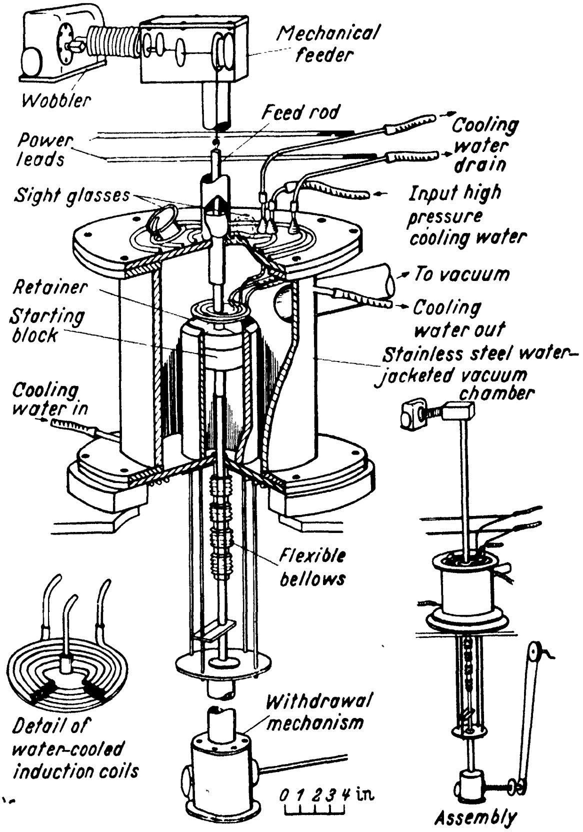

Figure 109. Details of auto-crucible melting apparatus. A 20 kW *generator is used, and a vacuum of* 1 micron *is maintained inside the stainless steel tank during the run (after* T. T. Magel *et al.*[11])

equipment is shown in *Figure 109.* A vacuum of one micron or less is maintained in the vessel during the melting.

Several methods of operating the furnace were tried. Continuous operation, in which a bar of metal is fed into the molten pool while the starting metal is lowered, did not prove very successful because of the tendency of the metal to pull apart at the high temperatures to produce very ragged ingots. It is possible that more careful control could produce good ingots. Another method employed for continuous operation used a cylinder having a diameter slightly greater than the pool to contain the starting metal. The container is lowered as new metal is fed in and an ingot built up. Successful operation depends primarily on careful adjustment of the cooling conditions at the surface of the billet. If the cooling is overdone or the billet diameter too large, cold shuts will spoil the metal. Overcooling could freeze the metal into irregular mounds which may short to the coil. Control is essential and if employed good results can be obtained. A 4½-in ingot of titanium has been produced satisfactorily by this method using a carbon container. Carbon analysis of the feed and ingot metal gave 0·062 and 0·068 per cent respectively. With a feed bar 1-in in diameter melting was at the rate of about 2 lb/h using about 15 kW from the generator.

There is no doubt that this method of melting has advantages over some of the others which have been described but as always one set of difficulties is overcome and another introduced. One of the main difficulties is to prevent arcing between the coil and the metal which must necessarily be very close to one another.

15.14. CASTING ZIRCONIUM

A method for the production of titanium and zirconium shapes by casting has recently been developed in the Titanium Alloy Manufacturing Division of the National Lead Co. of America[10]. The method may be employed for the production of castings from a few grammes to several pounds. The equipment used is shown in detail in *Figure 110.* The reactive metal is melted rapidly with an arc in an argon atmosphere on a water-cooled copper platform, shown in the arrangement, with the furnace inclined at an angle of 30° from the vertical so that the molten metal is contained between the cooled copper base and walls. Tilting the furnace causes the molten metal to flow from the crucible through the graphite sprue and into the mould.

Copper and graphite have been employed as mould materials without contaminating the castings.

Two methods of casting have been employed.

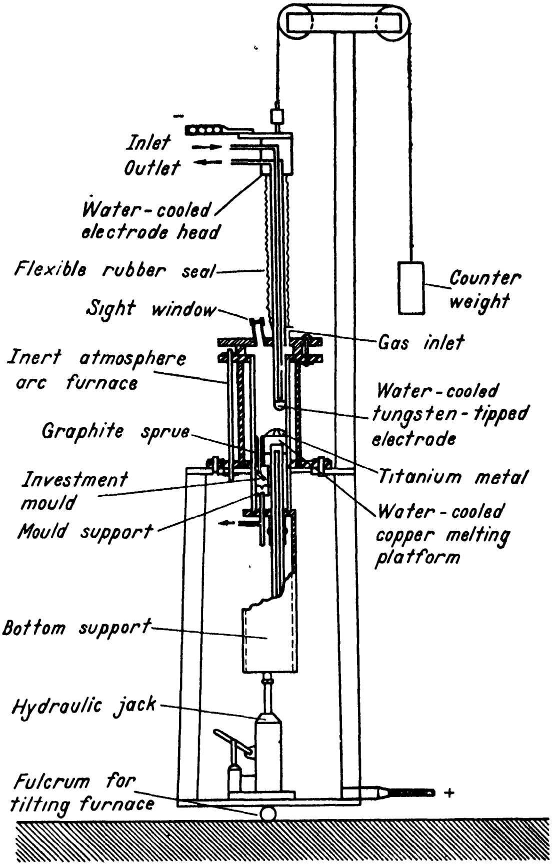

Figure 110. Arrangement of apparatus for casting zirconium (*after* W. E. KUHN[10])

15.14.1. *Vacuum casting*

After melting in argon the pressure is reduced by evacuating the argon and the molten metal cast by tilting the furnace. Relatively large castings are made by this method using pressures from the micron range to 20-in of mercury.

15.14.2. *Pressure casting*

In this method argon enters through a port in the cover of the furnace casing and is drawn through the sprue opening and a port below the mould by the suction created by a vacuum pump.

The flow of gas is maintained during melting and when the molten metal is poured into the sprue by tilting the furnace, the gas exerts a pressure on top of the metal while the reduced pressure on the lower side exerts a suction. The pressure difference ensures good castings and titanium rods 7-in long and ⅛-in in diameter have been produced by this arrangement.

15.15. PRECISION CASTINGS

The results obtained indicate that production of small precision castings of metals and alloys of zirconium and titanium is a definite possibility. Permanent moulds of graphite and copper have been found satisfactory and special cements for investment moulds are being developed. The rapid cooling obtained in the mould should make it possible to use ceramic materials which would be reduced if the reactive metal remained molten.

Scrap titanium metal was used in the investigation and was found ideal for such small scale operations.

It is suggested that the method could be applied to the production of many small complex parts such as zirconium dentures.

It is a relatively simple matter to cast simple zirconium shapes by bottom pouring from graphite crucibles heated in the split graphite tube resistor furnace. Graphite moulds have been used for this purpose with good results. If this method is used the metal will contain carbon which is avoided by the use of the technique first described.

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16

FABRICATION

THE methods of fabricating zirconium are essentially the same as those employed for titanium and as titanium is produced in much larger quantities a great deal more is known and has been published about the fabrication of this metal.

The crystal structure of titanium and zirconium is similar to that of magnesium, a metal which is not readily worked and it is usually necessary to use some heat to aid working. The ease of working depends on the purity of the metal as small additions of oxygen, nitrogen and carbon act as alloying agents, which have a considersiderable effect on the mechanical properties.

Zirconium produced by the van Arkel process in the form of crystal bars is fabricated much more readily than metal produced by the Kroll process. The fabrication of wire and sheet from crystal bar has been described by D. B. ALNUTT and C. L. SCHEER[1] who reported that two difficulties were encountered; the metal work hardened rapidly and seized on the die walls. Considerable annealing was required for wire drawing and it was necessary to form a thin coat of oxide on the wire to prevent adhesion to the dies.

Sheet zirconium was also produced by D. B. ALNUTT and C. L. SCHEER[1], and again it was necessary to anneal. The complication of vacuum annealing was overcome by placing the metal in a furnace heated to 816° C (1500° F) in air and as soon as the metal had attained this temperature (about one minute) the sheet was removed and rolled.

The oxide skin was removed by abrasion and acid treatment and final annealing of the thin sheet had to be performed *in vacuo*.

F. B. LITTON[18] indicates the variation in properties of zirconium produced by the iodide process. The maximum hardness value recorded for 29 samples of crystal bar was 140 Vickers, compared to a minimum of 72 and an average of 90 with standard deviation ± 17 units. Litton considered that it was impracticable to produce metal with a Vickers hardness of less than 72 by the iodide method. The effect of cold work on the hardness of specimens quenched from above and below the transformation temperature was investigated. Both crystal bar and arc melted samples were investigated; little difference was found in the work hardening curves except that approximate maximum hardness values were obtained at 70 and 60 per cent cold reduction respectively. Both materials worked to 90 per cent reduction and both had the same maximum hardness—Rockwell A52.

R. B. Gordon and W. J. Hurford[11] have described the development of zirconium fabrication technology from laboratory work on 2-lb ingots in 1949 to present conversion practices for 500-lb ingots.

16.1. ROLLING

The fabrication of zirconium produced by melting the sponge from the Kroll process has been performed on a fairly large scale. E. T. Hayes, E. D. Dilling and A. H. Roberson[13] described their work on forging and rolling 10-lb ingots. Later operations are described by E. T. Hayes, G. L. Frederick and E. D. Dilling[14]. In order to facilitate working, the zirconium ingots were enclosed in gas-tight steel sheaths which permitted working at higher temperatures than could be used with the unprotected metal, and this contributed to the ease of fabrication. The zirconium ingots are first machined down to a smooth surface and fitted into a clean section of seamless tube. Hayes used 3-in tubes and machined the ingots to 2·99 in; he stated that it was desirable not to have the steel tube too clean since the presence of a little oxide on the steel prevented the metals welding together. A typical arrangement is shown in *Figure 111.* The tube had a wall thickness of $\frac{3}{8}$in. The $\frac{3}{4}$-in end plugs are welded in position. The welds must be sound as the sheath is subjected to considerable stress during the fabrication.

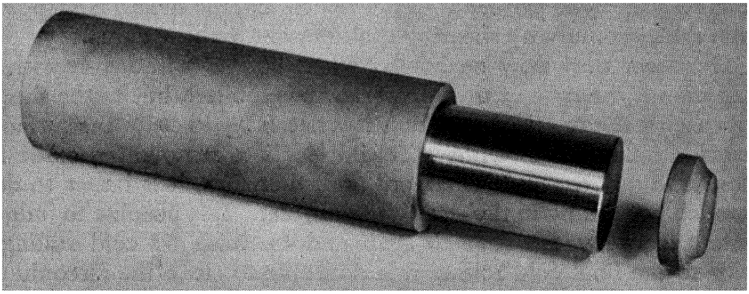

Figure 111. Typical arrangement of sheathed zirconium for rolling

The sheathed ingot is then heated in an open furnace to 850° C and forged on flat anvils to a rectangle of about 2-in total thickness; reheating to 850° C when necessary. The flat section, still in its sheath, is again soaked at 850° C and rolled.

It is important while the metal is being hot worked in the sheath that the temperature does not greatly exceed 850° C otherwise there is the possibility of forming the zirconium–iron eutectic which occurs at 935° C. If the eutectic is formed it is difficult to separate the sheath from the zirconium which would be contaminated with iron. There is even the danger of a molten alloy being formed which when rolled may burst the sheath with considerable danger to the operators.

Hayes used the conventional technique of cross rolling to produce the desired width of sheet and then rolling longitudinally to the required thickness.

Reductions per pass depend on the size of the rolls and may be 10 to 15 or even 30 per cent. After annealing, the sheath is stripped from the zirconium by shearing the sides and pulling apart.

The sheet may now be hot rolled at 650° C without excessive oxidation if the time at this temperature is limited, but as the sheet approaches the required thickness it is necessary to clean the surface before the final cold rolling. It is difficult to remove the oxide if present to any appreciable extent and, therefore, it is better to do as much hot rolling in the sheath as possible. It is possible to judge quite accurately the time to strip and to finish by cold rolling. Prior to the final cold rolling it is desirable to clean the zirconium by acid pickling in a mixture of dilute nitric acid containing a few per cent hydrofluoric acid.

E. T. HAYES *et al.*[14] listed the advantages and disadvantages of sheath rolling as follows:

Advantages	*Disadvantages*
(*1*) Metal is protected at high heat.	(*1*) Cost of sheath.
(*2*) Clean scrap is produced.	(*2*) Work load is increased.
(*3*) Cleaning costs for fabricated material are lower.	(*3*) There is some cross sectional variance in the finished material.

As Hayes indicated, the comparison varies depending upon the value of the zirconium, the more expensive it is, the more advantageous to use sheaths. Operating on a small scale it is probable that there is little difference in the cost of sheathing compared to the total cost of removing the oxide skin and additional scrap loss. When operating with large ingots the oxidation is relatively less important.

When the zirconium ingots are not sheathed, the temperature of hot working has to be reduced to 650° C. Higher temperatures may be used but there is the danger of promoting excessive oxidation; however, exposure for short periods at 1000° C with large ingots showed comparatively little oxide penetration.

The effect of temperature on the hardness of zirconium[13] is shown in *Figure 112.* The hot hardness may be used as a guide to strength at elevated temperatures and is shown with the values for other metals and alloys for purposes of comparison.

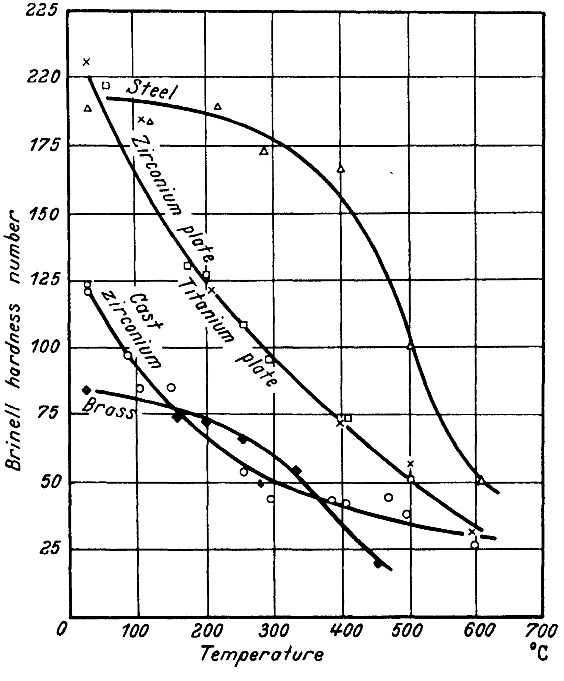

Figure 112. Effect of temperature on hardness of several metals (*after* E. T. Hayes *et al.*[13])

A typical rolling operating using a 10-in mill on sheathed graphite melted zirconium is as follows. Hot rolling with 10 to 15 per cent reduction and reheating to 850° C between passes. This is continued until the thickness of the sandwich is reduced, in this instance to 0·14 in. The sheath is stripped from the zirconium which is 0·10-in thick. The hardness at this stage is 170 VPN. The zirconium is acid pickled before proceeding with the cold rolling. After reducing to 0·08 in, the hardness increases to 219 VPN but cold rolling is continued to 0·02 in before vacuum annealing at about 850° C. The hardness is now 187 VPN and the sheet is rolled to the finished thickness of 0·005 in. Cold working produced very slow reduction; it required 80 to 90 passes to reduce the sheet from 0·08 in to 0·005 in.

The operation described involves no hot working of the bare zirconium because of the difficulty in cleaning the oxidized metal particularly when it is desired to produce thin sheet.

Hot operations with unsheathed zirconium are practicable and, in fact, the oxide penetration is less than is generally assumed. E. T. Hayes and A. H. Roberson[12] studied the effect of heating zirconium in air and found that several hours at 700° C or a short time at 800° C produced no detrimental effect on the ductility of the metal. Hayes forged zirconium in air at 700° C and hot rolled at 650° C and produced satisfactory sheet but this could not be applied to the production of thin sheet and would not be a sound proposition even with comparatively thick sheet. The best arrangement is to hot work the metal to the stage where it can be finished by cold rolling after cleaning. It is essential in order to produce a good finish, to remove the oxide surface before cold rolling. The effect of cold working and subsequent annealing on the properties of graphite melted zirconium[13] is shown in *Figure 113*.

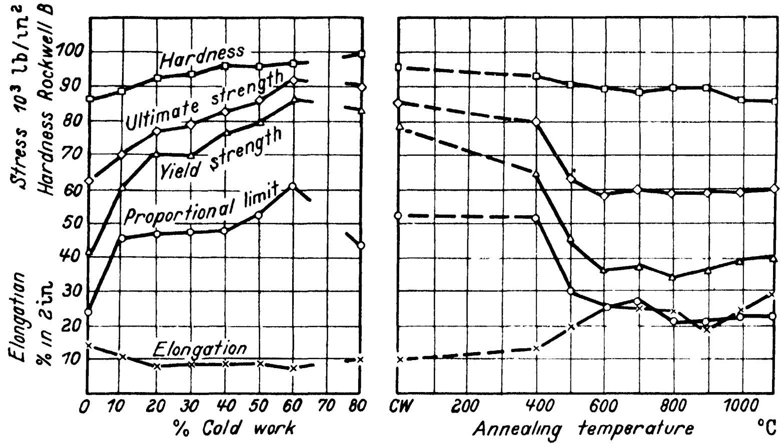

Figure 113. Effect of cold working and subsequent annealing on properties of zirconium rolled at 850° C (*after* E. T. Hayes *et al.*[13])

Hot rolling zirconium bar has been accomplished with steelworks equipment without difficulty using an ingot of unprotected graphite melted metal; 2¼-in diameter ingots were first heated to 630° C in a gas fired forge furnace and when soaked were transferred to an electric muffle furnace operating at 750° C where the ingot was quickly brought up to furnace temperature. The ingot was transferred to the anvil of a 7-cwt hammer and forged to a 1-in diameter bar without reheating. The bar was again heated in an open electric furnace to 750° C and then rolled in an 11-in mill to a square bar, next it was transferred to the round rolls, and continuing in round section to the finishing size of about 0·6-in diameter. No reheating between passes was necessary.

R. B. Gordon and W. J. Hurford[11] describe the fabrication of unsheathed zirconium ingots 4 to 12-in in diameter and weighing up to 500 lb. The ingots are rough machined; small local defects which remain are removed by grinding and if necessary a bad section can be removed by tapered machining.

