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Vol. II

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THE PRODUCTION OF BERYLLIUM AND ZIRCONIUM

Chairman - A. R. Kaufmann

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SESSION I-B

THE PRODUCTION OF BERYLLIUM AND ZIRCONIUM

Chairman - A. R. Kaufmann
PREPARATION OF CHEAP ALTERNATE FEED MATERIAL
FOR THE MANUFACTURE OF ZIRCONIUM CRYSTAL BAR

H. R. Hoge and Z. M. Shapiro

Abstract

The preparation, directly from zirconium oxide and zirconium carbide, of materials which are suitable for replacing zirconium sponge in the manufacture of zirconium crystal bar is discussed. The reactivity of these materials with iodine is compared with that of zirconium sponge, Bureau of Mines zirconium carbide and Titanium Alloys Manufacturing Company zirconium carbonitride. Two of the materials prepared were applied successfully to the preparation of crystal bar in a small deposition unit.

Introduction

The cost of crystal bar zirconium could be greatly reduced if Kroll process sponge which is presently used as a feed could be replaced by a cheap material. This report presents the results of a survey of some materials which can be prepared from zirconium oxide and be used as feed stock for the manufacture of crystal bar zirconium.

In order to be a satisfactory crystal bar feed, a material must have the following characteristics.

1) It must react readily with iodine to form zirconium tetraiodide.
2) It should react completely with iodine and leave no unreactive residue.
3) It must be able to withstand repeated washings and handlings without powdering.
4) It must not release any gases or contain elements which may be transported to the crystal bar and impair its properties.

Any cheap new feed material for low hafnium iodide zirconium must be made from zirconium oxide since this is the product obtained from the hafnium separation process. Accordingly, two approaches can be made toward the transformation of zirconium oxide into a useful feed material. One is the direct reduction of the oxide with one of the active metals such as aluminum, calcium, or magnesium. Material made by this method would be less costly than material made by the Kroll process since the oxide would not have to be first converted to zirconium tetrachloride. The other approach is to make a zirconium bearing compound which would react readily with iodine to form zirconium tetraiodide. The second approach was chosen for our initial investigations because it was felt that these materials could be produced at the lowest cost.
Reactions Investigated and Method Employed

Kroll and Schlechten (1) in some of their efforts to produce zirconium metal, tried to reduce zirconium oxide with zirconium carbide and concluded that zirconium metal could not be prepared by this method; stable complex products containing zirconium, oxygen, and carbon were obtained. Since it was not the object of this study to produce zirconium metal from the oxide, but rather a compound reactive to iodine, Kroll's experiments were repeated under slightly different conditions. The product obtained from this reaction was a hard metallic looking substance containing on the average less than four per cent carbon. X-ray analyses indicated that large amounts of free zirconium were present as well as zirconium carbide and zirconium oxide. From the chemical analyses it was calculated that 45 per cent free zirconium was present.

In addition to the reaction of zirconium oxide with zirconium carbide, Kroll and Schlechten studied the reaction of zirconium oxide with two moles of carbon. Although they were able to effect only a partial reduction, as in the case above, this reaction was also studied in an effort to produce a suitable feed. Unlike Kroll and Schlechten, however, who ran their reactions at temperatures no higher than 1300 degrees Centigrade, these studies were extended to temperatures in excess of 2200 degrees Centigrade. The product obtained was quite similar in appearance to the product obtained by the reaction of carbide with oxide. Again x-ray analyses indicated that large amounts of free zirconium were present in addition to zirconium oxide and zirconium carbide. On the basis of chemical analysis for carbon and zirconium, it was calculated that 40 per cent of the product was free zirconium.

Other reactions explored in this study were those involving the reduction of zirconium carbide with magnesium oxide and calcium oxide. In both cases the products obtained were again quite similar to those produced by the reaction of zirconium oxide with zirconium carbide.

The reactants used in conducting these studies were prepared in the following manner: The powders were first ball milled together for several hours following which the mixtures were screened and compacted. The compacts were then heated in a vacuum induction furnace, or if a larger amount was needed, in a graphite resistor furnace. The furnace was evacuated to a pressure of less than one micron before heating, however as the reaction proceeded the pressure in the system rose to about one millimeter. If lower pressures could have been maintained during the reactions, products of lower carbon content could probably have been produced.

Fig. 1 is a schematic drawing of the vacuum induction furnace used in these studies. The furnace consists of a silica tube 48 inches long and 11 inches in diameter sealed between two water cooled stainless steel plates by means of neoprene gaskets. The furnace is loaded and unloaded by lowering or raising the bottom steel plate which supports the silica tube, its contents, and the induction coil. Graphite powder is used for
insulating the bottom and sides of the charge, while silica wool is used for insulating the top. The furnace is evacuated through the top plate by means of a 700 liter per second diffusion pump backed up by a 100 liter per second booster and a 27 cubic feet per minute mechanical pump. The furnace is capable of maintaining a temperature of 2500 degrees Centigrade under vacuum.

It has been noted that the chemical and x-ray analyses indicated that several of the materials produced were chemically similar. Fig. 2 is a photomicrograph of the product obtained by reacting zirconium oxide with zirconium carbide. The rounded particles, which are probably a form of zirconium carbide, have a hardness of 1400 Vickers hardness number, while the matrix, which is probably a form of zirconium oxide, has a hardness of 800 to 900 Vickers hardness number. A photomicrograph of the product obtained by reacting zirconium oxide with carbon is shown in Fig. 3. Again the rounded particles have a hardness of 1400 Vickers hardness number and the matrix a hardness of 600 to 700 Vickers hardness number. In general it can be seen that the two structures are quite similar.

Iodination Rate Studies

Apparatus and Method

The relative reactivities of the various products with iodine were determined in the apparatus shown in Fig. 4. In order to minimize the effect on the rate of reaction of variations in surface area, samples were crushed and screened to a given mesh size, and approximately the same volumes were used in each case. The sample and iodine were placed in zirconia boats which were then weighed and located at the opposite ends of a pyrex tube. The tube was sealed at the larger end, evacuated and then sealed at the constriction. The sealed tube was placed into two adjacent split tube resistor furnaces, such that the sample was in one furnace and the iodine in the other. The temperature of the furnace surrounding the iodine, determined the iodine pressure in the system, while the temperature of the furnace surrounding the sample determined the reaction temperature. After one hour at temperature, the tube was removed from the furnace, cooled, and opened. The unreacted portion of the sample was then washed with dilute hydrochloric acid, dried and weighed. The weight loss of the sample was used as an index of the relative reactivities of all the materials.

Iodination Rate of Zirconium Sponge

Iodination rate studies were carried out on zirconium sponge at several temperatures and iodine pressures. These results were used as standards for the comparison of the reactivities of the various samples.
Fig. 5 is a plot of the weight loss of zirconium sponge versus iodine pressure at various temperatures. It can be seen that at low reaction temperatures the pressure has a pronounced effect upon the rate of reaction, whereas at higher temperatures the pressure has relatively little effect upon the rate of reaction.

Fig. 6 is a plot of the weight loss of zirconium sponge versus reaction temperature at various iodine pressures. It will be noted that the sensitivity of the reaction rate to temperature decreases with an increase in iodine pressure.

Iodination Rate of Zirconium Carbide

A similar series of experiments was run on zirconium carbide. A plot of weight loss versus iodine pressure at several temperatures is shown in Fig. 7. Although the points are quite scattered, it is apparent that the carbide is considerably less reactive than zirconium sponge.

Fig. 8 shows the relative rates of iodination of Bureau of Mines zirconium carbide, Titanium Alloys Manufacturing Company zirconium carbonitride, and Westinghouse zirconium carbide. It can be seen that the rate of iodination of the Westinghouse zirconium carbide is slightly greater than that of the other carbides. Since an attempt made to produce crystal bar from Westinghouse zirconium carbide was without success, it is highly unlikely that crystal bar could be made from Bureau of Mines zirconium carbide or Titanium Alloys Manufacturing Company zirconium carbonitride.

Iodination of Low Carbon Carbides

Since preliminary studies indicated that the reactivities of all the low carbon carbides (new materials) are similar regardless of the method of preparation, the iodination of the cheapest product, zirconium oxide, which was reacted with two moles of carbon, was studied more exhaustively than the other products. A plot of the weight loss of this material versus iodine pressure at several temperatures is shown in Fig. 9. The results are quite similar to those obtained with sponge, except that the reactivities do not appear to be as temperature sensitive. Fig. 10 is a plot illustrating the relative reactivities of carbide, new material (low carbon carbide) and sponge. Note that the iodination rate of the new material is of the same order of magnitude as that of sponge.

Variation of Reactivity with Free-Zirconium Content

In studying the reactivity of the various materials to iodine, it became evident that the reactivity increased with an increase in the
quantity of free zirconium present in these materials. This is illustrated in the graph shown in Fig. 11 in which the carbon content of the materials is plotted against their weight loss at 500 degrees Centigrade and at several different iodine pressures. Because the carbon analyses are much more reliable than the analysis for free zirconium, the carbon contents are used as an index of the amount of free zirconium present in the material, the assumption being made that the amount of free zirconium increases as the amount of carbon decreases.

Production of Crystal Bar

Based on the survey outlined above of the relative reactivities of the various materials, two of these materials were prepared in sufficient quantity for a study of their applicability as crystal bar feeds. Fig. 12 is a photograph of one of the six bars produced from these materials. The feed for the bar pictured was the product of the reaction of zirconium oxide with two moles of carbon, however other bars were made from the product of the reaction of zirconium oxide with zirconium carbide and mixtures of the two materials. As a more severe test of their applicability as crystal bar feeds, the materials were used, washed, and reused. This was accomplished with complete success.

The bar shown in Fig. 12 grew at approximately 80 per cent of the normal rate of growth using zirconium sponge as feed. All six crystal bars were grown at a filament temperature of 1350 degrees Centigrade and a bath temperature of approximately 300 degrees Centigrade. The carbon contents of these bars ranged between .02 and .05 per cent as compared to .02 for crystal bar prepared from sponge. The nitrogen contents of the bars were normal except in the cases where leaks developed during the runs. All of the bars, except those containing abnormal quantities of nitrogen, were found to have satisfactory corrosion resistance in 600 degree Fahrenheit water after fourteen days.

Conclusion

Although the work outlined above represents only a preliminary survey of possible cheap alternate crystal bar feed materials, it does serve to illustrate that such materials can be prepared in a practical manner and that further work along these lines may be very fruitful. Even though the methods of preparing the feeds discussed above were not thoroughly studied and developed, they could be prepared even now for only about fifty cents per pound as compared to about five dollars per pound for sponge.

Acknowledgment

This work was done under Atomic Energy Commission Contract AT-11-1-GEN-14.

Bibliography

Fig. 1
Vacuum Induction Furnace

1. Sight Tube and Sight Tube Shield
2. Water Cooled Steel Top
3. Stainless Steel Baffles
4. Water Cooled Gasket Well
5. Wood Supporting Frame
6. Silica Wool
7. Silica Tube
8. Split Graphite Cylinder
9. Graphite Powder
10. Graphite Baffles
11. Graphite Crucible
12. Induction Coil
13. Charge
14. Granular Graphite
15. Water Cooled Steel Plate
16. Scissors Jack
17. Movable Platform

TO VACUUM
Fig. 2
Product from the Reaction ZrO$_2$ + ZrC
250X

Fig. 3
Product from the Reaction ZrO$_2$ + 2C
250X
IODINATION APPARATUS

Fig. 4
Fig. 5
Fig. 6

IODINATION RATE OF ZIRCONIUM SPONGE

WT. LOSS OF ZIRCONIUM SPONGE (gms)

TEMPERATURE °C

0 100 200 300 400 500 600 700

10

1.0

0.1

0.01

0.001

679 mm
394 mm
217 mm
157 mm
111 mm
45 mm
15 mm

15 mm
45 mm
111 mm
157 mm
217 mm
394 mm
679 mm

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Fig. 7
Fig. 8
Figure 9: Iodination Rate of ZrO₂ + 2C

VAPOR PRESSURE OF IODINE (mm Hg)

WT. LOSS OF CHARGE (gms)
Fig. 10

The graph shows the vapor pressure of iodine in mm Hg as a function of weight loss of the charge in grams. The materials and conditions are labeled as follows:

- Zr SPONGE
- ZrO₂ + 2C
- ZrO₂ + 3C

The data is presented for iodination materials at 500°C.
Fig. 11

1. BUMINES CARBIDE
2. WAPD CARBIDE
3. ZR O₂ + 2 C
4. ZR O₂ + 2 ZR C
5. ZRC + MgO
6. ZR

Wt. Loss of Charge (gms) vs. % Carbon

45.5 mm IODINE PRESSURE
217 mm IODINE PRESSURE
679 mm IODINE PRESSURE

IODINATION RATE vs. CARBON CONTENT AT 500°C
A SYSTEMATIC STUDY OF THE DEPOSITION PROCESS FOR IODIDE ZIRCONIUM

Z. M. Shapiro

Abstract

The results of a systematic study of factors influencing the deposition process for iodide zirconium are discussed. The factors studied include filament temperature, bath temperature, quantity of iodine or zirconium tetraiodide introduced, type and condition of the feed material and the effect of the presence of inert gases in the deposition vessel.

Introduction

Although the iodide deposition process was invented 27 years ago and is now one of the two principal processes currently used for the production of ductile zirconium, relatively little was known about the factors governing the process. The work discussed in this report was undertaken to fill this gap in our knowledge and understanding of this process.

Description of the Apparatus and Its Operation

All of the studies made in connection with this project were carried out with the deposition unit illustrated in Fig. 1. It is 12 inches in diameter and four feet tall, and constructed mainly of Hastelloy B. However, the internal portion of the electrodes, and the sponge retaining screen are molybdenum.

The unit operates in the following manner: The space between the retaining screen and the vessel is filled with zirconium sponge approximately 90 to 100 pounds. A bottle containing approximately one and one-fourth rounds of zirconium tetraiodide, which has been previously evacuated and sealed is suspended from a small molybdenum wire stretched between a holder attached to the head and one of the electrodes. A zirconium filament 80 mils in diameter and five feet long is shaped in the form of a hairpin and suspended from the two electrodes through molybdenum transition tips.

The head is sealed to the tank by means of a .030 inch gold gasket and the vessel is evacuated to a pressure of $10^{-5}$ millimeters mercury while being heated in a salt bath to about 250° to 280°C.
Following the evacuation, the valve is closed and the bottle of zirconium tetraiodide is shattered by remotely dropping it to the bottom of the tank. The filament is then heated to the proper temperature by passing a current through it. In the process the zirconium iodide vaporizes, and some of it impinges on the filament where it decomposes and deposits zirconium and releases iodine. The iodine then migrates back to the sponge and reforms more zirconium iodide. Thus by countless repetitions of this process the iodine carries the zirconium from the crude and deposits it on the filament.

In order to minimize any effects which might have been due to variations in the feed material from run to run, a large batch of sponge was thoroughly mixed and used as initial feed and replenishing feed in all the experiments. In addition, the sponge was screened from run to run, and definite proportions of each size range were used in making up each batch. Only about 8% of the feed was consumed in each run, and this was replenished from the unused stock.

Unless otherwise indicated, approximately 540 grams of zirconium tetraiodide were used in each experiment. This was carefully leached in benzene to remove all traces of iodine just prior to each experiment.

The filament temperature was maintained at a constant value during its growth by holding the current and voltage on a curve obeying the relationship

\[ K = E I^{1/3} \]

This expression is derived by assuming that all the power put into the filament is lost by radiation, and by equating the electrical power input to the fourth power law. \( K \) varies with filament length and temperature. Its value was determined experimentally.

Experimental Results

Effect of Filament Temperature on the Rate of Deposition

The first study undertaken was the determination of the effect of variation of filament temperature on growth rate at constant bath temperature. The results are illustrated in Fig. 2. The conductivity is plotted against time at various filament temperatures, since the conductivity is proportional to the cross-sectional area, which is proportional to the weight. It will be noticed that there is a regular increase in growth rate with filament temperature. This is due principally to a regular increase in the equilibrium iodine pressure at the filament which increases the overall diffusion rate.
Probably the most striking thing about this plot is the constant rate of growth at any given temperature. This clearly demonstrates that the decomposition step cannot be the rate controlling one, for if it were, the increased area presented for decomposition as the growth proceeds would most assuredly influence the rate proportionately. The only other possible rate controlling steps are (1) the rate of movement of the gases to and from the filament, i.e. diffusion and (2) the rate of reaction of the liberated iodine with the sponge. Which of these is the rate controlling step appears to be a function of the type of feed material and the rate at which it reacts, as will be demonstrated later.

Fig. 3 illustrates how the growth rate of the bar, expressed as the change in conductivity of the bar per unit time, varies with temperature. Notice how the rate levels off at 1400°C. This levelling off is most probably due to a shift in the equilibrium constant of the iodide formation reaction at the sponge in the direction of decomposition as the surface of the sponge facing the filament becomes hotter.

Variation of Bar Structure with Filament Temperature

In making this rate study it was found that the external structure of bar varies progressively with growth temperature as illustrated in Fig. 4. Bars grown at a low temperature have well defined, large, hexagonal, crystals while those grown at higher temperatures became progressively more spiney as the filament temperature was increased. This phenomenon appears to be similar to that of crystallization of a salt from solution, in that the crystals are large when crystallization is slow and small when crystallization is rapid.

Variation of Growth Rate with Feed Material

Fig. 5 shows how the growth of crystal bar under identical conditions varies with the kind and condition of the feed material. Since the diffusion conditions in all cases should be almost identical, this experiment clearly demonstrates that the reaction of the feed material can be rate determining. Notice that the rate increases with increased surface area. It will also be noticed that the initial rate of growth with the chopped up crystal bar in both the etched and unetched conditions is greater than the final rate. This is probably due to the progressive masking of some of the feed surface with iodides as the deposition progresses. This effect would not be important in the case of the sponge because the surface area is so much greater than that of the chopped up crystal bar.
Effect of Inert Gases on Growth Rate

Shown in Fig. 6 is the effect on the growth rate of the addition to the vessel of an inert gas under various pressures. Notice that the initial slopes in all cases are very much the same, and that these are reduced with the addition of the gas. This demonstrates how in this case diffusion is rate determining since the addition of the gas has changed the feed in no way other than in the frequency of collision of the iodine with it.

Fig. 7 shows how the rate falls off from the normal with the addition of argon.

Variation of Growth Rate with Bath Temperature

In Fig. 8 is shown the variation of filament growth with time at various bath temperatures. Note that the 160°C and 200°C curves have breaks in them at approximately 5.5 kilowatts where the slope increases. This may illustrate that the internal sponge temperature must reach a certain point before the reaction can proceed at its maximum rate.

The variation of growth rate with bath temperature is shown in Fig. 9. The sharp rise in the deposition rate is probably due to an increase in the vapor pressure of the iodide with increasing bath temperature. The fact that the curve goes through a maximum and then starts to fall is probably due to a shift in the equilibrium at the higher sponge temperatures in favor of the decomposition of the iodides at the sponge.

Reaction of Sponge as a Function of Position in the Sponge Bed

Since the inner surface of the sponge bed facing the wire is hotter and more accessible to the iodine than the sponge behind it, it was suspected that this surface contributed most to the growth of the bar. This was demonstrated by two experiments designed to determine the reactivity of pieces of sponge relative to their position in the bed. In these experiments a small piece of titanium was inserted as a tracer, and the weight loss of the titanium was used as an index of its reactivity relative to a particular location in the bed. In the first experiment, the titanium was placed adjacent to the wall of the tank in the same plane as the legs of the filament, whereas in the second, the titanium was placed adjacent to the retaining screen. In the case where the titanium was adjacent to the wall, only 80 milligrams were lost during a 44 hour period. Analysis of the bar indicated only a slightly higher than normal titanium content with no particular distribution as a function of position.
However, in the case where the titanium was adjacent to the screen, the titanium lost four grams -- a fifty-fold increase. Analysis of the bar revealed a sharp gradation in titanium content as a function of position from the source as shown in Fig. 10. This experiment is also significant in that it reveals what sort of impurity distribution can be expected in the bar if a bad piece of feed is in the bed.

Variation of Effective Growth Time with Varying Amounts of Zirconium Tetraiodide

If the quantity of zirconium tetraiodide introduced in the deposition vessel is varied, and all other conditions are held constant, it is found that growth proceeds along the same slope, but that the bar stops growing after a certain period of time, the length of which increases with the introduction of increasing quantities of zirconium tetraiodide. This is illustrated in Fig. 11. If the effective growth time, as indicated by the arrows in Fig. 11, is plotted against the quantity of zirconium tetraiodide added, it is found (Fig. 12) that the effective growth time is directly proportional to the quantity of zirconium tetraiodide added, or in other words, the rate at which the active carrying agent is removed from the deposition process is constant. Furthermore, this rate is independent of the filament diameter. From this it can be concluded that the rate of the reaction by which the carrying agent is removed from the deposition process is independent of the filament diameter. This does not, however, exclude as one of the possible processes for the removal of the carrying agent, a reaction at the filament whose rate is governed by diffusion. Two other possible processes by which the carrying agent can be removed are (1) a reaction with the sponge to form a non-volatile product or (2) the diffusion of the material through the sponge to the comparatively cold wall of the vessel where condensation can occur.

Summary

In summary, the following general conclusions can be drawn from this work: (1) The decomposition of the iodide on the wire is not the rate determining step for the process. (2) In general, the rate of diffusion is probably rate determining, but the rate of reaction with the feed can be rate determining depending on the type of feed. (3) The rate of removal of carrying agent from the deposition process is constant and independent of the filament diameter.

Acknowledgement

This work was done under Atomic Energy Commission Contract AT-11-l-GEN-14.
Fig. 1
12" DEPOSITION UNIT

1 Cold Trap
2 Bottle
3 Valve
4 Electrode
5 Tank Cover
6 Inner Gasket
7 Tank
8 ZrLi Bottle and holder
9 Stud
10 Immersion Tank
11 Electrode Tips
12 High Vacuum Pump
13 Thermocouple
14 Coil
15 Flange
16 Flange
17 Gasket
18 Gasket
19 Gasket
20 O-Ring
21 O-Ring
22 Bellows
23 O-Ring
24 to 35 Hardware

CONFIDENTIAL
DECLASSIFIED
Fig 3
Fig. 4. PHOTOGRAPH SHOWING APPEARANCE OF CRYSTAL BAR GROWN AT VARIOUS TEMPERATURES
GROWTH OF CRYSTAL BAR VS TIME
WITH VARIOUS TYPE FEEDS
WIRE 1450°C   BATH 285°C
12" UNIT—SINGLE HAIRPIN FILAMENT 63.5" LONG

Fig. 5
EFFECT OF INERT GASES ON CRYSTAL BAR GROWTH - 12" UNIT -
SINGLE HAIRPIN FILAMENT - 63.5" LG - BATH TEMP 280°C - WIRE TEMP 1450°C

Fig. 6
EFFECT OF ADDITION OF INERT GAS ON GROWTH RATE
12" UNIT - SINGLE HAIRPIN FILAMENT - 635° LONG
WIRE TEMPERATURE 1450°C - BATH TEMPERATURE 280°C

PERCENTAGE NORMAL GROWTH RATE WITHOUT GAS
PRESSURE OF ARGON ADDED TO VESSEL - MM
0 10 20 30 40 50 60 70 80 90 100
0.0 0.5 1.0 1.5
CURVE NO. 2873-9280

Fig. 7
CRYSTAL BAR GROWTH VS TIME AT VARIOUS BATH TEMPERATURES
12° UNIT - SINGLE FILAMENT - WIRE TEMPERATURE 1450° C - WIRE LENGTH 63.5°

Fig. 8
DISTRIBUTION OF Ti IN Zr CRYSTAL BAR
12° UNIT - SINGLE HAIRPIN FILAMENT
BATH TEMPERATURE 200°C - WIRE TEMPERATURE 1450°C

FINAL AVERAGE BAR DIA. = 21 MM (V/E = 115.5)
EFFECTIVE GROWTH TIME = 44 HOURS

EXPERIMENTAL DISTRIBUTION OF Ti ON LEG CLOSEST TO SOURCE
EXPERIMENTAL DISTRIBUTION OF Ti ON LEG FARTHEST FROM SOURCE

Fig. 10
CRYSTAL BAR GROWTH VS TIME WITH VARIOUS QUANTITIES OF ZRI4
12" UNIT-SINGLE HAIRPIN FILAMENT-635" LONG-BATH TEMP 285°C WIRE

TEMP 1450°C

CONDUCTIVITY, MIHOS

TIME-HOURS

CURVE NO. 366576

x - 354 GMS
o - 252 GMS
- 154 GMS
- 52 GMS
EFFECTIVE GROWTH TIME vs WT OF ZR 14 INTRODUCED

12" UNIT - SINGLE HAIRPIN FILAMENT 63.5" LONG
WIRE TEMPERATURE 1450°C - BATH TEMPERATURE 285°C

Fig. 12
A THERMODYNAMIC STUDY OF THE VAPOR-PHASE REDUCTION OF ZIRCONIUM TETRACHLORIDE BY MAGNESIUM

R. H. Giffen and Z. M. Shapiro

Abstract

A new process for the production of inexpensive zirconium, suitable for arc-melting, has been investigated experimentally and studied thermodynamically. The reaction between zirconium tetrachloride and magnesium in the vapor state is exothermic, and zirconium can be produced in good yield as a powder, a sintered mass, or as a melt. The metal obtained is free of magnesium and magnesium chloride when the heat of the reaction raises the temperature of the reaction zone above the dew point of magnesium chloride.

