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UNITED STATES ATOMIC ENERGY COMMISSION

PROGRESS REPORT IN METALLURGY
APRIL 1, 1949 TO SEPTEMBER 30, 1949

By

B. A. Rogers, et al

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Ames Laboratory
Ames, Iowa

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PROGRESS REPORT IN METALLURGY

I. THORIUM METAL

(H. A. Wilhelm, D. Peterson and R. M. Walrath)

A. Production of Thorium

With the completion of an order for metallic thorium, production of this metal has been curtailed during the occupation of the new Metallurgy Building, where improved equipment for reduction and casting of thorium is being installed. However, the present equipment for reduction and casting is being maintained in operating condition to meet production requirements until the new equipment is ready to operate.

Progress on the construction of the calcium distillation unit has been much slower than anticipated as most of the crew working on this project were loaned to groups engaged in other work. The unit has been completed, however, and different parts of it subjected to tests although actual operation on a charge of calcium is still to be undertaken. A trial run will be made shortly.

II. THE PRODUCTION OF ZIRCONIUM

(H. A. Wilhelm, B. A. Rogers, R. H. Kraemer, J. W. Ross,
J. F. Smith, M. Stock, A. J. Stonehouse and K. A. Walsh)A. Production of Zirconium Fluoride1. Hydrofluorination of Zirconium Tetrachloride

As indicated in the previous report, ISC-45, the hydrofluorination of ZrO_2 , although a usable process, presents some difficulties. For this reason, an investigation of the hydrofluorination of $ZrCl_4$ was undertaken.

The reaction between $ZrCl_4$ and HF is exothermic and proceeds at low temperature. Graphite trays containing $ZrCl_4$ in layers about two inches deep were stacked inside a copper container which was heated to the desired temperature. Analysis of the exit gases offered a way of determining the rate of conversion as all of the

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HCl coming over originates from the reaction

The progress of conversion as calculated from frequent determinations of the HCl coming from the reaction chamber can then be compared with the amount of HF consumed. Information obtained in this way on the amount of HF required to produce different degrees of conversion of a charge of 1500 grams of ZrCl_4 is shown in Table 1 for 50°C., 80°C., and 100°C.

Table 1 - The Relationship Between Degree of Conversion and Consumption of Hydrogen Fluoride.

Percent of conversion of a 1500 g. charge of ZrCl_4 by the amount of HF shown in the top row of figures. (HF in grams)							
Temp., deg. C.	64	170	282	434	620	694	766
50	10.0	25.0	40.0	60.0	80.0	85.0	88.0
80	6.4	17.8	30.5	46.3	62.8	68.2	78.4
100	9.0	22.2	32.2	48.4	63.9	68.2	77.0

The range of temperature in which hydrofluorination of ZrCl_4 can be conducted satisfactorily is limited to about 50°C. If the temperature is reduced below 50°C., HF condenses in the trays; if the temperature rises, caking of the product hinders the movement of the reacting gases into the interior of the charge.

In accordance with the results shown in Table 1, 50°C. was selected as the temperature for hydrofluorinating operations. About 6 hours are required for 95 to 98 per cent conversion of a 1500 gram charge. Only 40 per cent of the HF passing through the hydrofluorinator is consumed in the reaction but the proportion could be increased to an economical value if several hydrofluorinating units were operated in series. The equipment was only slightly corroded after 40 batches of ZrCl_4 had been hydrofluorinated.

The product obtained in the 50°C. hydrofluorination is light and fluffy and requires no pulverizing. Its packing density is approximately 0.5 g./cc. It hydrolyzes rapidly with evolution of hydrogen fluoride if exposed to the atmosphere.

The tendency of the fluoride to react with moisture is reduced to negligible proportions if the material is heated to 300°C. under an atmosphere of HF. If the heating operation is conducted at 500°C. it has the added advantage that it drives off most of the titanium and silicon present. High temperature treatment also increases the degree of conversion slightly.

2. Hydrofluorination of Zirconium Carbide

A few experiments were made on the hydrofluorination of ZrC purchased from the Bureau of Mines. The reaction proceeds readily at 250°C. and above. At 400°C., titanium present in the charge is driven off as TiF_4 which condenses in cooler parts of the reaction vessel. Some unreacted ZrC and carbon can be removed from the product by screening but enough fine carbonaceous material remains in the fluoride to give it a gray color. Sublimation of the product probably would leave the carbon behind but tests have not been made yet.