Four-inch ingots are heated for not more than one hour at 980° C while ingots as large as 10-in in diameter are soaked at temperature for two hours prior to forging. Arc cast ingots are free from the centre burst difficulties found in round ingots of other metals made by conventional casting practice.

Forging temperatures are as follows:

Type of zirconium	*Starting temp.* °C	*Finishing temp.* °C
Iodide . . .	760	600
Sponge (Kroll) . .	840	650
Sponge alloy . .	870 to 1040	700 to 820

Ingots can either be hammer- or press-forged; ingots up to 10 in have been pressed on a 500-ton forge press, but several reheats were necessary to work down to 2½-in thick slabs. With a 1000-ton press, 12-in diameter ingots have been pressed easily into the same slabs without reheating. A 6000-lb air-operated forge hammer will also work the 12-in ingots.

The forging operation can be by-passed for production of bars and slabs by groove rolling or blooming of the ingots.

Billets for rolling into strip or sheet are cleaned by sandblasting, etching in mixed nitric and hydrofluoric acids and grinding the surface to remove local defects. Slabs 2½-in thick are heated for 40 to 60 minutes in either gas or electric furnaces and then rolled. Rolling should be completed without reheating to minimize contamination. The approximate rolling temperatures are:

Type of zirconium	*Starting temp.* °C	*Finishing temp.* °C
Iodide . . .	760	600
Sponge (Kroll) . .	790	650
Sponge alloy . .	840	700

Reduction per pass should be decreased or the rolling temperature increased for zirconium alloys.

The scale on hot rolled strip is very tenacious and must be sand- or shot-blasted before pickling with mixed nitric and hydrofluoric acid solution to remove about one mil (0·001 in) of metal. The pickling solution contains up to 12 per cent nitric acid and 4 per cent hydrofluoric acid.

16.2. EXTRUSION

Work on extrusion of zirconium at the Massachusetts Institute of Technology[21] deals with the hot extrusion of sheathed metal which included not only solid ingots, but small pieces and even compressed millings. The sheaths were copper-plated to facilitate the extrusion. Extrusions were made without difficulty at 800 and 1065° C at ratios up to 14 to 1. For U.S. Bureau of Mines zirconium (Kroll zirconium sponge graphite melted) the values of the extrusion constants were about 46,000 and 22,000 lb/in^2 at the lower and higher temperature respectively, the extrusion constant being the value K in the following formula

$$\text{Extrusion pressure} = K \ln \text{(Original area/Final area)}$$

The variation in extrusion temperature did not affect the properties of the extruded metal. Crystal bar zirconium extruded more readily than the Kroll metal but had less strength. In one experiment the tube was packed with lengths of crystal bar and when extruded appeared to be even more ductile than the as-deposited bar. The work suggested that extrusion methods might be used to produce structural sections of higher purity than can normally be obtained by remelting and working.

R. B. GORDON and W. J. HURFORD[11] describe the development of zirconium fabrication technology. They include a description of the consolidation of crystal bar by extruding a sheathed bundle of bars through a steel die at 815° C as already described, and in addition, mention a similar process developed by H. R. HOGE and B. LUSTMAN[16]. These investigators consolidated crystal bar by compacting in a graphite mould or by extrusion through a graphite die under relatively low pressures but at a temperature of 1650° C. This temperature appears to be much higher than is necessary.

Normal extrusion of zirconium ingot is described by Gordon and Hurford who point out that development has been limited by lubrication difficulties. Good lubrication is essential to prevent welding of the metal to the dies. This difficulty has restricted the preparation of tube billet bores to machining rather than piercing. Dies with entrance angles varying from 20 to 45° blended through radii into their bearings have been found more satisfactory for both zirconium rod and tube extrusions than square-faced dies. Tungsten-bearing hot work tool steels have generally been used as tooling materials. The basic lubricants used have been heavy oil suspensions of flake graphite, molybdenum disulphide or mica.

R. B. Gordon and W. J. Hurford[11] consider that the Ugine–Séjournet process which employs glass as a lubricant may become important. They have extruded arc-cast 7-in diameter Kroll zirconium alloy billets weighing about 120 lb at 995° C with this technique. The maximum tonnages recorded for the extrusions were 1470 tons for tube shells (2⅜-in o.d. by 0·18-in wall), 1120 tons for the 1¼-in diameter rod and 1160 tons for 2-in square bar. Reaction between the glass and hot zirconium would be expected but no comment is made.

16.3. Tube and Rod Fabrication

R. B. Gordon and W. J. Hurford[11] describe the production of tube. Iodide zirconium metal has been fabricated to tubes 0·61-in o.d. and 0·028-in wall by drawing extruded tube 1½-in o.d. and 1¼-in i.d. Kroll metal has been used to produce zirconium alloy tube 0·235-in o.d. by 0·03-in wall, and ⅜-in by 0·06-in wall has been manufactured by cold drawing. A molybdenum disulphide lubricant was used.

Zirconium tubes produced from Kroll graphite melted zirconium with a wall thickness of 0·002 in have been produced by cupping and cold drawing.

Tubes have also been produced by argon- or heli-arc welding.

Rods of zirconium have been produced by extrusion or forging followed by cold swaging or drawing. Hot working temperatures of 980° C and higher are required for alloys, compared to 815° C for iodide zirconium.

Intermediate anneals are required for Kroll zirconium at approximately 790° C after 35 per cent cold reduction, while iodide zirconium can be processed without annealing if the reductions are less than 20 per cent per pass.

A special lubricant-base coating was produced for this work, by immersing the zirconium in an aqueous solution containing 0·1 to 0·5 per cent hydrofluoric acid and 1 per cent orthophosphoric acid by volume. The phosphate coating thus obtained served as the base for commercially available lubricants such as chlorinated oil or soap drawing compound.

16.4. WIRE DRAWING

The normal reduction for each pass is 16 per cent. Wire is drawn down to 0·010-in diameter without difficulty, and with care 0·005-in or less can be drawn. Annealing can be achieved by heating *in vacuo* to about 850° C but for some purposes it is satisfactory to anneal by heating in air at 700° C for one minute. The oxide skin produced during the air anneal prevents galling and serves as a base for the lubricant. Solid bees-wax has been found to be suitable for this purpose.

The production of wire by this method has two disadvantages: (*i*) the oxide skin which is essential to prevent welding to the die causes excessive wear in the dies, (*ii*) the final wire is very difficult to free from oxide without marring the surface, and if it is not removed before the wire is heated to elevated temperatures, the oxide skin will dissolve in the metal and embrittle it. An alternative method of procedure which overcomes the disadvantages is to use a steel, or preferably, a copper sheath, and after drawing remove the sheath by dissolution in acid.

16.5. COLD WORKING AND FORMING

Zirconium work hardens quite rapidly during cold working as indicated by the hardness values for various reductions[11] given in *Table CI.*

Table CI. Brinell Hardness versus Percentage Reduction

Material		*Reduction* per cent				
	0	20	40	60	80	90
Iodide zirconium . . .	88	125	145	160	168	172
Sponge zirconium . . .	165	204	210	215	228	255

Kroll zirconium can be cold rolled with reductions per pass less than 10 per cent and with permissible total reductions of 35 per cent between anneals, while iodide crystal bar can be cold reduced 99 per cent without intermediate anneals.

Zirconium sheet can be slit and blanked with conventional equipment. It can also be deep drawn into cans using electroplated copper or a commercially available adhesive-type cement for lubrication. Cans 8-in long, 1-in in diameter with approximately 0·015-in wall have been drawn from Kroll zirconium using intermediate anneals at 650° C in a 50–50 lithium carbonate–potassium carbonate bath and commercially available waxes as lubricants. An oxide film on the metal was found necessary to achieve proper lubrication.

16.6. JOINING

It has been reported that zirconium may be arc welded[10], heli-arc welded[23] or spot welded[1]. The latest report on this work shows that ductile welds may be obtained if certain precautions are taken[6].

The production of ductile welds in zirconium and titanium has been mentioned in the technical press but no details were given beyond the fact that it was essential to shield the metal when heated above 650° C if ductility was to be obtained in the weld and preserved in the adjoining metal. F. G. Cox[6] used a standard *Mk. III Argonarc* welding torch, operating with argon of a purity not less than 99·80 per cent. It was shown that for welds in zirconium sheet of the order of 0·030 in or thinner, direct current welding gave superior results to those obtained with alternating current. The only precaution required when welding thin sheets with direct current was to ensure protection on the underside of the weld as well as on the top. Welding of thin sheet was performed with an argon flow of 14 ft³/hour and without the use of a filler rod. The welds so produced were ductile and could be cold rolled until all signs of the weld had vanished.

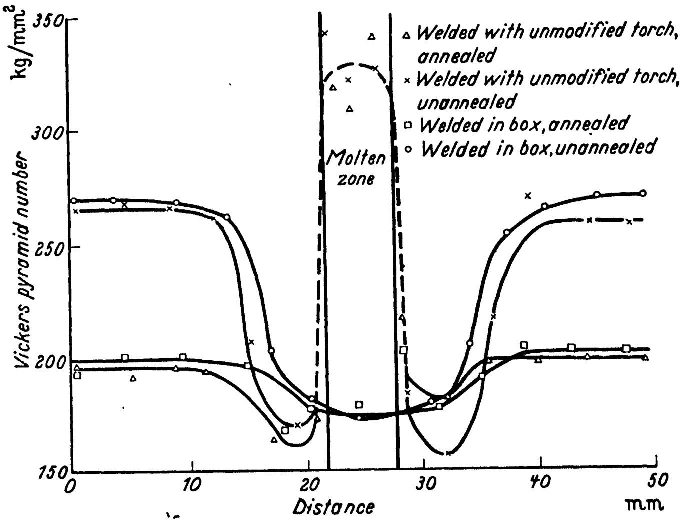

Figure 114. Variations in hardness (a.c.) (after F. G. Cox[6])

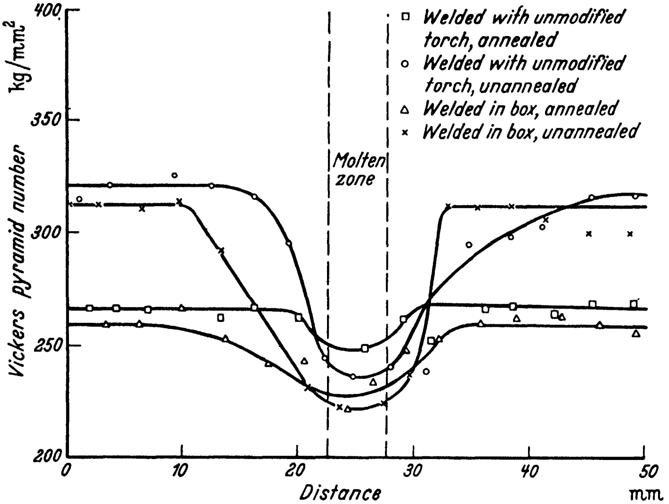

Figure 115. *Variations in hardness* (*d.c.*) (*after* F. G. Cox[6])

To obtain satisfactory results when welding thicker sheet, of the order of $\frac{1}{4}$-in thickness, it was necessary to ensure much more complete protection by performing the welding in a gas-tight box under a slight pressure of argon and in this case there were indications that the best results could be obtained only with purified argon.

Figures 114 and *115* show the variation in hardness across welds made in joining 0·030-in sheet using the normal argon arc torch technique and with the aid of the argon filled box. In one instance alternating current was used and in the other direct current.

Corrosion resistance of the welds was determined using concentrated hydrochloric acid with an addition of 1 g/l of added iron to intensify the corrosive action of the acid. The tests were done at room temperature, the specimens being rotated at 300 r.p.m. In the cases where ductile welds had been produced it was found that not only had the weld metal withstood corrosion, but also it withstood it better than the parent metal.

The zirconium sheets used in the tests were produced from Kroll sponge zirconium melted in a graphite crucible and contained 0·1 to 0·2 per cent carbon.

16.7. BRAZING AND SOLDERING

Using a suitable furnace brazing technique it is possible to produce a satisfactory joint between zirconium and other metals. Both silver and copper may be used as the brazing metal, the amount being carefully controlled by inserting a suitable shim of metal into the joint. The actual braze must be carried out either *in vacuo* or in an atmosphere of argon to prevent oxidation of the zirconium. If these precautions are observed, joints are obtained having strengths approaching that of the brazing metal used. Care must be exercised when brazing with copper or any copper alloy such as brass, *Sif-bronze* or silver solder, for if excess brazing metal is present the zirconium will be attacked strongly.

Two methods have been described for 'tinning' zirconium in preparation for brazing and soldering. One entails[7] dipping the zirconium through a flux of molten cuprous chloride into silver solder at 1100° C. A second method[24] consists of pretreatment in molten zinc chloride at 420° C for 1 to 10 minutes, depending on thickness of material, when a film of zinc is deposited on the zirconium.

It is claimed that both these methods of preparation enable the zirconium to be soldered or brazed by conventional methods using standard fluxes.

A development of the latter method, having some practical advantages for soft soldering, is to use a flux consisting of two parts sodium fluoride, two parts zinc chloride and one part ammonium chloride. The zinc coating is then deposited and tinned in one operation by normal soldering technique.

It is necessary to heat the work slightly above the melting point of the solder in order to deposit the zinc coating, but this has no deleterious effect on the zirconium.

16.8. Brazing Other Metals and Non-Metallic Materials with Zirconium

Experiments on the direct brazing of metals and non-metallic materials by means of the reactive metals zirconium, titanium, tantalum and niobium were made by C. S. Pearsall and P. K. Zingeser[22]. Such materials as diamond, sapphire, carbides, various ceramics, refractory oxides, glass, quartz, stainless steel *etc* have been successfully brazed to like materials or to other metals.

Pearsall and Zingeser report that the reactive metals have the property of wetting both metals and non-metallic materials equally well, producing exceptionally strong bonds which often exceed the strength of the non-metallic materials. Good vacuum seals with glass and ceramics have been obtained by this method.

Table CII. Brazing Experiments on Metals and Non-metallic Materials with Zirconium

Material	*Brazing materials*	*Atmosphere*	*Bond*	*Remarks*
CARBIDES				
Silicon carbide	ZrH + *pure silver*	*vacuum*	*good*	
	ZrH + *pure silver*	*dry tank nitrogen*	*good*	*Discoloration*
Boron carbide	ZrH + *pure silver*	*vacuum*	*good*	
	Zirconium–silver alloy (15% Zr)	*forepump vacuum*	*good*	
METALS				
Stainless steel	ZrH + *pure silver*	*vacuum*	*good*	*Bonded to steatite*
	ZrH + *lead-silver alloy* (2·5% Ag)	*vacuum*	*good*	*Bonded to* Pyrex
Molybdenum	*Zirconium–silver alloy* (15% Zr)	*dry tank nitrogen*	*good*	*Discoloration*
Copper	ZrH + *pure silver*	*dry tank nitrogen*		*No improvement over flow of pure silver*
	Zirconium–silver alloy (15% Zr)	*dry tank nitrogen*		*Dissolves copper*
PURE REFRACTORY OXIDES				
Alumina	ZrH + *pure silver*	*vacuum*	*good*	
	ZrH + *pure aluminium*	*vacuum*	*good*	*Bonded to tantalum*
Synthetic sapphire	ZrH + *pure silver*	*vacuum*	*good*	
	Zirconium–silver alloy (15% Zr)	*forepump vacuum*	*good*	
Beryllia	ZrH + *pure silver*	*vacuum*	*good*	
	ZrH + *pure aluminium*	*vacuum*	*good*	
	Zirconium–silver alloy (15% Zr)	*forepump vacuum*	*good*	
Thoria	ZrH + *pure silver*	*vacuum*	*good*	
	Zirconium–silver alloy (15% Zr)	*forepump vacuum*	*good*	
VITREOUS SUBSTANCES				
Pyrex	ZrH + *lead–silver alloy* (2·5% Ag)	*vacuum*	*good*	*Also bonded to molybdenum and to stainless steel*
	ZrH + *aluminium–silver alloy* (50–50)	*vacuum*	*good*	
	ZrH + *aluminium – tin alloy* (50–50)	*forepump vacuum*	*good*	

Table CII. Brazing Experiments on Metals and Non-metallic Materials with Zirconium—continued

Material	*Brazing materials*	*Atmosphere*	*Bond*	*Remarks*
VITREOUS SUBSTANCES—contd				
Quartz	ZrH + *pure silver*	*vacuum*	*good*	
	Copper – tin – zirconium alloy (10–85–5)	*vacuum*	*good*	
DIAMOND				
Dust No. 0 (80 *to* 100 mesh) *Dust No. 7 also used,* 0 *to* 2 micron	ZrH + *pure silver*	*vacuum*	*good*	*The silver wets the surface and completely covers the particles. A solid dense mass was formed*
Congo cube	ZrH + *pure silver*	*vacuum*	*good*	
	Zirconium–silver alloy (15% Zr)	*forepump vacuum*	*good*	
	Zirconium–silver alloy (15% Zr)	*dry tank nitrogen*	*good*	

The results indicated that for most purposes zirconium was preferred to the other metals because it had superior wetting and bonding qualities. The metal hydrides were used as well as alloys of the active metals. Brazing operations were performed *in vacuo* or in highly purified hydrogen, argon, helium and nitrogen as well as in commercial tank argon, helium and nitrogen.

Despite the reactivity of zirconium towards nitrogen successful results were obtained with this metal with ordinary commercial dry tank nitrogen although the result with the other metals was poor.

The general procedure using the hydrides involves coating the surface to be brazed with thin films of the hydride. A water paste or nitrocellulose solution binder appear to be equally satisfactory. A piece of suitable solder is then placed in contact with the hydride-coated surface and the work heated to approximately 1000° C or to a temperature at which the solder flows freely in a vacuum (approximately 10^{-4} mm of mercury or better) or in an atmosphere of pure hydrogen or pure inert gas. When the correct temperature is reached the brazing alloy will melt and flow over the hydride-coated surface. Copper–silver eutectic solder (melting point 779° C) and pure silver (melting point 960° C) are both very satisfactory.

Zirconium powder produced by decomposing the hydride in a vacuum at 800 to 1000° C proved to be equally as good as the hydride but titanium metal powder produced by the same method was not successful. As hydrogen was not necessary to produce satisfactory welds alloys of silver and zirconium were prepared by vacuum melting of the pure metals in tantalum or quartz crucibles. An alloy containing 15 per cent zirconium and 85 per cent silver was found to wet and bond ceramics, diamond, sapphire, carbides *etc.* Equally good results were obtained by placing pieces of zirconium metal and silver wire on the surface to be brazed and heating to the flow point.