Introduction

Since the first of July, 1950, the Bureau of Mines has produced approximately 200,000 pounds of clean zirconium sponge by the Kroll process. This process consists essentially of a fourteen hour reaction between gaseous zirconium tetrachloride and molten magnesium at a total pressure of one atmosphere. The reaction produces solid zirconium and liquid magnesium chloride. The zirconium is separated from the bulk of magnesium chloride by heat, under reduced pressure, for about forty hours, such that the magnesium chloride drains from the sponge while the magnesium boils away to a condenser. The sponge is then chipped out of the vessel, graded according to quality by inspection and analysis, and hand cleaned.

Although this process is satisfying the current demand for primary zirconium, several costly disadvantages are recognized:

1) The magnesium must be of premium purity, since non-volatile impurities tend to remain with the sponge.
2) Long process times and much labor and equipment are involved in the production and separation of the sponge from the other materials.
3) Some magnesium and magnesium chloride remain in the sponge as impurities which must be removed prior to arc-melting.
4) The quality of the sponge is not uniform within any one batch, varying also from batch to batch.
5) The yield of clean sponge from zirconium tetrachloride is about sixty-five per cent based on the zirconium content.
6) The current cost of clean zirconium is about $15 per pound.
Vapor-Phase Reduction

A new process, which may overcome these disadvantages, is the vapor-phase reduction of zirconium tetrachloride by magnesium. In essence, the proposed process consists of the reaction between zirconium tetrachloride vapor and magnesium vapor, flowing into a reaction chamber, at a temperature and pressure such that the magnesium chloride, formed as a product of the reaction will not condense.

The specific advantages of this process are:

1) The magnesium need not be of premium purity since non-volatile impurities remain in the boiler.
2) Process times should be short, since the reaction is homogeneous, and since the final product is directly obtained.
3) No magnesium nor magnesium chloride should contaminate the zirconium because it can be collected without condensing these compounds.
4) The quality of the zirconium should be high and hence uniform at all times.
5) The zirconium may be recovered as a powder, as a sintered mass, or as a melt, depending upon the temperature.
6) The cost should be lower than for sponge zirconium because less equipment and shorter process times are possible.

Brush Beryllium Company has experimented with vapor-phase reductions. They produced metal powders by condensing both the products and excess reactants, and subsequently leaching the mass to recover the metal.

Preliminary experiments to investigate the feasibility of the process were made at the Westinghouse Atomic Power Division. The first attempt was unsuccessful because the zirconium tetrachloride stopped subliming after the small amount touching the walls of the chamber was vaporized away.

Titanium tetrachloride, a liquid, was then substituted for zirconium tetrachloride rather than build a sublimer at this early stage. The use of a "stand-in" is justified by the fact that the free energies of reaction are in the same range. With this system, a small amount of a black powder was obtained before the feed nozzles clogged. An X-ray analysis of this powder showed it to be metallic titanium.

This degree of success warranted a two-fold attack on the problem:
1) A versatile apparatus was constructed with which controlled experiments could be performed using titanium tetrachloride as a stand-in. These experiments would provide useful information regarding appropriate techniques and equipment for future work.
2) A mathematical analysis of the thermodynamics of the zirconium reaction was made in order to determine the appropriate operating conditions and the potential yields of zirconium.

This paper gives the results of the thermodynamic study.
For the study of the zirconium system, the principal reaction was assumed to be that given in Equation 1.

\[
\text{ZrCl}_4(g) + 2\text{Mg}(g) \rightleftharpoons \text{Zr}(s) + 2\text{MgCl}_2(g) \tag{1}
\]

The equilibrium constant, \( K \), was related to the molar fraction of the zirconium in the reduced state, \( x \), by assuming that the activities of the gaseous components may be satisfactorily approximated by their mole fractions, and that the reduced zirconium was at unit activity.

\[
K = \frac{(1+2n-x)(x^2)}{(1-x)(n-x)^2} \tag{2}
\]

In Equation 2, the stoichiometric amounts of magnesium are represented by \( n \); and when \( n \) equals 2, for example, there are four moles of magnesium per mole of zirconium, so that 100 per cent excess magnesium is available over that required for complete reaction.

Values of the equilibrium constant were calculated from enthalpy and entropy data which were obtained from the literature and extended by calculation into areas where such data are missing. The standard states were chosen as the pure components at the temperature and pressure of the system. The basis for calculation was one gram molecular weight of monomolecular zirconium tetrachloride, as in Equation 1. The calculated values of the equilibrium constant were plotted as a function of temperature at the several pressures chosen for calculation as illustrated in Fig. 1. The range of temperatures at each pressure is limited at the lower end by the boiling temperature of magnesium chloride, and at the higher end by the melting point of zirconium. Outside this temperature range the reaction given above does not apply.

For a given total pressure and proportion of magnesium, the molar yield of reduced zirconium at various temperatures was determined from Fig. 1 and a working plot of Equation 2 which is the relation between the equilibrium constant and the molar yield. Fig. 2 illustrates the equilibrium conditions at 1.00 atmosphere total pressure. Observe that the yield is decreased at higher temperatures -- a typical phenomenon among exothermic reactions. Note too that the yield is increased by higher proportions of magnesium -- as is to be expected.

Fig. 3 illustrates the same type of plot, but at a total pressure of 0.10 atmosphere. There are two differences to be noted here: (1) the lower temperature has been decreased due to the reduced pressure; and (2) the yield at any given temperature has also been reduced. Fig. 4 shows the extension of the same trends to a lower pressure of 0.01 atmosphere.
Since the reaction is exothermic, the temperature attained by the reaction will increase with its progress toward equilibrium. A heat balance was computed for the general case to relate the temperature rise accompanying the reaction to the molar yield of reduced zirconium produced by the reaction under various conditions. It was found that the temperature rise was essentially linear with molar yield, and practically independent of the temperature, as illustrated by Fig. 5. The points plotted on the graph are the calculated values, but for each proportion of magnesium a straight line was intentionally drawn between the end points. Notice that no large deviations from the line are evident.

This plot was used to determine the adiabatic reaction temperatures. Fig. 6 shows a typical graphical solution for the adiabatic reaction temperature. For reactants entering the system at 1000 degrees Kelvin, the molar yield is zero, and as the reaction proceeds, the calculated temperature of the reacting materials and products rises approximately linearly until equilibrium is established at the intersection of the heat balance line with the equilibrium curve, where the temperature is seen to be approximately 2000 degrees Kelvin and the molar yield is about 60 per cent. Other initial temperatures will produce different results, and other proportions of magnesium will alter the end point.

Furthermore, heat losses from the reaction zone to its surroundings will change the conditions. Fig. 7 shows the effect of such heat losses on the reaction temperature and on the yield. The heat losses indicated thereon represent the percentage of the heat of reaction which is lost to the surroundings. Complete loss of heat of reaction would be represented by a vertical line -- an isothermal reaction.

Since no kinetic data are available to indicate the speed with which this reaction will reach equilibrium, and since the heat losses for these conditions are difficult to estimate, a set of operating conditions must be chosen somewhat arbitrarily. Then experiments under these conditions will provide the answers to the above problems.

With these considerations in mind, a system operating at 0.10 atmosphere total pressure and feeding the reactants at the boiling point of magnesium at this pressure, in proportion such that n equals 2, or 100 per cent excess, was selected as a starting point.

Fig. 8 shows the results of several predictions for this system. With no heat losses and assuming equilibrium is attained, the reaction would probably produce liquid zirconium with poor yield. However, if 50 per cent of the heat of reaction were lost, the yield would be 90 per cent at equilibrium and the reaction temperature would drop to 1910 degrees Kelvin. Heat losses of 80 per cent would increase the yield to above 99 per cent at equilibrium and the reaction temperature would be 1500 degrees Kelvin.
Furthermore, if due to unfavorable kinetics, the reaction proceeded to only 80 per cent of the equilibrium amount in each case, the corresponding yields and reaction temperatures would be 49 per cent at 2000 degrees Kelvin, 72 per cent at 1760 degrees Kelvin, 80 per cent at 1430 degrees Kelvin, respectively. It may be pointed out here that the corresponding yield for the Kroll process is about 65 per cent.

Thus by temperature measurements and chemical analyses of experimental runs, the real conditions can be determined, compared with the theoretical, and judged for the possibility of further improvement.

This type of vapor-phase reduction is a new process which may produce inexpensive zirconium of uniformly high quality, adequately suited for arc-melting.
APPENDIX

The reports of Brush Beryllium Company which are of interest in connection with this work are:
Kalischer, P. R. Report BBC-20. 1949
No date.

Data for the thermodynamic calculations was obtained from the following sources:

The calculations were based upon the methods given by:
CORRELATION OF CALCULATED EQUILIBRIUM CONSTANTS WITH TEMPERATURE

FIG. 1
FIG. 2 EQUILIBRIUM YIELD FOR VAPOR-PHASE REDUCTION

FIG. 3 EQUILIBRIUM YIELD FOR VAPOR-PHASE REDUCTION
FIG. 4 EQUILIBRIUM YIELD FOR VAPOR-PHASE REDUCTION

FIG. 5 EFFECT OF EXCESS MAGNESIUM & CONVERSION ON ADIABATIC TEMPERATURE RISE
FIG. 6 EQUILIBRIUM YIELD FOR ADIABATIC OPERATION

FIG. 7 EFFECT OF HEAT LOSSES ON EQUILIBRIUM YIELD
EXCESS MAGNESIUM = 100 PERCENT (n=2)
TOTAL PRESSURE = 0.10 ATM

FIG 8 ANTICIPATED OPERATING RESULTS FOR PROPOSED SYSTEM
THE POWDER METALLURGY OF BERYLLIUM

W. W. Beaver
Brush Beryllium Co.
Cleveland, Ohio

Introduction

The contents of this paper relate to the present production method for producing beryllium reactor parts, all of which fabrication processes are built around powder metallurgy. The information contained here is primarily based on experimental study of the effect of the degree of attritioning on the particle size and the consequent effect of particle size on the fabricating ability and mechanical properties of beryllium metal.

Production Powdering

The procedure for powdering beryllium consists of the multiple chipping of vacuum cast ingots which are made in sizes from 40 to 50 pounds, the size of the chips varying from a very fine powder to chips approximately 5/8" wide, 1/2" long and a few thousandths thick. The powder is then taken to the top of the attrition mill which is shown in schematic in Fig. 1.

The attrition mill consists of two beryllium-lined magnesium plates, one of which is stationary and one rotating. In the middle of the stationary plate there is a hole through which beryllium powder feed is introduced. The powder falls through the attrition mill by gravity and is moved by a series of Rotex shakers over a 200 mesh screen. The powder passing the screen is bottled, while the powder coarser than 200 mesh is moved by the rotary shakers across the inclined screen and is collected for return to the attrition mill. The entire operation is conducted under dry nitrogen having a dew point of around -50°C in an enclosure which is exhausted through a precipitron to avoid atmospheric dispersal of beryllium powder.

The use of -200 mesh powder evolved over a period of time during which it was found that +200 mesh powder was more difficult to hot press than the finer particles. However, during the last few years a number of improvements have been introduced in the production of beryllium metal resulting in a higher product assay than was heretofore available. With this in mind, it was deemed advisable to investigate the fabrication of powder of various particle sizes to determine whether or not powder of coarser size could be used and the value of the finer particles as far as the properties of finished beryllium products were concerned. The economic advantages of using coarser powder would, of course, arise from the
Fig. 1--Attrition Mill
decrease in the number of passes through the attrition mill and the resulting increased production capacity of the equipment. In general, -200 mesh powder takes from 15 to 20 passes through the attrition mill and is produced at a rate of 12 to 15 pounds per hour.

A coarser powder would also be more uniform in that there is no way of controlling the sub-sieve fraction of -325 mesh powder which constitutes at least 50% of the -200 mesh product. Work carried out to examine the sub-sieve size by elutriation and sedimentation methods substantiated this as there was considerable non-uniformity between various -200 mesh lots. In addition, the finer particles have more oxide impurity corresponding to the amount of surface they have exposed, which is inversely proportional to the size of the particle. Table 1 shows the decrease of assay which occurs during the attritioning operation due to oxidation.

Experimental Work

Attritioning

In the special test that was set up, about 500 pounds of chips were attritioned with ten consecutive passes through the mill. A departure from the normal procedure was made here in that the total amount of powder from the first pass was re-attritioned for the second pass and for further passes through the attrition mill, whereas in the normal technique the -200 mesh powder is continually removed. Consequently, for this test, the oxide content for any given powder would be greater in that the -200 mesh portion was re-attritioned several times. The mesh size percentages were determined after every pass and are shown in Table 2.

It is interesting to note that with the first, second and third passes a relatively large amount of -325 mesh powder was produced. Further passes, however, do not increase the amount of -325 mesh powder appreciably, indicating that there is a differential grinding action occurring in the first passes, presumably from such material as is contaminated by a beryllium compound, probably beryllium carbide or ferride. In examining hot pressed compacts made from first fractions of powder, a high density grain boundary constituent is noted which eventually disappears, as far as the radiographic delineation is concerned, as the powder becomes finer. In addition, screenings made of +400 and -400 mesh powder from the first pass analyzed for iron indicate that the -400 mesh powder in the first pass has about twice as much iron and appreciably more silicon than the +400 fraction. Consequently, the removal of a few percent of the total powder as +400 mesh fraction after the first pass is one method of getting some purification of beryllium metal in the solid phase.
TABLE 1 - Be METAL SPECIFICATIONS

<table>
<thead>
<tr>
<th>Determination</th>
<th>Damage Coefficient</th>
<th>Pebbles</th>
<th>Vacuum Castings</th>
<th>Hot Pressed Billets</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be Assay</td>
<td>--</td>
<td>96.0% Min.</td>
<td>99.0% Min.</td>
<td>98.0 Min.</td>
</tr>
<tr>
<td>Be$_2$C</td>
<td>--</td>
<td>1500 ppm Max.</td>
<td>2500 ppm Max.</td>
<td>--</td>
</tr>
<tr>
<td>Al</td>
<td>0.00074</td>
<td>1400 &quot; &quot;</td>
<td>1400 &quot; &quot;</td>
<td>1500 ppm Max.</td>
</tr>
<tr>
<td>B</td>
<td>5.96</td>
<td>2.0 &quot; &quot;</td>
<td>2.0 &quot; &quot;</td>
<td>--</td>
</tr>
<tr>
<td>Fe</td>
<td>0.0039</td>
<td>1300 &quot; &quot;</td>
<td>1500 &quot; &quot;</td>
<td>2000 ppm Max.</td>
</tr>
<tr>
<td>Mn</td>
<td>0.0205</td>
<td>175 &quot; &quot;</td>
<td>200 &quot; &quot;</td>
<td>250 &quot; &quot;</td>
</tr>
<tr>
<td>Ni</td>
<td>0.0069</td>
<td>450 &quot; &quot;</td>
<td>450 &quot; &quot;</td>
<td>500 &quot; &quot;</td>
</tr>
<tr>
<td>Total Danger Summation (TDS)</td>
<td>10.4 Max.</td>
<td>12.0 Max.</td>
<td>12.9 Max.</td>
<td></td>
</tr>
</tbody>
</table>
Table 2 - Particle Size Distribution of Each Pass Material

<table>
<thead>
<tr>
<th>Type of Powder</th>
<th>+20</th>
<th>-20/30</th>
<th>-30/60</th>
<th>-60/100</th>
<th>-100/150</th>
<th>-150/200</th>
<th>-200/250</th>
<th>-250/325</th>
<th>-325/400</th>
<th>-400</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chips</td>
<td>.71</td>
<td>1.05</td>
<td>.10 .87</td>
<td>.36 .78</td>
<td>.25 .82</td>
<td>.9 .02</td>
<td>.4 .04</td>
<td>1.68</td>
<td>1.84</td>
<td>1.37</td>
</tr>
<tr>
<td>1st Pass Be Powder</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>2nd Pass Be Powder</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>3rd Pass Be Powder</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>4th Pass Be Powder</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>5th Pass Be Powder</td>
<td>12.89</td>
<td>18.57</td>
<td>12.63</td>
<td>7.03</td>
<td>8.80</td>
<td>8.62</td>
<td>31.59</td>
<td>.70</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>6th Pass Be Powder</td>
<td>10.68</td>
<td>18.14</td>
<td>12.32</td>
<td>7.03</td>
<td>8.81</td>
<td>8.47</td>
<td>33.75</td>
<td>.72</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>7th Pass Be Powder</td>
<td>7.48</td>
<td>17.05</td>
<td>12.34</td>
<td>7.48</td>
<td>9.34</td>
<td>9.09</td>
<td>36.86</td>
<td>.81</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>9th Pass Be Powder</td>
<td>3.46</td>
<td>13.28</td>
<td>12.80</td>
<td>7.28</td>
<td>10.12</td>
<td>9.88</td>
<td>42.52</td>
<td>.96</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>10th Pass Be Powder</td>
<td>2.2</td>
<td>11.98</td>
<td>11.97</td>
<td>7.14</td>
<td>10.05</td>
<td>10.53</td>
<td>45.56</td>
<td>.89</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>— 200 Mesh Be Powder</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
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</tr>
</tbody>
</table>

Beryllium Oxide in Powder

Mesh Sizes % of Total
Fabrication by Powder Metallurgy

The beryllium powder produced as various fractions was then fabricated by the methods usually used for the production of reactor parts. These have been discussed in more detail in "The Mechanical Properties of Beryllium as Related to Fabrication Processes", but as far as this work was concerned, three processes were involved.

1) The hot pressing of beryllium powder at 1050° to 1100° C. under pressure of 75 psi or greater.
2) The further fabrication of hot pressed beryllium by extruding at 1400° to 1450° C. without canning.
3) The extrusion of canned hot pressed beryllium billet at around 1000° C.

Results

Beryllium powder from the various passes was analyzed as to the BeO content, the specific surface and average particle size attained by a Fisher sub-sieve analyzer (permeability principle), the packing density and the flowability of the powder. Table 3 illustrates these characteristics of beryllium powder, showing the hot pressed grain size and minimum pressure needed to achieve maximum density. These are compared with various normal -200 mesh powders and some recently made -100 mesh powder.

It is believed that the permeability principle of specific surface measurement is satisfactory for attritioned powder in that some earlier work on comparing iron attritioned powder as to specific surface made by resistance to gas flow vs. nitrogen adsorption showed similar values for attritioned powder. However, a reduced or electrolytic powder having appreciable sub-surface pores would have a much greater surface than obtained by permeability measurements. In general, it can be seen that the particle size and BeO content increase as the chip is attritioned, while the packing density and minimum pressure needed to achieve the maximum density decrease.

None of the powders as produced showed any flow, although through a 1/16" diameter orifice, flowability of the -200+325 fraction of the -200 mesh powder was indicated. In general, for a flowing powder, a narrow size distribution combined with a relatively coarse powder is needed. Production-wise, the flowability of the powder is important, as well as initial packing density, especially in fabricating intricate shapes by powder metallurgy. As such, the -200+325 powder seems to be the most satisfactory, as the coarser powders would require higher pressing pressures to reach maximum density.
<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>-200 Mesh</td>
<td>-200+325 Mesh</td>
<td>-325 Mesh</td>
<td>-100 (normal)</td>
<td>-100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| Packing Density (% of max.) | 1.54 | 1.42 | 1.09 | 1.10 | 1.12 | 1.09 | 1.09 | 1.09 | 1.08 | 1.07 |

| Specific Surface (cm²/m) | 0.17 | 0.18 | 0.18 | 0.18 | 0.18 | 0.18 | 0.18 | 0.18 | 0.18 | 0.18 |

| Average Particle Size (microns) | 7.6 | 9.57 | 11.70 | 12.90 | 14.10 | 15.50 | 16.00 | 16.50 | 17.00 | 17.50 |

| Hot Press Grain Size (microns) | 84 | 61 | 57 | 50 | 38 | 28 | 22 | 17 | 14 | 9 |

| Minimum Hot Pressing Pressure (psi) at 1050°C | 850 | 500 | 425 | 300 | 200 | 100 | 80 | 60 | 40 | 30 |

**Table 3 - Characteristics of Beryllium Powder**
THE POWDER METALLURGY OF BERYLLIUM

The grain sizes of the hot-pressed, warm-extruded and hot-extruded powders are shown in Fig. 2, 3 and 4. In general, the hot-pressed grain size obtained by microstructure analysis is greater than the average particle size obtained by permeability measurements. However, after hot work or cold work and recrystallization, the as-produced grain size is finer. Fig. 5 shows a relation between the specific surface plotted against ultimate tensile strength and tensile elongation for the various production techniques. A number of tensile samples were involved in each examination, as some of the processes, notably those involving hot extrusion, were quite erratic, especially in the finer powders with the better tensile properties.

The relatively surprising straight line relation was found in the hot-pressed powders, as far as ultimate strength was concerned. A similar but more erratic relation was obtained for the percent tensile elongation, but this is not shown here as the maximum tensile elongation obtained did not exceed 5%, while the minimum was not less than 1-1/2%.

Concluding Remarks

Therefore, it may be said that the largest particle size that can be used in order to fabricate attritioned beryllium powder successfully would be -100 mesh in that coarser powders appear to seriously depress the tensile properties. The straight line relation obtained with hot-pressed powder (Fig. 5) is believed to be due more to the increased pressure needed to obtain maximum density, in that lower pressures are needed with finer powders. Consequently, small variations in porosity in the hot-pressed powders are quite important as to their effect on the tensile properties.

