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RECENT PROGRESS IN THE METALLURGY OF MALLEABLE ZIRCONIUM *

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ABSTRACT

Improved methods in the various operations for the production of ductile zirconium from zircon sands are described. They are essentially an improved method of producing the zirconium carbide from zircon sand by use of an arc furnace and the melting of zirconium metal in graphite crucibles. The slight carbon contamination apparently does not appreciably impair the working properties of the metal. Other improvements are refinements of the process as described in an earlier publication.

INTRODUCTION

The successful production of malleable zirconium by the reduction of zirconium chloride vapor with magnesium under a helium atmosphere was outlined in a previous article,^{5,†} which described the status of the work as it was in December, 1945. A literature survey had been previously made.⁶ Considerable progress has been made in all aspects of the problem since that time and it is the purpose of this paper to describe the recent developments.

The research was conducted at the Northwest Electrodevelopment Laboratory of the Bureau of Mines at Albany, Oregon, under the supervision of Dr. B. A. Rogers, former Chief of the Albany Division of the Metallurgical Branch. The production of malleable zirconium from zircon by the Bureau of Mines process requires the following steps:

1. Production of zirconium carbide from zircon.
2. Chlorination of zirconium carbide.
3. Purification of raw zirconium chloride.
4. Reduction of pure zirconium chloride with magnesium.
5. Elimination of residual salts by vacuum treatment.
6. Melting of zirconium ingots.

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Discussion of new methods and discoveries will be taken up under these headings. Additional information is appended on methods of rolling zirconium and the determination of oxygen and nitrogen in zirconium metal.

1. Production of Zirconium Carbide from Zircon

As first reported, zirconium carbide was made by heating mixtures of zircon and graphite in a vertical graphite tube resistor furnace of special design.⁴ The capacity of this first furnace was so limited that a furnace of the Acheson type, such as is used for the commercial production of silicon carbide, was built. The Acheson furnace, consisting of a horizontal graphite rod clamped between water-cooled, copper blocks had several drawbacks. The electrode was badly at-

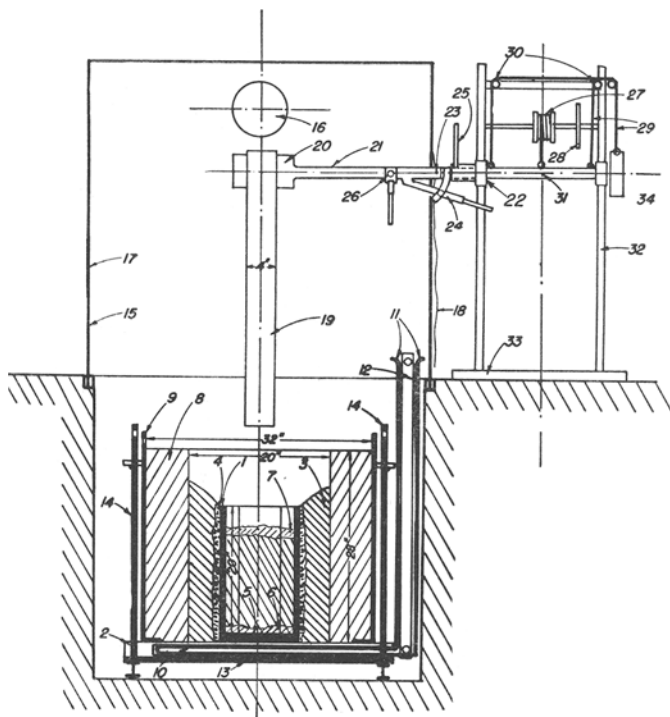


FIG. 1. Arc furnace for the production of zirconium carbide.
 1. Graphite plate crucible. 2. Graphite plate bottom. 3. Charcoal filling.
 4. Old batch filling. 5. Graphite bottom of crucible. 6. Graphite powder seal of bottom. 7. Graphite powder top seal. 8. Refractory lining. 9. Iron shell. 10. Water-cooled contact plate. 11. Water cooling. 12. Bus bar to bottom. 13. Iron bottom plate. 14. Vertical furnace columns. 15. Hood. 16. Exhaust duct. 17. Window opening for feed. 18. Asbestos cloth. 19. Graphite electrode. 20. Electrode holder, water-cooled. 21. Electrode arm. 22. Guide. 23. Hollow shaft. 24. Arm for horizontal movement in picture plane. 25. Arm for horizontal movement perpendicular to picture plane. 26. Cable contact. 27. Drum. 28. Hand wheel. 29. Counterweight and cables. 30. Rolls. 31. Cross bar for vertical electrode movement. 32. Vertical columns of electrode lift. 33. Base plate.

tacked by the carbide, and any fused product ran down and mixed with unreacted material. The separation of good carbide from unreacted charge was difficult.