Alloys of aluminium and zirconium containing 0·1, 0·28 and 0·8 per cent zirconium, and of aluminium–silver–zirconium (26 : 64 : 10) have also been prepared by vacuum melting and show good wetting and bonding properties.

The results of various brazing experiments are shown in *Table CII.* It was concluded that brazing with zirconium appears to offer a simple, inexpensive method of preparing tools and other devices which involve attaching non-metallic materials in the form of powders or solids to metals, at the same time producing strong bonds which will withstand reasonably high temperatures.

16.9. ELECTROPLATING

Methods for electroplating on zirconium were developed by W. G. SCHICKNER, J. G. BEACH and C. L. FAUST[25]. Normal methods of plating such as are applied to the metals chromium, stainless steels, aluminium or magnesium are not applicable to zirconium which is resistant to most acid and alkaline solutions. If the conventional plating methods are used the plated metal can be stripped easily. Heat treatment of the plated zirconium does not give adhesion, instead the plating either blisters or separates from the base metal.

Successful results were obtained by etching the surface of the zirconium, plating with iron or nickel followed by pre-baking and heating to form an alloy bond between the two metals. Other metals may be electroplated over the nickel or iron. The as-plated adhesion was about 6000 lb/in^2 and the heat treated nickel- or iron-plated zirconium bonds of almost 50,000 lb/in^2 as indicated by the modulus of rupture.

The following general procedure is recommended for producing adherent nickel electroplate on zirconium:

(*1*) Descale: (*a*) sandblast, (*b*) vapour blast, or (*c*) surface grind.
(2) Alkaline clean.
(*3*) Rinse.
(*4*) Chemical etch. Solution: NH_4F – 18 to 52 g/l, HF – 3 to 16 g/l; molar ratio: NH_4F:HF, 1·2:4·1; temperature: 38° C (100° F); time: ¾ to 3 min; metal removed: 0·6 mil; container: polyethylene.

(5) Rinse.
(*6*) *Nickel plate.* Solution: $NiSO_4 \cdot 7H_2O$ - 330 g/l, $NiCl_2 \cdot 6H_2O$ - 46 g/l, H_3BO_4 - 37 g/l, H_2O_2 added periodically to prevent pitting; pH 2·0; temperature: 60° C (140° F); current density: 40 A/ft^2; plate thickness 1 to 2 mils.
(*7*) Rinse and dry.
(*8*) Pre-bake. Temperature: 204° C (400° F)—air is satisfactory; time: 2 to 4 hours.
(*9*) Heat treat. Temperature: 704° C (1300° F)—air is satisfactory; time: 19 to 45 min; quench: air or water.

The strength of the alloy bond is related to the amount of diffusion. The best diffusion bonding of electroplated iron in zirconium occurs at 816° C (1500° F) in 10 to 45 minutes.

16.10. ANNEALING

When zirconium is heated above 862° C a transformation occurs, the hexagonal close packed or α modification changing to the body centred cubic or β modification which is unstable at room temperature.

According to A. E. VAN ARKEL[27] the grain size of zirconium is altered during the transition $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$, tiny crystallites being formed which increase in size by recrystallization.

Quenching from above the transformation temperature will not retain the β structure but a slight hardening results.

Water quenching from 1000° C increases the strength of Kroll zirconium[3]. Two samples were tested, poor agreement was obtained as shown in *Table CIII.*

Table CIII. Effect of Water Quenching from 1000° C

Material	*Treatment*	*Reduction in area* per cent	*Elongation* per cent	*Yield strength* (0·1 per cent *offset*) lb/in^2	*Ultimate strength* lb/in^2
*Kroll zirconium (Rockwell B*84)	*As received*	31·4	13·7	43,500	68,500
ditto	1000°C in vacuo, *water-quenched*	40·6 29·4	10·1 9·1	49,000 71,000	77,000 95,750

The heat treatment necessary to obtain the stress relief annealing of zirconium depends on the amount of cold work prior to annealing, but generally a short treatment of about 10 minutes (less for thin sheet) at temperatures above 500° C will soften the metal. Complete annealing is obtained on recrystallizing by heating for about one hour at 850° C or for a shorter period at higher temperatures; such treatment would have to be done in a vacuum or a pure inert gas atmosphere to avoid oxidation. Generally a temperature of 650° C is used to anneal metal in process of working; short periods at this temperature produce appreciable softening without much oxidation. The time of treatment will vary with the section, thin sheets are satisfactorily softened in one minute at temperature.

The effect of heat treatment on the hardness and grain size of zirconium is shown in *Table CIV*.

Table CIV. Effects of 2 h *Heat Treatments on the Hardness and Grain Size of Zirconium Sheet*[4]

Temperature °C	*Grain size* mm	*Hardness Rockwell B*
As rolled	*Cold worked*	84
500	*Cold worked*	73
550	*Recrystallized*	70
600	0·01	68
650	0·01	66
700	0·015	63
750	0·025	63

Note: Stock was prepared by the usual practice at the U.S. Bureau of Mines, melted in graphite, hot worked at 800° C and cold rolled to a 50 per cent reduction.

The annealing of heavy sections is described by R. B. GORDON and W. J. HURFORD[11]. The pieces are usually annealed in air at 700 to 850° C to restore the crystalline structure after hot rolling. An A.S.T.M. grain size of 7–8 can be obtained in iodide zirconium after hot rolling at 760° C by annealing for 10 min at 700° C whereas some Kroll zirconium alloys have the same grain size after annealing for 10 min at 850° C. Contamination of the metal by the atmosphere for these short periods and low temperatures can be ignored,

Table CV. Effect of Percentage Reduction on Recrystallization Temperature of Zirconium

Material	*Reduction* per cent					
	20		50		80	
	°F	°C	°F	°C	°F	°C
Iodide zirconium[15]	905	485	860	460	835	445
Iodide zirconium[9]	1020	550	840	450	—	—
Sponge zirconium[15]	1010	540	960	515	925	495

but light sections should be annealed *in vacuo* or inert gas atmospheres.

Recrystallization temperatures of zirconium after various degrees of cold working[11] are given in *Table CV*.

16.11. CLEANING AND FINISHING

There are two types of surface oxidation that may have to be removed from zirconium, a heavy coating produced by hot working in air and a thin coating produced during annealing in air at a relatively low temperature. The latter type of coating is easily removed by an acid pickling bath. Various techniques have been recommended but the one found most satisfactory is carried out by dipping the zirconium in a pickling bath composed of 47·5 parts by volume of water, 47·5 parts concentrated nitric acid, and 5·0 parts 40 per cent hydrofluoric acid. The zirconium is removed occasionally, rinsed and brushed to remove the loosened oxide before retreating with acid. This acid bath gives a bright finish and is preferred to a bath with greater concentration of hydrofluoric acid which attacks the metal more vigorously and causes deep pitting.

Lead vessels may be used to contain the pickle liquor but polythene is preferable.

With heavy oxide coatings it may be necessary to sandblast the surface or use abrading equipment before treating with the acid.

16.12. MACHINABILITY

When machining zirconium precautions must be taken against fire as the swarf produced will ignite if overheated. Generous clearance angles on all tools must, therefore, be used and care must be taken to avoid using badly worn or dull tools.

16.12.1. *Tooling recommendations for tungsten carbide tools*

	Roughing	*Finishing*
Approach angle	15°	30°
Top rake at right angles to approach angle	10 *to* 15°	25°
Side and end clearances	8°	8°
Plan relief angle	15°	15°
Nose radius	0·020 in	0·050 in

Peripheral speed of workpiece for both roughing and finishing 120 ft/min.

Feed of tool per revolution, for roughing should be 0·010 in, and or finishing 0·005 in.

The depth of cut is not critical except that it should not be a skimming cut which produces swarf in the form of a fine dust which is liable to spontaneous combustion.

Oxide scale on hot worked surfaces is extremely abrasive and should be removed by blasting prior to machining.

In machining flat surfaces of zirconium, vertical face milling is preferred to horizontal slab milling since metal can be removed at higher rates with excellent finish[11]. Face milling is done with surface feeds up to 250 ft/min when cutter and work are flooded with a suitable water-soluble coolant.

Because of the work hardening characteristics of zirconium, machine chips are harder than the base metal and these hard chips may abrade the machined surface. This may be avoided by adjusting the rake angles so as to form a lightly curled chip that is thrown out of the cutter and clears the work. In face milling this is accomplished by using a 5 to 6° negative radial rake and a 10 to 15° positive axial rake with a 45° chamfer on the cutting edge.

Drilling zirconium may be a little difficult as there is a tendency for chips to get fixed when using bushings. It is claimed that sharpening drills with a somewhat smaller angle than the normal 118° gives better results.

Zirconium is readily sawn by mechanical saws with high speed steel blades.

16.13. RECOVERY OF ZIRCONIUM FROM MACHINE TURNINGS

The recovery of machining scrap has been considered by R. W. DAYTON *et al.*[8]. During machining of zirconium the elements iron, carbon, silicon, aluminium and oxygen are all picked up and contaminate the cuttings. Examination indicated that aluminium, silicon and some of the iron were introduced as 'dirt', the rest of the iron was from the cutting tools, the carbon was from traces of cutting fluid and the oxygen was absorbed by exposure of the hot chips during machining. The increase in impurities during machining is shown in *Table CVI.* It appeared that the contaminants could be removed by a mixture of physical and chemical treatments. The cutting oil was completely removed by treatment with a solvent (carbon tetrachloride). This treatment did not remove the dirt but agitation on a gyratory sieve with openings 0·017 in by 0·060 in was quite effective. Sometimes iron oxide remained attached to the chips and could be removed by leaching with dilute hydrochloric acid.

Table CVI. Analyses of Zirconium Chips and Crystal Bar

Spectrographic analyses p.p.m.

Chip type	Fe	Al	Si	Ni	Sn	Zn	Cu	Mg	Mo	Mn
Sharon shaper	1100	310	170	80	<5	—	20	25	200	7
Sharon mill	840	510	840	40	<5	—	40	25	175	4
Straddle mill	1600	300	140	40	<10	<100	20	400	<10	<5
Face mill	700	700	80	5	<10	—	40	20	<10	5
*Crystal bar**	300	20	50	30	<10	—	5	10	<10	<10

Chip type	Cr	Pb	Ti	Hf	V	B	Be	Co	Ta	W
Sharon shaper	20	<10	40	<300	—	1	1	6	500	<50
Sharon mill	10	<10	40	<300	—	2	<1	<5	500	<50
Straddle mill	10	<10	90	<300	<10	<1	<1	<5	500	<50
Face mill	<10	<10	<10	<300	<10	2	<1	<5	—	<50
*Crystal bar**	30	<10	20	<400	—	—	—	—	—	—

Chemical analyses p.p.m.

Chip type	N_2	C	O_2
Sharon shaper	70	1300	—
Sharon mill	20	1200	—
Straddle mill	<20	700	1700
Face mill	30	1000	1000
*Crystal bar**	20	200	—

* For comparison

The oxygen contamination is the most difficult to remove. It is present as a very thin layer and since zirconium oxide is not readily attacked by acid treatment it is necessary to attack the metal under the oxidized skin and force the skin from the metal. This treatment, while reasonably successful, results in an unavoidable loss of about 10 per cent of the metal. The pickling solution used contained 50 per cent by volume of 70 per cent nitric acid and water with an addition of 1 per cent ammonium fluoride. The turnings were pickled for about eight minutes, using 1 to ½ gallon of liquor per pound of cuttings which were agitated slightly during the treatment. The bath was regenerated by adding 0·20 lb of ammonium fluoride per pound of metal treated. After pickling the metal is rinsed thoroughly with cold water and finally with alcohol, before drying.

Arc melting of the recovered zirconium produced ingots which were satisfactory, provided at least 9 per cent of the turnings had been removed by pickling.

A sample ingot produced from scrap turnings from which 6·1 per cent had been removed by pickling had a hardness of 115 BHN (3000 kg).

R. W. DAYTON[8] proposed analysis limits for treated cuttings and these values together with the analyses of material before and after treatment are compared with crystal bar metal and shown in *Table CVII.*

Table CVII. Analysis Limits and Result of Decontamination of Zirconium Chips

State	*Analyses* p.p.m.					
	O_2	N_2	C	Al	Fe	Si
Contamination limits	200	30	400	80	550	100
Prior to cleaning and pickling	1700	20	3400	300	1600	140
After decontamination	200	20	200	20	350	60
For comparison: crystal bar	—	20	300	20	300	50

It is probable that the oxygen could be removed by treatment with molten calcium as previously described. Thin cuttings would be very suitable for such treatment and this method would have the advantage that no loss in zirconium would be incurred.

16.14. GRINDING CHARACTERISTICS[26]

Although zirconium is soft in its pure form, it is extremely difficult to grind under conventional conditions, being very similar to titanium in its grinding behaviour. The principal difficulty is that under such conditions, the wheel wears at an extraordinarily rapid rate; fifty times as fast as for hardened carbon tool steel. Moreover, zirconium is easily smeared and burned when ground conventionally, and the surface finish is poor.

However, just as is true of titanium, zirconium can be ground very satisfactorily provided much lower wheel speeds than normal are used in combination with particular grinding fluids. The recommended[26] coolant is a straight grinding oil.

Surface grinding experiments have shown that the grinding ratio increases to a peak value as the wheel speed is decreased from 6000 s.f.p.m. to somewhere between 4000 and 2000 s.f.p.m., depending on the wheel and grinding fluid, and then decreases with further decrease in wheel speed. The increase from the value at 6000 s.f.p.m. to the peak value is relatively small for poor grinding fluids (like plain water or the commonly used dilute mixtures of general purpose soluble oils in water) but it can be extremely large for straight grinding oils.

16.14.1. *Surface finish*

Wheel speeds for which the grinding ratio is high are the ones that produce the best finish. Values of surface roughness as low as 25μin on the profilometer are obtained using grinding oil, the other grinding conditions being those described above. The best finish obtainable under comparable conditions with the water-base fluids was in the 60 to 75μin range. In no case was there any difficulty from burning and smearing of the surface.

16.14.2. *Fire hazard*

At conventional wheel speeds, the spark stream of zirconium is extremely bright and voluminous, practically the same as that of titanium, so that the use of a straight grinding oil under such conditions may well be hazardous. However, when the wheel speed is lowered considerably in order to raise the grinding ratio, then only a few faint sparks are given off so that there is no more fire hazard from the use of a straight grinding oil than if steel were being ground.

16.15. HEAT TREATMENT STUDIES

Grain growth and recrystallization characteristics of commercially pure iodide zirconium are reported by F. J. DUNKERLEY *et al.*[9]. The recrystallization and grain growth studies were made below the transformation temperature and all annealing treatments were carried out *in vacuo* or in a helium atmosphere. Iodide metal was used in the investigation with weight per cent impurities as follows: Hf 2·1, Mg 0·012, Fe 0·035, Si 0·095, Ti 0·023, Al 0·037, Ca 0·006 and a trace each of Mo, Ni and Cr. Dunkerley concluded:

(*1*) The isothermal grain growth data for zirconium follow the relationship

$$D = kt^n$$

(*2*) Second-phase inclusions have pronounced effects on grain growth. (*a*) In the presence of dispersed second-phase inclusions, grain growth of zirconium was retarded but growth was continuous at temperatures from 640 to 800° C. (*b*) The retarding effect of the second phase when agglomerated in the grain boundaries was less when it was dispersed throughout the grains. (*c*) The entire elimination of the second phase resulted in accelerated grain growth.

(*3*) The energy of activation for grain growth of zirconium in the presence of a dispersed second phase is 68,800 cal/gatom as compared with a value of 55,000 cal/gatom when the second phase is agglomerated in the grain boundaries.

(*4*) Increasing the temperature increases the rate of recrystallization of zirconium independently of prior heat treatment and deformation.

(*5*) The rate of recrystallization increases and the incubation period decreases with increased amount of cold work.

(*6*) Solid solutions of oxygen or a second-phase constituent increased the hardness early in the recrystallization anneal so that appreciable recrystallization occurred before it was revealed by softening. The two structures of zirconium heat treated above and below the transformation temperature contained appreciably different distributions of the second phase, and had different recrystallization characteristics. Heat treating above the transformation temperature results in more work hardening and slightly higher hardness readings than below, and this difference persists throughout the entire annealing period. When the second phase occurs as platelets, recrystallization is retarded.

R. K. McGeary and B. Lustman[19] studied the orientation relationships and rate of annealing of 97 per cent cold rolled zirconium.

It was shown that the process of annealing can best be explained by the formation of domains early in the annealing treatment and the subsequent growth of these domains without recrystallization. The results of the investigation are summarized as follows.

(*1*) Quantitative x-ray diffraction techniques have been used (*a*) to determine $\{10\bar{1}0\}$ pole figures of 97 per cent cold rolled zirconium, as rolled and as fully annealed, in order to establish the exact crystallographic relationships associated with the thermally activated texture changes that have been found to occur, and (*b*) to determine the rate of the reorientations for specimens heated for appropriate times at temperatures from 98 to 600° C.

(*2*) Metallographic observations, hardness measurements, and other results have been correlated with the x-ray results and the following processes occurring during annealing have been identified: (*a*) polygonization may occur in zirconium during cold rolling or during the very first stages of heating. This polygonization is not accompanied by reorientation nor is it detectable metallographically. (*b*) Recrystallization *in situ* (metallographic evidence of polygonization) occurs after annealing at relatively low temperatures and corresponds to a reorientation in which the ideal cold rolling texture is sharpened; this process may occur by selective growth of favourably oriented domains. (*c*) Further annealing causes a complete reorientation corresponding to 20 or 40° rotations about {0001} poles. This process occurs in two steps, the one at constant domain size, the other accompanied by domain growth. Data have been presented to show that the processes do not occur by nucleation and growth of reoriented grains, nor by discontinuous growth of favourably oriented domains.