3. Hydrofluorination of Products from Zirconium-Hafnium Separation Tests

Tests were made of the amenability of $\text{ZrCl}_4 \cdot \text{POCl}_3$ to hydrofluorination. This material is the product of one method employed for the separation of hafnium from zirconium. During reaction with HF at 50°C., the brownish lumps of the complex were converted into white, porous ZrF_4 . Decomposition of a 1680 gram charge was considered sufficiently near completion after 8 hours. The product, weighing 820 grams, was heated for an additional 2 hours at 300°C. under HF, after which it was found by analysis to contain 93.5 per cent ZrF_4 . The material obtained at 300°C. was then sublimed at 800°C. under a pressure of about 35 microns. The sublimate accounted for 97 per cent of the material charged and contained 44.1 per cent fluorine and 0.24 per cent chlorine corresponding to about 98.5 per cent ZrF_4 . Material left as residue weighed 3 per cent as much as the charge.

A hydrofluorination test was made also on the product from experiments by the chemical group on the separation of hafnium from zirconium in a silica-gel column. The solution of ZrCl_4 and methanol withdrawn from the column had been evaporated to dryness and the residue heated at 300°C. A 20 gram charge of this black, charry material was hydrofluorinated at 300°C. in the manner described above. From the analysis made for fluorine, the conversion was calculated to be 99 per cent complete after 4 hours. A small amount of carbonaceous material remained in the fluoride. Although the product obtained from the ZrCl_4 and methanol procedure reacted readily, the material remaining from similar separation tests in which acetone replaced the methanol was not amenable to hydrofluorination.

4. Sublimation of Zirconium Fluoride

Because of the embrittling effect of oxygen on zirconium, the presence of oxides in the ZrF_4 used for production of metal is objectionable. An apparatus for subliming charges of ZrF_4 has been constructed from a stainless steel tube. The charge to be sublimed is heated to about 800° to 850°C . and the sublimate collects at the cool end of the tube. The pipe is cooled by a water-jacket at the point of condensation so that the apparatus may be short and the deposit be formed in a smaller region.

The sublimed fluoride made from the chloride, has a packing density greater than 3 g./cc. A little over 1 per cent of the charge remains as residue. It contains iron, chromium, copper, manganese and magnesium according to spectrographic analysis. Fluorine content of the sublimed product is about 2 or 3 per cent higher than in the charge.

B. Bomb Reduction of Zirconium Compounds

Both ZrCl_4 and ZrF_4 have been used in the production of metallic zirconium in bomb-type reactions with calcium. An excess of 10 per cent of calcium was adopted as standard procedure as previous trials showed that maximum yields were obtained with an excess of 7.5 per cent or more. ZnCl_2 has given good results as a booster substance. In general, ZrF_4 gave more satisfactory results than ZrCl_4 . Not only did the fluoride give higher yields of metal as shown in Table 2, but less difficulty was experienced in its use. It reacted less readily with moisture and had less tendency to diffuse through the refractory liner and cause it to stick to the bomb.

Table 2 - The Yields of Zirconium obtained with ZrCl_4 and with ZrF_4 in Reactions with Calcium

Compound used	ZnCl_2 used mole per cent	Yield of zirconium, per cent
ZrCl_4	20.6	61.9
ZrCl_4	20.2	60.3
ZrF_4	20.7	77.4
ZrF_4	21.7	79.0

In reduction of ZrF_4 , a minimum of 11.2 mole per cent of ZnCl_2 is required as yields fall off rapidly if less is used. On the other hand, the yields increase gradually up to 20.0 mole per cent. Best results have been obtained with a charge composed of 4 moles of ZrCl_4 , 1 mole of ZnCl_2 , and 9.9 moles of calcium. With this charge zirconium yields greater than 85% have been obtained.

C. The Vapor Pressure of the Halides

Apparatus for determining the vapor pressure-temperature curves of the halides was described in a previous report, ISC-45. No additional description is necessary as no important alterations have been made.

Measurements of the vapor pressure of ZrBr_4 were obtained without difficulty. The bromide was prepared in much the same manner as the chloride; that is, by direct bromination of ZrC at about 400°C . Because of the relatively low vapor pressure of bromine at room temperature, the vessel containing it had to be warmed moderately to produce a suitable flow of vapor. Transfer of the product to the measuring apparatus required considerable care as the bromide is even more hygroscopic than the chloride. Measured values fell more closely on the mean curve than did those shown for ZrCl_4 in ISC-45. The sublimation temperature was found to be 356°C .