As was mentioned in our first article, the product of the vertical graphite tube furnace contained approximately 53% Zr and 14% Si. The product of the Acheson furnace varied over a wide range of composition, but it too had a relatively high silicon content. This carbide chlorinated well; recovery of more than 90% of the zirconium in the chloride was obtained regularly. However, the silicon was chlorinated along with the zirconium, causing a higher chlorine consumption than would be needed for silicon-free material. For this reason, it seemed desirable to produce a zirconium carbide low in silicon.

It is known that silicon can be driven off as monoxide at very high temperatures such as those obtained in an arc furnace. In order to utilize this principle, an arc furnace, shown in Fig. 1, was built.

The bottom of the furnace was made of heavy graphite blocks (5). Upon the blocks was placed a crucible (1) formed from 1½-in. (3.8 cm.) thick graphite plates arranged in a hexagon and held in place by the charcoal (3) packed between the crucible and the outer refractory shell (8). The crucible was 23 in. (58.4 cm.) high and the distance between parallel sides was 9¼ in. (23.4 cm.). A graphite powder layer (6) seals the bottom of the crucible. A second graphite layer (7) is placed on top of the carbide on completion of the run and prevents infiltration of air during cooling. The refractory shell (8) was made of a silicon carbide ramming mix and was enclosed in an iron shell (9). Current was supplied to the furnace through water-cooled copper strips (10) bolted to the bottom graphite blocks and through a 4-in. (10 cm.) diameter movable graphite electrode (19) held in a water-cooled clamp (20). The electrode could be lowered with a windlass arrangement and could also be moved horizontally in two perpendicular directions so as to direct the arc into any portion of the crucible. The furnace was placed in a pit and a hood (15) with an exhaust duct (16) provided to remove the fumes.

The furnace was usually operated with approximately 100 volts across the arc and a current averaging 2,500 amperes. Graphite was used exclusively as a reducing agent since it was available as scrap from burned out crucibles and electrodes. Coke may be used quite as well if the impurities of the ash, especially alumina, are not too high.

The charge to the furnace consisted of a mixture of unground zircon sand containing about 67% ZrO₂ and graphite powder that had been screened through 20 mesh (0.84 mm. opening). The graphite addition was varied with the intention of producing a carbide that would chlorinate well.

Table I gives the approximate carbon and silicon contents of the carbides that are obtained with a stated amount of graphite in the batch. The zirconium content seems to go through a maximum and the low carbon samples contain large amounts of oxide which remain behind in the chlorination.

It was found that the silicon could be driven off almost completely by allowing sufficient time between successive additions of the charge to the furnace.

TABLE I

*Effect of Varying Proportions of Zircon and Graphite
on Products Obtained in Carbide-making Furnace*

Graphite in the Batch	Carbon in the Carbide	Zirconium Content	Silicon Content
37%	28%	63%	8%
33	17	70	6
22	6	80	4
16.5	4.0	76	2

The chemistry of the reduction of zircon by carbon can be summarized by the following equations:

1. $\text{ZrO}_2 \cdot \text{SiO}_2 + 6 \text{ C} = \text{ZrC} + \text{SiC} + 4 \text{ CO.}$
2. $\text{ZrO}_2 \cdot \text{SiO}_2 + 5 \text{ C} = \text{ZrC} + \text{Si} + 4 \text{ CO.}$
3. $\text{ZrO}_2 \cdot \text{SiO}_2 + 4 \text{ C} = \text{Zr} + \text{Si} + 4 \text{ CO.}$
4. $\text{ZrO}_2 \cdot \text{SiO}_2 + 3 \text{ C} = \text{Zr} + \text{SiO} + 3 \text{ CO.}$
5. $2 \text{ SiO}_2 + \text{ZrO}_2 + 6 \text{ C} = \text{ZrSi}_2 + 6 \text{ CO.}$
6. $\text{SiO}_2 + \text{C} = \text{SiO} + \text{CO.}$
7. $\text{SiO} + \text{ZrO}_2 = \text{SiO}_2 + \text{ZrO.}$
8. $\text{ZrO}_2 + 6 \text{ SiO} = \text{ZrSi}_2 + 4 \text{ SiO}_2.$
9. $\text{SiC} \rightleftharpoons \text{Si} + \text{C.}$
10. $\text{ZrSi}_2 + \text{C} \rightleftharpoons \text{ZrC} + 2 \text{ Si.}$
11. $\text{ZrO}_2 + 3 \text{ Si} \rightleftharpoons \text{ZrSi}_2 + \text{SiO}_2.$
12. $\text{ZrO}_2 \cdot \text{SiO}_2 + \text{Si} = \text{ZrO}_2 + 2 \text{ SiO.}$