W. A. Bostrom and S. A. Kulin[2] studied the annealing of cold worked zirconium in the temperature range, room temperature to 575° C by electrical resistivity measurements at −196° C. The metal examined was arc melted iodide zirconium which was cold worked to various stages and stored in liquid nitrogen to prevent partial recovery before test. The effect of cold work by swaging on the resistivity of zirconium is shown in *Figure 116.*

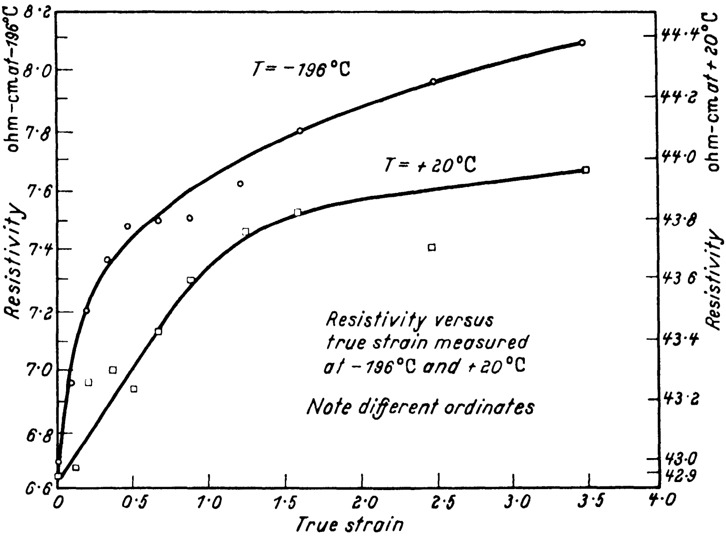

Figure 116. Effect of cold work by swaging on the resistivity of zirconium (after W. A. Bostrom *and* S. A. Kulin[2])

Bostrom and Kulin considered that, after cold working, zirconium recovered and recrystallized in four stages: (*a*) Recovery first occurred not associated with any hardness or microstructural change, but shown by changes in electrical resistivity. (*b*) The second stage was a partial recrystallization in which domains (defined as groups of grains of average diameter 2μ) showed differences in orientation between themselves sufficient to be recognized microscopically. There was an associated drop in hardness of about 30 per cent. (*c*) The third stage was one in which the grain size remained substantially constant, but the metal changed its texture by continuing reorientation of further domains. There was a 90 per cent recovery in hardness at this stage. (*d*) In the final stage, grain growth occurred.

16.16. Preferred Orientation in Zirconium

The textures produced in zirconium by cold and hot rolling and by recrystallization above and below the transformation temperatures were determined by R. K. McGeary and B. Lustman[20].

Two types of zirconium were investigated—iodide crystal bar and zirconium ingot produced by melting Kroll zirconium in a graphite crucible. The composition of the metals is shown in *Table CVIII.*

Table CVIII. Composition of Zirconium used in Preferred Orientation Investigation

Impurity	*Iodide crystal bar* per cent	*Zirconium ingot* per cent
Hf	1·5	1·5
C	0·02	0·09
O_2	0·02	0·08
Fe	0·01 *to* 0·05	0·14

X-Ray diffraction methods were used in the investigation, and the data were presented as pole figures. The following is a summary of the results obtained.

(*1*) The cold rolled texture indicated an average orientation that can be described as having the basal planes $\{0001\}$ parallel to the rolling direction, but inclined from the rolling plane of the sheet about 30° in the transverse direction, with a $\langle 10\bar{1}0 \rangle$ plane in the rolling direction.

(*2*) The recrystallization texture was different from the cold rolled texture. The average position of the basal planes was the same as for the cold rolled texture but a $\langle 11\bar{2}0 \rangle$ plane was in the rolling direction.

(*3*) The hot rolled texture was similar to the cold rolled texture but with more scatter, especially in the transverse direction.

(*4*) A specimen cross rolled at room temperature had a sharp texture with the basal planes parallel to the rolling plane and with the $<10\bar{1}0>$ plane in one rolling direction and the $<11\bar{2}0>$ plane in the other rolling direction.

(*5*) The recrystallization texture of the cross rolled zirconium showed the same basal plane orientation as the rolled material, but the $<11\bar{2}0>$ plane was in the $<11\bar{2}0>$ rolling direction.

(*6*) The texture of the surface layers of cold rolled zirconium was found not to differ fundamentally from that of the interior of the metal.

(*7*) Experimental evidence that the transformation mechanism of body centred cubic β- and hexagonal close packed α-zirconium is of a crystallographically reversible nature was presented. The transformation texture indicates that the orientation relationship is the same as that reported by W. G. BURGERS *et al.*[5], namely

$$\{0001\}_{\alpha}\|\{110\}_{\beta}, \quad <11\bar{2}0>_{\alpha}\|<111>_{\beta}$$

(*8*) By x-ray diffraction the thermal expansion of zirconium in the *c* axis direction was found to be $10{\cdot}3 \pm 0{\cdot}5 \times 10^{-6}$ per C° and $4{\cdot}5 \pm 0{\cdot}5 \times 10^{-6}$ per C° in the *a* axis direction. The thermal expansion was measured in the thickness, transverse, and rolling directions of all sheet materials the textures of which were determined, and the magnitude of expansion was found to be proportional to the degree of scatter in the three measured directions.

The finding of McGeary and Lustman has been to some extent supported by the observations of W. G. BURGERS, J. D. FAST and F. M. JACOBS[5] that the ideal fibre texture of zirconium wire is $<10\bar{1}0>$.

The textures of hot rolled, cold rolled and annealed cold rolled zirconium sheets were determined by J. H. KEELER *et al.*[17] using an x-ray spectrogoniometer.

The pole figures for the cold- and hot-rolled zirconium showed the $<10\bar{1}0>$ direction to be parallel to the rolling direction in agreement with R. K. McGEARY and B. LUSTMAN[20]. All textures showed a tilt of the basal planes ±40° from the rolling plane about the rolling direction. This 40° tilt compares with the 30° tilt determined by McGeary and Lustman.

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17

POWDER METALLURGY OF ZIRCONIUM

THE original method used for fabricating Kroll titanium was based on a powder metallurgy technique applied to the titanium powder recovered by leaching the reduced mass of titanium and magnesium chloride. The production of ductile titanium by this process is described by R. S. DEAN *et al.*[6]. Titanium powder compacts formed at 50 ton/in^2 were sintered for 16 hours at 1000° C in a vacuum of 5×10^{-4} mm of mercury and forged and rolled to thin sheet by hot and cold working. The method was satisfactory but with the future of titanium envisaged in thousands of tons there was little hope that powder metallurgy would be able to cope, particularly as the bulk of the metal would probably be required as sheet, tube, rod and wire. In the meantime Kroll had shown it was possible to recover zirconium as a sponge metal instead of powder, further, he melted the metal in a graphite crucible and with these examples it was not long before the powder metallurgical operations on titanium were completely superseded.

Although it is possible to melt and fabricate zirconium there are difficulties to be overcome because of the reactivity of the metal and it is possible by the use of powder metallurgy to reduce the difficulties. For example, sintering of zirconium powder occurs at a temperature very much lower than the melting point, and shapes can be produced without fabrication. While the melting and fabricating techniques for zirconium may change, there appears to be little chance that they will be replaced by powder metallurgy, especially as the bulk of the metal will be required in the usual forms, *viz* sheet, tube *etc.* However, for special applications, particularly as zirconium castings are not easily made, powder metallurgy may have a definite field; at least, it does provide a method of producing zirconium without any contamination either from a crucible or an electrode.

Very little work on the powder metallurgy of zirconium has been published. H. A. HAUSNER *et al.*[10] in 1951 showed that zirconium was readily fabricated by powder metallurgical methods.

The zirconium used for powder metallurgy must conform to certain standards: (*1*) highest degree of purity, (*2*) consistency in particle size and particle size distribution, (*3*) low compression ratio and (*4*) satisfactory strength of the compacted powder.

17.1. POWDER PREPARATION

Zirconium powder may be made by several methods. First, by applying the orignal titanium leaching process to the reduced mass obtained by the Kroll zirconium process. This method is not generally used but it has been proved to produce powder suitable for powder metallurgical operations[5].

Calcium reduction of zirconia is the most common method used for the production of zirconium powder. The method has been used to produce an intermediate metal for the van Arkel process[2]. A purity of 98·3 per cent zirconium was claimed with about 1·7 per cent oxygen and nitrogen but no doubt this result could be improved. G. MEISTER[15] claimed a high purity for metal produced by calcium reduction of the oxide in an inert gas atmosphere. W. J. KROLL[14] used an atmosphere of argon and reduced under a flux of calcium chloride. Zirconium of 99·5 per cent purity was obtained.

The reduction of zirconium by calcium hydride[1] provides a ready means of producing zirconium hydride which is converted to metal in the early stages of sintering.

The preparation of zirconium powder has been examined by H. S. KALISH[11]. In general, the methods mentioned are those that were used in the earlier attempts to produce ductile metal but which, with variation, may now be employed to produce suitable material for powder metallurgical purposes. Kalish describes the methods in fair detail making suggestions for improvements where necessary. The first essential is the production of pure zirconium tetrachloride or pure oxide from the tetrachloride.

The processes described for the production of powder are:

(*1*) Reduction of zirconia with calcium

(*2*) Reduction of zirconium tetrachloride with sodium

(*3*) Reduction of sodium zirconium fluoride ($Na_5Zr_2F_{13}$) or potassium zirconium fluoride (K_2ZrF_6) with sodium, and

(*4*) Hydrogen embrittlement of massive zirconium.

Most of the processes have been described under the 'Production of Zirconium Metal' (Chapter 5), but Kalish views the processes from the point of view of a powder metallurgist and his findings are important because of the interest in that field.

17.1.1. *Reduction of zirconia with calcium*

The method used by W. P. KIERNAN[13] to carry out the reduction process was regarded by Kalish as the best. Oxide was prepared by igniting zirconyl nitrate dihydrate $ZrO(NO_3)_2.2H_2O$ at 750° C and sieving through 150 mesh. Calcium chips were prepared by cutting with a Wiley cutter to pass $\frac{1}{8}$-in sieve. The calcium chloride was dehydrated by heating for several hours at 500° C. The calcium content of the final metal was largely determined by the extent of dehydration of the calcium chloride; if less than 0·1 per cent water was present in the salt the calcium content of the zirconium could be kept down to 0·05 to 0·1 per cent. According to the reaction

$$ZrO_2 + 2Ca = Zr + 2CaO$$

65 g of calcium is required to reduce 100 g zirconia. Kiernan used 1 g of calcium for every gramme of zirconia. The amount of calcium chloride is determined by experience and depends on the conditions of the reaction: it is added as a diluent to control the rate of reaction. In recent work 90 g of calcium chloride has been added to every 100 g of oxide.

It appears that the quantity of calcium chloride present determines the particle size of the powder presumably because it largely determines the ultimate temperature of the reaction. The reagents are mixed together and charged into an iron or molybdenum crucible and reacted in a partial pressure of argon. No pressure is developed.

The reacted mass is leached with 10 per cent hydrochloric acid, drained on a filter and rinsed with alcohol and ether and finally dried *in vacuo* at 60 to 70° C. According to Kalish zirconium powder produced by this method is the best made by any reduction process. A typical analysis of such powder is: Ca 0·05 to 0·11, Si 0·01 to 0·03, Fe 0·1 to 0·2, Ti 0·01 per cent. If a molybdenum crucible is used the iron content may be reduced to 0·03 to 0·04 per cent, the molybdenum content being 0·01 to 0·005 per cent. If calcium chloride is not employed the oxygen and nitrogen contents are 3·0, and 0·5 to 1·0 per cent respectively, whereas if calcium chloride is used together with the reduction vessel operated with a partial pressure of argon, the oxygen and nitrogen values become 0·3 and 0·03 per cent. Most of the oxygen is picked up during the leaching operation.

17.1.2. *Reduction of zirconium tetrachloride with sodium*

This method is regarded by H. S. KALISH[11] as one of the least favourable for the production of powder. The chloride and sodium are mixed (a difficult operation) and reacted in a bomb at 850° C.

Excess sodium and sodium chloride are removed by leaching with water and the metal is recovered as a mixture of powder and lumps. Kalish considers the metal produced is satisfactory but that the handling of sodium is difficult. It is probable that the main objection to the process is the use of a hygroscopic zirconium salt which makes it extremely difficult to avoid oxide in the final metal.

It is apparent that the method could not be employed as Kalish describes it, but would have to be done on a modified Kroll system where the chloride was densified and purified before reduction. The production of the final metal in lumps as well as powder is a considerable disadvantage.

17.1.3. *Reduction of sodium or potassium zirconium fluoride with sodium*

The sodium salt is preferred to the potassium salt as it is much less expensive. Both these methods of preparing zirconium powder are complicated and have little to recommend them, although the double alkali fluorides are probably better starting points than the tetrachloride which is hygroscopic.

17.1.4. *Hydrogen embrittlement of massive zirconium*

H. A. HAUSNER *et al.*[10] after preliminary tests concluded that none of the zirconium metal powders commercially available was suitable for their work and decided to produce a powder with suitable characteristics, particularly with a low compression ratio and high purity. Both van Arkel's crystal bar and Kroll's sponge are too soft and ductile to be finely comminuted by mechanical methods. However, zirconium hydride which may be formed without difficulty, is brittle and readily broken down to a powder which when heated *in vacuo* is decomposed to metal and hydrogen. Zirconium hydride forms in the temperature range 235 to 800° C, the absorption being most rapid at 400° C[8]. Hydride made at 400° C is primarily ZrH_2 while that produced at 800° C is ZrH but cooling in hydrogen from 800° C converts some of the hydride to ZrH_2 and the final product is a mixture of the two hydrides. Both hydrides are friable and can be ground to pass a 400-mesh sieve (0·037 mm).

Pure zirconium crystal bar is heated in a quartz tube electric furnace in a stream of hydrogen treated by passing through a purification train consisting of the following steps. Tank hydrogen containing 0·2 per cent oxygen is passed over (*i*) copper turnings at 600° C, (*ii*) activated alumina and (*iii*) calcium turnings at 700° C. The flow of gas is maintained through the heating and cooling periods.

Zirconium metal powder is prepared by decomposing the hydride *in vacuo* at 800° C. The pressure should be not more than 0·05 micron. During heating the pressure rises suddenly with the evolution of hydrogen; heating must be continued until at 800° C the pressure has returned to the original value.

Particle size can be varied by crushing the zirconium hydride to a relatively coarse powder and then removing the hydrogen by hot vacuum treatment and finishing the grinding on the recovered powder, this method yields less fines than crushing the hydride to the sieve size.

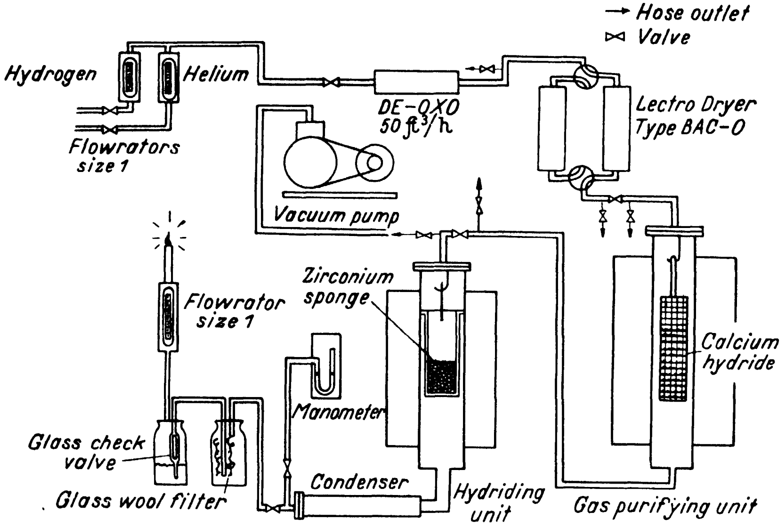

Figure 117. Schematic diagram of apparatus for hydriding zirconium (after H. S. KALISH[11])

H. S. KALISH[11] describes in detail the embrittlement of zirconium by hydrogen absorption. Iodide zirconium required much longer periods of treatment and higher temperatures than those employed for sponge zirconium produced by the Kroll process. Great care was taken to purify the hydrogen, the system consisting of a palladium catalyst, activated alumina, and calcium hydride operated at 700° C. The hydriding apparatus is shown in *Figure 117.* It was found for massive zirconium such as iodide bar or cast Kroll metal that a temperature of 800° C and a period of 20 hours were required. With sponge zirconium the treatment is carried out at 300° C, the absorption of hydrogen being very rapid and dilution of the hydrogen with helium is necessary to maintain control of the process.

The residual impurities in the sponge such as magnesium and magnesium chloride are removed by high temperature hydrogen treatment, but it is preferred to use the low temperature treatment and then leach out the impurities with dilute hydrochloric acid after comminution. If grinding is carried out in air, the oxygen content may increase by 0·1 to 0·2 per cent, but this for general purposes is no disadvantage; nitrogen is not absorbed under such conditions. Inert gas atmospheres should be used in mechanical grinding, but in practice this does not completely eliminate oxygen absorption. The hydride powder can be decomposed by heating at 800° C *in vacuo* as already described.

Kalish compares the hydrogen content of arc melted zirconium and sintered zirconium hydride and shows that the former may contain about 10 to 100 p.p.m. and the latter only 4 p.p.m. *Table CIX* shows the gas content at various steps in the production and sintering of zirconium hydrides. The principal change which occurs is in the oxygen content during comminution of the hydride.

Table CIX. Effect of Powder Preparation by the Hydride Process on the Gas Content of Zirconium[11]

State	*Iodide process crystal bar hydrided at* 800° C			*Sponge hydrided at* 300° C		
	Oxygen per cent	*Nitrogen* per cent	*Hydrogen* per cent	*Oxygen* per cent	*Nitrogen* per cent	*Hydrogen* per cent
Raw material . .	0·05	0·005	0·003 *to* 0·01	0·11	0·005	0·003 *to* 0·01
Hydride . . .	0·05	0·005 *to* 0·015	2·1	0·12	0·006	2·14
Hydride powder (–325 mesh)	0·2 *to* 0·4	0·005 *to* 0·015	2·1	0·2 *to* 0·3	0·006	2·14
Vacuum-decomposed hydride powder (–325 mesh)	0·3 *to* 0·5	0·005 *to* 0·015	<0·001	0·3 *to* 0·4	0·006	<0·001
Vacuum-sintered zirconium hydride powder	0·2 *to* 0·4	0·005 *to* 0·015	0·0004	0·3 *to* 0·4	0·006	0·0004
Vacuum-sintered zirconium powder	0·3 *to* 0·5	0·005 *to* 0·015	0·0004	0·4 *to* 0·5	0·006	0·0004

Kalish compared the properties of zirconium powder produced by the calcium reduction of the oxide and the hydride processes.