In order to reduce the effect of pressure under hot pressing, the finest powder practical must be used. However, as the finer particles have a lower assay and a greater BeO content, a point of diminishing returns is reached at which the BeO content itself is a factor promoting resistance to flow at the hot pressing temperature and the achieving of maximum density. However, from the data shown here, down to an average micron size of 1μ.2, this point does not appear to have been reached.
Fig. 2—Grain size of hot pressed (1050°C) beryllium powder

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DECLASSIFIED
Fig. 3--Microstructures of Extruded (1010°C.) Rod
Fig. 4—Microstructures of Extruded (400°C) Be Powder Annealed at 750°C.
Fig. 5 - Relation of Mechanical Properties and Particle Size of Beryllium Powder
THE MECHANICAL PROPERTIES OF BERYLLIUM
AS RELATED TO FABRICATION PROCESSES

Wallace W. Beaver
Brush Beryllium Co.
Cleveland, Ohio

Introduction

As illustrated in the companion paper, "The Powder Metallurgy of Beryllium," the methods for fabricating beryllium are based on powder metallurgy, and the method for powder production was illustrated therein. Fig. 1 shows the various processes for producing beryllium shapes. In general, these processes depend on pressing or working at temperatures around 300°-500° C., or at 900°-1100° C. These are respectively dubbed "warm" and "hot" processes. Cold compacting is used for making handleable objects for further processing by the warm or hot processes.

The earliest successful process used commercially for the production of large beryllium shapes was hot pressing. Hot pressing is accomplished to a density specification of about 99.5% of theoretical density, which density varies according to the purity of the beryllium used. Table 1 shows the beryllium specifications and actual values found for the commercial grades of fabricated beryllium.

Description of Processes

Hot Processes

In hot pressing, the powder is packed in a thin steel form which is backed up by a thicker, more rigid die. A plate is placed across the top and a load applied on the plate at temperatures between 1000° C. and 1100° C. A vacuum then is applied until an indicated pressure of 25 microns is reached. The beryllium hot pressing unit is shown in Fig. 2, a picture of the hot pressing unit is shown in Fig. 3, and a picture of the pressed billet is illustrated in Fig. 4. Pieces of beryllium approaching 100 pounds apiece have been made by this process, with a density of 1.84 g/cc.

The mechanical properties of beryllium produced by this method related to purity and method of production are shown in Table 2. Here it is illustrated that the effect of the rate of testing follows the general relation in that the greater the testing speed, the higher the ultimate strength and the lower the tensile elongation. The mechanical properties of metal produced by hot pressing are completely isotropic and show no directionality. Unfortunately, this is not true with products of any processes involving cold or hot-worked metal.
Fig. 1 - Fabrication Procedures for Beryllium
TABLE 1 - MTR BERYLLIUM REFLECTOR SPECIFICATIONS

Type of Beryllium - QMV - Hot Pressed (sintered) beryllium powder made from vacuum melted metal by The Brush Beryllium Company.

CHEMICAL COMPOSITION:

<table>
<thead>
<tr>
<th>Element</th>
<th>Specification</th>
<th>Actual Av.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Assay</td>
<td>98.0% Min.</td>
<td>99.2</td>
</tr>
<tr>
<td>Be₂C</td>
<td>0.25% Max.</td>
<td>0.18</td>
</tr>
<tr>
<td>BeO</td>
<td>1.50% Max.</td>
<td>0.9</td>
</tr>
<tr>
<td>B</td>
<td>2 ppm Max.</td>
<td>-0.5</td>
</tr>
<tr>
<td>Al</td>
<td>1500 ppm Max.</td>
<td>500</td>
</tr>
<tr>
<td>Co</td>
<td>2 ppm Max.</td>
<td>-1</td>
</tr>
<tr>
<td>Ca</td>
<td>500 ppm Max.</td>
<td>50</td>
</tr>
<tr>
<td>Fe</td>
<td>2000 ppm Max.</td>
<td>1500</td>
</tr>
<tr>
<td>Li</td>
<td>3 ppm Max.</td>
<td>-0.3</td>
</tr>
<tr>
<td>Mg</td>
<td>3000 ppm Max.</td>
<td>500</td>
</tr>
<tr>
<td>Mn</td>
<td>250 ppm Max.</td>
<td>150</td>
</tr>
<tr>
<td>Ni</td>
<td>500 ppm Max.</td>
<td>175</td>
</tr>
<tr>
<td>Si</td>
<td>700 ppm Max.</td>
<td>500</td>
</tr>
<tr>
<td>Ag</td>
<td>5 Ppm Max.</td>
<td>3</td>
</tr>
<tr>
<td>Zn</td>
<td>150 ppm Max.</td>
<td>-30</td>
</tr>
</tbody>
</table>

TDS SPECIFICATIONS:

Total of all above listed impurities (except Be₂C, BeO, and B) should not exceed 15. Actual average = 11.5 without B; 16 with B.

CORROSION TEST SPECIFICATIONS

All fabricated QMV pieces to be autoclave tested at 250° C. (482° F) for 96 hours. Tendency to crack, spall, blister, splinter, or pit excessively shall be cause for rejection.

DENSITY:

1.84 Minimum g/cc

RADIOGRAPH

All pieces are to be radiographed, and evidence of any crack or inhomogeneity shall be cause for rejection.
Fig. 2 - Apparatus for Hot Pressing Beryllium (Schematic)
Fig. 3 - Apparatus for Hot Pressing Beryllium
### TABLE 2 - MECHANICAL PROPERTIES OF HOT PRESSED BERYLLIUM

<table>
<thead>
<tr>
<th>Property</th>
<th>QPT</th>
<th>QRM</th>
<th>QMV</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ultimate Tensile Strength, psi</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.01&quot;/min. strain rate</td>
<td>35,500</td>
<td>32,900</td>
<td>41,500</td>
</tr>
<tr>
<td>0.10&quot;/min. strain rate</td>
<td>38,500</td>
<td>36,400</td>
<td>45,200</td>
</tr>
<tr>
<td>1.00&quot;/min. strain rate</td>
<td>39,700</td>
<td>39,700</td>
<td>49,300</td>
</tr>
<tr>
<td><strong>Tensile Yield (0.2%), psi</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.01&quot;/min. strain rate</td>
<td>28,600</td>
<td>30,400</td>
<td>30,500</td>
</tr>
<tr>
<td>0.10&quot;/min. strain rate</td>
<td>32,900</td>
<td>35,600</td>
<td>32,100</td>
</tr>
<tr>
<td>1.00&quot;/min. strain rate</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td><strong>Tensile Elongation, %</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.01&quot;/min. strain rate</td>
<td>2.2</td>
<td>1.1</td>
<td>2.7</td>
</tr>
<tr>
<td>0.10&quot;/min. strain rate</td>
<td>1.9</td>
<td>1.1</td>
<td>2.3</td>
</tr>
<tr>
<td>1.00&quot;/min. strain rate</td>
<td>--</td>
<td>1.1</td>
<td>2.0</td>
</tr>
<tr>
<td><strong>Tensile Modulus of Elasticity, psi</strong></td>
<td></td>
<td>44.3x10⁶</td>
<td>44.3x10⁶</td>
</tr>
<tr>
<td>psi at 20°C</td>
<td></td>
<td>7,700 psi/°C</td>
<td>7,700 psi/°C</td>
</tr>
<tr>
<td><strong>Temp. Coef. of Modulus</strong></td>
<td></td>
<td>8,500 psi/°C</td>
<td>8,500 psi/°C</td>
</tr>
<tr>
<td><strong>Compression Yield (0.2%) psi</strong></td>
<td>26,000</td>
<td>28,900</td>
<td>24,600</td>
</tr>
<tr>
<td><strong>Compression Modulus, psi</strong></td>
<td>44.2x10⁶</td>
<td>44.2x10⁶</td>
<td>44.2x10⁶</td>
</tr>
<tr>
<td><strong>Poisson's Ratio</strong></td>
<td>0.025</td>
<td>0.028</td>
<td>0.028</td>
</tr>
<tr>
<td><strong>Shear Ultimate (Torsion) psi</strong></td>
<td></td>
<td>31,300</td>
<td>38,900</td>
</tr>
<tr>
<td><strong>Shear Ultimate (Double Shear) psi</strong></td>
<td>40,600</td>
<td>40,600</td>
<td>36,800</td>
</tr>
<tr>
<td><strong>Shear Yield (0.2%) (Torsion) psi</strong></td>
<td></td>
<td>16,600</td>
<td>18,300</td>
</tr>
<tr>
<td><strong>Shear Modulus (Torsion)</strong></td>
<td></td>
<td>19.0x10⁶</td>
<td>21.5x10⁶</td>
</tr>
<tr>
<td><strong>Unnotched Charp Impact (ft.lb.)</strong></td>
<td></td>
<td>--</td>
<td>0.8</td>
</tr>
<tr>
<td><strong>Tensile Impact (ft.lb.)</strong></td>
<td></td>
<td>--</td>
<td>1.1</td>
</tr>
</tbody>
</table>
THE MECHANICAL PROPERTIES OF BERYLLIUM AS RELATED TO FABRICATION PROCESSES

Warm Processes

An illustration of the low temperature extrusion process known as warm extrusion is shown in Fig. 5. In this picture the die is cut away to illustrate the method of lubrication. In Fig. 6 are illustrations of various warm extrusions. As now set up, this method has been limited to a 3\(^\circ\) extrusion die, and rods and shapes somewhat lower than this dimension, depending on their amount of reduction, can be made. The warm extrusion process is primarily advantageous for special shapes in that a relatively close control over finish dimensions can be gained, and little or no machining is needed to achieve final uniformity of dimensions.

Envelope Pressing

Another process involving fabrication of beryllium shapes through powder metallurgy is illustrated in Fig. 7. This finned tube was made by packing beryllium around a central core in a finned die consisting of thin steel. An argon pressure up to 300 psi was placed on the outside, while the central core containing the metal was attached to a vacuum system. The temperature for consolidation is the same as that for hot pressing, namely, about 1050\(^\circ\) C. Very irregular surfaces can sometimes be obtained by this method, which may be attributed to the inability of some grades of beryllium (i.e., -200) to flow. For contoured pressing involving unequal pressures on various parts of the shape in order to get even flow under pressure, a free-flowing powder is needed. As a part of the standard grade (-200) powder, -200+325 mesh portion, is a flowable powder and the properties as far as mechanical strength is concerned are good, effective commercial utilization of the envelope technique may be possible. This also applies to the hot pressing of shapes around special dies in the ordinary hot pressing and sintering procedure. Because of the oxide film around beryllium, little increase in grain size is obtained until a temperature of 1100\(^\circ\) C. is approached. Consequently, the sintering temperatures used in production with the present grade of powders employed can be varied without influencing grain size.

As indicated in Fig. 1, a large number of the more recently developed processes involving fabrication of beryllium are centered around the use of powder as a feed material rather than hot-pressed billets. This is done in order to save metal by fabricating directly to size (rolling, extruding, etc.) instead of machining shapes out of a hot-pressed billet. In the former process the beryllium powder is first cold pressed and then pressed at 425\(^\circ\) C. in the shape of the extrusion or rolling billet. The density-pressure relation in cold pressing and warm pressing is shown in Fig. 8.
Fig. 5 - Die Assembly for Warm Extruding Beryllium
Fig. 7 - Beryllium Finned Tube Fabricated by the Envelope Technique.
Fig. 8 - Pressure Vs. Density Relationship for Compacting -200 Mesh Beryllium at Room Temperature and 425°C
Mechanical Properties of Extruded Beryllium

The mechanical properties of fabricated beryllium are shown in Tables 1, 3 and 4 in relation to hot pressed metal, extruded metal and those produced by miscellaneous fabrication processes. From Table 3 it can be observed that for extruded beryllium a wide variation of properties, especially in tensile elongation, can be achieved. Unfortunately, the rather high values for tensile elongation shown here are only for the direction of extrusion, as in the direction transverse to extrusion the tensile elongation runs between 0-2% and the ultimate tensile strength is about two-thirds of the tensile strength in the direction of extrusion.

The values of the mechanical properties of beryllium metal shown in Table 4 essentially follow the fabrication sequence in that initially cast metal is attritioned to powder, cold pressed into a green billet and repressed to shape at 450° C. Even by pressing at a temperature of only 450° C. the ultimate tensile strength achieved is greater than that of as-cast beryllium. After sintering, the ultimate strength again rises, even though the density may fall, while after extruding the powder to the maximum density the ultimate tensile strength rises greatly, showing a large increase in elongation after recrystallization.

Concluding Remarks

The rather erratic mechanical properties encountered, especially in the worked and recrystallized beryllium metal, may be caused by micro-fissures obtained by overworking during the fabrication process or it may be attributable to segregated zones or stress raisers caused by the impurities.

As normal beryllium has an assay of less than 99.5% beryllium, the principal advantages both for the optimum mechanical properties and for consistency may be looked for only with a higher purity metal.

The hot-pressed metal, although weaker and less ductile than the worked and recrystallized metal, has a number of advantages for specific applications. It is rather uniform in properties, is not subject to anisotropic effects, such as spalling under cycling thermal conditions, and has better corrosion resistance. For reflector parts in nuclear reactors, the hot-pressed beryllium appears to be the better material, but in order to obtain the greatest engineering properties in beryllium, it is believed that these will be found where a combination of high purity, fine grains, and a directionally stressed and recrystallized structure is involved.
<table>
<thead>
<tr>
<th></th>
<th>Hot Pressed</th>
<th>Hot &quot;Warm&quot;</th>
<th>Hot Pressed</th>
<th>Hot &quot;Warm&quot;</th>
<th>Hot Pressed</th>
<th>Hot &quot;Warm&quot;</th>
<th>Hot Pressed</th>
<th>Hot &quot;Warm&quot;</th>
<th>Hot Pressed</th>
<th>Hot &quot;Warm&quot;</th>
<th>Hot Pressed</th>
<th>Hot &quot;Warm&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultimate Tensile Strength, psi</td>
<td>83,600</td>
<td>59,000</td>
<td>79,000</td>
<td>101,800</td>
<td>90,000</td>
<td>81,800</td>
<td></td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>Tensile Yield Strength (0.2%), psi</td>
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<td>55,000</td>
<td>71,600</td>
<td>66,700</td>
<td>45,000</td>
<td>39,500</td>
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<td></td>
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</tr>
<tr>
<td>Tensile Elengation, %</td>
<td>1.0</td>
<td>2.5</td>
<td>6.8</td>
<td>8.8</td>
<td>11.7</td>
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<td>Modulus of Elasticity, psi</td>
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<tr>
<td>Compression Yield (0.2%), psi</td>
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<td>51,600</td>
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<tr>
<td>Compression Modulus, psi</td>
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<td>12.6 x 10^6</td>
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<tr>
<td>Poisson's Ratio</td>
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<td>0.030</td>
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<td></td>
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<td></td>
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<tr>
<td>Shear Strength, psi</td>
<td>66,900</td>
<td>66,000</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Shear Yield (0.2%), psi</td>
<td>31,100</td>
<td>18,100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Twist to Failure, Degrees</td>
<td>160</td>
<td>190</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Unnotched Charpy Impact</td>
<td>20.0 x 10^6</td>
<td>19.4 x 10^6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>Tensile Impact (Ft.-lb.)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

* Strain rate 0.1"/min. - All Tested Longitudinal to Working

** Recrystallization at 750° C

(This is a copy)
<table>
<thead>
<tr>
<th>Process</th>
<th>Yield psi</th>
<th>Ultimate psi</th>
<th>Elong. %</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cast</td>
<td>-</td>
<td>20,000</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pressed at 450° C. at 100 tsi</td>
<td>-</td>
<td>30,300</td>
<td>0.2</td>
<td>1.84 gm/cc</td>
</tr>
<tr>
<td>&quot;</td>
<td>-</td>
<td>28,100</td>
<td>0.2</td>
<td>1.81 gm/cc</td>
</tr>
<tr>
<td>Pressed at 450° C. at 100 tsi and sintered at 1050° C.</td>
<td>-</td>
<td>35,700</td>
<td>0.5</td>
<td>1.77 gm/cc</td>
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<tr>
<td>W.P.-S- Extruded at 4-1 reduction at 400° C.</td>
<td>95,000</td>
<td>110,000</td>
<td>1.0</td>
<td>-</td>
</tr>
<tr>
<td>W.P.-S- E. Recrystallized at 750° C.</td>
<td>65,000</td>
<td>101,300</td>
<td>8.8</td>
<td>-</td>
</tr>
<tr>
<td>W.P.-S- E. Recrystallized at 850° C.</td>
<td>48,000</td>
<td>92,500</td>
<td>11.2</td>
<td>-</td>
</tr>
<tr>
<td>Hot Rolled Sheet (60% reduction at 850-900° C.)</td>
<td>41,000</td>
<td>63,800</td>
<td>3.5</td>
<td>2-3 ft.lbs. unnotched charpy</td>
</tr>
<tr>
<td>Long.</td>
<td>41,000</td>
<td>63,800</td>
<td>3.5</td>
<td>2-3 ft.lbs. unnotched charpy</td>
</tr>
<tr>
<td>Transverse</td>
<td>36,000</td>
<td>44,200</td>
<td>1.8</td>
<td>-</td>
</tr>
<tr>
<td>Remarks</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
THE ROOM TEMPERATURE DEFORMATION OF SINGLE CRYSTALS
AND EXTRUDED RODS OF BERYLLIUM

A. R. Kaufmann and D. H. Woodard

At M.I.T., during the past year, we have been interested in the manner in which the room temperature ductility of beryllium single crystals and hot extruded rods of powder depends upon the orientation of the hexagonal close-packed lattice with respect to the test stress system. For this work, billets were cast in such a manner as to form several large single crystals. Slices of these crystals were cut, machined, etched and their orientations determined. Then by bending these slices, which imposed conditions of tension on the upper side and compression on the lower, the fracture faces were determined crystallographically. It was found that, at room temperature, beryllium fractures most easily on the basal plane. When the basal planes are nearly parallel to the axis of tension, these single crystals fractured along planes at right angles to them. Precise x-ray measurements showed that this fracture plane was a prismatic plane of the type (1120). The normal component necessary for fracture proved to be much higher for the prism planes than for the basal planes. A third type of fracture observed was that which occurred along the interface between twins and the matrix.

Attempts to bend single crystals around any axis which lay within the basal plane resulted in immediate failure without easily observable plastic deformation. However, a torsion specimen, machined with its basal plane at right angles to the axis of torsion, showed amazing ductility before fracture. Jillson,(1) in his study of the deformation of zinc single crystals observed this same ductility. More recently Burke and Hibbard(2) in their paper on magnesium, have described the ease with which the (1120) plane can be bent around an axis which is parallel to the "c" axis. This is shown by the diagram on the right of Fig. 1. If now a series of specimens are cut in such a manner that the specimen edge makes increasing angles with the (1120) plane, it is found that the amount of bending which is possible before fracture goes to a minimum for the bending of the (1010) plane and back to a maximum for a 60° range of cuts. This would be true only if there is competition between the critical resolved shear stress for slip and the normal stress for fracture on the prism planes. The figure on the left of Fig. 1 illustrates this competition. Here, the yield stress is the applied stress which will produce slip on the (1010) prism plane and the fracture stress is the stress which will produce fracture on the (1120) plane. Initial plastic flow and its resultant strain hardening can occur only in the region between the two curves. It must be remembered that in this case, the axis of tension lies within the basal plane. The stress necessary to initiate prismatic slip at room temperature is less than that needed
for basal plane slip. This will be discussed in a future paper.

An awareness of this competition between the applied stress which will produce slip on the (10\(\bar{1}0\)) planes and the applied stress needed for fracture on the (11\(\bar{2}0\)) planes forms the basis for an understanding of the relatively high ductility present in extruded powder rods. Such rods, extruded at M.I.T., have been giving an average measured elongation of approximately 20%.

When straight tensile specimens are made from extruded rods and carried to fracture in tension, the fracture planes make an angle of 60° with the tension axis instead of the normal 90° fracture which one obtains from brittle isotropic materials. Notch specimens made with different notch angles and therefore different radial stress components also fractured at the same 60° angle. There was no evidence in the microstructure of twinning. As fracture for each grain must be either a basal or prism face type, this indicated a strong preferredness in crystallographic alignment of either the basal or prismatic planes.

Previous x-ray studies at M.I.T. have shown that there was not only a strong basal plane alignment in the direction of extrusion but also a strong preferredness for (10\(\bar{1}0\)) plane to lie normal to the extrusion axis. This would mean that (11\(\bar{2}0\)) planes would make angles of 60° with the extrusion axis. Polarized light examination, the techniques of which will be described later, eliminated the possibility that the fracture plane alignment from grain to grain was that of the basal plane. The 60° alignment from grain to grain, therefore, must be of the (11\(\bar{2}0\)) type. This would satisfy the x-ray evidence of a (10\(\bar{1}0\)) texture where the slip angle would be the same but the slip direction would vary from grain to grain. A consideration of Fig. 2 will show that we have here a condition where the normal components for fracture on the (11\(\bar{2}0\)) planes are a minimum and the conditions for shear on the (10\(\bar{1}0\)) planes are an over-all maximum. Therefore, extruded powder rods satisfy the conditions for maximum unidirectional ductility at room temperature.

We would like to present at this point our concept of how this prism face alignment is achieved as a result of extrusion followed by recrystallization. To do this, we would like to describe recent work carried out at M.I.T. on the use of polarized light to determine basal plane orientations of beryllium single crystals. When a polished grain of beryllium is viewed under crossed-nicols, it is seen to go through four cycles of brightness and darkness for a 360° rotation. Extinction, i.e., minimum intensity, occurred when the intersection of the basal plane with the specimen surface coincides or is at right angles to the plane of vibration of the incident light. Furthermore, the magnitude of the maximum intensity depends upon the inclination of the basal plane to the specimen surface; being greatest for an inclination of 90° and least for one of 0°. This is similar to the well-known behavior of an absorbing uniaxial transparent crystal. It is thus possible to observe optically the basal plane alignment and approximate inclination of each grain. Basal plane preferredness of alignment can be measured from the over-all reflection from many grains.

(This is a copy)
With these factors in mind, let us consider a specimen extruded, with a basal plane fiber texture at such a temperature above that necessary to form kink bands that it would form the deformation bands shown in Fig. 3. Here the dark bands are a series of orientations whose basal planes lie close to the plane of the surface of the specimen while light bands have their basal planes close to the vertical. By observing the extinction pattern as the specimen is rotated and by studying sections polished at right angles, it was evident that the deformation bands are formed by the bending of the basal planes as shown in Fig. 4a with the maximum bending occurring at the band edge.

If the extrusion temperature is just high enough for polygonization to occur in the region of greatest bending, microscopically observable sub-grains (polygonized areas) appear in this region (see Fig. 4b and 5). At this stage, the basal and prismatic plane alignments would be very close to those in the original deformation bands. Before the metal can cool, these sub-grains grow through the bands as shown in Fig. 6.

Studies of rods, extruded at lower temperatures and quenched before appreciable grain boundary migration can occur, show a very strong basal plane preferredness of alignment in the direction of extrusion. Some evidence exists which indicates that polygonization is confined to the planes of maximum density i.e. basal planes. That is, there is no polygonization of the prism planes. With grain boundary migration of the polygonized areas, there should be a strong prism face preferredness retained since contiguous prism faces should have low interfacial energy. Spread of orientation through polygonization would thus be confined to the basal plane only.

Under polarized light, it can be easily seen that with continued grain boundary migration, those grains which grow the fastest are those whose basal plane alignment is farthest from the axis of the deformation band. While this would increase the scatter from the ideal (0001) orientation, the basic deformation texture is retained.

Although work during the past year has emphasized the acute dependence of ductility upon the orientation of the hexagonal close-packed lattice and thereby explained the high ductility of our extruded rods, a different approach must be made if the inherent ductility in beryllium rods is to be increased.
References

1. Jillson, D. C.
   JOURNAL OF METALS (Sept. 1950).

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   JOURNAL OF METALS (March, 1952).