The first four equations show the influence of decreasing additions of carbon. They correspond to 28.3%, 24.6%, 20.9% and 16.5% carbon in the batch. Of course, carbon is also picked up from the crucible and from the electrode. It can be seen that, in the first equation, carbides of both silicon and zirconium form; with less carbon only zirconium carbide is obtained besides free silicon; with still less carbon, free zirconium and silicon are made; and with the lowest possible carbon content, zirconium metal is produced and silicon monoxide escapes as a gas. These equations have been fully confirmed by experiment. With less than 22% carbon in the batch a new metallic product appears, which is frequently golden yellow, well fused and contains in selected samples up to 88% zirconium, about 2% silicon, sometimes up to 2% nitrogen, less than 6% carbon, and some oxygen. Old reports in the literature mention⁸ that zirconium metal can be made from zircon in the arc furnace by using deficient carbon. The alloy made in this way is really a solid solution of various elements in zirconium. It may find some commercial uses as a master alloy to introduce zirconium into other metals.

The zirconium carbide and the zirconium metal made in the arc furnace are both pyrophoric. Coarse carbide starts burning in air at 700° C and advantage is taken of this fact in the production of a cheap, fairly pure oxide. The burning sometimes causes losses in the arc furnace when air leaks through cracks during the cooling period. The batch has to be covered carefully with graphite powder after the run. Burned material must be recycled.

The other equations show side reactions that occur under different conditions when making carbide or zirconium metal in the arc furnace.

Low melting silicide is made at low temperature according to equation 5 by reduction of both oxides with carbon; according to equation 8, by reaction of silicon monoxide with zirconia; according to equation 11, by reduction of zirconia with silicon metal. The silicide, which is easily fused, causes much trouble in a resistor furnace, less in an arc furnace, because it separates and flows away from the charge. It stays in equilibrium with carbon as indicated by equation 10 and zirconium carbide appears as soon as the silicide reaches a concentration of more than 38% zirconium. The monoxide of silicon, which is much more volatile than silica,⁷ evaporates and burns to dioxide with a fuming flame at the mouth of the furnace. The dissociation of silicon carbide according to equation 9 takes place above 2,500° C. It is the last high temperature phase of the operation and free graphite forms. Silicon carbide can be obtained only with the highest additions of carbon as shown in equation 1.

The reduction of zirconia by silicon with formation of zirconium silicide, as shown by equation 11, has been demonstrated by heating a mixture of these substances under helium to about 1,200° C. The product obtained in this way develops large quantities of $ZrCl_4$ when heated in chlorine.

The reaction in equation 12 was established by Zintl,⁷ who showed that silica can be driven off completely from zircon by heating a mixture of zircon and silicon in vacuo at 1,500° C. The authors checked this result and could confirm it. Zircon, when heated without silicon in vacuo at 1,500° C, loses but very little weight.

It may be noted that ZrC melts above 3,500° C and does not undergo dissociation as does SiC . The use of ZrC as resistor material in electric resistance furnaces is limited because of its pyrophoric properties. However, it could be used as a resistor material in place of tungsten in high frequency furnaces operating with a noble gas atmosphere.

A typical run of the carbide furnace is shown in Table II.

TABLE II

Products Obtained in Typical Operation of Carbide Furnace

Charge: 75 kg. mixture of zircon and graphite containing 16.5% carbon, 83.5% zircon composed of 49.6% zirconium and 15.4% silicon. Total weight of zirconium = 31.05 kg. and of silicon = 9.65 kg.
 Recovery of zirconium = 90.0% Loss of silicon = 95.3%

Product	Weight of Product	Zirconium		Silicon		C	N ₂
Yellow Material	17.25 kg.	77.2%	13.30 kg.	0.2%	0.035 kg.	3.9%	0.93%
Gray Material	2.95	76.2	2.26	0.4	0.012	4.3	1.3
Mushy Carbide	14.10	72.5	10.20	2.8	0.225		
Burned (reoxidized) and fines	2.32	58.8	1.37	8.1	0.183		
			27.13		0.455		

2. Chlorination of Zirconium Carbide

The use of an arc furnace for the production of zirconium carbide or raw zirconium metal introduced some difficulties in the chlorination.

The literature mentions³ that zirconium carbide behaves erratically when chlorinated. We confirmed this as illustrated by the carbides shown in Table III, the one chlorinating with 77.8% efficiency, the other with only 26.0% efficiency, both being of almost the same composition.