Table CX

Analysis and Properties of Zirconium and Zirconium Hydride Powders

All −325 mesh powders[11]

	Gas content		*Average particle size* micron	*Density* g/cm³		*Compression ratio at* 50 ton/in²
Powder type	*Oxygen* per cent	*Nitrogen* per cent		*Apparent*	*Compacted at* 50 ton/in²	
Zirconium hydride from iodide process zirconium	0·2 *to* 0·4	0·005 *to* 0·015	10·3	2·2	4·9	2·2 : 1
Zirconium hydride from sponge zirconium	0·32	0·006	6·8	1·96	4·45	2·27 : 1
Zirconium from decomposition of iodide hydride	0·3 *to* 0·5	0·005 *to* 0·015	20·0	2·0	5·5	2·75 : 1
Zirconium from decomposition of sponge hydride	0·4 *to* 0·5	0·006	27·4	2·33	5·10	2·2 : 1
Calcium-reduced zirconia high purity	0·31	0·036	5·5	0·47	5·68	12 : 1
Calcium-reduced zirconia photoflash grade	2 *to* 3	0·5 *to* 2	3	—	—	—

Table CXI

Particle Size Distribution of Zirconium and Zirconium Hydride Powders as Determined on the Photometer[11]

Particle size micron	*Zirconium hydride powder made from iodide process zirconium*	*Zirconium powder made by vacuum decomposition of the hydride*	*Calcium-reduced zirconium*
0 *to* 1	10·2	1·5	3·3
1 *to* 2	10·3	2·8	9·3
2 *to* 3	13·3	2·0	5·9
3 *to* 4	19·0	4·3	24·4
4 *to* 5	8·3	3·8	14·1
5 *to* 6	5·0	5·4	9·6
6 *to* 8	5·4	6·6	18·5
8 *to* 10	1·8	5·5	8·4
10 *to* 12	1·1	5·3	1·8
12 *to* 14	1·3	5·6	1·4
14 *to* 16	1·5	5·5	1·3
16 *to* 20	1·8	8·0	2·0
20 *to* 30	7·7	15·4	0
30 *to* 44	10·5	19·4	0
>44	2·3	8·9	0

He points out that the bulk of the powder produced is used for photoflash lamps and that for this purpose it is desirable to have a powder with a high oxygen content. A powder containing 2 to 3 per cent oxygen has an ignition temperature of about 250 to 300° C which is suitable for the lamps. The much purer powder which can be made by the same method has an ignition temperature of about 85° C and is totally unsuitable for present photoflash lamps.

Tables CX and *CXI* show the analysis, properties and particle size distribution of zirconium powders produced by the calcium reduction and hydride processes.

17.2. HAZARDS IN HANDLING ZIRCONIUM POWDER

It is important to handle zirconium powder with care in all stages of processing, because although the metal is resistant to oxidation at room temperature the powder has a low ignition temperature. Kalish states that it is erroneous to consider zirconium hydride to be more stable than zirconium powder and even claims that the ignition temperature of the hydride powder is a few degrees lower than that of the metal powder[9]. This is surprising in view of the fact that hydride powder has been shipped for some years without precautions while zirconium powder has been covered with water. Kalish gives the ignition temperature of both hydride and zirconium powders as 75 to 300° C, depending upon the particle size and purity.

H. C. ANDERSON and L. H. BELZ[3] who also investigated the combustion of zirconium powders, compared zirconium and zirconium containing hydrogen and reported little difference in the ignition temperature until the metal was almost completely converted to ZrH_2, when the ignition temperature was raised from about 200° C to above 400° C.

The handling of zirconium powder used in the flashlamp industry is described by W. C. FINK[7]. Great care is taken and the first step is to keep down to a minimum the amount of powder in process. The maximum quantity of powder which may be handled in an 8-hour shift is 25 lb; the quantity handled by one operator at a time is limited to 1½ lb. The powder is received in 50-lb batches in wooden kegs, suspended in water which is considered much less dangerous than suspension in inflammable liquids such as alcohol. Alcohol has the advantage that when drained from the powder, the adhering liquid is readily evaporated, but the water can be fairly readily eliminated if the drained powder is rinsed with alcohol before low-temperature drying.

The handling operations are divided into areas and most of the work is done in hoods fitted with venting doors to relieve sudden pressure which would result from an explosion. Precautions are taken to prevent explosions due to ignition by static charges. The humidity of the air is controlled at around 50 per cent at about 25° C. All exit doors are fitted with emergency showers.

While it is not necessary for everyone who handles zirconium powder to have a laboratory fitted like the one described by Fink, it is important to take great care in handling the material. Quantities being handled should be kept at a minimum. Comminution of small quantities may be carried out cautiously but larger quantities should be crushed or milled under an inert gas. The powder should be stored under argon or water.

17.3. EXPLOSIVE CHARACTERISTICS OF ZIRCONIUM POWDER

The precautions required in the handling, storage and shipping of zirconium powder have been summarized in a National Safety Council publication[16].

The major hazard with zirconium is fire and explosion. It has a comparatively low ignition temperature, is highly inflammable in the dry state and burns with an intensely brilliant flame. Like other finely divided metals, the powder will produce an explosive mixture with oxidizing agents such as barium nitrate or potassium chlorate.

Ignition temperatures of the dry powder are reported[16] to range from 151 to 160° C, according to the grade. The dry powder is ignitible at low temperature by heat, static electricity, or simple friction. It is reported to be more easily ignited than magnesium powder. When dispersed into the air as a cloud, it explodes spontaneously, ignited by the static charges generated during dispersion.

Zirconium powder damped with water is much safer to handle than dry zirconium powder because it is more difficult to ignite. Once ignited, however, the damp powder will burn even more violently than the dry powder, partly because the metal will decompose the water and use the oxygen for its own combustion and partly because the steam formed within the burning mass will scatter the metal. The powder containing about 5 to 10 per cent of water is stated to be the most dangerous.

The minimum explosive concentration was 0·16 g/l (0·15 oz/ft^3), and a cloud containing 1 g/l when ignited in a closed chamber produced a maximum pressure of 2·9 atmospheres (42 lb/in^2).

The explosive characteristics of zirconium and other metals and their hydrides have been studied by I. HARTMAN *et al.*[9]. Several samples of zirconium powder and hydride were examined. Four of the zirconium powder samples ignited at room temperature when dispersed as a dust cloud. One sample, prepared by decomposing hydride, ignited at 350° C and another, coated with copper, ignited at 480° C. Two samples of hydride were dispersed as dust clouds, one ignited at 350° C and the other at 430° C. Oxygen content did not appear to be important as one sample of zirconium which ignited at 20° C was reported to contain 3 per cent oxygen while the one prepared by decomposing hydride contained only 0·29 per cent oxygen and ignited at 350° C. The results indicate that of the samples tested the zirconium powder was the more liable to ignite.

H. C. ANDERSON and L. H. BELZ[3] studied the activity of sub-sieve zirconium powders by measurements of ignition temperature,

Table CXII. Effect of Alloying Constituents on Zirconium Powder

Alloying constituent (*A*)	*Zirconium* per cent	*A* per cent	*Particle size or range* micron	*Ignition temp.* °C	*Burning time* sec/10 in	*Ignition energy* J
Ti	44·7	40·0	2 *to* 8†	228	7	0·000125
Ti	21·8	66	2 *to* 8†	279	9·9	0·000045
Ti	11·8	73·5	2 *to* 8†	>400	30·5	0·00045*
Ti	8·1	75·2	2 *to* 8†	>500	45·2	0·0025*
Ti	0	86·0	2 *to* 8†	>500	81	>21·9
Ni	87·2	6·2	<44	176	9·4	0·00016
Ni	79·1	13·8	<44	250	60	0·00036
Ni	64·5	29·9	<44	>400	202	12·5*
Ni	54·9	38·9	<44	>400	324	21·9*
Ni	34·7	54·3	<44	*Would not burn*		
Cu	85·3	7·7	<44	210	21·2	0·000625
Cu	72·1	15·1	<44	194	25·8	0·00125
Cu	64·0	31·4	<44	200	18·2	0·00144
Cu	49·2	46·0	<44	210	47·5	0·0025*
Fe	86·7	6·1	<44	132	31·0	0·000625
Fe	81·6	11·9	<44	162	23·4	0·000625
Co	89·0	13·5	<44	188	32·6	0·00025
H_2‡	90·0§	0	3·77†	218	11·8	0·00009
H_2‖	89·9	0·07	3·77†	200	6	0·000045
H_2	89·9	0·08	3·77†	204	11·5	0·000045
H_2	89·9	0·13	3·77†	208	8	0·000045
H_2	89·4	0·55	3·77†	230	42·5	0·000080
H_2	88·9	1·1	3·77†	224	51	0·000125
H_2	88·6	1·5	3·77†	260	73·1	0·00050*
H_2	88·5	1·8	3·77†	>400	81	0·0225*

* Ignition not sustained. † By air permeability method. ‡ Degassed at 1100° C.
§ Free zirconium, as determined by gain on ignition. ‖ Degassed at 700° C.

burning time and ignition energy. These authors reported that a particle diameter of 10 microns represented approximately the dividing line between hazardous and non-hazardous powder; this did not apply to powders consisting of agglomerates of particles smaller than 10 microns. The presence of residual oxide had no effect on the temperature of ignition, in fact, some of the lowest ignition temperatures noted were for incompletely reduced powders. Alloying additions had little or no effect on the ignition temperature, unless very large additions were made.

The effect of such additions is shown in *Table CXII.*

17.3.1. *Shipping regulations*

The Interstate Commerce Commission[17] classifies zirconium as an inflammable solid, and its regulations for transportation state that as a sludge, or in the wet form, it must be packed in wooden boxes with inside containers of screw cap metal cans containing not over 8 lb each with a gross weight of not more than 150 lb per package, or in wooden kegs containing not over 75 lb net.

For dry zirconium the Commission requires wooden boxes with inside metal cans with push in covers soldered in place at four points, or screw cap metal cans, not more than 75 lb gross per package.

17.3.2. *Storage*

The metal powder in the form of sludge should be stored in a fireproof room kept above freezing temperature. Unit quantities should preferably be kept separated to limit the amount of damage in case of fire. Only enough for current use should be removed from the storage room at any time.

17.3.3. *Personal protective equipment*

A person who handles zirconium powder should wear goggles or a face shield of flame-resisting material, gloves of leather or asbestos, and a smock or jacket with one-piece front to protect him from flash burns.

17.3.4. *Handling*

When zirconium is to be mixed with other materials, the sludge form should be used if possible. The unit quantities used in any process should be kept small. Some users report limits of 100 to 400 g for a single operation.

When the batch is to be dried, the sludge should be filtered on a Buchner funnel with a slight suction. After as much water as possible has been sucked out, the rest of the water can be displaced with absolute methanol. The filtering flask should be left under vacuum until the liquid is removed from the filter cake.

Each filtering unit should be completely separated from the others in the line, and filtering, as well as subsequent operations, should be carried out behind a shield of shatter-proof glass.

After the filter cake has been sucked dry, it should be dumped from the funnel on to a smooth, clean, non-sparking metallic surface, and the filter paper should be removed from the cake and scraped as clean as possible with a non-sparking spatula. The cake may also be broken up with the spatula.

The filter cake can be dried at 60 to 70° C (140 to 158° F) for two hours in a hot-water oven. After it is dry, the material should cool to room temperature before it is removed from the dryer.

The hot-water oven used for this purpose should have a vented top to relieve possible explosions, and the interior should be smooth non-sparking metal so that it can be readily cleaned after each use.

Dust balls or soft lumps of the dry zirconium can be broken up with a wooden roller on a board or with a non-sparking metal roller or spatula. The powder can be sifted in an enclosed and grounded mechanical shaker under an atmosphere of nitrogen. The exhaust nitrogen should be bubbled through water to trap any zirconium powder which might be carried out as dust.

The work place should be kept scrupulously clean. Any accumulation of dust should be picked up by a moist cloth which is kept immersed in a can or covered bucket of water.

The dry powder should be transferred from the sifter to small unit containers under an atmosphere of nitrogen or helium.

Paper should never be used for handling or transferring zirconium because it can be readily ignited by being poured off a sheet of paper.

17.3.5. *Extinguishing fires*

If the zirconium is handled in small quantities and the individual units are properly isolated, as they should be, it is probably best to let an ignited unit burn out quietly without interference.

Fire in a comparatively small amount of zirconium can be controlled by a large amount of foam applied very rapidly and in such a manner as not to disturb the powder. Such fires can also be controlled by dry sand.

Generally, the methods effective in extinguishing magnesium fires should also be effective for small zirconium fires. Carbon tetrachloride, carbon dioxide, soda and acid extinguishers are ineffective.

Although a sprinkler system might be expected to intensify the fire rather than extinguish it, the spread of flames in quantities of zirconium not exceeding 400 to 500 lb in one fire would be minimized by the wetting and consequent cooling of adjacent combustibles.

17.3.6. *Toxicity of zirconium*

The small amount of work which has been done indicates that the toxicity of zirconium is very low[16].

17.4. COMPACTING AND SINTERING

Zirconium powder and zirconium hydride powder prepared by the methods described are free flowing powders which can be compacted without the aid of a binder to give strong compacts. The compression ratio is excellent, varying between 2 to 1 and 2·5 to 1 with pressures of 40 to 50 ton/in^2.

The green strength of compacted zirconium powder is considerably better than that of zirconium hydride for equal compacting pressures; mixtures of zirconium powder and hydride powder yield intermediate green strengths. At 50 ton/in^2 the green strengths for zirconium hydride, 50/50 hydride–zirconium, and zirconium were approximately 1700, 2500 and 3600 lb/in^2 (modulus of rupture).

The disadvantage of low green strength of the compacted hydride is entirely outweighed by the advantage to be obtained in sintering. H. A. HAUSNER *et al.*[10] claimed that sintered zirconium of good density could be obtained by pressing hydride at lower pressures than zirconium.

The pressed compacts are sintered in an atmosphere of inert gas or *in vacuo*. Hausner found that despite employing extreme precautions to purify argon the zirconium sintered in the gas was invariably contaminated with nitrogen. Sintering in a vacuum of 5×10^{-5} mm of mercury or better, at above 1300° C, gave good sintered products practically uncontaminated with oxygen or nitrogen. Pieces of zirconium crystal bar when heated for 10 hours at 1260° C in a vacuum of 2×10^{-5} mm of mercury showed no change in their oxygen and nitrogen contents. In addition, Hausner reported that if vacuum sintering is employed zirconium hydride may be sintered directly without prior decomposition.

Stabilized zirconia boats and slabs were used for sintering without much trouble from oxide contamination, but it was not considered good practice, and other materials were investigated. An obvious choice was graphite in view of the fact that zirconium can be melted in crucibles of this material with relatively little contamination. Tests in graphite boats showed that while the graphite tended to adhere to parts of the compacts carbon penetration was never more than a few mils even after sintering at 1390° C. Samples were usually sintered in graphite boats, without any covering except a graphite lid, and this method yielded sintered products with bright shiny surfaces.

Hausner's work showed that zirconium hydride when pressed and sintered yielded much less porous metal than when zirconium metal powder was used. It had been noted in earlier work that samples of sintered products from hydride were superior in most respects, including ductility and corrosion resistance, to those obtained from zirconium metal powder.

It was assumed that the difference was due to the higher oxygen and nitrogen content of the zirconium powder because of the additional pulverization step required to produce this powder. This point is not very clear, unless it means the pulverization required to break down the partially sintered material produced by the decomposition of hydride *in vacuo* at 800° C. The improved results obtained by direct sintering of the hydride are also due to the clean active surfaces produced during the decomposition of the hydride.

The optimum conditions for sintering zirconium hydride were investigated by H. A. HAUSNER *et al.*[10]. Zirconium hydride formed

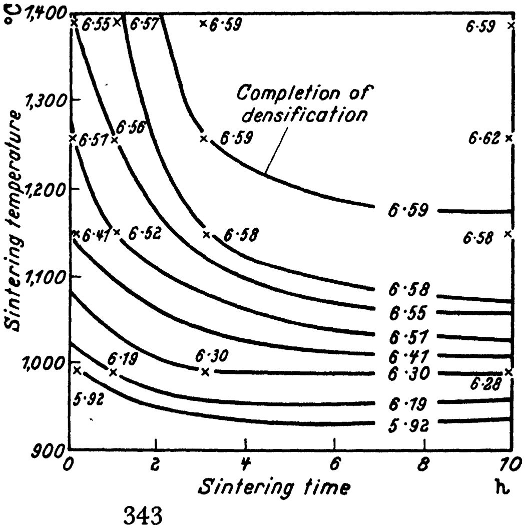

Figure 118. Constant density lines as a function of sintering time and temperature for zirconium. Vacuum sintered from − 325 mesh *zirconium hydride powder compacted at* 50 ton/in² (*after* H. A. HAUSNER *et al.*[10])

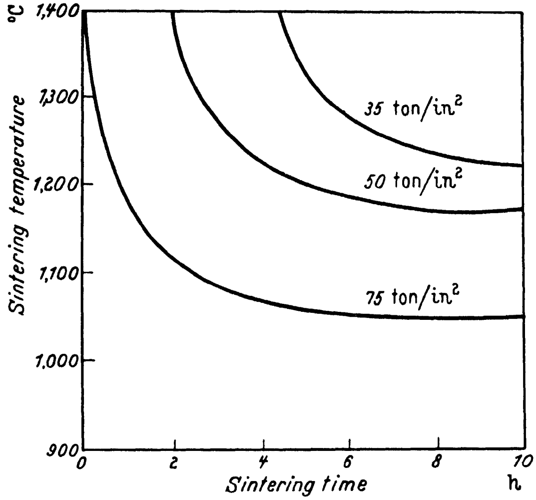

Figure 119. Isodense lines representing 6·59 g/cm^3 *(complete densification) for three compacting pressures. Data for* −325 mesh *zirconium hydride compacted as indicated and vacuum sintered (after* H. A. HAUSNER *et al.*[10])

at 800° C was crushed to pass a 325-mesh sieve and samples pressed at 35, 50 and 75 ton/in^2 and sintered *in vacuo* at temperatures ranging from 990 to 1390° C for periods ranging from 5 minutes to 10 hours. Full densification was obtained by sintering for three hours at temperatures as low as 1100° C if a high compacting pressure of 75 ton/in^2 was used. The same density could be obtained by lowering the pressure to 50 ton/in^2 and increasing the temperature to about 1260° C but if the temperature was maintained at 1100° C the best density attainable would be about 6·35. The results obtained are shown in *Figures 118* and *119.*

The zirconium metal obtained by sintering hydride was ductile and could be cold rolled in 5 per cent passes to an average of 62 per cent reduction in thickness before it showed edge cracking. The hardness was about Rockwell B92, with the range 90 to 94.