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**Figure I**

Orientation dependence of fracture stress and yield stress.
Figure 2

FRACTURE PLANES AFTER EXTRUSION

SLIP DIRECTIONS AFTER RECRYSTALLIZATION

PRINCIPAL SHEAR PLANE
Figure 3: Deformation bands formed by extrusion at 500°C followed by an immediate quench. X250.

Figure 4: Sketch showing: (A) basal plane orientation in a deformation band. (B) The location of new grains in the region of greatest bonding.
Figure 5. Microstructure of a rod extruded at 1750°F and quenched, x250.

Figure 6. Microstructure of a rod extruded at 1850°F, x250.

UNCLASSIFIED

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SESSION II

PHYSICAL PROPERTIES AND ALLOYS OF URANIUM

Chairman - H. W. Russell
APPLICATION OF ALPHA CANNING TO PREPARATION OF SLUGS
FOR ORNL REACTOR

E. J. Boyle*, D. E. Hamby*, F. H. Eckert*

Introduction

Since the start of the Oak Ridge National Laboratory air-cooled, graphite-moderated reactor, there have occurred about 100 ruptures of the aluminum-canned, unbonded fuel slugs. These ruptures are a direct result of air's gaining access to the uranium slug through a break in the aluminum can. Since the reactor operates with a maximum slug-surface temperature of 250°C, the oxidation of the uranium core proceeds at a rapid rate and results in swelling and tearing of the aluminum can. In the case of several ruptures, this swelling has resulted in blockage of the slug channels with overheating of the remainder of the slugs in that channel, thereby causing failure of the entire line of slugs.

In a previous report (1), data were obtained for the causes and solution of the slug-rupture problem. This work has shown that the major cause of slug failure was faulty welds at the end-cap closure. A secondary, but equally important, cause of failure was the penetration of the aluminum can by interdiffusion of uranium and aluminum. The recommended solution to this problem was the use of aluminum-silicon bonded slugs for the following reasons:

1. The welding closure is structurally sounder, since there is a double protection against air leakage into the uranium core by virtue of the fact that there is present an aluminum-silicon layer between the core and the inert-gas, arc-weld bead on the end cap.

2. The uranium-rich compound layer formed on the surface of the uranium core when in contact with molten aluminum-silicon acts as an effective diffusion barrier between the core and the aluminum can.

Experimental Procedure

A. Triple-Dip Canning (2)

In line with the above recommendation, the decision was made to replace the present slugs in the reactor with aluminum-silicon bonded, triple-dip slugs. All production was carried out in the Chemical Department at the Y-12 Plant.

*Metallurgy Division, Oak Ridge National Laboratory

Paper presented at Ames Metallurgy Information Meeting, March, 1952
1. Bronze bath—The machined and etched uranium slugs are immersed in a bronze bath for a period of 44 seconds at a temperature of 725°C.

2. Tin bath—Slugs from the bronze bath are quenched into molten tin at a temperature of 600°C and are held for a period of 40 seconds.

3. Centrifuge—From the tin bath, the slugs are transferred directly to a centrifuge and spun at 650 rpm for a period of six seconds.

4. Aluminum-silicon dip bath—After centrifuging, the slugs are immersed in an aluminum-silicon (11.2% silicon) bath at 600°C and are held for a period of eight seconds.

5. Aluminum-silicon canning bath—After the slugs have been wet with aluminum-silicon in the dip bath, they are transferred to the canning bath where they are inserted into a preheated aluminum can inside of a steel sleeve. Just prior to insertion, the aluminum can is filled with aluminum-silicon by lowering the mouth below the surface of the bath. The final operations are to insert a preheated aluminum cap, which was pretreated with aluminum-silicon, into the end of the can and quench the entire assembly into water.

6. Welding—After cutting end caps to proper length, a weld is made at the end cap-can interface with inert-gas, shielded arc welding.

Two of the standard Hanford inspection tests, i.e., visual inspection and autoclaving, were used. A third Hanford test, the frost test, was eliminated. Finally, a test consisting of holding the slugs for one week at 400°C was employed to determine whether diffusion between the uranium core and the aluminum can would occur.

B. Alpha Canning (3)

Because of difficulties to be discussed later, associated with the triple-dip canning process, it was decided to use the alpha-canning process. This process, so named because all canning operations are carried out at temperatures below the alpha-beta transformation temperature in uranium, consists of the following steps:

1. Beta heat treatment—This step, considered a preliminary step prior to canning, is carried out by immersing slugs in a salt bath at 720--720°C for a period of three minutes. The salt used is Houghton's Liquid Heat No. 980. The technique used in the present work employed slugs machined to size prior to this salt bath treatment, since the slugs had already been machined for the triple-dip process. If the Y-12 Canning Group were starting anew, the salt bath treatment would be carried out prior to machining, as there is some pitting of the slugs during the salt bath treatment.

2. Duplex bath—After chemical cleaning (50% nitric acid) following the salt bath treatment, the slugs are immersed in a duplex bath consisting of a ten-inch thick lead layer at the bottom and a 15-inch
thick aluminum-silicon layer at the top. A cover of Eutectic 190 flux (manufactured by Eutectic Welding Company) is kept on top of the aluminum-silicon layer. The slugs are held for 35 seconds in the lead layer at 600°C, are raised into the aluminum-silicon layer, and are held in this layer for five seconds at 600°C.

3. Aluminum-silicon dip bath--Slugs are transferred from the duplex bath to the dip bath where they are held for 13 seconds at 600°C.

4. Aluminum-silicon canning bath--The time, temperature, and procedure here are exactly the same as for the triple-dip process.

5. Welding--The same procedure is followed as used in triple-dip, canned slugs.

The same inspection techniques, i.e., visual, autoclave, and heat treatment of one week at 400°C, are used as were used for triple-dip, canned slugs.

The furnaces used in the canning line consist of an electrical resistance furnace with a graphite crucible for the salt bath and Ajax-Wyatt low frequency, induction furnaces with rammed linings for the duplex bath, dip bath, and canning bath.

Results and Discussion

A. Triple-Dip Canning

The production of triple-dip, bonded slugs was begun in the Chemical Department at Y-12 in June, 1951. Testing of the first 5,886 slugs for one week at 400°C resulted in diffusion blistering of 18.6%. The external appearance of a typical blistered slug is shown in Fig. 1. The microstructure at the area of a diffusion blister is shown in Fig. 2.

The structure at the can-slug interface in Fig. 2 shows that there is a layer of UA1_3 between the aluminum-silicon and uranium. It will be noted that there is no uranium-rich compound, i.e., U(Al, Si)_3, at the uranium surface. The absence of this layer, which acts as a diffusion barrier, has led to interdiffusion between the aluminum-silicon and/or aluminum layer and uranium to form the UA1_3 layer. The formation of UA1_3 results in an increase in volume and, hence, blister formation. This diffusion can lead to penetration of the can and rapid oxidation of the uranium to form a ruptured area, as shown in Fig. 3.

In the course of investigating the cause of the diffusion blisters in triple-dip, canned slugs, it was found that tin content at the bonding layers had a very significant effect on diffusion blister formation. Two slugs which showed diffusion blistering after heat treatment of one week at 400°C were sectioned, and the bond layers were submitted for examination by spectrographic analysis. Blistered areas and blister-free areas were both examined. It was found that in every case where a blister had formed a high concentration of tin was present; but no
Fig. 1, Typical Diffusion Blisters on Triple-Dip Slug

Fig. 2, Center Section of Typical Diffusion Blister
Magnification 100X
Fig. 3, Can Rupture Caused by a Diffusion Blister
detectable amounts of tin were observed in blister-free areas. In order to obtain a more quantitative idea of the amounts of tin present in blistered slugs, as compared with blister-free slugs, five slugs which had blistered in the seven-day heat treatment at 400°C and five which did not blister were stripped from the cans and the bonding layers removed by filing. Chemical analysis of these samples revealed that the blistered slugs contained from 75 to 300 mg. of tin, whereas non-blistered slugs had less than one mg. of tin.

Since it appeared that localized concentrations of tin were associated with the blistering problem in triple-dip, canned slugs, various techniques were employed to eliminate residual tin on the slugs. These techniques were as follows:

1. Lowering of bronze-bath temperature from 720 to 710°C.
2. Increasing time of slug immersion in aluminum-silicon dip bath from six to 12 seconds.
3. Redesign of fixture which held the slug during centrifuging to permit point contact only between the slug and fixture.

When these changes were incorporated one at a time, a significant decrease was noted in the number of slugs which blistered during the standard heat treatment of one week at 400°C. When, however, a production lot of 550 slugs was made, using the first two techniques but not the last one, 25% of the slugs blistered during the seven-day heat treatment at 400°C. The results of this test made it apparent that the control of tin content in triple-dip slugs during production runs could not be controlled sufficiently well to insure complete freedom from blistering difficulties. At this point in the experimental work it was decided to abandon the triple-dip canning technique and explore the possibilities of using the alpha-canning technique which eliminates completely the use of tin.

During the heat treatment of the lot of 550 slugs described above, a second type of blistering was noted. As may be seen from Figs. 4 and 5, these blisters do not contain diffusion products and may be ascribed to gas formation. It was noted that the aluminum-silicon baths used for preparation of this lot of slugs were made up from virgin ingot which was not preheated prior to melting. Also, the incidence of blisters from heat treatment decreased markedly in the last slugs canned as compared with the first. It was concluded that the trouble arose from hydrogen absorption in the aluminum-silicon baths. This gas was released on heating of the slugs and caused the blisters in question. The well-known techniques for eliminating hydrogen from

*Although no direct evidence was obtained about the mechanism involved, it was felt that localized concentrations of tin probably represented non-wet areas on the slug. These areas would, therefore, not have a barrier layer of U(Al, Si) present; and blister formation would result from diffusion.
Fig. 4, Radiograph of Slugs with Typical Gas Blisters (top) and Typical Diffusion Blisters (bottom)

Fig. 5, Edge of Gas Blister between Aluminum-Silicon and Aluminum Can. Magnification 100X
molten aluminum, i.e., flushing the melt with either nitrogen or chlorine, were employed in several tests and were found to be effective in removing the absorbed hydrogen. The simpler techniques, however, of preventing moisture from entering the bath by preheating the charge and also allowing the bath to stand for a period of approximately 24 hours prior to the start of canning to allow any absorbed hydrogen to diffuse out were equally effective and are used at present.

B. Alpha Canning

As pointed out previously, the decision to investigate alpha canning was made when it was found impossible to control, at a low level, the tin content of triple-dip, canned slugs. A lot of 553 slugs was canned by the alpha process under the following conditions:

1. Beta heat treatment—Three minutes at 730°C in Houghton’s Liquid Heat No. 980
2. Cleaning—Nitric acid (50%) etch
3. Aluminum-silicon duplex bath—35 seconds in lead bath, five seconds in aluminum-silicon. No flux on bath
4. Aluminum-silicon dip bath and canning bath—Standard procedure

After heat treatment of seven days at 400°C, 14.6% of these slugs showed diffusion blisters. It was noted during the canning and by stripping of as-canned slugs that the major difficulty was non-wetting of the slugs by aluminum-silicon in the duplex bath. When blistered slugs from the seven-day heat treatment at 400°C were stripped, it was found that the diffusion blisters were invariably associated with non-wet areas on the slug surface. As pointed out previously, the absence of the U(Al, Si)3 compound layer on the uranium surface, because of non-wetting by aluminum-silicon, invariably leads to diffusion blistering during heat treatment at 400°C.

Various attempts were made to insure that a clean, nonoxidized uranium surface was presented to the aluminum-silicon layer in the duplex bath. These included the following:

1. Electrolytic etching following the salt bath treatment—As beta heat treated and quenched in water, the slugs show a stained surface which is not completely cleaned by a nitric acid etch. Electrolytic etching was found to improve this situation very markedly.
2. Flowing water quench—If slugs from the salt bath treatment are quenched in static water, considerable pitting of the surface by corrosion from the water-soluble salt results. The use of flowing water alleviated this behavior.
3. Redesign of handling tools—The first tools used had a large contact area with the slugs during canning. It was found that the use of point contacts eliminated the oxidation and consequent non-wetting of the slugs in the duplex bath. The oxidation occurred when the slugs
were put into the hot tongs prior to dipping in the aluminum-silicon bath.

4. Use of flux on duplex bath—This was the most important change made and completely solved the non-wetting problem. Eutector 190, aluminum brazing flux (made by Eutectic Welding), was employed as a cover on the aluminum-silicon layer on the duplex bath. This flux—composed of sodium, lithium, potassium, aluminum chlorides and/or fluorides—cleans the uranium surface when the slug is immersed in the duplex bath and results in complete wetting of the slug by the aluminum-silicon. Large numbers of slugs canned with this technique have been stripped and examined for non-wetting. No cases of non-wetting have been observed.

Some difficulty was encountered with crucible erosion at the flux line. The original clay-graphite crucibles had a relatively short life of two-to-three weeks. Low carbon steel crucibles were tried but gave poor service because of reaction with the aluminum-silicon and contamination of the flux cover. The rammed linings in the low-frequency, induction furnaces used at present, however, give very satisfactory service. These furnaces have now been in service for several months and have shown no observable attack from the flux.

The success obtained with the solution of the problem of obtaining complete wetting of the uranium by aluminum-silicon prompted a trial production run of 1,000 slugs using this technique. A heat treatment of three weeks at 400°C of these slugs resulted in a single blister on one slug. A photomicrograph of this blister is shown in Fig. 6. There is some doubt about the cause of this blister, but it appears to be a result of oxidation from a leak in the can or cap rather than diffusion. Fig. 7 shows the structure at the bonding layer of a typical alpha-canned slug. It will be noted that the compound layer is cracked and separated with a layer of aluminum-silicon between the separation. This condition is typical of alpha-canned slugs but, apparently, does not lead to diffusion blistering during heat treatment at 400°C, since there is always a continuous layer of U(Al,Si)₃ compound at the uranium surface.

The summary listed in Table 1 illustrates the behavior of production lots of alpha-canned material as compared with triple-dip, canned slugs:
**Fig. 6**, Oxidation Blister on Alpha-Canned Slug  
Magnification 150X

**Fig. 7**, Structure at Bonding Layer of Typical Alpha-Canned Slug  
Magnification 250X
### Effect of Canning Technique on Blistering of Aluminum-Silicon Bonded Slugs During Heat Treatment at 400°C

<table>
<thead>
<tr>
<th>Method of Canning</th>
<th>No. of Slugs Tested</th>
<th>Time at 400°C</th>
<th>% Blistered</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard triple-dip, canned at Y-12</td>
<td>5,886</td>
<td>7 days</td>
<td>18.6</td>
<td></td>
</tr>
<tr>
<td>Alpha-canned, with no flux, at Y-12</td>
<td>648</td>
<td>7 days</td>
<td>11.6</td>
<td></td>
</tr>
<tr>
<td>Alpha-canned, flux on duplex bath, at Y-12</td>
<td>2,288</td>
<td>7 days</td>
<td>0</td>
<td>Two slugs failed from leaky welds</td>
</tr>
<tr>
<td>Retest of 977 of above for additional 2 weeks</td>
<td>977</td>
<td>21 days</td>
<td>0.1</td>
<td>One slug showed oxidation blister from can leaks</td>
</tr>
<tr>
<td>Alpha-canned, flux on duplex bath, at Y-12</td>
<td>8,801</td>
<td>7 days</td>
<td>0.1</td>
<td>Eleven slugs showed oxidation blisters from can leaks</td>
</tr>
</tbody>
</table>

It will be noted from examination of this table that no cases of diffusion blistering have occurred with slugs prepared by alpha canning with a flux on the duplex bath. All blistering of these slugs was associated with either porosity in the welds or leaks in the end caps. Some end caps were prepared from defective aluminum rod which contained porosity which permitted access of air to the uranium during heat treatment. This situation has been corrected by rigid inspection of end-cap stock.
Conclusions

On the basis of the experimental work carried out in connection with the present problem, the following conclusions appear to be justified:

1. The compound layer, $U(Al, Si)_3$, formed on the surface of uranium when in contact with molten aluminum-silicon, is an effective diffusion barrier between uranium and aluminum-silicon or aluminum at 400°C.

2. The diffusion blisters are invariably associated with localized concentrations of tin in the bonding layers. It is thought that localized tin concentrations prevent contact of molten aluminum-silicon with the uranium and result in discontinuities in the $U(Al, Si)_3$ diffusion barrier.

3. Gas blistering will occur in triple-dip canned slugs heated to 400°C when the aluminum-silicon layer contains dissolved hydrogen. This defect may be avoided by careful attention to the prevention of moisture's entering the aluminum-silicon baths and by "aging" of the bath for 24 hours prior to the start of canning.

4. The use of a flux on the surface of the duplex bath in the alpha-canning process insures complete wetting of the uranium surface by molten aluminum-silicon. This complete wetting is very important in insuring that the $U(Al, Si)_3$ diffusion-barrier layer is continuous over the entire slug surface.

5. There have been no definite cases of diffusion blistering, during heating at 400°C, of slugs canned by the alpha-canning method with a flux on the duplex bath. All blisters and ruptures examined to date appear to be associated with leaks in the weld closures or porosity in the end caps.

Acknowledgments

All of the present work was carried out as a cooperative venture between the Operations and Metallurgy Divisions at Oak Ridge National Laboratory and the Chemical Department at Y-12. Messrs. Cox and Tench, of the Operations Division, performed the heat treatment tests and specified standards for slug quality. Messrs. Strasser, Williams, and Kite, of the Chemical Department at Y-12, carried out all the slug production work.

Bibliography

1. ORNL-269 Interim Report--Clinton Slug Ruptures, Causes and Prevention
I. Introduction

A hot-pressed uranium rod was used in the investigation and evaluation of preferred orientation techniques (SEP-88). Since this material was fine-grained and of random orientation it offered an ideal starting material for the examination of textures in rolled uranium rod. The development of preferred orientation with increasing degree of deformation was thus investigated.

II. Specimen Preparation

Specimens of rolled uranium rod with various degrees of preferred orientation were prepared as described in detail in SEP-88. The reductions in area were achieved by rolling at 300°C after a ten-minute soak at 300°C at the Argonne National Laboratory. Cross-sectional specimens about 0.150" thick were cut from the rod after 0, 5, 10, 15, 20, 25, 35, 55, and 70% reductions of area. Each specimen was electropolished to remove at least 0.010" from the thickness.

III. Experimental Technique

A modification (1,2) of the Schulz reflection preferred orientation technique(3) was used in conjunction with the Geiger counter spectrometer to determine the intensities of planes whose poles were inclined from 0° to 25° to the rolling direction. As stated in SEP-88, it was felt that from a time and material standpoint a cross-sectional specimen would yield sufficiently sensitive indications of preferred orientation since it was felt that in a rod, the planes which were parallel to the rod axis tended to be random about the rod axis, whereas the planes which were parallel to the cross section tended to be parallel to each other. It was therefore felt that examination of the cross section only would yield sufficient data for examining the effect of increasing reductions of area on the texture of a hot-pressed uranium rod.

All specimens were individually mounted on the rotating specimen table of the preferred orientation specimen holder and were integrated by rotation about the rod axis. Data for plotting pole charts were obtained by setting the goniometer at the proper 2θ value for a given reflection and recording intensities as the position of the cross section was changed with respect to the spectrometer circle. A description of the technique and apparatus is given in references (1) and (2).
III. Experimental Technique (Cont'd.)

The Hanford technique (4) was used to interpret a portion of the data obtained with the modified Schulz technique.

TABLE I

Variation of Intensity With Increasing Reduction of Area

<table>
<thead>
<tr>
<th>(hkl)</th>
<th>0</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
<th>35</th>
<th>55</th>
<th>70</th>
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<tr>
<td>010</td>
<td>1.4</td>
<td>1.8</td>
<td>2.8</td>
<td>3.6</td>
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<td>110</td>
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<td>021</td>
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<td>51.8</td>
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<td>14.1</td>
<td>11.4</td>
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<td>111</td>
<td>16.8</td>
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<td>15.1</td>
<td>14.7</td>
<td>12.3</td>
<td>11.2</td>
</tr>
</tbody>
</table>

IV. Results and Discussion

In the present investigation, only one uranium rod was examined. The intensity variation at the rolling direction of five reflections with increasing reduction of area is given in Table I.

"D", the per cent deviation from theoretical intensity, as a function of reduction of area is plotted in Figs. 1-3. "D" is defined as \( \frac{R_o - R_t}{R_o} \) where \( R_o \) is the observed intensity ratio and \( R_t \) is the theoretical intensity ratio. It is seen from these curves as well as from Fig. 4, a plot of the intensity variation of the five examined reflections as a function of increasing reduction of area, that there is an apparent tendency toward a duplex fiber texture with the (010) and (021) poles parallel to the rod axis. This apparent duplex texture could result from a wide scatter about the mean orientations of an (010) fiber texture, especially at low deformations, since the angle between an (021) and (010) pole is 31°. The similarity between (021) and (010) curves of Figs. 1-4 (up to 60% reduction of area) lends further support to the contention that the (021) intensity maximum at the rolling direction is most probably caused by the above mentioned scatter about the mean (010) pole positions. At 70% reduction of area, both (010) and (021) intensity maxima at the rolling direction begin to decrease. This decrease can be attributed to an (041) fiber texture (to be discussed below) in which the (010) pole is 15°-1/2° to the rod axis.

The pole charts of Figs. 5-9 summarize the variation of intensities of the different reflections as a function of the tilting angle \( \phi \) (1,2). Background intensity has been subtracted and the proper tilting angle correction (1) applied.

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IV. Results and Discussion (Cont'd.)

The (111) pole chart exhibits first an increase in intensity at low reductions of area, and then a decrease in intensity at higher reductions in all examined regions of the pole chart up to 70% reduction of area. This might indicate the possibility of a compression texture in the as-hot-pressed rod. At 70% reduction of area, the (111) intensity maximum lies outside the range of \( \phi \) values investigated.

It is seen from the (010) pole chart that the concentration of (010) poles increases in all examined areas of the pole chart with increasing reduction of area. At 70% reduction of area, there is a tendency toward alignment of the (010) poles 15° from the rod axis.

The (021) pole chart indicates an increase in concentration of (021) poles in all examined areas of the pole chart with increasing reduction of area up to 70%. At 70% reduction there is a tendency for (021) poles to be aligned 15° to the rod axis.

The (001) pole chart reveals a tendency toward a decrease in intensity with increasing reduction of area. At 70% reduction of area, the (001) maximum is outside the range of \( \phi \) angles investigated. It should be noted that the as-hot-pressed rod reveals a tendency for (001) poles to be aligned about 6° to the rod axis, another indication of the possibility of a slight compression texture.

The (110) pole chart reveals a tendency for (110) poles to be aligned in the vicinity of the rod axis for deformations up to 15%. At higher deformations, the tendency is for the (110) poles to exhibit intensity maxima in the \( \phi \) angle range of 20 to 25° and possibly outside the range of \( \phi \) values investigated. At 70% reduction of area, there is an indication of an intensity maximum outside the range of \( \phi \) angles investigated. It has been proposed [5] that working uranium at 300°C produces a duplex (010), (110) fiber texture and that as soon as the (110) poles become parallel to the rod axis they would be favorably oriented for twinning on the (130) plane. (130) twinning would cause a marked decrease in the (110) component and a corresponding increase in the (010) component. It is possible that (130) twinning is responsible for the decrease in the initial tendency of (110) poles to lie in the vicinity of the rod axis and contributes toward the increase in the tendency for (010) poles to lie in the vicinity of the rod axis as the deformation is increased.