TABLE III

Difference in Efficiency of Chlorination of Two Carbides of Similar Composition

Carbide No.	Zr	Composition Si	C	Efficiency
1	75.5%	0.60%	16.5%	77.8%
2	75.2	5.50	16.8	26.0

The physical condition of the carbide evidently has a considerable influence on the chlorination recoveries. The thickness of the residual carbon layer as well as its density plays an important role. Furthermore, channeling was observed, with the result that chlorine was found in the exhaust gas while unreacted material remained in the charge. As yet, no remedy has been discovered to control these factors, but recycling after slight regrinding seems to be a temporary solution for these difficulties. In this way, chlorination efficiencies above 70% are obtainable.

The chlorination of carbide proves to be much cheaper and more efficient than that of a mixture of zircon and carbon. The chlorine consumption is lower, the chlorinator has a much higher capacity, and the reaction is thermally self-sustaining. Furthermore, there are fewer steps from the ore to the chloride. The chlorination of an ore-carbon mixture necessitates the briquetting of the mixture with a binder and firing the pellets in absence of air. Also, the formation of large quantities of waste gases, CO and SiCl₄, certainly cause considerable losses of zirconium chloride, which may be carried away by partial pressure or mechanically.

As described in the first report, the original chlorinator consisted essentially of a vertical silica reaction tube connected at the top through a graphite elbow to a horizontal, heated, cylindrical condenser, and at the bottom to an iron discharge elbow. This arrangement was considerably improved by making the upper elbow entirely out of nickel. The new elbow was heated internally by an inserted quartz tube heater element of 1-in. (25 mm.) inner diameter. Its base was held down on the ground, horizontal joint of the quartz chlorinator tube by means of two nichrome straps and springs. The construction of the chlorinator gave satisfaction, except that the bottom of the silica tube frequently cracked where the iron elbow was attached. During continuous runs, exhausted material was removed from the bottom of the chlorinator; this procedure caused the hot residue in the reaction zone to drop into the iron discharge elbow and the thermal expansion and contraction of the iron cracked the silica tube. This difficulty was overcome by using a water-cooled Invar ring to hold the silica tube; the ring was in turn soldered to the iron base.

The chlorine consumption of a carbide with a low silicon content, 2% to 4%, was generally less than 20% in excess of the theoretical amount needed for the chlorination of the zirconium and in some cases practically no excess was required.

The zirconium oxide content of the chloride produced has been as high as 10%. The use of such heavily contaminated chloride in the reduction operation yields a metal that contains an excessive amount of oxygen, because the zirconium oxide is mechanically carried over with the chloride vapor. It is important, therefore, to keep the oxide content of the chloride as low as possible.

The source of the oxide contamination of the chloride was investigated. Although some contamination was caused by reaction of $ZrCl_4$ with moisture of the air while the chloride was being handled or briquetted, most of the contamination was a result of the reaction of zirconium chloride with oxygen of the air in the condenser of the chlorination apparatus, according to the equation: $ZrCl_4 + O_2 \rightleftharpoons ZrO_2 + 2 Cl_2$.

This reaction was checked and it was found that, at the sublimation temperature of zirconium chloride, quantities of chlorine are given off and zirconium oxide is formed. This experiment confirms reports in the patent literature⁷ which state that many oxides can be made by the reaction of anhydrous chlorides with oxygen at elevated temperatures. It was noted that in chlorination runs made with high-silicon carbide the chloride product contained but little oxide. The emission of large quantities of silicon chloride prevented air from entering the condenser. Thus, some silicon or nitrogen is desirable in the carbide as a means for excluding air from the condenser, which otherwise must be sealed fairly tightly.

3. Purification of Raw Zirconium Chloride

Dense chloride has considerable advantage over the powder or briquetted material. It entraps less gas, does not pick up such large quantities of moisture when exposed to air, and takes up less space. Such dense chloride was produced quite easily in a separate operation in the reduction furnace itself by subliming the zirconium chloride powder onto a hot metal core suspended in the furnace. Because of the slowness of the operation, which lasts about 12 to 16 hours, very little oxide was carried mechanically into the condensate.

In adapting the reduction furnace for this operation as shown in Fig. 2, the floating top (5) was provided with a condenser made of pipe. The condenser was cooled with compressed air (7) to about 100° C. Since the weight of the top increased steadily with the deposition of chloride (8), counterbalancing with a weight (11) was provided.

Iron can be eliminated from the chloride in the same operation by subliming the chloride in a very light flow of hydrogen. The volatile iron trichloride is reduced in this way to the less volatile dichloride which remains behind in the residue. The reducibility of the iron trichloride was checked in a separate experiment. Raw zirconium chloride powder was mixed in a rotating heated drum in a hydrogen

atmosphere at different temperatures. The reduction of trichloride to dichloride was almost complete at 250° C.

The dense chloride works very well in the reduction operation. The loss of chloride by volatilization, which was above 8% in the runs reported in our first publication, was reduced to less than 2%. The hydrogen consumption is almost negligible, and the iron content of the final product is generally below 0.05%.