According to a later paper by H. S. KALISH[12] the properties of sintered zirconium are as shown in *Table CXIII.*

Further work on the powder metallurgy of zirconium has been done by Y. C. CHUANG[5] who prepared specimens from two types of powder, one was hydride prepared by hydriding zirconium turnings and the other was zirconium metal powder prepared by leaching the reduced mass of zirconium and magnesium chloride obtained in the Kroll process.

The hydride powder was graded into two sizes, '*A*' to −100 to +200 mesh *B.S.S.* and '*B*' −200 mesh *B.S.S.*, while the zirconium metal powder was much finer, 20 per cent +300 mesh and 80 per

Table CXIII. Properties of Sintered Zirconium Compacts

Density	6·59* g/cm^2
Resistivity	58 *to* 60 microhm-cm *at* 68° F
Hardness	92 *Rockwell B*
Tensile strength	95,000 lb/in^2 91,000† lb/in^2
Yield strength, 0·2 per cent *offset*	77,300 lb/in^2 73,000† lb/in^2
Reduction in area per cent	6·1 33·5†
Elongation per cent	5·3 22†
Cold reduction in thickness before the first sign of edge cracking per cent	50 *to* 75

* Density of zirconium varies considerably with hafnium content. This density is for a hafnium content of about 2·5 weight per cent. The density of pure zirconium is reported as 6·50.

† Hot rolled at 1300° F. 50 per cent reduction. As-sintered metal made from −325 mesh zirconium hydride powder compacted at 50 ton/in^2 and sintered 3 h at 1250° C in a vacuum.

cent − 300 mesh. The hydride particles were angular and irregular while the metal particles were rounded and there was little variation in size. The pressed density at 64 ton/in^2 with hydride was 5·17 g/cm^3 compared to 5·0 obtained by Hausner but the metal powder at the same pressure gave a value of 5·62. The rupture strength for the hydride compact obtained by Chuang at 64 ton/in^2 was only 1750 lb/in^2 compared to Hausner's 2000 lb/in^2, and it is possible that the difference was due to a difference in technique. However, the metal powder gave 2070 lb/in^2 rupture. Chuang preferred the metal powder to the hydride for the reasons given and the sintered results confirmed his preference. The sintering schedule used by Chuang was as follows:

The compacts were sintered in a recrystallized alumina boat while protected by zirconium turnings covering the compact. The boat was heated in a *Nimonic* tube in a vacuum of better than 5 × 10^{-5} mm of mercury. The temperature of the tube was raised to 800° C and held there until the charge attained the same temperature, and all the hydrogen had been expelled. The compact was raised to the sintering temperature and maintained for the required period. After sintering the furnace was cooled to 700° C before removing the *Nimonic* tube, which was allowed to cool in air before breaking the vacuum.

Samples of fine and coarse hydride and zirconium metal powder compacts pressed at 32 and 48 ton/in^2 were sintered at 1150° C; the maximum working temperature of the *Nimonic* tube under vacuum was 1200° C.

The results obtained with fine hydride powder confirmed that it had remarkable sintering characteristics, sintering much more rapidly than either of the other powders. The superior sintering properties may be ascribed to the energy change associated with the decomposition of the hydride, this being more apparent in the fine powder.

Samples from sintered compacts of the fine and coarse hydrides were analysed for oxygen. The – 100 mesh powder sintered compact contained 0·06 per cent, the – 200 mesh sample 0·04 per cent, and the original zirconium turnings 0·026 per cent. The hydride powder prepared by H. A. HAUSNER *et al.*[10] contained 0·2 to 0·4 per cent oxygen and it may be assumed that the lower oxygen content of Chuang's hydride is due to the use of an inert gas while milling.

The highest density obtained with hydride powder was 6·10 using a pressure of 48 ton/in^2 and sintering at 1150° C for six hours. This result compares unfavourably with that obtained by Hausner and may be due to the fact that Hausner used very pure metal for hydriding while Chuang used Kroll zirconium which had been melted in a graphite crucible and contained 0·15 per cent carbon. The hardness of the sample with the density of 6·10 was 225 VPN (equivalent to about Rockwell B96) and the rupture strength was 43·7 ton/in^2.

The results obtained with the zirconium powder were unusual, maximum densities were attained at low temperatures and 1050° C appeared to be sufficient. Samples pressed at 48 ton/in^2 sintered at 1000° C had densities of 6·16, increasing the temperature to 1200° C resulted in a drop to 6·03, while at 950° C a density of 5·98 was obtained. The hardness of the 6·16 density sample was 212 VPN (Rockwell B94), rupture strength 45·7 ton/in^2. According to H. A. HAUSNER *et al.*[10] (*Figure 118*) fine hydride powder pressed at 50 ton/in^2 sintered at 950° C for four hours gave metal with a density of 6·19 and at 1050° C the density would be about 6·35.

A few samples of the zirconium metal powder were sintered in an aluminous porcelain tube *in vacuo* for three hours at 1300° C. The compacts pressed at 48 ton/in^2 had, when sintered, a density of 6·2 g/cm^3, hardness 212 VPN (Rockwell B94), and rupture strength 74·6 ton/in^2 with a deflection of 6·1 per cent on 1·125-in span. Samples were cold rolled to 53 per cent reduction in thickness before edge cracking occurred.

The work of Hausner and Chuang shows that it is possible to produce satisfactory sintered products from zirconium and a commercial process could be based on their results.

As Hausner rejected powder produced by the calcium reduction of zirconia on the basis of high compression ratio, there appear to be two possible powders for powder metallurgical applications. First, the hydride produced from pure solid zirconium and secondly the metal powder recovered from a Kroll reduction by acid leaching. The second choice would be cheaper. If van Arkel crystal bar was used as the basis of the hydride production, the powder would be very expensive. Hydride production from scrap zirconium would probably be the cheapest source of powder.

Oxidation of the hydride powder during milling can be limited by the use of an inert gas in the mill.

Sintering in a high vacuum with a pressure not greater than 5×10^{-5} mm of mercury is preferable to sintering in an inert gas owing to the difficulties involved in purification, and as a vacuum-tight furnace is required for use with pure gas atmospheres, it is wasteful to use inert gases where vacuum is possible. The compacting pressure required is rather high at 50 ton/in^2 and die wear may be severe.

The most suitable temperature for sintering to dense metal is 1200 to 1300° C while graphite boats appear to be the most convenient containers for the compacts.

The zirconium metal powder prepared by leaching the product of the reduction of zirconium tetrachloride and magnesium contains a small amount of magnesium, about 0·5 per cent, which cannot be removed by acid leaching. In attempts to remove this by controlled heating in a high vacuum it was found that when the loose powder was heated in a molybdenum or graphite crucible at 1000° C, an ingot of metal with practically full density was obtained, thus illustrating the ease with which zirconium metal may be utilized in powder metallurgical techniques.

It was found impossible to eliminate all the magnesium at temperatures below that at which appreciable sintering took place and therefore it is impossible to produce a powder free from magnesium, but the powder containing the magnesium may be used directly so long as the sintering of the compacts takes place *in vacuo* and at above 1000° C. The vaporized magnesium provides an excellent gettering atmosphere.

Another instance of the ease of fabricating zirconium powder may be shown by packing the powder in a steel tube which is then sealed and worked at below 1000° C to produce dense metal. Similarly, zirconium sponge may be broken into small pieces up to ½-in, and hot worked in a steel case to yield dense metal; this unfortunately contains small amounts of magnesium chloride and magnesium which are difficult to remove from the sponge even by prolonged hot vacuum treatment.

17.5. HOT PRESSING

The hot pressing of zirconium was examined briefly by H. A. HAUSNER *et al.*[10]. The pressings were made in a graphite-lined steel die at 650° C for 15 minutes *in vacuo* at a pressure of 25 ton/in^2. The powder compacted to a density of 6·53 g/cm^3. The specimen had a uniform fine grain size, less than that of the specimens obtained by cold pressing followed by sintering. The hardness of the hot pressed sample was slightly more than normal, indicating that there had been contamination from the die.

Hot compaction of zirconium powders in cermet dies heated by radiation was investigated at the Atomic Energy Research Establishment[4]. A pressure of 17·5 ton/in^2 was used at temperatures of 500 to 850° C. The compacts produced from zirconium hydride disintegrated after ejection from the die due to stress caused by the hydrogen remaining in solid solution. Strong compacts with a density up to 6·45 and rupture strength up to 37 ton/in^2 were formed from zirconium powder under the same conditions.

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5 [illegible]

radiation was investigated at the Atomic Energy Research Establishment[4]. A pressure of 17·5 ton/in^2 was used at temperatures of 500 to 850° C. The compacts produced from zirconium hydride

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18

SPECIAL COMPOUNDS OF ZIRCONIUM

THE compounds zirconium nitride, zirconium carbide, zirconium boride and zirconium silicide are all hard, high melting point, metallic substances which may become important as materials for high temperature purposes. Although there is a tendency in some quarters to regard these compounds as ceramic materials, they are essentially metallic in character with good electrical conductivity, high elasticity modulus and fair alloying properties with auxiliary metals. Components are usually produced by powder metallurgical techniques.

18.1. ZIRCONIUM NITRIDE

18.1.1. *Production*

Zirconium has a strong affinity for nitrogen and when heated in this gas a solid solution is formed up to about 20 atomic per cent nitrogen followed by the formation of zirconium nitride, ZrN. Other nitrides reported are Zr_3N_2, Zr_3N_4, Zr_2N_3 and Zr_3N_8. In the case of Zr_3N_2 it is probable that this represents a mixture of ZrN and solid solution. The existence of the higher nitrides is doubtful.

Several methods for the preparation of zirconium nitrides have been described. E. WEDEKIND[46] prepared a nitride by heating the metal in a stream of pure nitrogen at 1050° C. The same method was used by K. MOERS[30] and P. CLAUSING[11] who preferred to operate at 1100 to 1200° C and 1700° C respectively.

E. FRIEDERICH and L. SITTIG[14] prepared zirconium nitride by heating a mixture of lamp-black and zirconium dioxide in a tungsten or graphite boat at 1300° C in a stream of nitrogen. The nitride crystals produced by this method were of doubtful purity. Friederich and Sittig described the colour as 'golden-yellow' while 'citron-yellow' was the description applied by Moers[30]. E. WEDEKIND[46] also produced nitride by heating the hydride in nitrogen at 1050° C.

A. E. VAN ARKEL[39, 40] produced zirconium nitride by the decomposition of zirconium tetrahalide vapour by contact with a hot tungsten filament in an atmosphere of nitrogen and hydrogen.

The reaction is shown by the following equation

$$2ZrCl_4 + N_2 + 4H_2 \rightarrow 2ZrN + 8HCl$$

K. Moers[30] investigated the method thoroughly. He found the optimum conditions for operation to be as follows: filament temperature 2300 to 2800° C; zirconium tetrahalide ($ZrCl_4$) at 300 to 350° C gave most favourable vapour pressure; gas mixture 75 per cent nitrogen and 25 per cent hydrogen. The presence of hydrogen greatly facilitates the reaction on the hot filament because of its reducing properties; the reaction temperature being greatly lowered.

K. Moers[30] found that a mixture of the composition

$$ZrCl_4 + N_2 + C_6H_5CH_3 + H_2$$

within certain temperature limits produced only the nitride with no carbide formation.

According to R. Kieffer and F. Benesovsky[24] both metal chlorides and oxychlorides can be reacted with ammonia to produce metallic nitrides:

$$MeCl_4 + NH_3 \rightarrow MeN + HCl$$
$$MeOCl_3 + NH_3 \rightarrow MeN + HCl + H_2O$$

No details are given, nor are specific metals mentioned; it is probable that the first reaction could be applied to zirconium but not the second. Another reaction mentioned by Kieffer and Benesovsky which might be applied successfully to the production of zirconium nitride is that which occurs between oxides and calcium nitride

$$MeO + Ca_3N_2 \rightarrow MeN + CaO$$

According to F. P. Venable[41] the compound $ZrCl_4.8NH_3$ gives off fumes of ammonium chloride when heated to redness in a stream of nitrogen. The residue, a pearl-grey powder, yielded ammonia when heated in a stream of hydrogen. The analysis of the compound indicated its composition as Zr_3N_8. When $ZrCl_4.4NH_3$ was similarly treated the product appeared to be Zr_2N_3. All ammonia compounds react with zirconium tetrachloride on heating to 195° C to yield $Zr(NH_3)_4Cl_4$. This is also true for the iodide. At higher temperatures the halogen acid and not ammonia is expelled.

A more recent method for the production of nitride is described in a patent by P. P. Alexander[3]. The method is described for titanium nitride but could be applied equally well to zirconium nitride. Finely divided titanium dioxide is reduced with calcium hydride to produce titanium metal dispersed in lime and while the reaction product is still hot, pure nitrogen is admitted to the reaction vessel to react with the metal to form nitride. The titanium nitride is recovered by leaching the lime with a dilute acid such as acetic acid.

18.1.2. *Properties*

Lattice—ZrN; cubic NaCl type

Lattice constant—$a = 4{\cdot}567$ kX[13]

Density—Calculated from x-ray data[6]	6·97 g/cm^3
Measured[6]	6·93 l/cm^3

Melting point—3255 ± 50° K[6]

Hardness—	(*a*) Moh's scale[6]	+8
	(*b*) Knoop microhardness[24]	K100/1510
	(*c*) Microhardness (30 g load)	19·83 kg/mm^2 (18 mean square deviation)[38]

Specific electrical resistance—Low temperature measurements:

At room temperature	13·6 microhm/cm[6]
Liquid air temperature	3·97 microhm/cm[6]

(The conductivity of the nitride is much better than that of the metal.)

Other low temperature measurements[6]:

°K . . .	273·16	78	20·4	9·3
$R/R_0 = r$ . .	1	0·170	0·087	0·000

High temperature measurements[6]:

°K	$\varrho/\varrho_{+20°}$ $=\varrho/0{\cdot}136$	°K	$\varrho/\varrho_{+20°}$ $=\varrho/0{\cdot}136$
1452	7·52	2392	10·44
1803	8·14	2628	11·21
2135	9·82	2835	11·95

Critical superconductivity temperature[6] 9·45° K

Magnetic properties—Magnetic susceptibility[6]:

$K \times 10^6$	+ 0·6
$\frac{1}{2}K \times 10^6$/mole	+30

Solubility of zirconium nitride—Zirconium nitride (ZrN) is completely soluble in the carbides of titanium, zirconium, hafnium and tantalum[24]. P. DUWEZ and F. ODELL[13] studied the binary systems of nitrides and carbides of zirconium, niobium, titanium and vanadium and formed the following conclusions:

(*1*) The binary nitride systems ZrN–NbN and ZrN–TiN form continuous series of solid solutions.

(*2*) In the binary nitride system ZrN–VN the solubility of ZrN in VN is less than 1 per cent and the solubility of VN in ZrN is approximately 5 per cent.

(*3*) The carbide–nitride system TiC–ZrN forms a continuous series of solid solutions.

(*4*) The system VC–ZrN shows very limited solubility.

(*5*) In the system NbC–ZrN no reaction took place at a temperature of 2450° C.

18.2. ZIRCONIUM CARBIDE

18.2.1. *Production*

Zirconium carbide is produced from zirconium dioxide by mixing and heating with carbon. K. BECKER[6] states that a temperature of 1900° C is required. R. KIEFFER[22] described the production of zirconium carbide as follows. Zirconia was wet milled in a hard metal-lined mill using hard metal balls. The mixture contained 85 per cent of the theoretical amount of carbon as carbon black. The milled mixture was dried and heated to 1800° C in a graphite crucible in an induction furnace. The carbide was milled and assayed for carbon and the amount of carbon required (approximately 3 per cent) to reach the theoretical value of 11·7 per cent carbon was added and the mixture recarburized at about 1700° C in a vacuum graphite tube furnace. The final product assayed 11·8 per cent carbon of which about 0·5 per cent was free carbon. It has been suggested that there are two carbides, ZrC and ZrC_2 but R. KIEFFER[22] failed to produce the higher carbide and concluded that it did not exist below 2000° C.

A marked solubility of carbon in zirconium carbide has been reported by C. AGTE and K. MOERS[2]. Owing to solution of carbon in the carbide the melting point may be reduced by as much as 1000° C. On cooling some of the carbon which dissolves in melting is precipitated.

Reduction of zirconium oxide with carbon may produce material which on analysis gives the correct composition but such material has been found to contain varying amounts of free carbon up to nearly 50 per cent of the total carbon. This would indicate that either free zirconium is present, which is most unlikely, or that a lower carbide than ZrC has been produced. X-Ray examination indicates that the sample is wholly ZrC which cannot be correct on the basis of the chemical analysis. The free carbon determined by chemical analysis was present in two forms, the bulk being graphitic in appearance. This anomaly has not, as far as is known, been reported by any other investigators.

Zirconium carbide is formed during the melting of zirconium in graphite crucibles but only to a very limited extent.

While the principal method of production is the zirconium dioxide–carbon reaction, other general methods can be applied. Zirconium alloys such as ferro-zirconium may be carburized and the iron and iron carbide dissolved with acids leaving zirconium carbide. Another method which can be employed is to react the hot metal powder with hydrocarbons.

A very pure zirconium carbide can be produced by heating a mixture of zirconium tetrachloride, hydrogen and carbon monoxide in a tube containing a heated tungsten filament. Hydrocarbons can be used instead of carbon monoxide and would appear to be preferable. K. MOERS[30] produced zirconium carbide by treating zirconium tetrachloride with the vapour of hydrocarbons such as toluol, methane and acetylene

$$ZrCl_4 + CH_4 \ (+H_2) \rightarrow ZrC + 4HCl \ (+H_2)$$

The presence of hydrogen serves two purposes, it removes the hydrogen chloride and prevents the side reactions[30]. The temperature of the filament and ratio of the concentration of the reactants are of the utmost importance. By careful control very pure carbide can be obtained.