Fig. 10 illustrates a possible grain orientation which is compatible with the textures reported above for a uranium rod which had a 70% reduction of area by rolling at 300°C. The (100) plane is the plane of the drawing. It is seen from this drawing that both the (010) and (021) poles are inclined 15°-1/2° to the rod axis. This corresponds closely to an (041) fiber texture. Fig. 11 is a mean orientation pole figure compatible with the texture shown in Fig. 10.
V. Textures of Beta-Treated Material

A beta-treated rod was examined at the Argonne National Laboratory. The grain size in this rod varied from 0.09 to 0.30 mm from outer surface to core respectively. It was felt that examination of ten or more cross sections of this rod might yield sufficient information to indicate the type of texture present in this rod even in the presence of a large grain size. Table II summarizes the intensities of the reflections from three cross sections of this rod. It is obvious from this table that there is no resemblance of consistency in the data, indicating that it is not possible to determine the texture in this material by examining one section alone, even with integration. Statistically it would probably be necessary to examine in order of ten or more cross sections and an average of the intensities obtained from these ten sections might then be a measure of the average throughout the rod. It is interesting to note that averaging as few as three cross sections yield intensity ratios approaching those of a theoretically random rod. Neither the deviation from theoretical nor the approach toward theoretical ratios is deemed significant of the presence or absence of a texture in this material since only three cross sections were examined.

<table>
<thead>
<tr>
<th>(hkl)</th>
<th>Cross-Section #1</th>
<th>2</th>
<th>3</th>
<th>Average</th>
<th>Theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td>(010)</td>
<td>1.3</td>
<td>2.9</td>
<td>0.2</td>
<td>1.47</td>
<td>-</td>
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<tr>
<td>(110)</td>
<td>25.7</td>
<td>31.3</td>
<td>17.7</td>
<td>24.9</td>
<td>-</td>
</tr>
<tr>
<td>(021)</td>
<td>4.6</td>
<td>67.8</td>
<td>7.1</td>
<td>26.5</td>
<td>-</td>
</tr>
<tr>
<td>(001)</td>
<td>32.9</td>
<td>5.4</td>
<td>6.4</td>
<td>14.9</td>
<td>-</td>
</tr>
<tr>
<td>(010)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>.099</td>
<td>.107</td>
</tr>
<tr>
<td>(001)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.67</td>
<td>1.43</td>
</tr>
<tr>
<td>(021)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.77</td>
<td>2.05</td>
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<tr>
<td>(001)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
VI. Conclusions

A. The texture of the rolled rod which had a 70% reduction of area at 300°C could best be described as an (041) fiber texture with the (100) pole perpendicular to the rod axis and the (001), (021) and (010) poles 74-1/2°, 15-1/2° and 15-1/2° respectively from the rod axis.

B. The possibility exists that there is a slight compression texture in hot-pressed uranium rods in the as-hot-pressed condition.

C. Examination of three cross sections of a beta-treated rod revealed inconclusive evidence of the absence or presence of preferred orientation, but strongly indicated an inhomogeneity of preferred orientations along the length of the rod.

Acknowledgements

The authors wish to express their appreciation to Dr. Frank Foote, Mr. J. Schumar, Dr. S. Sidhu, Dr. W. H. Mueller and Dr. H. Chiswick of the Argonne National Laboratory, and to Mr. R. Van der Laan of the E. I. du Pont de Nemours Co., Inc. for their cooperation in this investigation. The authors also wish to thank the Argonne National Laboratory for the use of their facilities.

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5. KAFI-370, June 1950
Fig. 1 Percent Deviation of Intensity Ratios as a Function of Percent Reduction of Area at 300°C (111) Base Plane at $\phi = 0^\circ$
Fig. 2  Percent Deviation of Intensity Ratios as a Function of Percent Reduction of Area at 300°C (001) Base Plane at $\phi = 0^\circ$
Fig. 3 Percent Deviation of Intensity Ratios as a Function of Percent Reduction of Area at 300°C (010) Base Plane at $\phi = 0^\circ$
Fig. 4 Variation of Intensity With Percent Reduction of Area at 300°C at $\phi = 0^\circ$
Fig. 5 (111) Pole Chart for 300°C Rolled Rod
Fig. 6 (010) Pole Chart for 300°C Rolled Rod
Fig. 8 (021) Pole Chart for 300°C Rolled Rod
Fig. 9 (001) Pole Chart for 300°C Rolled Rod
Fig. 10 Texture in Hot Pressed Rod After 70% R. A. at 300°C.
THE CRYSTALLOGRAPHY OF THE BETA TO ALPHA TRANSFORMATION IN URANIUM

A. N. Holden

Abstract

The orientation relationships between beta uranium single crystals containing small amounts of chromium and their alpha transformation product are established. Two transformation mechanisms are observed, a martensite mechanism at low temperatures and a conventional nucleation-growth mechanism at high temperatures. The efficacy of beta treatment in both alloy and pure uranium for improving distortion stability is explained. A new x-ray method for rapidly determining preferred orientations was used to study the transformation product and the method is described in detail.

Introduction

It is well known that the beta phase of uranium, normally stable in the range 660°C to 770°C, can be quenched to room temperature and retained in a metastable condition for long periods if the uranium contains but small amounts of chromium. This fact has been extremely useful, permitting the growth of beta uranium single crystals stable at room temperature(1) and the subsequent determination of the crystal structure of beta uranium(2) and the crystallography of deformation of beta uranium(1). An additional use of these crystals, namely to study the mechanism of the beta to alpha transformation, will be described in this paper.

One reason this transformation is of particular interest and importance is because much of the standard heat treating practice for the uranium slugs used in reactors involves heating into the beta range. It is well known, for example, that a beta range heat treatment followed by quenching produces a more random grain structure than can be obtained by alpha working or annealing. Furthermore, this randomly-oriented beta-treated material is less likely to distort and roughen during either irradiation or thermal cycling than alpha worked metal. The beneficial effect of a random structure is to be expected since the distortion is primarily a consequence of the anisotropy of the uranium. However, the complete explanation of the beneficial effects of beta range heat treatment must describe the transformation of beta to alpha.

A second important reason for studying the transformation of uranium using alloys of very low chromium content is that certain isothermal treatments of these low chromium alloys produce structures even more stable to the distortion induced by thermal cycling than beta-quenched pure uranium(3).

As a result of this study, both the beneficial effect of a beta-treatment and the advantage of the heat treated uranium-chromium alloys can be explained.
Cross Features of the Beta Alpha Transformation

Beta uranium crystals containing small amounts of chromium will transform at room temperature into what, upon etching, appear to be small plates of alpha. These plates are not distributed randomly, but rather are consistently parallel to certain planes in the parent beta crystal. If a polished crystal transforms at room temperature, the transformation product produces considerable surface distortion as well as bending of the specimen. Under high power microscopic examination with polarized light, the plates appear much like martensite, distorting the surface and frequently appearing with a characteristic midrib.

A beta crystal containing only 0.3 atomic percent chromium generally requires about three hours at room temperature for the formation of the first alpha plate. The rate of transformation may be increased by heating the crystal, and at 400°C the crystal transforms completely to alpha in ten minutes. The crystal will also transform at room temperature simultaneously with the application of stress, the amount of transformation being crudely proportional to the amount of stress.

The increasing transformation rate with increasing temperature is entirely consistent with the kinetic studies of the transformation made dilatometrically by White.(3) The general shape of the TTT curves for these low chromium alloys is that of a double "C"; an upper "C" for one transformation mechanism and a lower "C" for another transformation mechanism. The formation of plates of alpha at room temperature corresponds to transformation by the lower "C" mechanism and at the slow rate dictated by the bottom of the "C". The increasing rate of plate formation with increasing temperature corresponds to the approach to the nose of the lower "C" curve.

It is interesting to speculate that if the transformation is martensitic, it can be completely suppressed in the Kurdjumov fashion and will occur isothermally at higher temperatures.

Experimental Technique

Beta crystals of 0.3 atomic percent chromium content were grown in the form of 50 mil square wires several inches long by the method described previously.(1). The orientation of these crystals was determined immediately after growing by a back-reflection Laue method. The crystals were then transformed isothermally at several temperatures; in a lead pot at 400°C, 450°C, 500°C, and 550°C; in boiling water at 100°C; in Woods metal at 200°C; and at room temperature. The transformation product was studied either by microscopic examination or by x-ray methods or by both in some cases.

These specimens studied microscopically were given a metallographic polish on two adjacent faces of the square wire before the crystals were grown. It was necessary to repolish these crystals for a few moments electrolytically to restore an excellent surface for microscopic examination. The crystals studied
microscopically were transformed only at room temperature to prevent serious oxidation.

Habit planes of the transformation plates were determined from the directions of these plates observed in adjacent faces of the beta crystal.

X-ray work was carried out in several ways initially, but ultimately a new pole figure technique was evolved to simplify the work and this technique is described in the Appendix.

The first attempts were to orient large isolated plates by a back reflection Laue method using a very fine beam. These attempts failed because the plates were evidently strained sufficiently to give distorted patterns that could not be oriented, and furthermore, the exposure times with the fine beam were so long that excessive oxidation of the crystal occurred.

Attempts were then made to obtain a pole figure of the transformed alpha after the transformation was complete, using cylindrical rather than square crystals, and using standard film techniques. These attempts were not successful because the simple planes \{110\} and \{002\} occur in a triple reflection together with the \{021\}, making it very difficult to separate the three on film and almost impossible to correctly assign indicia to isolated diffraction spots of the triplet group.

The final successful procedure was to use a completely modified Schulte-type goniometer in conjunction with a Geiger counter spectrometer (see Appendix). The goniometer was designed to automatically move the specimen through a spiral path on a stereographic projection, and a record of the reflected intensities along this spiral path was made for several planes of interest and pole figures plotted from this record. Good resolution of the \{110\} \{021\} \{002\} triplet was obtained with this instrument.

**Experimental Results**

The results of the x-ray work are presented as a series of typical pole figures. The \{002\} alpha pole figure for the room temperature transformation is shown in Fig. 1, plotted directly over the projection of the beta crystal matrix. The principle relationship shown is that \{002\} alpha planes are parallel to \{140\} beta planes, and also parallel to \{101\} beta planes with considerable scatter about the latter. The \{040\} alpha planes for the room temperature transformation are shown in Fig. 2 to be parallel to the vicinity of either a \{101\} or a \{411\} type beta plane, with considerable scatter about the \{101\} observed. In Fig. 3 the \{110\} alpha pole figure for the room temperature transformation is shown, and the important relationships are: \{110\} alpha planes are parallel to \{140\} beta planes, parallel to \{132\} \{142\} regions of beta, and also parallel to \{341\} \{441\} \{331\} regions of beta. The scatter of the pole figure has been accounted for by specifying a region, as in the foregoing, for the relationship between beta and alpha. Where no other planes are nearby, as in the case of \{140\} beta planes, the relationship has been stated more precisely.
Several crystals have been examined in this fashion after room temperature transformation and agree with the results presented here.

At all other temperatures of transformation up to 400°C the product of transformation gave precisely the same pole figure as for room temperature. An example is shown in Fig. 4 for the \{110\} poles obtained for a beta crystal transformed at 400°C in a lead pot, and this pole figure can be compared with the data for the room temperature transformation in Fig. 3.

At 450°C and above the transformation product of a beta crystal is a completely random, fine grained, equi-axed structure when examined by either x-rays or microscope. The exact temperature at which the mechanism changes from a martensite-like transformation to a random nucleation type transformation is not known, but for 0.3 atomic percent chromium must lie in the range 400°C to 450°C. The change in mechanism agrees with the kinetic observations of White -- that a double "C" TTT relation exists with one mechanism for the upper "C" and another for the lower "C". The upper "C" mechanism is, in fact, random nucleation and growth characteristic of many solid-state transformations.

From x-ray evidence the transformation of pure uranium has been deduced to be the same as the lower "C" or martensite-like transformation of the chromium alloy of uranium. It was found that 50 mil wires of pure* uranium given a gradient transformation treatment from gamma to beta, a treatment that always produces single beta crystals in the alloy, upon quenching to room temperature, had sharp textures not unlike the textures of Figs. 1 - 4. One might expect randomness in the sample if the crystal transformed by the upper "C" mechanism or if the sample had actually been polycrystalline beta; however, since the sample was highly textured and similar to the lower "C" transformation product, the only conclusion must be that it was a single beta crystal that transformed by the lower "C" mechanism.

Other evidence obtained by White(3) also suggests that pure uranium transforms by a lower "C" mechanism. White observed that as the percentage of chromium in uranium was decreased the temperature range of the lower "C" mechanism increased, and that it would probably extrapolate to 0% chromium as the only mechanism remaining.

The pole figure data for the martensite-like transformation can not be explained with a single simple orientation relationship, but they can reasonably be explained with two types of orientation relationships. These two proposed relationships are plotted in Figs. 5 and 6, in which the two alpha orientations are projected on an \{001\} beta projection, and in which the \{110\} pole figure obtained from the proposed relationships is compared with the observed \{110\} pole figure.

From symmetry considerations a single beta crystal may transform to 16 distinct alpha orientations by these two relationships and the variety of orientations obtained are illustrated in Fig. 7.

*Remelted electrolytic crystals supplied by A. P. Beard
Two habit planes in the beta which coincide with the general spatial location of the alpha plates have been found. These planes, as with martensite, bear no simple index. The closest approximate indices have been assigned to the habit plane from a plot of the normals to plate-matrix interfaces in adjacent faces of the square cross-section wires. A typical plot is shown in Fig. 8, in which an approximate $\{321\}$ beta habit plane was found. The other habit plane has been of the type $\{142\}$.

Discussion

From the observations that 16 orientations may result from a single beta uranium crystal transforming by the lower "C" or martensite-like mechanism, the efficacy of a beta treatment and quench in randomizing a textured polycrystalline alpha uranium specimen is apparent. Of more interest is the fact that even greater randomization can be obtained in dilute chromium uranium alloys using transformations of the upper "C" type that are not of a martensitic variety. This latter point probably accounts for the observation by White that dilute chromium alloys isothermally transformed in this temperature region were even more stable towards distortion during thermal cycling than beta quenched pure uranium. One would predict similar satisfactory results for the chromium heat treated alloys in pile irradiation. White is currently performing irradiation experiments on this material.

APPENDIX

A Description of the Spiral-Scanning Goniometer

The goniometer is designed to move a specimen in such a fashion that all the planes within that specimen whose normals would trace a spiral path (Fig. 9) in a stereographic projection are brought sequentially into reflecting position. This movement is accomplished by linking the drive of both circles of the goniometer through a cam and follower nut system.

A photograph of the spiral tracking goniometer in position on the spectrogoniometer is presented in Fig. 10, from which the operation may be simply explained. A synchronous motor D drives a threaded rod (not visible) through gear box E which in turn is connected to the small circle and specimen mount A. As the small circle and threaded rod rotate, the cam follower nut F, only a small part of which is visible in the photograph, moves against the cam C at a rate controlled by the pitch of the threaded rod. This action against the cam tilts the large circle B. The pitch of the threaded rod and the shape of the cam are such that one revolution of the small circle specimen mount A causes a $10^\circ$ tilt of large circle B.

Radiation always strikes the sample at the center of the small circle and reflection occurs whenever planes in the sample corresponding to the appropriate $2\theta$ setting of the spectrogoniometer are brought into a position so that their normals are a bisector of $2\theta$. A fixture for leveling a specimen at the center of the x-ray beam is used when setting a specimen in place and removed during operation.
In operation, the goniometer is generally set at a 70° tilt and moves to 0° tilt in seven full rotations of the specimen. Greater angles of tilt introduce considerable error in intensity.

A speed change consisting of a stepped idler between the driving and driven gears in the gear box permits the selection of rates of three, six, or 12 minutes per revolution of the specimen mount, or of 21, 42, or 84 minutes per complete spiral path.

**Goniometer Operation and Some Results with Cube-Textured Copper**

A specimen of copper that had been rolled 98% and then annealed was selected as a good material on which to test the goniometer. The specimen was scanned spirally in the goniometer for reflections from {220} and {222} planes, and a record of intensity of reflection versus position along the spiral path was made with the rate meter recorder.

In Fig. 11, the actual recorded data for each of these planes is presented. The zero on the right corresponds to a tilt of 70° on the large circle of the goniometer. After one full revolution of the small circle indicated by position marked 1, the tilt of the goniometer is 60°, and after two revolutions, 50°, etc.

Fig. 12 is a conventional pole figure obtained by reploting the data of Fig. 11, although the data actually present more quantitative information on the original record. This operation is performed by setting the spiral track of Fig. 9 under a sheet of tracing paper and indicating the intensity maxima in their proper location on the spiral path. This particular goniometer is designed so that when looking down at the surface of the specimen in the goniometer, it rotates clockwise as the tilt decreases from 70° to 0°, and therefore the spiral path of the normals to all reflecting planes in the specimen moves counter-clockwise when moving from 70° to 0°. Furthermore, if the top of the tracing paper is designated as parallel to some reference direction in the specimen such as the rolling direction, and if that reference direction is initially set up to point toward the x-ray tube parallel to the incident x-ray beam when both the spiral scanning goniometer and the spectrogoniometer are set at zero, then the starting point for tracing the normal path of the spiral scanning goniometer will be 70° out from the center directly to the left side of the paper. These relations are illustrated in Fig. 13.

While the rapid determination of preferred orientation in cube textured copper is reasonably simple, other metals with less sharp textures have required slower and more precise determinations.

If greater precision is required than can be obtained with a spiral path of 10° spread between loops, the simple expedient of remounting the specimen on the goniometer with its reference direction rotated 180° will provide a second spiral path interlocking the initial path but displaced 5° to a position midway between the initial loops. Such a system of interlocking spirals is shown in Fig. 14. Of course, four settings of the specimen 90° apart in rotation will produce four interlocking spiral paths only 2 1/2° apart.
A distinct advantage of the spiral path is that it scans all four quadrants of a pole figure and permits the study of asymmetrical preferred orientation. A good example is provided by the work reported in this paper in which the goniometer is employed to study the orientation relations that exist when single crystals wires of the beta phase of uranium transform to alpha with a martensite-like transformation. In this work the single crystal need not be initially rotated to a symmetry position, but may be studied with only its external form (wire axis for example) as a reference direction for initial orientation and subsequent transformation.

All too frequently in other techniques of collecting preferred orientations of rolled and recrystallized metals, twofold or fourfold symmetry has been assumed to lessen the work. The spiral path collects data that assures the experimenter of the veracity of such an assumption with no extra effort. And if fourfold symmetry does indeed exist, the spiral path scans the reflected intensity in four quadrants with an effective gap between loops of only 2 1/2°. It should be possible to study cube textured copper (fourfold symmetry) with four separate mountings of the sheet, each rotated 90°, and, allowing 21 minutes per spiral trace and five minutes to remount the specimen, collect sufficient data in less than two hours for a pole figure which would have an effective gap between unscanned regions of only 0.6°.

It is to be noted that the central 70° radius of 140° diameter region of a pole figure is obtained in the fashion described. In order to fill in the remainder of the pole figure, a specimen cut with its reflecting face at 90° to the first may be used. With sheet it is convenient to slice out several square cross-section wires, mount them with one face exposed for the first run and then, for the second run, lay all wires on their sides. Other techniques will, of course, occur to anyone operating a device such as this, and the speed of scanning far offsets the bother of specimen manipulation.

REFERENCES


FIG. 1--POLE FIGURE FOR ROOM TEMPERATURE TRANSFORMATION OF BETA TO ALPHA 002 POLES
FIG. 2--POLE FIGURE FOR ROOM TEMPERATURE TRANSFORMATION OF BETA TO ALPHA 040 POLES
FIG. 3--POLE FIGURE FOR ROOM TEMPERATURE TRANSFORMATION OF BETA TO ALPHA 110 ALPHA POLES
FIG. 4--POLE FIGURE FOR 400°C TRANSFORMATION OF BETA TO ALPHA
110 ALPHA POLES
Fig. 5--110 Alpha Pole Figure Plotted on [001] Beta Projection for All Possible Orientation Relations of the Type Shown
FIG. 6--110 ALPHA POLE FIGURE PLOTTED ON [001] BETA PROJECTION FOR ALL POSSIBLE ORIENTATION RELATIONS OF THE TYPE SHOWN
FIG. 7--SIXTEEN ALPHA ORIENTATIONS RESULTING FROM THE BETA ALPHA TRANSFORMATION PROJECTED ON THE 001 BETA UNIT CELL
FIG. 9--STEREOGRAPHIC PLOT OF SPIRAL TRACK
FIG. 12--POLE FIGURE OF CUBE TEXTURE COPPER OBTAINED BY SPIRAL SCANNING GONIOMETER METHOD
FIG. 13--RELATION BETWEEN SPECIMEN POSITION AND SPIRAL PATH ON STEREOGRAPHIC PROJECTION FOR NORMAL OPERATION
FIG. 14—INCREASED RESOLUTION OF TWO INTERLOCKING SPIRALS OBTAINED BY REMOUNTING SPECIMEN AT 180° ROTATION FROM INITIAL MOUNTING
The compounds of uranium have long been regarded by the ceramist as coloring agents for ceramic glazes, giving beautiful yellows and browns which have been difficult to duplicate, however, attention is now being drawn to the refractory properties of the pure dioxide of uranium, which make it suitable for special applications, such as the melting of pure uranium.

Properties of Uranium Dioxide

Proper fabrication of UO₂ refractories is contingent upon consideration of certain characteristic properties of the raw material, which indicate the fabrication techniques that can be employed. UO₂ is a dark brown, granular, non-plastic material. It is quite active chemically and is, of course, radioactive since it contains uranium.

Of major consideration from the fabrication standpoint, however, are the erratic oxidation properties of UO₂. Uranium forms a continuous monophasic series with oxygen from UO₁.₇₅ to UO₂.₃. This means that uranium dioxide can take up more oxygen than the stoichiometric formula indicates up to a composition of UO₂.₃ without changing from the face centered cubic lattice, except for slight changes in lattice dimensions. While the members of this series are reasonably stable at room temperature in contact with air, this stability decreases with increasing temperature, and oxidation proceeds rapidly even at comparatively low dryer temperatures. The blueish-black oxygen saturated form of the series, UO₂.₃, is reached at the low temperature of 150°C. At higher temperatures in air, oxygen content increases further thru a diphasic region up to a composition corresponding to U₃O₈. Then above 750°C U₃O₈ begins to decompose again, losing oxygen. This radically unstable nature of the uranium-oxygen system precludes the determination of moisture content by forced drying to constant weight, it limits drying temperature of finished ware to room temperature only, and it makes a vacuum or neutral atmosphere mandatory for firing.

The chemical activity of UO₂ also presents some minor difficulty in fabrication. UO₂ should not be left in contact with dies or metal containers any longer than necessary to avoid corrosion. Even though dies are cleaned immediately after use they soon show the inevitable signs of pitting. Chrome plating of dies and stainless steel containers are helpful in this respect, but are not permanent insurance against corrosion.
Both pressing and slip casting techniques can be used for forming UO₂ refractories. Pressing offers the advantages of simple preparation of raw material and freedom from contamination, however wall thickness and design are limited. Slip casting supplements pressing in that it can provide the thin walls and some design features not possible with pressed ware.

Pressing

A -325 U. S. STD sieve fraction is used exclusively for pressing small crucibles up to about two inches in diameter. On larger crucibles up to about five inches in diameter a distribution of particles approximating a maximum density mixture is employed (see Table 1). This particle sizing is quite roughly done, but it serves the purpose well for the larger crucibles which have thicker walls and can accommodate the larger particles.