4. Reduction of Pure Zirconium Chloride with Magnesium

The previous section has described the method of making dense zirconium chloride in the furnace designed for the reduction operation. The actual reduction is carried out in this apparatus by placing a

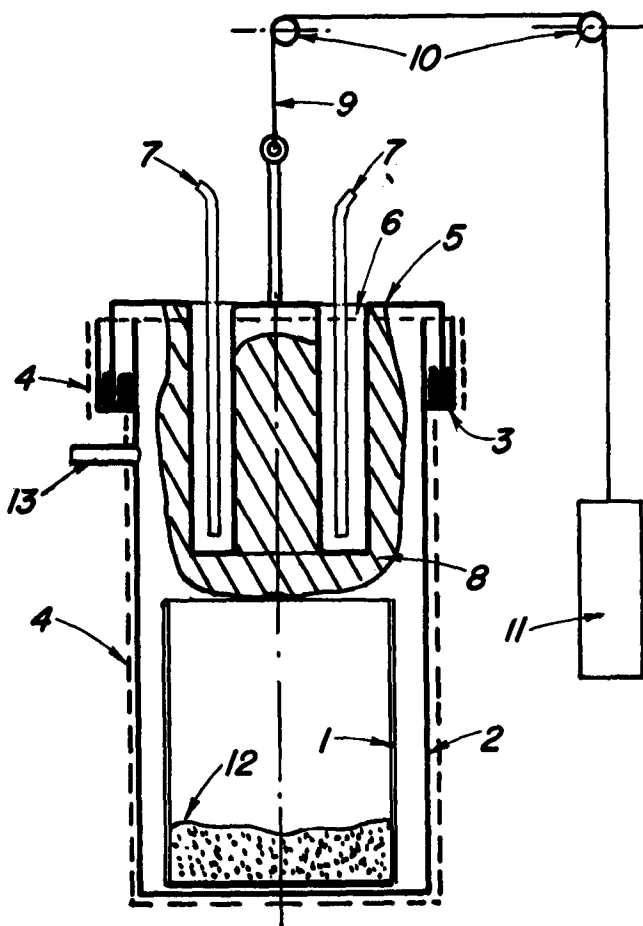


Fig. 2. Apparatus for producing dense zirconium chloride. 1. Crucible. 2. Reduction furnace. 3. Fusible metal seal. 4. Heating coil. 5. Floating top. 6. Condenser. 7. Compressed air. 8. Zirconium chloride ingot. 9. Steel wire suspension. 10. Pulleys. 11. Counterweight. 12. Oxide residue. 13. Needle valve stem.

crucible of magnesium in the bottom of the furnace vessel and setting on top of it the can originally used for holding the $ZrCl_4$. This latter container now serves to catch any residue from the dense chloride mass as it is slowly evaporated from the iron core attached to the floating lid. Such residue would contain any zirconium oxide left in the $ZrCl_4$ which is usually less than 1% by weight of the original chloride. The use of dense chloride containing very little moisture eliminates almost entirely any formation of HCl gas during the heating period. As a consequence of the use of low-oxygen, dense chloride, the hardness of the zirconium ingots has been reduced to 156 Brinell.

5. Elimination of Residual Salts by Vacuum Treatment

While there have been no fundamental changes in this phase of the process, it was found that certain precautions must be taken to avoid contamination with iron and to avoid ignition of the zirconium metal product.

The iron content of the zirconium was normally less than 0.2%. In several runs, however, the iron was found to be much higher, in the order of magnitude of 1% or 2%. Iron at these higher concentrations does not interfere with the malleability of zirconium metal, but as its general effect is unknown, it is desirable that such contamination be avoided. It was presumed that the source of the iron was the iron crucible of the reaction furnace and some consideration was given to the feasibility of lining the crucible with molybdenum or of using a graphite crucible. To check the possibility of zirconium being contaminated by the iron crucible, a briquetted mixture of iron and zirconium turnings was heated under helium. It reacted spontaneously at 1,125° C with such heat evolution that the mixture melted.* It was also found that zirconium chloride reacts with iron at 1,100° C, producing iron dichloride and a layer of an iron-zirconium alloy containing about 2% zirconium. This reaction may also contribute to the iron content of the zirconium metal.

Alloys of iron and zirconium with approximately 17% iron have a melting point as low as 1,000° C and frequently globules of molten eutectic have been found in the reduction crucible in the form of droplets or tears welded together in a string. Such fusible alloys of zirconium with iron group metals could possibly be used as master alloys or as brazing or soldering materials. Their corrosion resistance is good and they show some hot malleability.