The behavior of the corresponding hafnium compound was much less satisfactory. No difficulty was encountered in its preparation but in the measuring apparatus its performance was quite erratic. In particular, the vapor pressure did not continue to rise in the anticipated manner. Whether this behavior was caused by dissociation of the tetrabromide into a lower bromide with lesser vapor pressure or whether it resulted from reaction with the tin used as a manometric liquid remains to be determined. The addition of cadmium to the tin in the apparatus altered the behavior somewhat and at times appeared to cause an increase in pressure above the normal vapor pressure of HfBr_4 . Its use was abandoned after two or three runs.

As a substitute for tin and tin alloys, trials were made of the characteristics of two silicones that appeared promising. One of these has a vapor pressure of only 35 mm. Hg at 350°C . but cracks badly in a relatively short time with a resulting high viscosity. The other silicone has a higher vapor pressure but is more stable and may be useful if a considerable correction to the vapor pressure readings is accepted.

An experiment was made to test the possibility of separating hafnium from zirconium by reaction of the bromide with tin but

difficulties in analysis were encountered and the project was dropped when more promising methods of separation were developed by the chemical group.

Preparation of ZrI_4 was found to be relatively easy although the procedure differed from that used for the chloride and bromide. Iodine does not react readily with the carbide but does combine with metallic zirconium in the presence of carbon at a rapid rate in the 300° to 400°C . range. No measurements of the vapor pressure of the iodide have been made yet.

Some preliminary trials have been made on ZrF_4 prepared by hydrofluorination of the oxide and subsequent sublimation. The results were erratic and suggested that gas was being liberated from some source, possibly because of a reaction of the fluoride with the glass apparatus.

D. Experiments on Liquefaction and Distillation of Zirconium Chloride

1. Liquefaction

Some tests have been made on the temperature of liquefaction of ZrCl_4 under its own vapor pressure. Information on this point was desired in connection with experiments on the distillation of the liquid chloride as a means of separating hafnium from zirconium. A glass tube was filled with chloride, sealed off and placed in a bath of molten sodium and potassium nitrates. The container for the molten salt bath was also glass. It was set in a large, split combustion tube furnace in such a way that the tube of chloride was continuously visible.

With a charge of the relatively impure chloride received from the manufacturer, melting of the powder became complete in the vicinity of 450°C . On cooling, the chloride first showed evidence of solidifying at 421°C . and appeared to be completely solid at 399°C . This considerable range of values was partly due to a non-uniform distribution of temperature.

A test with resublimed chloride of a crystalline character and with improved stirring action in the salt bath gave 433°C . for the beginning of solidification and 427°C . for its completion. Uncontaminated chloride probably would show a solidifying temperature several degrees above the values for this material. Air was not removed from the containers in these tests.

2. Distillation under pressure

Two glass distillation units were made but both cracked before the distillation operation was completed. Both units were made of

heavy-walled glass tubing with charging bulbs having a capacity of about 20 cc. and receiving bulbs somewhat smaller. Connecting the bulbs was a straight length of glass tubing of smaller diameter filled with glass beads. A third unit of slightly different design is being constructed for trial.

Some interesting preliminary results were obtained with a glass tube of the approximate form shown in Fig. 1. This tube was filled with sublimed chloride, pumped out and sealed. It was then heated in such a manner that the bottom portion was a few degrees warmer than the upper. After the chloride had become completely liquid, it was allowed to cool slowly. The solid took on the form shown by the cross-hatched area of the figure. Spectrographic analysis of samples taken from three different locations indicated a variation of hafnium content as indicated on the sketch.

3. Differential sublimation

Three simple tests were made on the effect of subliming commercial $ZrCl_4$ at different temperatures under a comparatively rapid stream of hydrogen. The experiments demonstrated a tendency for the $HfCl_4$ to come out in greater proportion at low temperature. In one test, the deposits formed in the cool end of the tube at successively higher furnace temperatures had the hafnium contents shown below.