Table 1 - Particle Size Distribution Of Maximum Density Mixture

<table>
<thead>
<tr>
<th>Sieve Fraction</th>
<th>Per Cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>U. S. STD</td>
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</tr>
<tr>
<td>Plus 30</td>
<td>25.3</td>
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<tr>
<td>Minus 30 plus 200</td>
<td>36.7</td>
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<td>Minus 200 plus 325</td>
<td>32.8</td>
</tr>
<tr>
<td>Minus 325</td>
<td>5.1</td>
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</table>

Tempering with six to eight per cent distilled water is the only step taken to prepare the UO₂ for pressing. The purity requirements of these pressed crucibles are very high and therefore no additives, lubricants, or binders of any type are used, and since UO₂ has no plasticity, it is essential that the proper amount of tempering water be added, if the pressing operation is to be successful. The proper amount of tempering water is not constant but varies from day to day depending, it is assumed, on the relative humidity, and/or the original moisture content of the UO₂. As stated above UO₂ gains weight due to oxygen absorption when subjected to dryer temperatures, and it is therefore difficult to determine moisture content, at least as a routine measure preparatory to tempering. The simplest procedure is to make several trial pressings until the optimum water content is determined, and use this quantity in all subsequent pressings made the same day.

After tempering, the UO₂ is tamped in the inverted die using a uranium rod to minimize contamination, and the crucible is pressed in this inverted position using pressures from 6 to 20 tons/in², depending on the size of the die. Pressure is applied intermittently to allow escape of entrapped air and avoid "pressure cracking". After pressing, the mandrel and base plunger are removed and the crucible extracted by pushing up on the base with an extraction ram.
The importance of proper die design should be emphasized when pressing without binders. Only a very slight taper can be tolerated, so that when the crucible is extracted, the sides will be in direct compression and will not shear from the base, as will happen if the taper is too large.

The green UO₂ crucibles are extremely fragile, but with care and a little practice can be extracted readily. However, even the small pressure used in extraction is sometimes sufficient to crush the base, and it has been necessary to incorporate a support for the base in the form of a chrome plated brass ring (see Figure 1) which is beveled at a 45° angle where it meets the crucible. This ring protects the base during extraction and allows the crucible to be handled without danger of breakage. The ring is easily removable after extraction and does not stick to the crucible. Extraction of the large sized crucibles (4-3/4" by 8-1/2") cannot be performed by hand because of the excessive weight of the die. A mechanical die stripper was therefore devised to perform this operation. It consists of a clamping arrangement for the crucible die and an extraction plunger actuated by a hydraulic bumper jack. All pressed crucibles should be handled only by the extreme base to avoid breakage.

**Slip Casting**

The acid leaching technique commonly employed for slip casting of other non-plastic materials is used for preparing slips of UO₂. The -325 U. S. STD sieve fraction is ground in a steel mill; four hours grinding being sufficient for heavy walled solid castings and as much as 16 hours required for thin walled castings. The mill product is then leached with 5N HCl for 24 hours after which the acid is decanted and the leaching repeated three or four times. The slip is then washed until the proper pH is obtained, four washings being usually sufficient. The specific gravity is then adjusted and any additives included.

The pH-viscosity relationship² for UO₂ in the acid range is shown in Figure 2. The minimum point occurs at about pH 3.6 and satisfactory castings have been made at this pH, however, the shrinkage of the cast crucible is barely sufficient for mold release and the finer particles in the slip tend to clog the mold pores. Both of these conditions improve toward the acid end of the curve and it has been suggested² that a satisfactory compromise can be made at pH 2.1 and this is recommended for a medium sized casting, however, with an acid leached slip the settling rate is not too high even at the extreme acid end, and castings can be made at pH 1.5.

Small percentage additions of organic dispersion agents may be used to improve the dry strength and also help prevent cracking by slowing down the rate of water removal by the plaster. The addition of two per cent (dry by dry weight of solids) of Carbowax 40000W to the slip exerts a slight defloculating effect, aids in dispersion, as well as improving the dry strength. Using Carbowax, it is possible to cast very thin shapes, such as thermocouple protection tubes and crucibles with walls 1/16" thick (see Figure 3 and 4).

**Firing**

The urania refractories are allowed to dry slowly for several days at room temperature and are then fired in a molybdenum resistance furnace to
maximum temperature of 1750°C. A hydrogen atmosphere is used to prevent oxidation of both the furnace elements and the urania. The commercial hydrogen is purified by passing thru two Puridryers and one catalytic unit for oxygen and water removal. The hydrogen atmosphere also serves the useful purpose of reducing oxygen in excess of UO$_2$.15, which may have formed on the surface (oxygen above UO$_2$.15 is comparatively loosely bound) and may possibly reduce higher oxides to stoichiometrically pure UO$_2$. The urania pieces are set on alumina setting slabs with a thin sheet of molybdenum metal intervening to prevent any reaction between the alumina and urania. When slip cast ware containing Carbowax is being fired, the furnace temperature is raised slowly for the first 600°C to volatilize the Carbowax. This requires about eight hours. The furnace may then be heated fairly rapidly to reach 1750°C in about 20 hours. A nominal soak at temperature is allowed of about two hours to insure thermal equilibrium. The furnace must be cooled to essentially room temperature before the crucibles are removed when the furnace has cooled to 50°C, but are immediately transferred to desiccators which are then evacuated for storage.

Properties of Fired Ware

Linear shrinkage measurements of pressed crucibles indicate an average 11.6 per cent shrinkage in height and 11.9 per cent shrinkage in diameter on ware fired to 1750°C. Shrinkage of slip cast ware is slightly higher averaging 15.2 per cent for crucibles cast with a specific gravity of 4.0 and 16.2 per cent for thermocouple protection tubes which were cast with a more fluid slip of specific gravity 3.8. All measurements are based on fired size.

Density measurements made on pressed ware fired at 1750°C indicate an average of 9.13 or 83.8 per cent of the maximum theoretical UO$_2$ density taken as 10.9. With slip cast ware this average is 9.6 or 88.2 per cent of theoretical.

The variation of density with firing treatment is shown in Figure 5. The effect of temperature is much more pronounced than soak time as would be expected. Ware fired at 2000°C was badly deformed.

The variation in density along the height of pressed crucibles caused by differences in pressure is not large, but is measurable. The effect is not as pronounced for crucibles fired at the higher temperatures.

The contamination of UO$_2$ in fabrication is negligible for pressed crucibles, but is measurable for slip cast crucibles, particularly with respect to iron, silicon, lithium, magnesium, and manganese. Analyses of UO$_2$ before and after fabrication are shown in Table 2.

Analyses of Hanford uranium metal that has been melted in various types of crucible materials as compared with that melted in UO$_2$ crucibles are shown in Table 3. The analysis of uranium melted in graphite shows a rather high carbon content, as would be expected. The UO$_2$ and Al$_2$O$_3$ crucible materials are both superior to graphite in this respect, but metal melted in Al$_2$O$_3$ shows a rather high aluminum pickup. UO$_2$ also shows some superiority to MgO, particularly with regard to manganese pickup. Note the length of time the metal was held at temperature in each case; sixty-five hours for UO$_2$ as compared to four hours for MgO.

Table 4 shows analyses of electrolytic uranium before and after melting in pressed UO$_2$ crucibles. The pickup of impurities by the metal is extremely low. The alkali metals potassium and lithium have been eliminated.
Health Hazards

UO$_2$ is, of course, radioactive since it contains the element uranium and definite precautions are necessary to avoid injury to health. Uranium is an alpha emitter of rather long half life and therefore the level of activity is quite low. Alpha particles cannot penetrate the skin so no direct radiation danger is imminent in ordinary handling, however, if UO$_2$ should become fixed inside the body it can cause serious radiation damage by its presence over a long period of time. For this reason all dusty operations must be performed in a hood or dry box and all operations performed outside the hood should be periodically checked for dust count. Open wounds also present a hazard and should be suitably protected by rubber gloves or fingers. Under normal conditions UO$_2$ passes quite readily through the digestive tract, but sensible precautions are nevertheless advisable to prevent the contamination of food. The hands should be scrupulously washed when work is completed and care taken to prevent the contamination of street clothing. An alpha counter can be used as a check on cleanliness.

Table 2 - Analysis of UO$_2$ (in parts per million)

<table>
<thead>
<tr>
<th>Element</th>
<th>A</th>
<th>Cero. 5</th>
<th>Cero. 38</th>
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<td>L1</td>
<td>L1</td>
<td>2</td>
</tr>
<tr>
<td>Al</td>
<td>L20</td>
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<td>L10</td>
<td>L10</td>
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<td>L 0.1</td>
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<tr>
<td>Be</td>
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<td>L 0.5</td>
<td>L 0.2</td>
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<td>L 2</td>
<td>L 1</td>
</tr>
<tr>
<td>Ca</td>
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<td>L20</td>
<td>L20</td>
</tr>
<tr>
<td>Co</td>
<td>L 5</td>
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<td>L 5</td>
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<td>Cr</td>
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<td>L 1</td>
<td>L 1</td>
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<tr>
<td>Mg</td>
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<td>L 0.5</td>
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<tr>
<td>C</td>
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<td>11</td>
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A - UO$_2$ analysis provided by Special Materials Department
Cero. 5 - UO$_2$ analysis as received
Cero. 38 - Analysis UO$_2$ slip cast ware after firing
Table 3 - Analysis of Uranium Metal (Hanford)  
(in parts per million)

<table>
<thead>
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<tr>
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<td>50</td>
<td>20</td>
<td>20</td>
<td>10-50</td>
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<tr>
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<td>2</td>
<td>—</td>
<td>10</td>
<td>0.5</td>
<td>1-5</td>
</tr>
<tr>
<td>Mg</td>
<td>L 0.5</td>
<td>—</td>
<td>L 0.5</td>
<td>L 0.5</td>
<td>0.5-2</td>
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<td>1130-1300</td>
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<tr>
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<td>4</td>
<td>65</td>
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<tr>
<td>Crucible Material</td>
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<td>UO₂</td>
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</table>

*E Average analysis of Hanford Metal

Table 4 - Analysis of Electrolytic Uranium Metal  
(in parts per million)

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<td>Cu</td>
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<tr>
<td>Fe</td>
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<td>K</td>
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<tr>
<td>Li</td>
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<tr>
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<td>1 or less</td>
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<td>Mn</td>
<td>L0.5</td>
<td>L0.5</td>
</tr>
<tr>
<td>Si</td>
<td>1 - 3</td>
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<tr>
<td>Oxygen</td>
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<td>8</td>
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<tr>
<td>Fluorine</td>
<td>—</td>
<td>4 - 10</td>
</tr>
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</table>

A - Electrolytic Uranium Crystals  
B - Electrolytic Uranium after Melting in UO₂ Crucibles
Acknowledgements

The authors wish to express their appreciation to Mr. Ralph G. Kraft for his contribution on the determination of density and its variations, and also to the Chemistry Division of ANL for the analyses.

Bibliography


Figure 7 - Large Crucible Die. Note the beveled brass ring in front of the base plunger. Mandrel is hollow to reduce weight. (Negative No. 106-433)
Figure 2 - pH-Viscosity Relationship of UO₂ Casting Slip. (Negative No. 106-469)
Figure 3 - Unfired Slip Cast UO₂ Crucibles. (Negative No. 106-269)
Figure 4 - Fired UO₂ Crucibles and Shapes. Two largest crucibles in background are pressed, all others are slip cast. Thermocouple protection tubes left foreground. Large crucible cover at right.
(Negative No. 106-432)
Figure 5 - Variation of Density with Firing Treatment. (Negative No. 106-468)
NOTE ON THE URANIUM-TITANIUM BINARY SYSTEM.

R. W. Buzzard, R. B. Liss and D. P. Fickle

The portion of the uranium-titanium system covered by this report was limited to alloys which could be prepared by melting in beryllia crucibles with induction heating. A preliminary series of alloys prepared with Bureau of Mines titanium and covering the ranges 0.15-68.5 atomic percent titanium, were prepared by conventional induction melting methods to determine the alloy ranges for which the use of beryllia crucibles was feasible. All the alloys of this series slid free of the crucibles with no visual sign of crucible attack. Spectrographic analysis showed an increasing beryllium pickup with an increase in titanium above 30 atomic percent. Excessive crucible attack was noted in melting point determination for alloy containing above 35 atomic percent titanium. Metallographically excessive contamination was noted in alloys containing in excess of 30 atomic percent titanium. It was concluded from these results that the scope of this investigation would cover that portion of the system within the composition range of 0-30 atomic percent titanium. An arc-melted uranium-titanium master alloy (50 weight percent) using iodide titanium prepared at Battelle Memorial Institute was used in the preparation of subsequent alloys. The alloys were annealed for eight days within 100°C of the solidus in a purified argon atmosphere. The liquidus determinations were made in an induction furnace under a purified argon atmosphere. Time-temperature determinations were obtained using thermocouples and a Brown recorder. Platinum couples were used for the lower ranges and tungsten-molybdenum couples for the higher ranges.

The thermal analysis above the solidus, using induction heating, indicated that an invariant existed in the neighborhood of 1200-1250°C extending to 18-19 atomic percent titanium, terminating in a rapidly rising solidus. Due to the peculiarities of the alloys, determinations below the liquidus obtained by this procedure were inaccurate. All liquidus determinations were made with alloys composed of Bureau of Mines titanium.

Thermal analysis of the solid phase regions were made in a resistance furnace under vacuum using platinum couples. A consistent arrest was observed in the vicinity of 850°C for alloys made from iodide titanium, and some 20°C lower in alloys made of Bureau of Mines titanium. The type of titanium used in the alloy exerted little influence on the temperatures of the uranium transformations, although the arrests were sharper for the iodide titanium alloys. The beta-gamma transformation temperature was lowered with increased titanium content, becoming constant at 718°C in the vicinity of eight atomic percent titanium. The alpha-beta transformation appeared consistently at 667°C.

The solid phase boundaries were explored metallographically and confirmed by X-ray. The limit of the gamma solubility range was 8.8 atomic percent titanium at 1180°C. The gamma solid solution decomposed eutectoidly at 718°C, the eutectoid composition being five atomic percent.
titanium. At 600°C the alpha solubility was about 3.9 atomic percent titanium, changing little at room temperature. The alloys of four atomic percent titanium and higher were of a martensitic type structure when quenched from the gamma solid solution. A two phase field appeared in all the specimens of the 9.2 atomic percent titanium alloy quenched from above 830°C. Alloys containing less than eight atomic percent titanium, quenched from 800°C, all showed solid solution, while the alloys of eight atomic percent titanium and more, quenched from 800°C, all contained eutectoid. At 800°C, the 16.5 atomic percent titanium alloy was composed of uranium and eutectoid whereas the 18.75 atomic percent titanium alloy contained eutectoid and compound. This located the eutectoid composition within these compositions. The compound phase appeared in the 23.1 atomic percent titanium alloy quenched at 850°C, locating the eutectoid temperature between 800°C and 850°C.

To summarize, the uranium-titanium system, within the range 0-30 atomic percent titanium was developed by thermal, metallographic and X-ray analysis. (Fig. 1) The liquidus rises from the melting point of uranium to a peritectic at 1180°C and 2.6 atomic percent titanium, rising sharply to 1925°C at 30 atomic percent titanium. The peritectic horizontal terminates in a sharply rising solidus at approximately 15.4 atomic percent titanium. The system is characterized by two solid solution phases which decompose eutectoidly: The gamma solid solution has a solubility of 8.8 atomic percent titanium at 1180°C and decomposes eutectoidly at 718°C, the eutectoid composition being five atomic percent titanium. The delta solid solution decomposes eutectoidly at 830°C having an eutectoid composition of 18.3 atomic percent titanium. The delta solid solution appears to be the high melting phase rather than the compound (epsilon). The compound apparently forms peritectically and appears in the extreme titanium end of the alloy range covered by this investigation. The beta-gamma temperature was lowered, appearing at 718°C. The alpha-beta transformation was slightly raised as compared to the uranium values obtained in this investigation, appearing at 667°C, the beta appearing to decompose peritectoidally. The alpha solubility of approximately four atomic percent titanium appeared to extend to room temperature.
Fig. 1  Uranium-Rich Side of Uranium-Titanium
Diagram
PREPARATION OF URANIUM SINGLE CRYSTALS BY A GRAIN COARSENING METHOD

E. S. Fisher

Introduction

A method for producing single crystals of alpha phase uranium by grain coarsening has been developed at Argonne. This method is a result of a long investigation during which attempts to make single crystals by the strain-anneal and the modified Bridgeman technique proved unsuccessful. Although some single crystals were made by the modified Bridgeman technique, making use of the beta to alpha transformation, these crystals were undesirable because of the high degree of lattice imperfection. The single crystals produced by the grain coarsening method have considerably less lattice imperfection.

The method has been developed for producing single crystals in the shape of rods. Fig. 1 is a photograph of a single crystal specimen. The large crystal at the center is over ten mm. in length and four mm. in diameter. A number of other single crystals have been made of the same diameter and of lengths varying from five to twelve mm.

Basis of Method

The method is dependent upon grain coarsening or discontinuous grain growth in uranium rods which have been fabricated and recrystallized in the alpha temperature range. To establish conditions for grain coarsening to occur, it is necessary to heat treat the rods prior to fabrication. The process of heat treating also provides the conditions necessary for obtaining single crystals by controlling the growth of the coarse grains.

Inhibition dependent coarsening occurs on annealing if continuous grain growth following primary recrystallization is inhibited by a dispersed second phase and the inhibiting particles are gradually removed. The gradual removal of inhibition allows abrupt growth of a few grains at the expense of the fine grained matrix. The mechanism of inhibition dependent coarsening was studied in detail in aluminum-manganese alloys. The results of isothermal grain growth studies of a 1.1% manganese alloy are reproduced in Fig. 2. The curve obtained in plotting grain size versus time at three annealing temperatures shows the marked effect of the aluminum-manganese second phase. At this composition the second phase dissolves in the aluminum matrix at approximately 627°C. As is shown in Fig. 2, grain growth at 650°C is continuous as would be expected for a single phase structure. At 600°C the second phase is present as a very large number of small particles, which inhibit grain growth. At 625°C grain growth is inhibited while most of the second phase remains undissolved. At this temperature considerable dissolution of the second phase occurs after a long period, so that grain growth can then resume at isolated points of the matrix. The grains that resume growth increase in size at the expense of the still inhibited matrix and continue to grow until the...
large grains meet at common boundaries. Fig. 3 shows the grain structure at the surface of an aluminum-manganese sheet specimen after coarsening has started.

Grain Coarsening in Uranium

One of the important factors in the success of this method for making uranium crystals is the availability of high purity uranium ingots produced by melting of high purity electrolytic crystals. It is very convenient that the ingots contain some impurity phase. In order to have an effective grain growth inhibitor, it is necessary to first dissolve the impurity phases in gamma uranium and retain the solute in the alpha structure by quenching from the solution temperature. On subsequent alpha fabrication and heat treatment the solute precipitates as very fine particles which are very effective inhibitors. As the inhibition is decreased by prolonged heating after primary recrystallization, grain coarsening occurs. Fig. 4 shows the microstructure in a specimen showing incomplete grain coarsening. The large grain at the left of the figure appears to have been in the process of consuming the fine grained matrix when the heating was interrupted. Fig. 5 shows the grain structure at a transverse section of a rod specimen in which grain coarsening is complete. The structure consists of large grains with only a few dispersed smaller grains.

To obtain single crystals of rod shape by this method, it is necessary to control the grain coarsening mechanism so that coarse grains first grow near the axis of the rod. Under optimum conditions, a single coarse grain grows radially towards the rod surface, consuming the matrix of fine grains without encountering other coarse grains. To obtain the optimum conditions, further impurities are added to the rod prior to final fabrication. On subsequent alpha fabrication and heat treatment, the new phase or phases exist as fine particles which are heavily concentrated at the surface of the rod and decrease in concentration towards the rod center. The gradient of grain growth inhibitor is very effective in controlling the coarsening mechanism.

Fig. 6 is a photograph of a transverse section of a rod in which a gradient of inhibitor existed from surface to center. The single coarse grain at the center of the section is surrounded by a matrix of fine grains. This matrix is surrounded by a "skin" of still finer grains, close to the rod surface. In the area surrounding the coarse grain more continuous grain growth has occurred than has occurred in the "skin" area. To prevent this undesirable continuous growth, the rods are subjected to a diffusion anneal prior to fabrication, during which no further impurities are added, but the impurities added in the previous anneal are allowed to diffuse towards the rod center.

Because of the allotrophic transformation at approximately 660°C, the maximum temperature of the final coarsening anneal is limited. It is, therefore, important that the extent of inhibition should not be excessive. An excessive amount of inhibition increases the time necessary for coarsening to occur at the highest alpha temperatures and decreases the rate of growth of the coarse grains once coarsening begins. Impeding the growth of the coarse grains allows time for other grains to start growing and a multi-grain structure results. If the extent of inhibition is too small, grain
coarsening is limited by continuous grain growth and a multi-grain structure results.

As the number of inhibiting particles varies directly with the amount of impurity dissolved prior to fabrication, the optimum amount of grain growth inhibitor is controlled by adjusting the solution temperature in the pre-fabrication heat treatments. It has been found that the optimum solution temperature varies with the original composition of the ingot. Consequently, it is necessary to determine this optimum temperature for each new ingot. When the optimum inhibitor distribution is present, grain coarsening results in a single grain occupying the whole cross section of the rod as shown in Fig. 7.

Because it is desirable to retain a fine grain size in the rods prior to grain coarsening, the rods are swaged at 300°C using steps of increasing reductions in area with intermediate recrystallization anneals at as low a temperature as possible. This schedule of fabrication breaks down the large grains produced in the high temperature heat treating and provides a uniform structure of fine grains on primary recrystallization after the final reduction.

The final grain coarsening temperature is important because of the relative rates of inhibitor coalescence and coarse grain growth. It has been found that the rate of coalescence of the inhibiting particles varies slightly with increasing temperatures above 600°C, whereas, the coarse grains show a marked increase in rate of growth with temperature. Consequently, the highest coarsening temperatures give the best results.

To control the growth of the coarse grains along the rod axis, the coarsening anneals are carried out in a temperature gradient. Because of the undesirable balance of the rates of particle coalescence and coarse grain growth at the lower temperatures, small temperature gradients are used.

**Status of Investigation**

At present the identity of the inhibiting phase or phases has not yet been determined. An investigation is now underway to determine the phase components and to determine those factors in the process which are important, but which have as yet not been recognized.

The method produces a high yield of single crystals in specimens cut from rods which have an optimum distribution of inhibitor. Although the best annealing treatment must be determined for each new ingot, the high yield and ease of specimen preparation are attractive features of this method for producing single crystals. The back reflection Laue patterns in Figs. 8a and 8b indicate the relative perfection of the crystals obtained by coarsening, as compared with crystals made by the modified Bridgeman method.

**References:**

Fig. 1. Single Crystal Specimen.
Crystal at center is 11 mm.
long x 4 mm. diameter.

Fig. 2. Average grain diameter (mm. log scale) versus annealing time
for 1.1% manganese in aluminum. Vertical dashed line indicates
approximate start of coarsening.
Fig. 3. 3065 ND. Start of grain coarsening in Al-Mn alloy.

Fig. 4. 11,920. Start of grain coarsening in uranium. 100x
12,530 Macro-etched. 9x
Fig. 5. Large grains at transverse section of rod specimen after completed grain coarsening.

12,513 Macro-etched. 9x
Fig. 6. Start of grain coarsening in rod containing a gradient in concentration of impurity phases.