A survey of the results of a number of distillation runs indicated that there was a relationship between the maximum temperature of the furnace and the iron content of the product. When the temperature of the furnace, as measured outside of the vacuum vessel was kept below 950° C, the iron content of the product was less than 0.2%, but in those runs in which the furnace temperature was allowed to reach 1,025° C, the iron content of the zirconium increased to an average of about 2.0%. Thus, contamination by iron can be greatly reduced

* Similar reactions are known to occur between silicon and iron, and the well known Krupp "Thermosilit" process for making silicon iron castings is based on an analogous exothermic combination of silicon with iron.

by keeping the temperature below 950° C. This lower operating temperature also prolongs the life of the distillation retort.

The second difficulty has its source in the black, more pyrophoric portion of the zirconium which is found on top of the crucible. It is formed in the last stage of reduction when the magnesium is nearly exhausted and the reaction slows down. When brought in contact with air, this porous material heats up to such an extent that it may start burning. This occurrence can be avoided by conditioning the metal slowly with air which is admitted gradually into the vessel. The oxidation resulting from this procedure is undesirable, and an investigation was made of methods to passivate or poison the metal surface with less objectionable gases. It was thought that the active, or catalytic, centers of the metal surface could be neutralized in some way with gases such as nitrogen, hydrogen, or chlorine, or with catalyst poisons such as H₂S. These gases diluted with helium were tried at various times. Nitrogen was not absorbed by the cold, active metal. It was found that cold zirconium metal absorbs hydrogen steadily, and the metal becomes friable. Hydrogen did not prevent the tendency of the zirconium to ignite, nor did any other gas that was tried; the question is being investigated further.

6. *Melting of Zirconium Ingots*

The vacuum arc furnace described in the previous article was used successfully for the melting of a large number of ingots. Such a device has certain limitations and operating difficulties that should be mentioned. The lower copper electrode, on which the zirconium is melted, is pitted when struck by the arc; furthermore, when the arc is formed on the copper, it persists there because copper is more volatile. The water-cooled copper electrode also tends to gather a condensate of magnesium chloride that causes the molten zirconium to spatter. These difficulties were partially solved by making the lower electrode of iron with a tungsten plate brazed on the top. This arrangement worked fairly well, but the tungsten had a tendency to spall when struck by the arc because of the differential expansion of iron and tungsten.

There are some practical limitations to the size of a vacuum arc furnace. In the first place, it is not easy to obtain a large supply of direct current of the desired characteristics. Arc welders that will give up to 1,500 amp. are available at fairly reasonable cost. They would be sufficient for melting ingots weighing about 4 lb. (1.8 kg.). Attempts at using alternating current have not been successful. The a.c. arc could not be maintained, possibly because of the low vapor pressure of the zirconium at its melting point. It may be possible to stabilize an a.c. arc with a superimposed direct current. If it develops that direct current must be used for arc melting, the process will be handicapped by the necessity of either making small size ingots, or of using special, expensive generators that will give heavy currents over a wide voltage range.

Another limitation is imposed by the fact that the largest tungsten rods now available for use in the upper electrode are only $\frac{7}{8}$ in. (2.2 cm.) in diameter. This limits the maximum current to about 500

amp. For larger currents it is possible that the electrodes could be bundled into larger units.

The tungsten electrodes accumulate a covering of zirconium which occasionally fuses and runs down into the batch, especially if the furnace becomes very hot. Since this zirconium is slightly alloyed with tungsten, the ingot is contaminated. While most ingots contained less than 0.1% tungsten, as much as 2% was found in some of them. This impurity does not harm the corrosion resistance of the metal, but it increases the hardness considerably. In an attempt to avoid such contamination, the tungsten electrode was replaced by a zirconium carbide rod. This rod was made from zirconium carbide which was briquetted, sintered, and impregnated with zirconium metal to make it more dense. The rod was brazed in a vacuum furnace to a copper base which was soft-soldered into the water-cooled terminal. Such an electrode performed well but was fairly brittle, an objection that would not be important in a large furnace.