Deposit formed	Hafnium content, percent
below 260°C.	2.7
in range 260°C. to 300°C.	1.7
above 300°C.	1.3

III. RARE EARTH METALS

(F. H. Spedding, A. H. Daane and C. F. Miller)

A. Production of Neodymium and Yttrium

Approximately 347 grams of neodymium were produced by the reduction of $NdCl_3$ in bomb type reactions. The usual charge put into the bomb was composed of 49.4 per cent $NdCl_3$, 31.5 per cent of iodine and 19.1 per cent calcium by weight. It was mixed in an atmosphere of dry nitrogen and loaded into the bomb while still in this atmosphere. The weight of the resulting biscuit was about 175 grams.

Fig. 1 - Difference in hafnium content of different parts of a mass of zirconium tetrachloride formed when the salt, molten under its own vapor pressure, was allowed to solidify.

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Attempts were made to reduce yttrium but without much success. Apparently, this element has a high melting point as it does not collect as a biscuit but remains mixed with the slag. In co-reductions with zinc or cadmium the yttrium did not appear to alloy with its co-metal but was entrapped mechanically with it. The product of co-reduction with cadmium was heated until the cadmium was driven off but the remaining black, spongy material would not melt.

Purification of rare earth metals from calcium, magnesium, iron, zinc and cadmium is being carried out by repeated precipitation from 2N or 3N hydrochloric acid solutions. The oxide obtained by igniting the oxalate from the third or fourth precipitation usually contains about 10 ppm of iron, less than 0.1 per cent CaO and less than 0.05 per cent MgO. Neither zinc nor cadmium can be detected.

B. Casting of Rare-Earth Metals in a Vacuum

An all-tantalum apparatus has been constructed for casting rare earth metals inside an evacuated chamber and the first ingots cast with it. The operations are carried out in 3 steps. First, the biscuit is placed in a tantalum crucible which is in a coil connected to a source of high frequency power. After it has melted, the biscuit is held in the liquid state at about 1300°C. under a pressure less than 1 micron for from 15 to 30 minutes depending on the size of the biscuit. When the metal has cooled, the chamber is opened and the crucible placed in an inverted position over a tantalum funnel having its spout directed into a tantalum mold. The mold is formed from sheet 0.001 inch thick welded into shape by a spot welder or a Heliarc welder. It is so easily deformed that it must be supported by being packed in granular magnesium oxide so that the liquid metal will not deform it. Lanthanum has been cast in this way quite successfully.

The mold can be stripped from the ingot readily except at points where it was bent or folded. At these places, some filing and cutting must be done if the tantalum is to be removed completely. Lanthanum cast in this apparatus did not contain sufficient tantalum or calcium to be spectroscopically detectable. It had a hardness of H-55 on the Rockwell Tester, and is the softest lanthanum obtained so far. The yield by this method of casting amounts to about 97 per cent.

C. Apparatus for Measurements of Vapor Pressure

Some problems in the fabrication of tantalum have been encountered in the construction of the apparatus for determining the

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vapor pressure of the rare earth metals by an effusion method similar to Knudsen's. As the method depends on weighings made in a vacuum with a magnetically controlled, quartz-fiber micro-balance, the tantalum container must be extremely light. Spot welding does not give a completely tight container and atomic hydrogen welding produces excessive embrittlement of the tantalum. Some experiments have been carried out with an argon-shielded arc but the proper combination of current and voltage for welding such thin sheet has not been found yet.

IV. ALLOY STUDIES

(H. A. Wilhelm, B. A. Rogers, P. E. Armstrong, O. N. Carlson,
P. Chiotti, J. M. Dickinson, E. S. Hodge, W. N. Miner,
D. Peterson, E. L. Pike and M. A. Schoenbeck)

A. The Crucible Problem

As stated in the previous report, graphite crucibles have been used for melting zirconium and zirconium-titanium alloys. However, graphite undergoes some corrosion and produces a corresponding contamination of the metal. As this contamination is undesirable for some purposes, an investigation of possible refractory materials was undertaken.

Usual crucible materials like magnesia, alumina and beryllia were tested although reports in the literature indicated that they were unsatisfactory for melting zirconium. The reported behavior was confirmed by the results of the investigation.

Because some of the compounds of uranium are of a refractory nature, experiments were made with crucibles formed from the nitride, oxide and carbide of this element. No details need be given of the preparation of these crucibles as other reports have given adequate descriptions. Uranium nitride gives up nitrogen to zirconium. The zirconium charge was converted, on its exterior to bright, golden zirconium nitride and the crucible suffered considerable disintegration. A crucible made of uranium carbide also reacted with the melt to some degree and showed evidence of deterioration. Furthermore, it was very porous and allowed large amounts of molten zirconium to enter its walls.