12,529 Macro-etched. 9x
Fig. 7. Single grain at transverse section as a result of grain coarsening under optimum conditions.
Fig. 8. Comparison of Laue spots from single crystals produced by (a) grain coarsening and (b) modified Bridgeman techniques. Photograms enlarged 1x.
SESSION III-A

FABRICATION OF FUEL ELEMENTS

Chairman – R. B. Gordon
THE FABRICATION OF FUEL SLUGS FOR
THE EXPERIMENTAL BREEDER REACTOR

A. B. Shuck

Introduction

The initial fuel charge for the Experimental Breeder Reactor consisted of solid enriched uranium cylinders measuring 0.364" diameter by 1.872" long and 0.384" diameter by 1.666" and 2.515" long, nominal dimensions. A special fabricating shop was set up at the Argonne National Laboratory to manufacture these slugs.

The great value of the enriched uranium, plus the fact that the quantity of material allocated for the job was very nearly the amount needed in the reactor, made it necessary to achieve a high degree of quantitative efficiency in manufacturing the fuel and to establish a rigorous system of accounting for the material in each step of the process.

An additional requirement was that the slugs be dimensionally stable to thermal cycling and irradiation effects.

Method

The equipment, manufacturing method and accounting procedure were developed in a series of preliminary fabrication runs using normal uranium. The normal slugs were thermal cycled and tested metallurgically before beginning operations on enriched uranium. All weighing was done to the nearest milligram and then rounded off to the nearest 1/100 of a gram for the accountability record. A more complete description of the equipment and development of the methods is contained in report number ANL-4617(1).

Melting and Casting

The feed material consisted of Oak Ridge reduction buttons of 93 to 94 percent enrichment. Furnace charges were made up of two reduction buttons weighing approximately 1 kilogram each or of one reduction button and approximately 1 kilogram of return process scrap. After weighing, the reduction buttons were chilled in liquid nitrogen to make them more brittle and broken into quarters using a hooded hydraulic press. Analytical samples were taken from the clean chips formed in breaking. The remelt stock consisted of rod ends and scrap slugs from previously fabricated castings. This material was electrocleaned in sulfuric acid-glycerine-water solution to remove oxide or burned-in oil before melting. All materials were weighed before and after the preparation of the charge.

The furnace charge was packed loosely around the stopper rod of a previously weighed magnesia crucible, which was then placed in the quartz tube vacuum furnace shown in Fig. 2. The furnace was pumped down to an indicated pressure of about \(10^{-7}\) mm of Hg. Power was supplied to the furnace...
by a 15 kW, 220 volt, 10,000 cycle motor-alternator through a conventional induction coil and was received by a tantalum heater around the crucible.

The furnace was heated at a rate of about 700°C per hour to allow the ceramics to come to temperature uniformly and to maintain a vacuum below 10⁻⁴ mm of Hg. No crucible breakage was experienced in the 32 heats made. Temperature was read directly upon the metal through sight holes in the crucible cover and furnace top by means of a prism and optical pyrometer. When a temperature of 1365°C was reached, the uranium was poured into the water-cooled copper mold shown in Fig. 3.

The furnace was allowed to cool under vacuum and then brought to atmospheric pressure. The casting, crucible assembly, shot and skull were removed and the weights balanced against the total weight going into the furnace.

The castings produced by this method had mirror-bright metallic surfaces and were largely free of laps or surface defects. A casting is shown in Fig. 4. The castings were radiographed using a cobalt-60 source.

Fabrication of Rod

The castings were rolled directly, without cropping or surface machining. They were preheated for 10 minutes in an oil bath at 300°C and then rolled from 1-1/4" diameter to 0.66" diameter in nine passes on hand rounding rolls, with a one minute soak in the oil bath between each pass. After rolling to 0.66" diameter, the rods were vacuum annealed for one hour at 725°C. After annealing, the rods were again soak rolled at 300°C in eight passes from 0.66" diameter to 0.395" or 0.385" diameter depending upon the finished diameter of the slugs.

The rolled rods were not straight and were usually out of round between 0.005" and 0.010". The rods were then reheated to 300°C and swaged through a rotary swaging machine to 0.363" or 0.383". The swaging operation produced a straight rod, round to within 0.001". Weights were taken after each step of the fabrication.

Breaking Slugs From Bar

It was desirable to part the rod into slugs with a minimum of turnings. The method used was to cut circumferential notches about 1/32" with a 60°-sharp threading tool at intervals of 0.050" longer than the finished slug. This allowed about 0.020" for the contraction in length which takes place later when the slugs are beta treated, plus machining allowance for facing the ends of the slugs. After notching, the rods were chilled in liquid nitrogen, and slugs were snapped off using the hooded press. This operation is shown in Fig. 5. The slugs and notch turnings were weighed and the slugs were inspected for cracks or other internal defects which would show at the fractured surfaces. The rod ends and any reject slugs were reserved as remelt stock.

Beta Treatment

The acceptable slugs were beta treated by heating in an argon atmosphere.
at 725°C for 15 minutes and quenching in water. This was done by enclosing the slugs in stainless steel tubes which were then evacuated and filled with purified and dried argon. The tubes were inserted in a 725°C lead bath for 15 minutes, after which they were opened and the slugs dropped into a recirculating water quench. The slugs were then dried, weighed, and then annealed for 2 hours at 575°C in the vacuum annealing furnace shown in Fig. 6.

Beta treating increased the diameter of the fuel slugs about 0.0015" and decreased their length from 0.0121" to 0.020". There was some surface reaction with the quench water and to make certain that this surface oxide would not be rubbed off and lost in subsequent handling, it was removed by electrocleaning in a 46% sulfuric acid-9% glycerine-45% water solution. The slugs were water rinsed, dried and weighed after electrocleaning and the weight compared to that before cleaning to determine the quantity of uranium in solution.

Final Machining

The ends of the slugs were faced to length and chamfered in the hooded lathe shown in Fig. 7. No machining was done on the cylindrical surfaces.

Dilatometer Test

Properly beta treated slugs had a coefficient of expansion of between 12 microinches/°C and 13 microinches/°C, while the coefficient of expansion of the alpha rolled slugs was approximately 6.5 microinches/°C in the rolling direction. A dipping dilatometer made of nickel (coefficient of expansion 13.3 microinches/°C) was used in a screening test to determine whether all of the slugs had been through the transformation. The dilatometer with the slug in place was dipped in ice water and zeroed, then transferred to boiling water. Properly treated slugs gave very little differential movement while an untreated slug caused a differential deflection of about 0.0012".

The slugs were then weighed individually and inspected dimensionally using a comparator and gage blocks.

Just before assembly into the fuel rods, the slugs were electropolished in the sulfuric acid-glycerine-water solution, rinsed through distilled water and dried with acetone. A finished fuel slug is shown in Fig. 8.

Upsetting

The first tests of the fuel rods in the breeder pile indicated the need for a slight change in the geometry of the fuel section. This required that the diameters of certain slugs be enlarged to 0.384". This was accomplished by upsetting 0.364" diameter slugs to 0.384", reducing the lengths to 1.666". This was done by pressing in double acting dies at 300°C from the oil bath. A split die was used to allow easy extraction of the slugs. After upsetting, the slugs were re-beta treated and then coined to the exact length desired. After coined, the slugs were electropolished before assembly into the fuel rods.
Utilization of the Material

The distribution of material in useable metal and in unprocessed residue is shown as a percentage of the total weight of reduction metal process in Table 1.

Table 1. Utilization of Material, Melts 1 Through 25.

<table>
<thead>
<tr>
<th>Material</th>
<th>Yield</th>
<th>Residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>Finished Fuel Slugs</td>
<td>95.226%</td>
<td></td>
</tr>
<tr>
<td>Unused Remelt Samples</td>
<td>0.475%</td>
<td></td>
</tr>
<tr>
<td>Samples</td>
<td>0.057%</td>
<td></td>
</tr>
<tr>
<td>Melting &amp; Casting Residue</td>
<td></td>
<td>1.650%</td>
</tr>
<tr>
<td>Fabricating Residue</td>
<td></td>
<td>0.108%</td>
</tr>
<tr>
<td>Beta Treating, Annealing and Sampling Residue</td>
<td></td>
<td>0.007%</td>
</tr>
<tr>
<td>Turnings</td>
<td></td>
<td>2.368%</td>
</tr>
<tr>
<td>Electropolishing Solution</td>
<td></td>
<td>0.109%</td>
</tr>
</tbody>
</table>

| Total Yield                                  | 95.758% | 4.242%   |

References

Flow Sheet of Operations for Manufacturing Fuel Slugs

1. Melt and Cast
   1. Vacuum Melting Furnace
   2. H. T. Generator

2. Casting
   1. Liquid N₂

3. Heating Oil
   1. ROLL FROM 1/8" DIA. TO 0.040" DIA.
   2. Rolling Mill
   3. Break-Rod Milling
   4. Oil Heating Bath

4. Weigh and INDIVIDUALLY

5. Reduce and Electrolysis
   1. Polishing Solution
   2. Acid
   3. Electrolyte
   4. Solutions

6. Wipe Oil, Heating Oil
   1. Castings
   2. Wiping Rags

7. Chemical and Isotopic Analysis
   1. Chemicals
   2. Wipes

8. Reduce and Remelt Scrap
   1. Remelt Scap
   2. Vacuum Furnace

9. Cast and Anneal
   1. Vacuum Casting Furnace

10. Weigh
    1. norge and Break to 1.015" Length
    2. Heated Lathe
    3. Forging

11. Weigh and individually
    1. Heated Lathe
    2. Tools

12. Inspect Dimensionally
    1. Comparator
    2. Micrometer

13. Weigh Individually
    1. Electrolyte
    2. Solutions

14. Weigh
    1. Electrolyte
    2. Solutions

15. Weigh Individually
    1. Electrolyte
    2. Solutions

16. Weigh Individually
    1. Electrolyte
    2. Solutions

17. Finished Fuel Slugs

Fig. 1 - Flow Sheet of Operations for Manufacturing Fuel Slugs.
Fig. 2 - Vacuum Melting Furnace. (Negative Number AS-2)

Fig. 3 - Water-Cooled Copper Mold. (Negative Number AS-5)
Fig. 4 - Enriched Uranium Casting (Negative Number AS-6)
Fig. 5 = Breaking Fuel Slugs From Rolled and Swaged Rod.
(Negative Number A5-16)
Fig. 7 - Hooded Lathe for Machining Fuel Slugs. (Negative Number AS-20)

Fig. 8 - Finished Fuel Slug. (Negative Number AS-21)

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LIQUID METAL COOLING OF URANIUM METAL FUEL ELEMENTS

L. R. Allen

The work on liquid metal cooling of uranium fuel elements was started at M.I.T. to determine the feasibility of removing large amounts of heat from uranium at elevated temperatures. A tentative goal was set at 1 kw/cm² heat throughput while maintaining the coldest portion of the uranium at 400°C, the hottest portion still to be solid. The thickness of the uranium layer was to be between 1/8 and 1/4 inches thick. After achievement of cooling rates of this order of magnitude, thermal cycling of the system was started to determine stability in regard to interface coefficients.

The particular methods selected formed a secondary goal. The use of lead-bismuth eutectic alloy as a cooling fluid, necessitated determination of materials and methods to contain and control a large volume of such a coolant.

The apparatus used is block-diagramed in Figure 1.

All tanks, including metal reservoir, boiler shell, vacuum tanks and most of the pipes, are made of low carbon iron. The oxide was not removed from the hot-worked condition.

The molten metal impeller pump is driven by a 5 h.p. motor with an enclosed long shaft in which the windage space is water cooled as is the motor housing. The coolant flow can be varied between 0 and 12 gals. at 400°C.

The vacuum system permits evacuation to .02 μ using a variety of seals including rubber gaskets, expanded metal bellows and welding. Sight ports allow optical temperature readings to be taken on the test specimens. Due to occasional failures in the lead-bismuth lines it was necessary to install a vacuum line filter.

The power source used is a 3000 cycle motor-generator set with a maximum rating of 100 kw.

A system of Bourdon gauges was used as a measure of the flow rate. These had to be calibrated by direct measurement.

A number of different type samples were tested for throughput: (1) cylinders of uranium cast around a tantalum liner, (2) a finely machined shrink fit tube assembly, and finally (3) a coextruded uranium tube clad inside with zirconium.

The cast-on piece of uranium failed due to rupture of the tantalum sleeving at a large scored mark on the sleeve. The shrink fitted assembly gave a throughput of 40 kw on the first run, 20 kw on the second run and less than 5 kw on the third. This, plus the distortion of the piece,
indicated a sufficiently large interface coefficient to rule out shrink fitting as an assembly method.

The most successful sample used to date is a coextruded uranium-zirconium complex. A 20-mil layer of zirconium lines a 7/8 inch hole in the extruded tube. The outside is not clad. This type specimen has been used at throughputs of 80 kw or 1.05 kw/cm² for a number of hours without a measurable increase in interface coefficients. The same sample was cycled between approximately 260° and 900°C for 50 cycles without measurable growth and later flux density measurements indicate no increase in interface coefficient with cycling. Further work on this specimen type is projected.

Work to be done here involves running the above sample to destruction for flux density measurements and cooling of liquid uranium in an effort to raise the flux density measured to 2 kw/cm².
SCHEMATIC DIAGRAM OF URANIUM COOLING SYSTEM

- WATER BOILER
- VACUUM LINE FILTER
- DIFFUSION PUMP
- FOREPUMP

- STEAM VENT
- WATER DRAIN
- GAGES MEASURE H₂O FLOW IN G.P.M.
- 220 V. PREHEAT
- COLD WATER
- COOLANT SUMP
- 220 VOLT PREHEAT
- PUMP
- DRAIN
- COOLANT FLOW THROTTLE
- SAMPLE
- 100 KW 3000 CYCLE
- TEMPERATURE MEASUREMENTS

Figure 1
SESSION III-B

PHYSICAL METALLURGY OF ZIRCONIUM

Chairman - Earl T. Hayes
SOME OBSERVATIONS ON THE ZIRCONIUM-NIOBIUM ALLOYS

B. A. Rogers and D. F. Atkins

Introduction

At the Metallurgical Meeting at Oak Ridge in 1951, E. S. Hodge reported some results on the zirconium-niobium alloys that he had obtained at the Ames Laboratory. He proposed the partial, tentative diagram shown in Fig. 1, which is reproduced from the proceedings of the Oak Ridge meeting (1). Some additional results described in this report are concerned with the arrangement of lines that exist as a consequence of the transformation in zirconium at about 860°C. For this area, Hodge reported some inconsistency in his data and stated that a selection was made of the values that seemed most reliable.

Effect of Temperature on Electrical Resistance

Consideration of methods that might be used in a re-determination of the composition and temperature of the eutectoid in Fig. 1 led to the decision to make additional resistance-temperature measurements. This method has the advantages that specimens can be maintained at a fixed temperature for as long as necessary to reach equilibrium and that readings are taken while the specimen is at temperature.

The Apparatus

Because of the possibility that residual gas in the vacuum chamber containing the specimen might introduce contamination, the pumping system was designed to keep the pressure below 10⁻⁵ mm Hg. Usually the pressure did not exceed 10⁻⁶ mm Hg. Under these conditions, the specimens did not appear to become contaminated even when held at temperature for long periods.

Resistance was measured by the potentiometric method. The circuit is illustrated in Fig. 2. Specimen H has the form of a wire about 0.75 millimeters in diameter and 12 or 15 centimeters long bent into the shape of a hairpin. Attached to the ends of the hairpin are two 2-centimeter long pieces, F and G, of No. 14 gage Chromel A wire which
Fig. 1  The tentative diagram of the zirconium side of the zirconium-niobium alloy system according to Hodge(1).
Fig. 2  Diagram of the circuit used for resistance-temperature measurements.
have been drilled to receive the specimen and then squeezed down on it. Current leads, B and C, are attached to the ends of F and G in the same manner. Potential leads, A and D, are attached to the same pieces by spot welding. All four lead wires are No. 28 gage Chromel P wire. Wire E is Alumel and with wire D provides a thermocouple for measuring the temperature of the specimen. The entire unit is sealed in a Vycor tube about one inch inside diameter which rests in a furnace of the combustion tube type.

The potential drop across the specimen was compared with the drop across a standard resistance of 0.100 ohm in series with it, the current being kept at 50 milliamperes. Both potential measurements were made with a Rubicon Type B instrument. The output of the thermocouple was measured with a Rubicon precision portable potentiometer. The temperature of the furnace was maintained constant for some time previous to each reading by means of a separate thermocouple connected to a strip-chart controller-recorder.

Results

Some data have been accumulated with the apparatus described above but their interpretation is still uncertain. For this reason the title mentions "Observations" only and the graphs are presented with a minimum of description.

The first three graphs represent unalloyed zirconium specimens. Fig. 3 shows the resistance-temperature curve obtained on a piece of wire swaged from some first grade iodide zirconium furnished by the Argonne Laboratory. The pronounced decrease in resistance at the transformation point begins slightly below 850°C. A similar curve for a wire swaged from some iodide zirconium that had been melted under helium in a tungsten-electrode arc furnace is presented in Fig. 4. The decrease in resistance in this curve is slightly less than in Fig. 3 and begins slightly below 845°C. This difference in behavior may be partly the result of arc-melting but the original bar stock probably was a little less pure than the metal corresponding to Fig. 3.

A wire made from Bureau of Mines sponge that had been arc-melted under helium gave the curve shown in Fig. 5. The decrease in resistance is much less and the temperature of the beginning of transformation is definitely higher - about 860°C - than for iodide zirconium.

Alloying produces a marked change in the temperature and character of the break at the transformation point. The addition of 2 per cent of niobium reduces greatly the sharpness of the change in phase and lowers its temperature.
Fig. 3 The resistance-temperature curve for annealed zirconium wire swaged directly from iodide bar.
Fig. 4. The resistance-temperature curve for annealed zirconium wire from arc-melted iodide bar.
Fig. 5 The resistance-temperature curve for annealed zirconium wire from arc-melted Bureau of Mines sponge.

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by about 200°C as illustrated by Fig. 6. Four per cent of niobium has a still greater flattening effect as is evident from Fig. 7.

The curves for the 7 per cent niobium alloy are shown in Fig. 8. At elevated temperatures, the position of the curve is about the same regardless of the prior history but, at any temperature below 600°C, the resistance depends upon the prior heat treatment. The thermal treatment for each curve is indicated in the legend. This sensitivity to previous thermal treatment was not observed on the unalloyed specimens nor on the 2 or 4 per cent niobium alloys.

Curves for the 15 per cent niobium alloy are presented in Fig. 9. If the alloy is cooled from 800°C its resistance-temperature behavior is indicated by the smooth line, B. If it is reheated, its resistance follows approximately the same path. If it is held in the vicinity of 500°C or 525°C for perhaps 20 hours, it yields the jagged curve, A. However, once the specimen is carried to a temperature beyond the foot of the abrupt descent, its resistance follows along the smooth curve again. Should the specimen, while following the smooth path, be held for 24 hours at a temperature not much below 600°C its resistance increases but does not reach the value on the jagged curve. In general, one may say that any temperature between 525°C and 600°C gives less complete transition from the smooth to the jagged curve. Lowering of the temperature of holding below 500°C causes the effect to die out.

The 20 and 30 per cent alloys behave similarly to the 15 per cent one.

Effect of Temperature on Modulus of Rigidity

Some experiments were made on the effect of temperature on the modulus of rigidity of the zirconium-niobium alloys. For this purpose, coil springs were made up from wires of the same diameter as those used in the resistance measurements—about 0.75 millimeters. The mean coil diameter was about 8 millimeters and each coil had 6 turns. The modulus was calculated from the formula

$$ G = \frac{R \times 8ND^3}{d^4} $$

in which

- R = rate of extension in pounds per inch
- N = number of turns
- D = mean diameter of coil in inches
- d = diameter of wire in inches
Fig. 6 The resistance-temperature curve for zirconium-niobium wire containing 2 per cent niobium.
Fig. 7. The resistance-temperature curve for zirconium-niobium wire containing 4 per cent niobium.
Fig. 8 Resistance-temperature curves for zirconium-niobium wire containing 7 per cent niobium:

- Curve A - After cooling rapidly from 900°C
- Curve B - After cooling slowly from 900°C
- Curve C - After holding at 525°C for 40 hours and cooling slowly

All curves taken with rising temperature
Fig. 9  Resistance-temperature curves for zirconium-niobium wire containing 15 per cent niobium:  A.  after being cooled slowly from 900°C;  B.  after being held at 525°C for 20 hours and cooled slowly.

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Figure 10 shows the change in modulus of rigidity with temperature for the 15 per cent niobium alloy. Curve A is for the alloy after it had been cooled at a moderate rate from 900°C. The modulus decreases only slightly up to 500°C but begins to diminish more rapidly at about that temperature. At all temperatures it is low by comparison with the room temperature values for carbon steel and stainless steel - 18,000,000 and 14,000,000 psi, respectively. If the spring is held for a time at 525°C so that it is in the condition corresponding to the jagged curve of Fig. 9, its modulus is initially higher but decreases a little more rapidly with temperature as indicated by curve B.

Although according to these tests, the modulus holds up well in comparison with the modulus of either carbon steel or cold-worked stainless steel wire springs, a spring made of zirconium-niobium could be operated at 500°C for only very light loads. This is indicated by the fact that a short life test of about 50,000 operations under the same load that was used in determining the modulus of rigidity caused a permanent extension of approximately 50 per cent.

A spring made of 30 per cent niobium alloy behaved in about the same way as the spring just described. A spring made of 7 per cent niobium alloy showed a rapid decrease in modulus in the vicinity of 400°C as illustrated by Fig. 11.

For comparison, curves for piano wire, the material used in ordinary coil springs, and for 18 per cent chromium-8 per cent nickel stainless steel wire are shown in Fig. 12 and Fig. 13, respectively. Although the piano wire spring has several times as high a modulus or rigidity as 15 per cent niobium or 30 per cent niobium wire at room temperature, its value at 500°C is lower. The cold swaged stainless steel wire undergoes a rapid decrease in modulus above 450°C. A coil of this material has no spring action if taken to 900°C and cooled again to room temperature.

Reference

Fig. 10: Modulus of rigidity-temperature curve for zirconium-niobium alloy containing 15 per cent niobium:

A. alloy cooled slowly from 900°C;
B. alloy held 20 hours at 525°C and cooled slowly.
Fig. 11 Modulus of rigidity-temperature curve for zirconium-niobium alloy containing 7 per cent niobium. Alloy cooled slowly from 900°C.

MODULUS OF RIGIDITY—TEMPERATURE CURVE FOR ZIRCONIUM—NIOBium CONTAINING 7 PERCENT NIOBium AFTER COOLING SLOWLY FROM 900°C
6 COILS-8.60 MM. O.D.-0.85MM. WIRE
Fig. 12 Modulus of rigidity-temperature curve for carbon steel spring wire.
Fig. 13  Modulus of rigidity-temperature curve for stainless (18-8) steel in cold worked condition.
When cold-worked metals are annealed they return to an essentially strain-free state. The process is generally attributed to recovery and recrystallization, but in the past few years another thermally activated process for the removal of internal strains in cold-worked metals has been extensively studied. Numerous investigators have revealed subgrain formation after annealing cold-worked metal crystals, and have described the results in terms of a dislocation mechanism of polygonization. Recent investigations at Westinghouse Atomic Power Division indicate that similar results and mechanism seem to be applicable for zirconium.

To obtain these results, quantitative x-ray diffraction techniques have been used to (a) determine \{10\ 10\} 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) determine the rate of the reorientations for specimens heated for appropriate times at temperatures from 98 degrees Centigrade to 600 degrees Centigrade. Metallographic observations and hardness measurements for all the heat-treated specimens have been correlated with the x-ray results.