18.2.2. *Properties*

Lattice—ZrC; cubic NaCl type

Lattice constant—$a = 4{\cdot}685$ kX[13]

Density—Calculated from x-ray data[6]	6·51 g/cm^3
Measured[6]	6·90 g/cm^3
Measured[22]	6·70 g/cm^3

Melting point—3805 ± 125° K[6]
3523° K[22]

Hardness—(*a*) Moh's scale[6]	8 to 9
(*b*) Microhardness[26] (50 g load)	2600 kg/mm^2

Specific electrical resistance—Low temperature measurements[6]:

At room temperature	63·4 microhm/cm[6]
Liquid air temperature	37·8 microhm/cm[6]

(R. Kieffer and F. Benesovsky[24] quote 65 microhm/cm, presumably at room temperature.)

Other low temperature measurements[6]:

°K	$R/R_0 = r$	°K	$R/R_0 = r$
273·16	1	3·77	$9{\cdot}3 \times 10^{-2}$
78	0·355	3·68	$6{\cdot}1 \times 10^{-2}$
20·4	0·181	3·26	$1{\cdot}7 \times 10^{-3}$
4·21	0·177	2·86	$6{\cdot}9 \times 10^{-4}$
3·80	0·120	2·52	$5{\cdot}2 \times 10^{-4}$
		2·26	$1{\cdot}1 \times 10^{-4}$
		2·13	1×10^{-6}

High temperature measurements[6]:

°K	$\varrho/\varrho_{+20°}$ $= \varrho/0{\cdot}69$	°K	$\varrho/\varrho_{+20°}$ $= \varrho/0{\cdot}69$
1208	2·13	1962	2·51
1312	2·21	2185	2·60
1528	2·30	2408	2·68
1743	2·40	2630	2·75

Critical superconductivity temperature[6] 2·1 to 4·1° K

Thermal conductivity—0·049 cal/cm²/cm/sec/C°[37]

Magnetic properties—Magnetic susceptibility[6]:

$K \times 10^6$	$-0{\cdot}22$
$\frac{1}{2}K \times 10^6$/mole	-13

Solubility of zirconium carbide—J. T. Norton and A. L. Mowry[34] investigated the solubility relationship of the refractory monocarbides and concluded that:

(*1*) The binary carbide systems TiC–ZrC, ZrC–NbC and ZrC–TaC form continuous series of solid solutions.

(*2*) The binary carbide system ZrC–VC shows very little solubility, the limits at 2100° C being 5 per cent at the zirconium rich end and less than 1 per cent at the vanadium rich end.

In a later paper J. T. NORTON and A. L. MOWRY[35] investigated the systems ZrC–VC–TiC, ZrC–VC–TaC and ZrC–VC–NbC by x-ray methods and determined the boundary of the phase fields at 2000° C. This is shown in *Figure 120.*

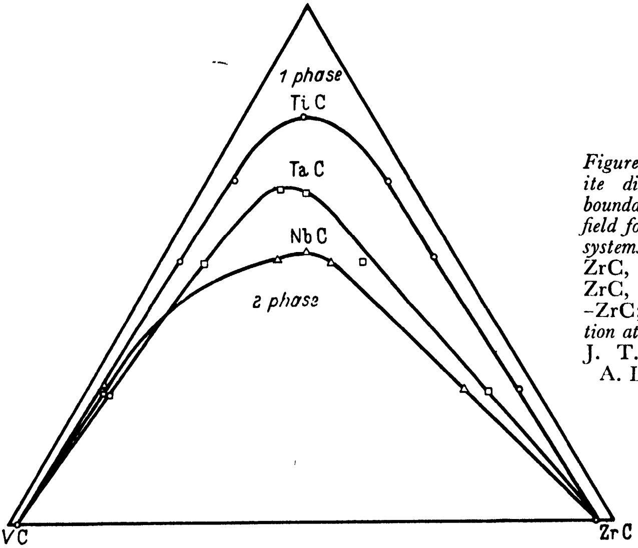

Figure 120. Composite diagram showing boundary of two-phase field for pseudo-ternary systems: TiC–VC–ZrC, TaC–VC–ZrC, *and* NbC–VC–ZrC; *isothermal section at* 2000° C (*after* J. T. NORTON *and* A. L. MOWRY[35])

Investigation of the system zirconium carbide–tungsten carbide is reported by K. BECKER[6]. *Table CXIV* shows the melting points.

Table CXIV. Melting Points of ZrC–W_2C *System*

Molecular components ZrC : W_2C .	0 : *a*	1 : 1	4 : 1	*a* : 0
Melting point °K	3130	3130	3130	3805

There was no solubility or mixed crystal formation at the melting point. The melting points of niobium carbide and zirconium carbide are almost identical and the melting points of the ratios 1 : 1,

Table CXV. Melting Points of TaC–ZrC *System*

Molecular components TaC : ZrC . .	0 : *a*	1 : 1	2 : 1	4 : 1	8 : 1	*a* : 0
Melting point °K .	3805	4045	4048	4205	4180	4145

2 : 1 and 4 : 1 were practically identical, and it was presumed by K. BECKER[6] that there was a mixed crystal series.

The values for the melting points in the tantalum carbide–zirconium carbide system are shown in *Table CXV*[6].

It is noteworthy that the melting points of the mixed carbides pass through a maximum.

P. DUWEZ and F. ODELL[13] reported that they could not investigate systems involving ZrC because this compound decomposed when heated in nitrogen.

18.2.3. *Hot pressing zirconium carbide*

Experiments on the hot pressing of zirconium carbide are described by A. R. HALL and W. WATT[18]. The hot pressing unit consisted of a simple graphite die and plunger which was contained in an alumina cylinder with the intervening space packed with crushed magnesite brick. Heating was by means of a spark gap high frequency unit. Pressures up to 6·9 ton/in^2 were used at a maximum temperature of 2050° C. The density of the product was up to 98·5 per cent of the true density of the zirconium carbide used in the tests. No appreciable grain growth occurred during the pressing.

A. R. HALL and W. WATT[19] in another paper quote values of 6·4 and 7·1 ton/in^2 at 1000 and 1200° C determined by A. R. BOBROWSKY[7] for the tensile strength of sintered zirconium carbide. The results of bend strength determinations by A. R. HALL and W. WATT[19] at room temperature, 1050 and 1600° C for sintered compacts of zirconium carbide show a considerable scatter, the majority falling in the range 11 to 15 ton/in^2. The maximum strength is reached before the sintering is complete as determined by the electrical resistivity measurements of the specimens. There is no drop in the bend strength of sintered zirconium carbide at 1050 to 1600° C, nor is there evidence of plastic flow under stress of short duration at these temperatures.

18.2.4. *Applications*

The properties of zirconium carbide have been examined critically by R. KIEFFER[22] who compared it with other hard carbides as shown in *Table CXVI.*

Kieffer also prepared hot pressed (1500° C and 200 kg/cm^2) specimens of the carbides bonded with the same weight of cobalt and compared their properties as in *Table CXVII.*

Cutting tests with tools made from the hot pressed zirconium carbide–cobalt (10 per cent) material were not made owing to the difficulty of brazing the tool to the steel shank, and reproducibility

Table CXVI. Properties of Some of the more important Metal Carbides

Carbide	*Carbon content* per cent	*Lattice*	*Lattice parameter*		Density g/cm³	*Hardness*		*Melting point* °C *approx.*	*Young's modulus* kg/mm²
			a Å	*c* Å		*Rockwell A*	*VPN* kg/mm²		
ZrC	11·70	NaCl	4·669	—	6·70	92·5	2,600	3,250	14,000
TiC	20·04	NaCl	4·315	—	4·85	93·5	3,200	3,250	32,200
WC	6·12	*Hexagonal*	2·897	2·27	15·60	92	2,200	2,900	72,200
Mo_2C	5·88	*Hexagonal close packed*	3·012	4·35	8·82	88	1,500	2,500	22,700
VC	19·00	NaCl	4·165	—	5·36	92	3,000	2,800	26,000
NbC	11·40	NaCl	4·48	—	7·76	91	2,400	3,800	24,700
TaC	6·20	NaCl	4·42	—	14·05	89	1,800	3,800	40,000

Table CXVII. Properties of Pressure-Sintered Hard Metal with 10 per cent Co *as Binder*

Composition per cent	*Rockwell A*	*Bending strength** kg/mm²	*Density* g/cm³	*Colour of fracture*
90 ZrC, 10 Co . .	91	80	6·83	*light grey*
90 TiC, 10 Co . .	92	80	4·96	*mouse grey*
90 Mo_2C, 10 Co . .	87	60	8·62	*light silvery*
90 WC, 10 Co . .	91	170	14·41	*blue-grey*
90 VC, 10 Co . .	89†	70	5·45	*silvery*
90 NbC, 10 Co . .	88	100	7·74	*brown-mauve*
90 TaC, 10 Co . .	85	75	13·00	*yellowish-gold*

* Values obtained with vacuum sintered specimens.

† For sintering temperature 1300° C. At higher temperatures strength diminishes due to grain growth.

with clamping methods was unsatisfactory, but it was considered that the material would be satisfactory for cutting.

Zirconium carbide was substituted for titanium carbide in WC–TiC–Co hard metal. With equal weight substituted, the resulting tool was somewhat inferior but with molecularly equivalent weights (*i.e.* 1·7 to 2 times the weight of TiC) the result was similar to that obtained with the standard TiC-containing product. The results of the tests are shown in *Table CXVIII.*

Zirconium carbide has been examined for its high temperature properties; R. KIEFFER and F. BENESOVSKY[25] summarized the results by stating that the hot pressed compacts showed good resistance to thermal shock but poor resistance to scaling at elevated temperatures and concluded that titanium carbide was a much superior material for use at high temperatures.

Table CXVIII. Mechanical Properties and Machining Performance of ZrC-*Containing Hard Metals Equivalent to the Usual* TiC-*Containing Hard Metal Alloys S1, S2, S3*

Chemical composition per cent	*Rockwell A*	*Density* g/cm^3	*Bending strength* kg/mm^2	*Working of Siemens–Martin steel of UTS* 85 kg/mm^2 $a = 5$ mm $s = 0{\cdot}8$ mm $t = 10$ min	
				Width of chip mm	*Cutting speed* metre/minute
78 WC 16 ZrC 6 Co	90	11·3	95	0·300	140
78 WC 16 TiC(*S1*) 6 Co	91	11·2	110	0·205	140
75·5 WC 16 ZrC 8·5 Co	89	11·3	100	0·395	120
75·5 WC 16 TiC(*S2*) 8·5 Co	90·5	10·9	120	0·255	120
87·5 WC 4 ZrC 8·5 Co	89·0	13·0	125	0·250	85
87·5 WC 4 TiC(*S3*) 8·5 Co	89·5	13·4	155	0·185	85

a = depth of cut, mm. s = feed, mm/rev. t = cutting time, min.

18.2.5. *Sintered zirconium carbide and niobium*

An investigation of the sintering of zirconium carbide–niobium mixtures has been made by H. J. Hamjian and W. Lidman[20]. The specimens used were prepared by hot pressing at a pressure of 2000 lb/in^2 and temperatures from about 2000 to 2250° C for periods of 5 to 90 minutes. The zirconium carbide used in the investigations had the following chemical analysis: Zr 85·13, C 12·58, Nb 0·22, Ti 0·48, Fe 0·03 per cent, leaving a balance of 1·56 per cent which is probably mainly oxygen. No value is given for free carbon. The mixtures contained approximately 12·5 per cent by weight of niobium. Study of the sintering mechanism indicated that:

(*1*) Niobium atoms diffuse into the zirconium carbide lattice, displace Zr atoms, and form niobium carbide and zirconium metal.

(*2*) The niobium carbide which forms during the reaction dissolves completely in the matrix of zirconium carbide and a homogeneous solid solution of the carbides is formed.

(*3*) The zirconium metal forms in the grain corners of the carbide structure at a sintering temperature of 2150° C.

(*4*) The size and distribution of the metal phase formed during sintering are of importance in obtaining good strength properties and can be controlled by the two variables, temperature and time. The specimens with a fine dispersion of metal have the highest strength.

The strength and density of some of the specimens studied are shown in *Table CXIX.*

Table CXIX. Strength and Density of Hot Pressed ZrC–Nb *Ceramals*

Sintering time min	*Sintering temperature* °C	*Density* g/cm^3	*Room temperature modulus of rupture* lb/in^2
5	2040	5·77	*Improper sintering*
5	2150	6·15	37,100
5	2150	6·05	37,400 32,400
5	2210	6·24	32,900 31,000
15	2150	6·08	51,000 49,400
15	2150	6·14	47,500 52,300
30	2150	6·18	45,600 52,800
45	2150	6·33	57,800 56,600
45	2150	6·22	58,800
90	2150	6·29	37,700
90	2150	6·22	32,400

18.3. ZIRCONIUM BORIDE

18.3.1. *Production*

One of the methods used for the production of zirconium boride is to heat the pure metal with boron in the necessary proportions[30]. The most suitable furnace is a tungsten vacuum furnace. The temperature required is in the region of 2000° C. Zirconium hydride may be used to replace zirconium. A temperature of 1600° C for pressed compacts appears to be ample. High grade zirconium boride can be produced by using a tungsten filament heated in an atmosphere of zirconium tetrachloride, boron tribromide and hydrogen. Less pure boride is obtained by the reduction of zirconia with carbon at about 1600° C in the presence of boric oxide, the product usually containing small amounts of carbon. P. McKenna[29] describes the process as follows. A mixture of zirconium dioxide and carbon with an excess of boric oxide is heated at about 2000° C to obtain the reaction

$$ZrO_2 + B_2O_3 + 5C \rightarrow ZrB_2 + 5CO$$

Three times as much boron oxide as indicated by the equation was employed. The heating was carried out in a graphite crucible. A charge containing 492 g ZrO_2, 840 g B_2O_3 and 120 g carbon black yielded a grey friable mass weighing 446 g. (If the charge is prepared according to McKenna's instructions there would be 240 g of carbon black.) Boiling hydrochloric or nitric acids had no effect on the material. Chemical analysis showed: Zr 78·55, B 18·15, C 1·89, Si 0·03 per cent. The density of the product was 5·64 g/cm³. Retreatment of a portion (170 g) with boron oxide (8·5 g) in a vacuum furnace at 1530° C lowered the carbon content to 1·09 per cent.

Zirconium boride may be produced[31] by heating boron carbide, B_4C, with zirconium oxide at 1900° C under a pressure of 1000 lb/in². The boride produced by this method contains a small amount of free carbon and carbide.

J. L. Andrieux[4] prepared zirconium boride by electrolysis using fused salt baths of various compositions, as shown in *Table CXX*, with bath conditions.

Table CXX. Bath Compositions and Operating Conditions for Production of Zirconium Boride

Bath composition g mole	*Temperature* °C	*Potential difference* V	*Current* A	*Time* h	*Weight of crystals obtained* g
$\frac{1}{4}ZrO_2 + 2B_2O_3 + MgO + MgF_2$	1000	9·5	18	2½	5·125
$\frac{1}{4}ZrO_2 + 2B_2O_3 + CaO + CaF_2$	1050	9·0	20	1½	3·210
$\frac{1}{4}ZrO_2 + 2B_2O_3 + Li_2O + LiF$	990	3·5	25	2	9·850

Andrieux obtained metallic-like silvery-white crystals which were isolated by treating the product with dilute hydrochloric acid. During the leaching a large quantity of the crystals was destroyed as the boride, Zr_3B_4, is attacked by dilute acids. Analysis of three samples of the crystals showed boron contents of 13·8, 13·4 and 13·7 per cent compared to a calculated value of 13·66 per cent for Zr_3B_4.

The zirconium contents were 86·0, 86·2 and 85·8 per cent compared to the theoretical 86·34 per cent.

The hardness of the boride obtained by Andrieux on Moh's scale was 8. The density was 5·97 g/cm³.

R. Kieffer *et al.*[23] described a method for the production of titanium and zirconium borides by reacting metallic titanium or zirconium with boron carbide (B_4C) and boric oxide. The favoured mix contained 7 parts Zr, 3 parts B_4C, and 3 parts B_2O_3. This was pressed into bars and heated in a carbon tube resistance furnace in an atmosphere of hydrogen at 2000° C for about 15 minutes. The product contained about 0·3 per cent carbon. Retreatment of a pressed mixture of the finely powdered product (9 parts) and B_2O_3 (1 part) at 2000° C reduced the carbon to less than 0·08 per cent in the titanium boride.

18.3.2. *Properties*

Lattice—ZrB_2; hexagonal AlB_4 type[27]

Lattice constant—$a = 3{\cdot}169$ Å[27] $c = 3{\cdot}530$ Å[27] $c/a = 1{\cdot}11$[27]

Density—Calculated from x-ray data[33]	6·09 g/cm³
Measured[33]	6·17 g/cm³

Melting point—3265 ± 50° K[1]

Hardness—(*a*)	Moh's scale[6]	+9
(*b*)	Microhardness (30 g load)	2252 kg/mm² (22 mean square deviation)[38]

Specific electrical resistance—Low temperature measurements[6]:

At room temperature	9·2 microhm/cm
Liquid air temperature	1·8 microhm/cm

(J. T. Norton *et al.*[33] report 38·8 microhm/cm for specific resistance at room temperature.)

Other low temperature measurements[6]:

°K	$R/R_0 = r$	°K	$R/R_0 = r$
273·16	1	3·05	$2{\cdot}0 \times 10^{-2}$
78	$8{\cdot}66 \times 10^{-2}$	2·92	5×10^{-4}
20·4	$4{\cdot}21 \times 10^{-2}$	2·92*	7×10^{-7}
4·25	$4{\cdot}17 \times 10^{-2}$		

* As in K. Becker's book[6].

High temperature measurements[6]:

°K	$\varrho/\varrho_{+20^\circ}$ $=\varrho/0{\cdot}092$	°K	$\varrho/\varrho_{+20^\circ}$ $=\varrho/0{\cdot}092$
1510	7·86	2580	12·83
1875	9·53	2720	14·41
2100	11·10	2920	15·12
2460	12·33		

Critical superconductivity temperature[6] 2·8 to 3·2° K

Thermal conductivity—0·055 cal/cm^2/cm/sec/C° at 20° C[33]

18.3.3. *Stability and solubility of zirconium boride*

L. Brewer *et al.*[8] studied the refractory borides, including zirconium boride. The borides were prepared by heating the elemental powders. After heating for 5 minutes at 1600° C in 0·5 atm of argon a sample containing about 68 atomic per cent boron lost the excess boron to form ZrB_2 but no further decomposition occurred. Only one intermediate phase, ZrB_2, was found. It was noticed that there was appreciable solubility of boron in zirconium as indicated by expansion of the metal lattice.