Crucibles of UO_2 were not attacked strongly by zirconium but had other disadvantages, of which the most serious was a tendency to give off oxygen almost indefinitely with a resultant high

pressure in the vacuum furnace and contamination of the charge. They also had poor resistance to thermal shock. Preheating improved their resistance to thermal shock but did not reduce the degassing action that appeared to result from a slow decomposition of the uranium oxide. The addition of 10 per cent of MgO to the UO_2 from which the crucibles were pressed did not give a better product. A similar negative result was obtained by the addition of 10 per cent of molybdenum powder.

A crucible made from zirconium nitride was attacked strongly by metallic zirconium and the carbide of zirconium yielded no better results.

Zirconium sulfide was investigated also as a material for crucibles. The sulfide was prepared by the reaction of H_2S with $ZrCl_4$ in a simple apparatus in which gaseous H_2S passed through a silica tube containing $ZrCl_4$ at $300^\circ C$. This product was heated for 1 hour at $400^\circ C$. under argon as a means of driving off excess H_2S and any unreacted $ZrCl_4$. The cinnamon brown powder obtained in this way was then heated under a vacuum for $2\frac{1}{2}$ hours at $1000^\circ C$. for removal of any substances not eliminated by the previous heating.

Small crucibles formed from the reheated powder pressed in steel dies could be heated satisfactorily to $1500^\circ C$. under vacuum, but showed little increase in strength and a slight tendency to crack. If the temperature were increased to $1600^\circ C$. the crucibles failed completely but whether from simple decomposition of the sulfide or because of reaction with the large crucible in which they were placed was not determined. The failure occurred in both graphite and tantalum crucibles and also when the sulfide crucible was protected from the graphite by a thoria liner. Microscopic examination indicated that some zirconium metal was produced but was not conclusive.

Thoria was the most satisfactory of the refractory substances tried. A small crucible with very dense walls showed little if any evidence of attack; however, thoria crucibles made from powder less thoroughly sintered were not so satisfactory.

Crucibles made from tantalum may be usable under restricted conditions. A crucible made of pressed tantalum powder absorbed considerable molten zirconium into its pores but chemical analysis of the solidified charge did not show the presence of tantalum. A small tantalum crucible drawn from sheet did not show any microscopic evidence of attack when a charge of zirconium was melted quickly and allowed to solidify immediately but another crucible in which the metal was allowed to remain molten for about 7 minutes appeared to alloy with the charge as illustrated in Fig. 2. In the

Fig. 2 - Wall of tantalum crucible with zirconium inside and outside. Metal outside leaked through a hole in the crucible.

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section shown in this figure, the wall of the crucible appears as a band with zirconium on each side. The zirconium on the exterior of the crucible is the result of an overflow of metal through a hole that developed at the liquid surface. This hole probably developed because of a thin place in the wall rather than because of more vigorous alloying of zirconium with tantalum.

Molybdenum crucibles appear to be usable in much the same manner as those made from tantalum but seem to be inferior in their resistance to alloying. Tungsten rod for use in making crucibles has been ordered and the possibility of using this metal will be studied.

B. The Zirconium-Uranium System

The previous report mentioned preliminary tests on the production of uranium-zirconium alloys by the methods of powder metallurgy. Compacts of uranium powder mixed with fine zirconium turnings were prepared but when given a diffusion treatment in carbon crucibles they picked up an excessive amount of carbon and when heated in beryllia crucibles, the zirconium turnings became oxidized.

Melting of uranium and zirconium together in either carbon or beryllia was found to be unsatisfactory for the same reason. Reluctance of the metals to alloy was also observed in melting experiments. Zirconium containing some zinc would not dissolve completely in uranium up to 1200°C. An attempt to produce alloying by melting uranium in a zirconium crucible was unsuccessful because the uranium took up very little zirconium even when heated up to 1500°C.

Co-reduction of the fluorides in a bomb with iodine as an agent for raising the temperature has yielded alloys that appear quite homogeneous and free from contamination. The zirconium fluoride available for these alloys was much superior to the product on which trials were first made. Alloys with higher zirconium contents were annealed at temperatures slightly below their melting points in graphite crucibles lined with thin zirconium sheet.

Evidence for the eutectoid reaction described in the previous report, ISC-45, as being slightly below 700°C. still appears valid. A suitable etching reagent for the higher zirconium alloys has not been found, however.