After encountering all of the problems and limitations that have been described, it was decided that if large ingots were to be produced, a radically new method had to be discovered. It had been observed during the production of synthetic zirconium carbide that, although finely ground zirconium metal reacts violently with carbon when the mixture is heated above 1,800° C, the reaction between coarse zirconium of about 20-mesh (0.84 mm. opening) and carbon under the same circumstances is very sluggish. This seemed to indicate that the solubility of zirconium in carbon and that of carbon in zirconium is low. To check the possibility of melting zirconium in contact with carbon a number of lumps of the metal were melted on a graphite plate in the vacuum arc furnace, both with a tungsten and with a graphite electrode. The ingots showed a low carbon content, 0.03% with the tungsten electrode and 0.15% with the carbon electrode. On the basis of these results, zirconium was melted directly in a graphite crucible. This was done both in a high frequency vacuum furnace and in a carbon resistor vacuum furnace of the type previously described by three of the authors.⁴ The only difficulty was caused by the volatilization of the carbon when it was heated in a vacuum. When carbon vapor comes in contact with the hot oxide refractories, a reaction takes place and CO and eventually SiO are evolved. The CO and SiO in turn react with the zirconium, introducing oxygen, silicon and carbon. It was found that this reaction could be avoided by protecting the vitreous silica or other refractory with shields of some refractory metal such as molybdenum in the regions where the refractories were subject to attack. In the high frequency furnace, a split, cylindrical molybdenum screen was placed between the crucible and the silica tube. In the carbon resistor furnace, concentric molybdenum cylinders were placed between the insulating refractory and the resistor. There would be some advantage in substituting molybdenum or tungsten for the graphite as the resistor material. Carbon evaporation could be reduced greatly if melting were done under a noble gas.

The average carbon content of 12 ingots made in the high frequency furnace was 0.23%. A microscopic examination of the ingots cooled in a graphite crucible showed that any carbide formed is deposited

mainly at the contact surface between the zirconium and the graphite. This suggested that a cast ingot would probably be lower in carbon than one that was allowed to cool in the crucible. By casting the molten zirconium into a separate mold, much of the carbide remained on the walls of the graphite crucible.

The carbide in the metal appears as inclusions in stringers that are stretched and broken up when the metal has been rolled. There is apparently only a slight solubility of zirconium carbide in the metal. Since the percentage of zirconium carbide present is about $8\frac{1}{2}$ times the percent of carbon, small amounts of carbide are immediately visible under the microscope. The hardness and malleability of the zirconium are only slightly affected by the presence of small amounts of carbide inclusions.

The possibility of melting zirconium metal in graphite crucibles and the use of the resistor furnace instead of more expensive equipment for heating means that ingots can be made at low cost.

Investigations showed that titanium and thorium can be melted on a graphite layer or in graphite crucibles with results similar to those for zirconium. Silicon, however, penetrates deeply into the graphite and forms carbide. Very poor results were obtained with beryllium and vanadium which carburized greatly.

THE ROLLING OF ZIRCONIUM

Heavy sections of zirconium are usually rolled hot, although hot rolling has several disadvantages. The ingot, if heated to 700°C in air, becomes coated with an oxide layer which is yellow to brown on the outside and black at the contact with the metal. The yellow color is probably caused by iron. The outer layer is soft and is readily removed with abrasives, but the black inner layer is very hard and neither acids nor ordinary abrasives remove it easily. A silicon carbide grinding wheel cleans the surface slowly. Obviously, thin sections cannot be cleaned in this fashion; they must be rolled cold with intermediate annealings in pure helium or in a good vacuum. Cold rolling is only practical for metal that is soft. Ingots should be hot worked in order to break up the cast structure, after which cold rolling can take place. The oxide skin which is always present diffuses into the metal during annealing and a small amount of oxygen can be found in the metal that has been treated in this way.

It is, however, very easy to roll zirconium, and titanium as well, out of contact with air by enclosing it in a metal sheath, a practice which has been recommended and successfully applied to other metals such as beryllium.² A cylindrical zirconium ingot is inserted into a length of pipe or a cavity made by drilling a steel rod, or a flat zirconium cake is placed in a box shaped iron container. The iron or steel casing is then welded to exclude air and the whole assembly rolled hot or cold. If the seal is perfect, no oxygen penetrates to the metal. Thin sections can be cold-rolled with intermediate annealing. Soft ingots can be reduced 50% before reheating. If the sheath cracks at the edge, as it sometimes does, the zirconium may be taken out and rewrapped. Sections as thin as 0.01 in. (0.25 mm.) can readily be

obtained, and, since no oxygen reaches the metal, the original composition of the ingot material is maintained. After rolling, the sheets are taken out of the sheaths by cutting the edges of their envelopes with shears. They may be cold-rolled afterwards to give them a polished surface. A sheet 0.01 in. (0.25 mm.) thick from an ingot having a Brinell hardness of 180 can be bent sharply at an angle of 180° without cracking.

It is important that zirconium sheathed in iron should not be rolled at temperatures higher than about 950°C . A zirconium sheet which was sheathed in iron and rolled at $1,025^\circ\text{C}$ suddenly ignited and burned vigorously. Care should be taken in the rolling of zirconium sheathed in iron because the excess heat developed in the deforming process may result in this vigorous burning taking place. This tendency of the iron and zirconium to unite can be used to plate iron on zirconium by carefully rolling a zirconium ingot encased in iron at temperatures between 800° and $1,000^\circ\text{C}$ with heavy reductions that cause local welding. The iron on one side of the sheet can be removed by dissolving it in acid, or if the rolling is stopped while the ingot is still fairly thick, the ingot can be cut in the middle through the zirconium, and the two halves may be rolled separately after they are rewrapped in iron. The same procedure can be applied to plate a number of other metals on zirconium.