The relative stabilities of ZrB_2 and W_2B were determined by L. Brewer *et al.*[8] by melting zirconium in W_2B crucibles. The zirconium reduced the W_2B to W forming ZrB_2.

J. T. Norton *et al.*[33] considered that the zirconium boride had well developed metallic properties. An interesting aspect reported by Norton is the possibility of metal atom replacement to form solid solutions. On the basis of limited experiments on the series ZrB_2–TiB_2 it appeared that a continuous series of solid solutions can be formed when the borides are mixed and heated together. F. W. Glaser and W. Ivanick[17] confirmed that the diborides of titanium and zirconium form a continuous series of solid solutions. It was also found that the melting point/composition relationship for the system is nearly linear. In addition, the curve electrical resistivity/composition has an inverted U-shape and was very similar to those observed for metal–metal solid solutions. Glaser and Ivanick suggested that during the formation of metal diboride solid solution only a substitutional interchange of metal atoms takes place, with boron layers remaining relatively undisturbed.

18.3.4. *Hot pressing zirconium boride*

The pressure sintering of zirconium boride has been investigated by F. W. GLASER[16]. The zirconium boride powder used in the work was produced by the method described by J. L. ANDRIEUX[4] and milled to a particle size of about 5 microns. After comminution the analysis of the material was: Zr 80·3, B 18·9 and Fe 0·45 per cent. Samples were heated in graphite moulds under a pressure of 1·3 ton/in^2 for periods of 30 to 180 seconds. Final densities ranged from 87 to 95·5 per cent of the calculated density of 6·09 g/cm^3. The results of experiments in which the effect of time and temperature on transverse rupture strength were studied are shown in *Table CXXI.*

Table CXXI. Transverse Rupture Strength of Binder-Free (Uncemented) Zirconium Boride Compacts

Sintering temperature °C	*Sintering time at temperature* sec	*Transverse rupture strength at room temperature* lb/in^2
2550	30	8,000
	60	11,000
	180	11,500
2800	30	14,500
	60	19,000
	180	21,000
2865	30	22,300
	60	22,800
	180	25,100

Carbon contamination was small being about 0·3 per cent confirming the relatively high stability of the boride in the presence of carbon. Electrical resistivity measurements were used to follow the progress of sintering. A value of about 9 microhm/cm was calculated for the electrical resistivity of zirconium boride, this being the value obtained by extrapolation of a curve for resistivity/sintering temperatures.

Zirconium boride appears to have good high temperature properties. One laboratory[5] investigating materials capable of withstanding the high temperatures encountered in turbine and rocket power plants has reported that zirconium boride was the most promising material examined. No details are given.

18.3.5. *Metallographic preparation of zirconium boride*

K. WACHTELL[42] describes the experience of his laboratory in preparing specimens of zirconium boride for metallographic examination. Due to a tendency for the particles to break away from the surface when conventional polishing methods were used, the material showed more porosity than was known to exist. A successful method was developed and is described as follows. The specimen is rubbed against a flat glass plate which has previously been lapped with *FFF* carborundum made up as a slurry with water. The lapping plate is another piece of flat plate glass and the lapping operation is continued until a fine matte surface is developed on the work plate. Specimens are polished dry by simple abrasion, no compound is added to the plate, but it is necessary to wash and dry the plate before polishing. No cloth belts are used; the specimen receives no further treatment.

Polishing is quite rapid but time can be saved by producing a flat surface with diamond or green grit wheel before polishing. It is necessary to re-lap the glass plate when polishing becomes slow. An electrolytic etch is used to develop the structure. The solution consists of 40 per cent concentrated hydrofluoric acid, 40 per cent ethyl alcohol and 20 per cent water. The work is the anode at about 4·5 A/in^2 for 2 to 5 seconds.

18.4. ZIRCONIUM SILICIDE

18.4.1. *Production*

E. WEDEKIND[43] first prepared zirconium silicide by reducing the double salt, potassium zirconium fluoride with an excess of silicon. Free silicon in the reaction product was removed by treatment with caustic potash. Wedekind also prepared the silicide by two other methods: (*i*) a high temperature reaction between zirconia and silicon, which he claimed[44] produced the monosilicide, ZrSi, and (*ii*) heating the elements together[45] at 1000 to 1200° C. Probably the simplest method for the preparation of commercial grade zirconium silicide is by the aluminothermic reduction of zirconia with aluminium and silicon, with an addition of barium peroxide to boost the heat of reaction. O. HÖNIGSCHMID[21] used a complex mixture of ZrO_2, SiO_2, Al and S for his investigations.

The reaction of silicon tetrachloride, in the presence of hydrogen, with zirconium heated to 1100 to 1500° C yielded a zirconium disilicide coating as reported by I. E. CAMPBELL *et al.*[9].

Zirconium silicide may be produced by the method used by L. E. LUNDIN *et al.*[28] to produce zirconium–silicon alloys for their investigations (see Section 14.3.4.) *i.e.* to melt the elements in helium in an arc furnace. Zirconium disilicide was prepared by M. DODERO[12] by fusion electrolysis using a bath of alkali fluosilicates, with zirconium dioxide or fluoride.

18.4.2. *Properties*

Lattice—$ZrSi_2$: orthorhombic[36]
$ZrSi$: hexagonal[28]

Lattice constants—

$$ZrSi_2{}^{32}\begin{cases} a = 3{\cdot}72\text{ Å} \\ b = 14{\cdot}61\text{ Å} \\ c = 3{\cdot}67\text{ Å} \end{cases} \qquad ZrSi^{28}\begin{cases} a = 7{\cdot}01\text{ Å} \\ c = 12{\cdot}77\text{ Å} \\ c/a = 1{\cdot}823 \end{cases}$$

Density—($ZrSi_2$). Measured[10] 4·88 g/cm^3

Hardness—($ZrSi_2$). Microhardness[10] (100 g load) 1030 kg/mm^2

Specific electrical resistance—($ZrSi_2$). (Hot pressed[15]) 161 microhm/cm

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APPENDIX : METALLOGRAPHY

ZIRCONIUM is difficult to prepare for examination under the microscope due to the tendency of the metal to flow and smear during grinding and polishing. Nevertheless several authors have described methods which they claim to be successful. Experience indicates that it is doubtful if any one of these methods can be used exclusively for all types of zirconium specimens. It is sometimes desirable to combine some of the methods to obtain the optimum result.

A. H. ROBERSON[8] has recommended that grinding and polishing be prolonged beyond the normal time required to remove the scratches from the preceding step, to ensure the complete removal of flowed metal from the surface. Up to 0·030-in of metal was removed from specimens in order to eliminate all traces of cold work. His technique consisted of grinding on silicon carbide papers to grade *0* paper followed by a three-stage polishing operation:

(*a*) canvas-covered lap with 280-mesh alumina at 250 r.p.m.
(*b*) felt-covered lap with 600-mesh silicon carbide at 600 r.p.m.
(*c*) *Gamal* cloth lap at 600 r.p.m. with Linde type *B* alumina suspension in water as the abrasive.

Chemical etching was used to reveal the microstructure and only solutions containing hydrofluoric acid were found to be satisfactory, the most versatile etchant being 6 parts glycerine, 2 parts hydrofluoric acid (48 per cent), 1 part concentrated nitric acid. The solution was applied by swabbing for 3 to 5 seconds since it was found that swabbing helped to prevent staining of the surface.

P. A. JACQUET[5] claimed that electropolishing in a commercially available apparatus (*Disa-Electropol*) using a solution containing 350 ml 95 per cent ethyl alcohol, 100 ml perchloric acid (density 1·20) and 50 ml of 2-butoxy-ethanol ('Butyl Cellosolve') gave the most satisfactory results. After grinding to grade *0* emery the specimen was polished in 10 to 20 seconds at 30 V. When the same electrolyte was used in a simple cell the results obtained were not as good as with the commercial apparatus, presumably because the temperature was more readily controlled in the latter. With a simple cell Jacquet obtained some success using a bath containing 1000 ml pure acetic acid and 50 ml perchloric acid (density 1·59) at 0·6 to 0·8 A/cm^2 and 60 V. Examination of scratches on polished specimens revealed that the metal was sensitive to cold work, slip lines being easily detected by this method of polishing.

H. P. ROTH[9] finished grinding with grade *3/0* emery, as anything finer tends to smear zirconium rather than to cut it. Electropolishing is done in a freshly prepared solution containing 1 part 60 per cent perchloric acid to 10 parts glacial acetic acid for 45 seconds at 12 to 18 V d.c. using 0·03 to 0·5 A depending mainly on the size of the specimen immersed. The procedure produces a result which is particularly suitable for examination by polarized light. Roth has noted that, as with most electrolytic etching techniques, it is difficult to obtain reproducibility. His own technique has a very narrow working range of current which must be determined for each sample by trial and error. The technique was found to preserve the carbides unless they were cracked.

Reduced polishing times are claimed by D. B. METZ and H. W. WOODS[6] who mixed dilute hydrofluoric acid with abrasive for the final polishing steps. Their grinding procedure consists of grinding on a 180-grit belt followed by *2/0* and *3/0* jeweller's papers on rotating discs. For polishing, a silk lap is first used with Linde *A* alumina and dilute hydrofluoric acid; this is followed by polishing on a *Gamal* cloth lap with Linde *B* abrasive and dilute hydrofluoric acid.

The dilute perchloric acid solutions used by Roth and Jacquet were improved by B. W. MOTT and H. R. HAINES[7] by adding ethylene glycol, in order to reduce the amount of relief on the surface caused by differential rates of attack. Their most satisfactory solution contained 50 ml perchloric acid, 175 ml acetic acid and 100 ml ethylene glycol, and this was used at a current density greater than 1 A/cm^2. It was found that this method was more suitable for cast zirconium than for recrystallized wrought material.

O. N. CARLSON[4] uses normal grinding procedures terminating in a mechanical polish on a felt-covered wheel using 600-grit carborundum. This procedure is followed by an electrolytic polish in a solution containing 8 parts ethyl alcohol, 5 parts ethylene glycol and 5 parts phosphoric acid. It is reported that current density is not critical but 1 A/cm^2 for 20 seconds is generally used.

F. W. BOULGER[2], having tried electropolishing, found mechanical polishing more satisfactory. After grinding on a partially dulled 80-grit silicon carbide disc, specimens were ground wet on dulled 240- and 400-grit papers. Dulling the papers was necessary to prevent embedding abrasive in the specimen. Polishing was carried out at 1750 r.p.m. on a wheel covered with *Microcloth*, or equivalent, using stannic oxide suspended in water as the abrasive (1 part stannic oxide to 3 or 4 parts water). There was found to be a slight etching effect from the stannic oxide and this was increased by electrolytic etching in a saturated sodium tetraborate solution using 12 V for 5 to 30 seconds.

The metallographic procedure used by the Armour Research Foundation[1] to prepare numerous zirconium alloys was as follows. After grinding on a 120-grit silicon carbide belt to obtain a flat surface, samples containing large amounts of intermetallic compound were ground on silicon carbide papers down to the 600-grit paper. Silicon carbide papers were used for rough polishing of samples containing zirconium–tungsten, zirconium–chromium and zirconium–silicon since it was found that *Alundum* papers had a tendency to crumble these hard and brittle phases. *Alundum* papers proved satisfactory for other binary alloys. The final polishing procedure consisted of two steps; diamond compound (5 to 8 micron) was used on the first wheel which was covered with aeroplane silk, paraffin being used as the lubricant. It was noticed that when softer cloths, such as billiard cloth, were used there was a tendency to relief polish, whereas the hard cloth backing minimized this effect. Gamma phase synthetic sapphire made under the name of Linde *B* abrasive was employed on the final wheel which was covered with Buehler *Microcloth*, water being used as a lubricant.

The etchant which proved most generally useful was 60 ml glycerine, 20 ml nitric acid, 20 ml hydrofluoric acid. The reaction rate was controlled by heating or cooling the specimen and also by altering the etchant composition.

A method of specimen preparation which eliminates mechanical and electrolytic polishing has been reported by F. M. CAIN[3]. A specimen for routine grain size determination need not be mounted and requires only a 180-grit silicon carbide or a good machined surface. Specimens to be examined in detail are ground to grade *3/0* emery and subsequently dipped in, or swabbed with, polishing solution. Three compositions of polishing solution are recommended. The first contains 45 ml of glycerine with 45 ml concentrated nitric acid and 8 to 10 ml hydrofluoric acid (48 per cent) and the others are the same except that the glycerine is replaced by the same volume of water or hydrogen peroxide (30 per cent). The first solution is used for alloys containing small amounts of zirconium, the other two are both used for pure zirconium and zirconium rich alloys. Time required to develop the microstructure is about 10 to 15 seconds. Specimens can be observed under bright field or polarized light illumination. The method is versatile since remote controlled metallography of irradiated specimens,

Table CXXII. Metallographic Procedures for Zirconium and Zirconium Alloys

Polishing method	*Used by*	*Grinding procedure*	*Polishing procedure*	*Preferred etchant*	*Notes*
Mechanical	*U.S. Bureau of Mines*[8]	*Grades* 2, 1 *and* 0 *silicon carbide* (SiC) *papers*	*Canvas lap* – 280-mesh *alumina*, 250 r.p.m. *Felt lap* – 600-grit *silicon carbide*, 600 r.p.m. Gamal *cloth lap—Linde* B *abrasive*, 600 r.p.m.	6 parts *glycerine* 2 parts HF 1 part HNO_3	*Etchant may be used successfully for carbon free, or graphite melted zirconium, and many alloys such as* ZrSi, ZrB, ZrNb, ZrFe, etc
	Battelle Memorial Institute[2]	*Dulled* 80 grit. SiC *disc. Wet grinding on* 240- *and* 400-grit *papers*	Microcloth *wheel. Stannic oxide abrasive* (1 part SnO_2—3 *or* 4 parts *water*). 1,750 r.p.m.	*Electrolytic etch in saturated sodium tetraborate.* 12 V 5 *to* 30 seconds	*No detailed information available*
	Argonne National Laboratory[10]	120; 180; 240; 400; 3/0 *and* 4/0 *papers*	*Silk lap* – 600-grit SiC Microcloth *Linde* A *abrasive* Microcloth *Linde* B *abrasive*	5 ml HF 3 ml HNO_3 92 ml H_2O	*No detailed information available*
	Westinghouse[10]	240 *and* 400 SiC *wet belts*; 600-grit SiC *wax lap*	Gamal *cloth lap* *Linde* B *abrasive*	60 ml H_2O_2 (30 per cent) 30 ml HNO_3 30 ml *ethyl alcohol* 2 drops HF (48 per cent)	*No detailed information available*
	Armour Research Foundation[1]	120-grit SiC *belt.* 280, 320, 400, 600-grit SiC *papers, or* 1, 1/0, 2/0, 3/0 Alundum *papers*	*Silk lap*—5 *to* 8-micron *diamond paste in paraffin.* Microcloth *Linde* B *abrasive*	60 ml *glycerine* 20 ml HNO_3 20 ml HF	*Standardized procedure for zirconium and zirconium-base alloys*
Electrolytic	O. N. CARLSON[4]	*Normal grinding with final polish on felt wheel with* 600-grit Carborundum	8 parts *ethyl alcohol* 5 parts *ethylene glycol* 5 parts *phosphoric acid* 1 A/cm^2. 20 seconds	*No subsequent etching: or electrolytic with* 10 per cent *oxalic acid*	*Developed for uranium–thorium–zirconium alloys*

Table CXXII. Metallographic Procedures for Zirconium and Zirconium Alloys—continued

Polishing method	*Used by*	*Grinding procedure*	*Polishing procedure*	*Preferred etchant*	*Notes*
Electrolytic	P. A. JACQUET[5]	*Normal grinding to grade* 0 *paper*	(a) 350 ml 95 per cent *ethyl alcohol* 10 ml perchloric acid ($d = 1{\cdot}20$) 50 ml 2-butoxy-ethanol 10 *to* 20 seconds. 30 V (b) 1000 ml *acetic acid* 50 ml *perchloric acid* 0·6 *to* 0·8 A/cm². 60 V	*No subsequent etching*	*Temperature control critical*
	A.E.R.E., Harwell[7]	*No information*	50 ml *perchloric acid* 175 ml *acetic acid* 100 ml *ethylene glycol* 1 A/cm²	*No subsequent etching*	*More satisfactory for recrystallized wrought material than for cast. Carbide is attacked*
	Massachusetts Institute of Technology[9]	*Normal grinding to grade* 3/0 *paper*	1 part *perchloric acid* 10 parts *acetic acid* 12 *to* 18 V *and* 0·02 *to* 0·5 A *depending on size.* 45 seconds	*No subsequent etching*	*Good for recrystallized and cast materials. Carbide retained and polished. Tends to attack the zirconium–iron precipitate more than the less concentrated perchloric acid solutions used by Jacquet*
Chemical polish	F. M. CAIN[3] *Westinghouse*	*Normal grinding to grade* 3/0 *emery or* 600-grit SiC	10 *to* 15 seconds *swabbing in* 45 ml *glycerine, water or* H_2O_2 (30 per cent); 45 ml *concentrated* HNO_3; 8 *to* 10 ml HF	*Stain with dilute polishing solution* (1 part *polishing solution to* 3 *to* 5 parts *water*); *or heat tint*	*With glycerine suitable for zirconium poor alloys* *With water and* H_2O_2 *suitable for pure zirconium and zirconium rich alloys* *Particularly suitable for remote polishing and for photomacrographs* *Carbides are attacked*
Attack polish	*Sylvania Electric Products Inc.*[6]	180-grit *belt,* 2/0 *and* 3/0 *jeweller's papers on rotating discs*	*Silk lap—Linde* A *abrasive, dilute* HF Gamal *cloth lap—Linde* B *abrasive, dilute* HF	*No subsequent etching*	*Developed to reduce polishing times*

non-destructive examination of large sections and macro-preparation can all be performed by this technique. The method has the advantage over electropolishing techniques that a wide range of alloys can be polished but carbides present are heavily attacked by the strong acid solution.

F. M. CAIN[3] states that the use of high pressures of the order of 2000 to 3000 lb/in^2 for mounting zirconium specimens may cause cold work, resulting in the production of numerous twins. Pressures of 300 lb/in^2 or lower are suggested to avoid the cold work.

Table CXXII summarizes the techniques given. The table includes the procedures used by the Argonne National Laboratory[10] and Westinghouse[10] which are described by Cain.

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