C. The Zirconium-Thorium System

Since the previous semi-annual report was written, additional zirconium-thorium alloys have been prepared. Up to about 50 per

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cent zirconium, these were made by co-reduction from the fluorides with calcium as a reductant and zinc chloride as a booster substance. Alloys of higher zirconium content were prepared by addition of zirconium to the co-reduced alloys. All alloys were heated to the molten state under vacuum for removal of residual calcium and zinc. Graphite crucibles were used for melting operations.

Melting points of the alloys were determined by observations with an optical pyrometer on a small hole in an electrically heated bar of material as described in the previous report. The bars used for this purpose were cut from the cast ingots. Thermal arrests were determined in the usual manner except that the specimens were tested in a vacuum. A summary of the melting points and thermal arrest temperatures is presented in Table 3.

The nature of the arrests is not completely understood. If one may judge from the photomicrographs of a 30 per cent zirconium alloy quenched from above 900°C. and from about 700°C., the alloys, in the range from 15 to 45 per cent, at least, are solid solutions above the upper transformation but decompose into two constituents

Table 3 - The Melting Points and Thermal Arrest Points of Some Zirconium-Thorium Alloys

Zirconium content, per cent	Melting point, deg. C.	Thermal arrests	
		deg. C.	deg. C.
13.8	1370	907	653
18.8	1300	891	649
23.2	1290	888	630
29.9	1350	884	645
31.6	1360	879	607
35.0*	1370	---	---
44.2	1400**	851	649
55.0*	1530	---	---
58.1	1580	802	649
72.5	1610	756	638
86.2	1770	752	642
95.0*	1820	None	None

* Intended composition, not analyzed

** Uncertain

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in going through that transformation. This behavior is illustrated by the series of three photomicrographs presented as Figures 3, 4, and 5. The first figure shows the alloy as cooled slowly after solidification. Fig. 4 shows the same alloy quenched from about 900°C . under vacuum and Fig. 5 shows a specimen quenched from about 700°C . The evidence for a solid solution above 900°C . is apparent. The constituents in Fig. 4 probably are thorium and zirconium as the lattice spacings calculated from x-ray patterns for a slowly cooled, 50 per cent alloy are those of the elemental metals.

D. The Zirconium-Titanium System

Although somewhat contaminated with carbon, the zirconium-titanium alloys did give approximate data for a melting point-composition curve. For the most part the points agreed with the curve estimated by J. D. Fast.* Apparatus has been set up for determining thermal arrests caused by transformations and other reactions in the solid alloys but no reliable data have been obtained.

As an alternative method for preparation of zirconium-titanium alloys, apparatus has been constructed for the simultaneous reduction of ZrCl_4 and TiCl_4 by magnesium according to the method used by Kroll for producing these metals separately. A glass apparatus was set up first but gave so much difficulty at the seals that the equipment was abandoned. Also the glass apparatus was found to offer little advantage in visibility as the walls coated so quickly with chloride that the inside parts could not be observed. A second apparatus constructed of silica gave so much trouble with breakage that it also was considered impractical. Metal equipment is nearing completion at the present time.

E. The Zirconium-Tantalum System

Eight melts of zirconium-tantalum alloys have been prepared in graphite crucibles. Charges for these melts were made from the mixed powders which were pressed together into a pellet. Melting points of the charged pellets were observed with an optical pyrometer. The solidus line obtained from these measurements cannot be very accurate as the unalloyed zirconium pellet melted about 40°C . above the value obtained for ingot metal.

* "The Transition Point Diagram of the Zirconium-Titanium System", J. D. Fast, Recueil des Travaux Chimique des Pay Bas, Vol. 58, 1939, pp. 973-983.

in many cases, the transformation of the alloy is accompanied by a change in the shape of the grains. In the case of the zirconium-thorium alloy, the grains are elongated in the direction of the applied stress. This is due to the fact that the grains are composed of a mixture of zirconium and thorium, and the zirconium grains are more ductile than the thorium grains. As a result, the zirconium grains are elongated, while the thorium grains remain relatively spherical. This elongation of the grains is a characteristic feature of the zirconium-thorium alloy, and it is observed in all specimens of this alloy that have been subjected to a tensile stress.

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Fig. 3 - A 30 percent zirconium, zirconium-thorium alloy after cooling slowly from solidification temperature.