Platings of zirconium on molybdenum or tungsten can be obtained readily by fusing zirconium on these metals and rolling the bonded metals down in an iron wrapping.

OXYGEN AND NITROGEN IN ZIRCONIUM

A method for the determination of oxygen in zirconium is being investigated. It depends on the chlorination of the metal with purified chlorine that is especially free of oxygen, nitrogen, and carbon dioxide. This purification is performed by condensing the cylinder chlorine with dry ice. Oxide-bearing material is left as a residue. The method is limited to zirconium that is free of carbon, tungsten, and the metals of the fifth group of the periodic table, as these elements form volatile oxychlorides. The method, which is also suitable for the determination of oxygen in titanium, will be described in a later report.

Nitrogen in zirconium is readily determined by the Kjeldahl method. It has been found that zirconium made by the Bureau process is easily held below 0.05% nitrogen. Zirconium nitride starts to dissociate in a vacuum at 500°C , but complete elimination of the nitrogen by vacuum heating is problematic. A nitride made by the reaction of pure sublimed zirconium chloride with ammonia gas showed a nitrogen content of 3% after it had been heated to $1,800^\circ\text{C}$ in a vacuum of a few microns. A dissociation of nitride may take place at the melting point of zirconium, since a slight gas evolution is sometimes perceptible when zirconium is melted even though it is very low in nitrogen. It is questionable whether all of the nitrogen can be removed from molten zirconium even by holding it for a long period of time in a vacuum. Nitrogen absorption by zirconium is very slow. Thin sheets of zirconium heated for one hour at 800°C in pure nitrogen were still malleable.

Zirconium oxide is stable in fused zirconium in the presence of carbon and no noticeable deoxidation can be obtained with carbon. This finding has bearing on the question of whether or not zirconium can be made by reduction of the oxide with carbon in a vacuum.¹ A metal which contained 0.3% oxygen did not evolve any gas when it was fused in a graphite crucible in a vacuum, although it contained 0.25% carbon.

Oxygen is known to harden zirconium to a considerable extent but accurate data as to the hardness as a function of the oxygen content are not yet available. Ingots of pure zirconium have a hardness below 135 Brinell (3,000 kg., 10 mm., 60 sec.). Ingots containing 0.1% oxygen have a hardness of about 190 to 200 Brinell, those with 0.2% oxygen, about 250, and ingots with 0.3% are about 300 on the Brinell hardness scale. Thus, oxygen may be considered as a suitable hardening agent for many applications. For example, springs made of zirconium alloyed with oxygen show good elasticity. Soft zirconium would be entirely unsuitable for this purpose, even though it was cold rolled. On the other hand, oxygen embrittles zirconium and it is questionable whether tools made from oxide-hardened zirconium would keep a cutting edge. Surface hardening of zirconium by either oxygen or nitrogen may be possible.

CONCLUSIONS

Considerable progress has been made on the method for producing malleable zirconium by reduction of chloride vapors with magnesium in a furnace with a noble gas atmosphere. The chief improvements and developments are: the production of low-silicon zirconium carbide, or crude zirconium metal, in the arc furnace; the precaution against oxidation of zirconium chloride at its subliming temperature; the production of dense, low-oxide chloride; the fusion and casting of zirconium in graphite vessels, which overcomes limitations as to the size of the melted ingots; the use of a carbon resistor furnace for the fusion of the ingots which reduces the investment in equipment; the perfection of a method of rolling thin sheet by sheathing zirconium in iron; the discovery of probably useful low-melting eutectics of zirconium with iron group metals; and the plating of zirconium on iron. A pilot plant is under construction that will permit establishing the commercial possibilities of the method. Part of the methods described above may be used for or adapted to the production of a number of other metals, especially titanium.

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Resumen del artículo: "Progreso Reciente en la Metalurgia de Circonio Maleable."

Se describe el progreso conseguido en el último año y media en el procedimiento de producir circonio maleable por la reducción de vapor de cloruro de circonio por magnesio en atmósfera de helio.

En la primera etapa del procedimiento, la producción de carburo de circonio partiendo del óxido, se ha conseguido un horno de arco (Fig. 1) que rinde un carburo con menor contenido de silicio. Otro horno nuevo (Fig. 2) produce cloruro de circonio más denso, con menos pérdida por volatilización en la reducción. Ahora se producen los lingotes de circonio en moldes de grafito. El poco de carbono disuelto así no empeora las propiedades físicas.