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Fig. 4 - The alloy of Fig. 3 after being reheated and quenched from 900°C .

Fig. 5 - The alloy of Fig. 3 after being reheated and quenched from 700°C.

3. The Zirconium-Molybdenum System

Three compositions of zirconium-molybdenum alloys have been made in graphite crucibles. The charges were made up from scraps of thin plates of Bureau of Mines zirconium and pieces of Commercial molybdenum sheet. The ingots, weighing from 10 to 12 grams each, contained, respectively, 25, 50 and 75 per cent zirconium. All of the alloys were relatively hard, a fact which suggests contamination by graphite. Degassing of the charge and crucible by slow heating would have been desirable but the minimum power input from the Lepel converter melted the charge very quickly. Only intermittent operation of the converter prevented the charge from reaching the melting temperature within 2 or 3 minutes. As this difficulty was encountered in other alloy systems, means for reducing the power input are being considered.

3. Miscellaneous Zirconium Alloy Systems

In addition to the above alloy systems which are being actively investigated, materials and some additional equipment are being assembled for work on the systems zirconium-copper, zirconium-silver, zirconium-aluminum and zirconium-bismuth.

4. The Thorium-Carbon System

A preliminary constitutional diagram of the thorium-carbon alloys was included in the previous semi-annual report. Recent work has been concerned with verifying and extending the data used in the construction of the diagram.

The melting points of several alloys in the range from 0.25 to 1.6 per cent carbon have been remeasured. Longer periods of heating at high temperature were allowed so that the alloys would approach equilibrium more closely and several readings were obtained for each composition. The later values do not differ greatly from the earlier ones but do indicate that the short peritectic horizontal shown in Fig. 9 of the previous report (ISC-45) as being at 1975°C. actually does not exist. Instead, the liquidus line follows a smooth curve of the type to be expected if a solid solution is formed.

The solid solution formed during solidification must break down at relatively high temperatures as the alloys with carbon content from about 0.25 to 3.75 per cent always show two-phase structures even when cooled rapidly from near the melting point. For this reason a tentative boundary of the two phase region has been drawn with its highest point not far below the liquidus line. The close approach of this boundary to the solidus line may be signifi-

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cant in the variation observed in melting point values as the change in phase would probably delay the establishment of equilibrium at the liquidus temperature. The changed constitutional diagram is illustrated in Fig. 6.

As the crystalline structure of ThC_2 is still doubtful, attempts were made to produce a single crystal of the compound to be used in an x-ray examination. The most successful method was relatively simple. Thorium was melted in a graphite crucible and held at approximately 2400°C . for 4 hours. During this period, the thorium reacted with the crucible wall to form carbides. The layer of dicarbide near the wall contained many rather large crystals which could be broken off from the main mass. Several of these crystals were sent to the x-ray laboratory for a determination of their structure.

Apparatus has been constructed for determining the electrical resistance of bars of alloy at high temperature. The specimen chamber belonging to this apparatus is shown with its cover off in Fig. 7. The specimen S is clamped between two large copper electrodes E which lead current into the chamber. The clamping action at one electrode is sufficiently light that the specimen can lengthen or shorten during changes of temperature. Wires W, customarily, of the same composition as the material being tested, press lightly on the specimen at points a short distance to either side of its center. They are connected through vacuum seals to a vacuum tube voltmeter of low range. When measurements are made, simultaneous readings are taken of the current passing through the specimen and the potential drop over the section between the contact wires. From these data, the resistance can be calculated. As the specimen has a small hole in its upper side, its temperature can be measured with an optical pyrometer sighted through the window in the center of the cover C in the manner outlined in ISC-45. Before all runs, the pressure in the specimen chamber is reduced to a few microns.

A number of trial runs have been made and resistance-temperature curves drawn from simultaneous electrical and temperature readings. As a test of the apparatus, a curve was obtained for unalloyed iron. It showed sharp discontinuities in the vicinity of 770°C . and 900°C . corresponding respectively, to the Curie point and the A_3 transformation in iron. The curves for thorium showed changes in slope near 750°C . and 1400°C . These discontinuities suggest transformations that have escaped notice previously but other possible reasons are being sought.

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Fig. 6 - The revised constitutional diagram of the thorium-carbon system.

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Fig. 7 - The apparatus for determining electrical resistance at high temperature

- 1 - cover
- 2 - copper electrodes
- 3 - specimen
- 4 - electrical leads

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