When zirconium is drastically cold-rolled a high degree of preferred orientation results in which prism poles, \{10\ 10\}, are perpendicular to the rolling direction. After fully annealing this material an entirely new texture develops which can be represented as a 20 degree or 40 degree rotation of the deformation texture about hexagonal axes of the annealing texture. In the present work the decrease in transmitted x-ray diffraction intensity from the prism poles perpendicular to the rolling direction, for the specimens heated at various temperatures for various times, has been used as a measure of the rate of thermally induced reorientation. Likewise, for the same series of specimens, the increase of \{10\ 10\} intensity from a minimum in the cold-rolled condition to a maximum in the fully annealed condition, for an orientation corresponding to a maximum on the pole figure of fully annealed material, has been used as a measure of the rate of formation of the annealing texture.

From these data it has been found that during the first stages of low temperature annealing of drastically cold-rolled polycrystalline zirconium, there occurs complete recrystallization of the matrix, as evidenced metallographically, to slightly disoriented domains about two microns average diameter. Even though further annealing leads to complete reorientation, no metallographic evidence of primary recrystallization nor
discontinuous growth of existant favorably oriented domains was found.

From the domain growth measurements, and x-ray rate of reorientation measurements, activation energies for domain growth and for reorientation were calculated.

Acknowledgment

This work was done under Atomic Energy Commission Contract AT-11-1-GEN-14.
BENEFICIAL EFFECT OF ALLOY ADDITIONS TO ZIRCONIUM ON
THE CORROSION RESISTANCE IN 600°F WATER

D. S. Kneppel and T. T. Magel

Results obtained at M.I.T. have indicated that additions of iron, nickel or chromium will allow higher levels of impurities in zirconium and still maintain good corrosion resistance in 600°F water. The effects of these alloying elements are even greater in steam corrosion. Results have also been obtained which indicate the feasibility of producing corrosion resistant graphite-melted alloys.

Some time ago it was shown that additions of about 0.1 wt.% iron or nickel showed some improvement in corrosion resistance over similar material which had none of these additions. When the amounts of these alloying agents were increased, the results showed considerable promise as can be seen in Table 1. It should be pointed out that samples 774 and 761 have had over 3,000 hours of exposure time. The corrosion rate is comparable with that obtained on good crystal bar.

Table 1. Beneficial Effect of Fe and Ni on Corrosion Resistance of Drip-Melted Zirconium in 600°F Water

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>N₂</th>
<th>Al</th>
<th>Fe</th>
<th>Ni</th>
<th>Corrosion Rate (mg/cm²/mo)</th>
</tr>
</thead>
<tbody>
<tr>
<td>762</td>
<td>16</td>
<td>295</td>
<td>290</td>
<td>&lt;20</td>
<td>3.5</td>
</tr>
<tr>
<td>467</td>
<td>35</td>
<td>290</td>
<td>120</td>
<td>860</td>
<td>0.76</td>
</tr>
<tr>
<td>774</td>
<td>38</td>
<td>305</td>
<td>345</td>
<td>4300</td>
<td>0.07</td>
</tr>
<tr>
<td>761</td>
<td>23</td>
<td>440</td>
<td>7300</td>
<td>310</td>
<td>0.05</td>
</tr>
<tr>
<td>796</td>
<td>207</td>
<td>40</td>
<td>155</td>
<td>&lt;25</td>
<td>6.6</td>
</tr>
<tr>
<td>470</td>
<td>215</td>
<td>90</td>
<td>2300</td>
<td>150</td>
<td>2.3</td>
</tr>
</tbody>
</table>

Recent results have indicated that when the iron and nickel contents are low, zirconium is more susceptible to corrosion. In connection with the problem that WAPD has been having where some metal fabricated from WAPD crystal bar corroded for reasons unknown, whereas, in general, the metal fabricated from Foote crystal bar showed good corrosion resistance, four samples of zirconium were sent to M.I.T. for study. Chemical analyses showed that the only differences in the two types of materials were in the iron and nickel contents. The results are shown in Table 2. Experience at M.I.T. has shown that in over 50% of the analyses made at M.I.T.
on Foote crystal bar zirconium, the nickel contents were over 50 ppm. Similarly, it has been found that iron generally was about 300-400 ppm. Thus it can be seen that WAPD crystal bar has very much lower iron and nickel content if these four samples are representative of the WAPD and Foote production.

Table 2. Corrosion and Analytical Study of WAPD Samples

<table>
<thead>
<tr>
<th>WAPD Sample No.</th>
<th>Description</th>
<th>Spectrographic Analysis in ppm</th>
<th>Corrosion in 600°F Water-</th>
<th>600°F Water-</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Fe</td>
<td>Ni</td>
<td>After 969 Hrs.</td>
</tr>
<tr>
<td>867</td>
<td>Annealed cover plate, Footo crystal bar, tested good at 650°F</td>
<td>160</td>
<td>50</td>
<td>Good</td>
</tr>
<tr>
<td>897</td>
<td>Annealed cover plate, WAPD crystal bar, tested bad at 600°F and 650°F</td>
<td>45</td>
<td>2</td>
<td>White Oxide, High Wt. Gain</td>
</tr>
<tr>
<td>652</td>
<td>Annealed cover plate, WAPD crystal bar, tested good at 650°F</td>
<td>35</td>
<td>10</td>
<td>Some White Oxide, Low Wt. Gain</td>
</tr>
<tr>
<td>1150</td>
<td>Unannealed strip, recent WAPD Prod'n., tested good at 600°F</td>
<td>65</td>
<td>15</td>
<td>Small amount White Oxide, Low Wt. Gain Acceptable</td>
</tr>
</tbody>
</table>

It is significant that the breakdown of corrosion resistance in 600°F water at M.I.T. did not occur until after 3 or 4 weeks' exposure, whereas differences in corrosion of these samples tested in 600°F steam showed up in one week of testing. Nickel definitely improves the corrosion resistance of zirconium in 600°F water, but the beneficial effect in steam corrosion is decidedly more pronounced. The low iron and nickel contents in the WAPD crystal bar are therefore a matter of concern. This effect of nickel in steam had been confirmed by WAPD, who at the same time, found that iron was also beneficial in steam corrosion. Table 3 shows the inhibiting effect of nickel in 750°F steam corrosion. This table is part of a memorandum prepared at M.I.T. in 1950, evaluating the proposed B.M.I. accelerated corrosion test in 750°F steam. It was roughly estimated at that time that only 75 ppm of nickel was needed to give an appreciable inhibiting effect. The effect of nickel, iron and chromium appeared so promising that testing of these alloys in 900°F steam was tried. Initial exposures showed relatively high weight gains; additional exposures gave steady increases of weight. However, no white oxide appeared, whereas by comparison, samples
Table 3. Inhibiting Effect of Nickel on Corrosion in 750°F Steam

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Analysis in ppm</th>
<th>Wt. Gain after 18 Hrs. in 750°F Steam (mg/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
<td>Al</td>
</tr>
<tr>
<td>3</td>
<td>&lt;20</td>
<td>100</td>
</tr>
<tr>
<td>40</td>
<td>395</td>
<td>130</td>
</tr>
<tr>
<td>4</td>
<td>&lt;25</td>
<td>150</td>
</tr>
<tr>
<td>37</td>
<td>310</td>
<td>155</td>
</tr>
<tr>
<td>11</td>
<td>&lt;20</td>
<td>330</td>
</tr>
<tr>
<td>44</td>
<td>925</td>
<td>325</td>
</tr>
<tr>
<td>9</td>
<td>&lt;25</td>
<td>270</td>
</tr>
<tr>
<td>38</td>
<td>320</td>
<td>270</td>
</tr>
</tbody>
</table>

corroded in 600°F water having those weight gains would show a heavy oxide coat. Since 900°F is in the range where hydrogen could conceivably be absorbed, it was thought that the weight gain was due to hydrogen pickup. However heating the corroded sample in a static vacuum gave no indication of hydrogen evolution. Another corroded sample was analyzed for oxygen. The increase of the oxygen content of the corroded sample checked with the calculated oxygen value when it was assumed that the weight increase of the corroded sample was due to oxygen pickup. This was further checked by heating samples in air at 900°F. Here again the relatively high weight gains were observed but no formation of white oxide. Thus it would seem that the alloys in 900°F steam present a protective film which prevents rapid oxidation. However, the absorption and diffusion of oxygen at these temperatures is relatively high.

From Table 4, however, we see that nickel, iron and chromium are over 100 times more effective than tin in steam corrosion at 900°F. Both the non-alloyed zirconium and the tin alloy gave a heavy, white oxide layer after only 41 hours, whereas by comparison, sample 855 with only 0.43 Wt.% nickel showed practically no white oxide up to 827 hours. Iron and chromium are about equally as effective in steam corrosion at this temperature.

The addition of tin to zirconium allows a higher level of impurities which can be tolerated in the metal and still maintain good corrosion.
resistance in 600°F water. Nitrogen, of all the impurities which can cause poor corrosion resistance, is probably the most important in that it is the most difficult to control and is most effective in accelerating corrosion. A study of the amount of nitrogen which can be tolerated for a given tin alloy has been undertaken. The results given herein are not to be considered as final since in many cases corrosion samples have not accumulated sufficient time to be able to say definitely that they are or are not corrosion resistant.

Table 4. Corrosion of Zirconium Alloys in 900°F Steam

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Percent Alloy</th>
<th>Time (Hours)</th>
<th>Wt. Gain (mg/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>856</td>
<td>None</td>
<td>41</td>
<td>785</td>
</tr>
<tr>
<td>857</td>
<td>5.83% Sn</td>
<td>41</td>
<td>167</td>
</tr>
<tr>
<td>855</td>
<td>0.43% Ni</td>
<td>827</td>
<td>2.75</td>
</tr>
<tr>
<td>871</td>
<td>0.86% Ni - 0.4% Fe</td>
<td>589</td>
<td>1.95</td>
</tr>
<tr>
<td>874</td>
<td>0.22% Cr</td>
<td>62</td>
<td>2.57</td>
</tr>
<tr>
<td>933</td>
<td>0.63% Ni</td>
<td>150</td>
<td>1.91</td>
</tr>
<tr>
<td>936</td>
<td>0.93% Cr</td>
<td>267</td>
<td>2.35</td>
</tr>
<tr>
<td>937</td>
<td>2.94% Fe</td>
<td>307</td>
<td>1.73</td>
</tr>
<tr>
<td>938</td>
<td>1.02% Fe</td>
<td>281</td>
<td>1.63</td>
</tr>
</tbody>
</table>

The alloys were all prepared by the vacuum drip melting method. Pure nitrogen gas was added to grade I crystal bar by diffusion at 1500°-1600°C. The metal was then drip melted once. Holes were drilled in the ingot and the correct amount of tin placed in the holes. The ingot with the tin was redrilled a total of five additional times in order to get a homogeneous alloy with respect to tin and nitrogen. During each drip melt, an undetermined amount of tin was lost due to volatilization and deposition on the walls of the quartz tube. For this reason it was difficult to make an alloy of exact tin composition by the drip melting method. After drip melting, the final ingot was given an additional homogenization treatment at about 1300°C for 20 minutes, the purpose of which was to eliminate drop boundaries. The latter have occasionally been observed to cause corrosion especially after a few thousand hours.
The samples for corrosion and chemical analysis were taken close together to minimize errors due to segregation. Two random analyses were made for tin on each of the samples submitted. A study of the results on tin analysis shown in Table 5 indicates that in spite of the numerous drip melts some inhomogeneity was apparent on a number of samples. This fact has been taken into consideration in the preparation of Table 6. It is believed that the nitrogen analysis represents the true nitrogen content of the corrosion sample.

Table 5. Nitrogen Tolerance Versus Tin Content Corrosion in 600°F Water

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>sum N₂</th>
<th>% Sn</th>
<th>Corrosion Rate (mg/cm²/mo)</th>
<th>Total No. Hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>877</td>
<td>1365</td>
<td>2.03-2.51</td>
<td>1.3</td>
<td>352</td>
</tr>
<tr>
<td>876</td>
<td>1156</td>
<td>0.83-0.86</td>
<td>32</td>
<td>43</td>
</tr>
<tr>
<td>921*</td>
<td>975</td>
<td>1.91-2.16</td>
<td>2.6</td>
<td>130</td>
</tr>
<tr>
<td>977*</td>
<td>970</td>
<td>1.65-3.14</td>
<td>3.5</td>
<td>132</td>
</tr>
<tr>
<td>920*</td>
<td>975</td>
<td>2.32-2.60</td>
<td>1.2</td>
<td>404</td>
</tr>
<tr>
<td>976*</td>
<td>990</td>
<td>2.62-3.12</td>
<td>Low</td>
<td>292</td>
</tr>
<tr>
<td>878</td>
<td>864</td>
<td>0.30-.35</td>
<td>13</td>
<td>34</td>
</tr>
<tr>
<td>875</td>
<td>892</td>
<td>.43-.46</td>
<td>23</td>
<td>43</td>
</tr>
<tr>
<td>974*</td>
<td>900</td>
<td>1.73-2.24</td>
<td>1.5</td>
<td>292</td>
</tr>
<tr>
<td>918*</td>
<td>870</td>
<td>2.07-2.13</td>
<td>Negligible</td>
<td>1085</td>
</tr>
<tr>
<td>975*</td>
<td>880</td>
<td>2.73-2.75</td>
<td>Low</td>
<td>292</td>
</tr>
<tr>
<td>893</td>
<td>906</td>
<td>2.83-2.96</td>
<td>.07</td>
<td>1384</td>
</tr>
<tr>
<td>840</td>
<td>820</td>
<td>1.19-3.58</td>
<td>3.5</td>
<td>97</td>
</tr>
<tr>
<td>860</td>
<td>791</td>
<td>1.60-1.70</td>
<td>5.3</td>
<td>657</td>
</tr>
<tr>
<td>972*</td>
<td>810</td>
<td>1.98-2.45</td>
<td>Low</td>
<td>292</td>
</tr>
<tr>
<td>973*</td>
<td>790</td>
<td>2.21-2.55</td>
<td>1.4</td>
<td>292</td>
</tr>
<tr>
<td>895</td>
<td>752</td>
<td>2.32-2.97</td>
<td>Negligible</td>
<td>1384</td>
</tr>
<tr>
<td>879</td>
<td>676</td>
<td>.86-.88</td>
<td>5.6</td>
<td>79</td>
</tr>
<tr>
<td>919*</td>
<td>725</td>
<td>2.22-2.48</td>
<td>1.2</td>
<td>731</td>
</tr>
<tr>
<td>896</td>
<td>671</td>
<td>2.42-2.93</td>
<td>Negligible</td>
<td>1384</td>
</tr>
<tr>
<td>881</td>
<td>427</td>
<td>.35-.36</td>
<td>2.2</td>
<td>151</td>
</tr>
<tr>
<td>883</td>
<td>368</td>
<td>2.40-2.41</td>
<td>Negligible</td>
<td>1951</td>
</tr>
<tr>
<td>882</td>
<td>306</td>
<td>.72-.89</td>
<td>Negligible</td>
<td>1951</td>
</tr>
<tr>
<td>870</td>
<td>197</td>
<td>.87-1.07</td>
<td>Negligible</td>
<td>2316</td>
</tr>
</tbody>
</table>

*Cold rolled 30%, annealed 2 hours at 700°F.
After this investigation had been under way for a short time, it was felt that previous metallurgical history might have a serious effect on the corrosion resistance of tin alloys. For this reason it was desirable to have all corrosion samples in a "standard metallurgical state." The treatment adopted was a 30% cold reduction by rolling the drip-melted specimen, followed by a two-hour anneal at 700°C. Samples which had this treatment are marked with an asterisk in Table 5.

Analytical and corrosion data on the samples are given in Table 5. Because of the difficulty in preparing tin alloys of an exact composition by the drip melting method, a regular series could not be presented. However, by interpolation, it was possible to make a calculated guess at the nitrogen tolerance for a given tin content. The tentative tolerance limits are shown in Table 6. All other impurities were, in general, low and of the same order of magnitude so that it was improbable that they would change the tolerance limits to any extent. Work on this problem is continuing.

Table 6. Tentative Tolerance Limits for Nitrogen in Zr-Sn Alloys

<table>
<thead>
<tr>
<th>% Sn</th>
<th>Tolerance Limit for N₂ in μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>60 - 100</td>
</tr>
<tr>
<td>1/2</td>
<td>200</td>
</tr>
<tr>
<td>1</td>
<td>300</td>
</tr>
<tr>
<td>2</td>
<td>600</td>
</tr>
<tr>
<td>2 1/2</td>
<td>700</td>
</tr>
<tr>
<td>3</td>
<td>800</td>
</tr>
</tbody>
</table>

Early work at M.I.T. showed that carbon was detrimental to the corrosion resistance of zirconium. This is shown in Figure 1. The impurities in both samples were about the same except for the carbon and the penetration of corrosion due to carbides is plainly visible. In spite of the fact that induction graphite melting is one of the best methods for producing massive zirconium, it was necessary to exclude this method because of carbon pickup with the resulting poor corrosion resistance in 600°F water. However, with the advent of the tin alloy first introduced by Ames and Battelle, it seemed that it would be possible to make corrosion resistant graphite-melted zirconium-tin alloys. It is suspected that the conflicting and sometimes discouraging corrosion results obtained by the various persons working on this problem may have been in large part due to the lack of emphasis placed on the history of the sample. This is perhaps shown more clearly by comparing samples of graphite-melted metal in...
Bureau of Mines Cast Billet No. 218
(0.04%C) corroded 509 hours in 300°C water — Transverse section 6X

Bureau of Mines Cast Billet No. 197
(0.13%C) corroded 345 hours in 300°C water — Transverse section 6X

Figure 1
the as-cast state and after extrusion. (See Table 7.) Extrusion has the effect of breaking up the continuity of the carbides. From Table 7 it is seen that even in the case of the graphite-melted non-alloyed sample extrusion reduces the corrosion rate about ten times.

Table 7. Comparison of Corrosion Rates of Graphite-Melted Zirconium in the As-Cast and Extruded States

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>State</th>
<th>C (%)</th>
<th>Ni (%)</th>
<th>Sn (%)</th>
<th>Total No. of Hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>939</td>
<td>As Cast</td>
<td>0.17</td>
<td></td>
<td>1.99</td>
<td>11</td>
</tr>
<tr>
<td>902</td>
<td>Extruded</td>
<td></td>
<td></td>
<td>0.03</td>
<td>1200</td>
</tr>
<tr>
<td>956</td>
<td>As Cast</td>
<td>0.16</td>
<td></td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>957</td>
<td>Extruded</td>
<td></td>
<td></td>
<td>0.9</td>
<td>438</td>
</tr>
<tr>
<td>940</td>
<td>As Cast</td>
<td>0.26</td>
<td></td>
<td>1.07</td>
<td>14</td>
</tr>
<tr>
<td>903</td>
<td>Extruded</td>
<td></td>
<td></td>
<td>0.05</td>
<td>1200</td>
</tr>
<tr>
<td>945</td>
<td>As Cast</td>
<td>0.26</td>
<td>0.51</td>
<td>&lt;1</td>
<td>544</td>
</tr>
<tr>
<td>908</td>
<td>Extruded</td>
<td></td>
<td></td>
<td>0.3</td>
<td>1065</td>
</tr>
</tbody>
</table>

Since the possibility exists of obtaining the as-cast structure in welded sections, it is important to know something of the corrosion characteristics in the as-cast state. Some data are given in Table 8. It is seen from this table that good corrosion resistant graphite-melted tin alloys in the as-cast structure can be obtained if the carbon content can be kept low. The value of higher tin additions is small when the carbon content becomes too high. It can be seen that the nickel alloys give the same order of magnitude of protection. This fact is better seen in Table 9 where the carbon contents are approximately the same. The carbon contents are too high for good corrosion resistance for the amounts of nickel and chromium additions, but the improvement is apparent when compared with sample 942 containing no alloying agent.

In Table 10 some corrosion results are given on graphite-melted extruded tin alloys. All the samples presented in this table show good...
corrosion resistance. However, it should be pointed out that even in the case of the extruded alloy, if the carbon content was too high the material would corrode. Here again it seems that raising the tin content of the alloy will not completely overcome the effect of very high carbon content.

Table 8. Corrosion Data of Graphite-Melted Zirconium Alloys in the As-Cast State

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>%C</th>
<th>%Sn</th>
<th>%Ni</th>
<th>%Cr</th>
<th>Total No.</th>
<th>Hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>900</td>
<td>0.48</td>
<td>2.9</td>
<td></td>
<td></td>
<td>0.4</td>
<td>1328</td>
</tr>
<tr>
<td>840</td>
<td>0.39</td>
<td>2.48</td>
<td></td>
<td></td>
<td>0.34</td>
<td>2590</td>
</tr>
<tr>
<td>866</td>
<td>0.29</td>
<td>0.73</td>
<td></td>
<td></td>
<td>0.54</td>
<td>2049</td>
</tr>
<tr>
<td>812</td>
<td>0.28</td>
<td></td>
<td>0.95</td>
<td></td>
<td>8</td>
<td>112</td>
</tr>
<tr>
<td>945</td>
<td>0.26</td>
<td></td>
<td>0.51</td>
<td></td>
<td>&lt;1</td>
<td>544</td>
</tr>
<tr>
<td>958</td>
<td>0.19</td>
<td>2.97</td>
<td></td>
<td></td>
<td>Low</td>
<td>438</td>
</tr>
<tr>
<td>964</td>
<td>0.17</td>
<td>2.84</td>
<td></td>
<td></td>
<td>1.4</td>
<td>322</td>
</tr>
<tr>
<td>939</td>
<td>0.17</td>
<td>1.99</td>
<td></td>
<td></td>
<td>11</td>
<td>177</td>
</tr>
<tr>
<td>944</td>
<td>0.17</td>
<td>2.25</td>
<td>0.66</td>
<td></td>
<td>Low</td>
<td>513</td>
</tr>
<tr>
<td>950</td>
<td>0.16</td>
<td>2.80</td>
<td></td>
<td></td>
<td>Low</td>
<td>322</td>
</tr>
<tr>
<td>947</td>
<td>0.16</td>
<td>2.24</td>
<td>0.40</td>
<td></td>
<td>Low</td>
<td>544</td>
</tr>
<tr>
<td>948</td>
<td>0.12</td>
<td>2.23</td>
<td></td>
<td></td>
<td>Low</td>
<td>544</td>
</tr>
<tr>
<td>943</td>
<td>0.11</td>
<td>1.0</td>
<td></td>
<td></td>
<td>Low</td>
<td>513</td>
</tr>
<tr>
<td>970</td>
<td>0.072</td>
<td>2.42</td>
<td></td>
<td></td>
<td>Low</td>
<td>487</td>
</tr>
</tbody>
</table>

Table 9. Effect of Alloy Additions on Corrosion Rate of Graphite-Melted Zirconium in the As-Cast State (Note High Carbon Content)

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>%C</th>
<th>%Sn</th>
<th>Other</th>
<th>Corrosion Rate</th>
<th>Total No.</th>
<th>Hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>942</td>
<td>0.26</td>
<td></td>
<td></td>
<td>44.3</td>
<td>177</td>
<td></td>
</tr>
<tr>
<td>702</td>
<td>0.287</td>
<td>5.59</td>
<td></td>
<td>16</td>
<td>2163</td>
<td></td>
</tr>
<tr>
<td>940</td>
<td>0.26</td>
<td>1.07</td>
<td></td>
<td>14.1</td>
<td>177</td>
<td></td>
</tr>
<tr>
<td>945</td>
<td>0.26</td>
<td></td>
<td>51% Ni</td>
<td>&lt;1</td>
<td>544</td>
<td></td>
</tr>
<tr>
<td>812</td>
<td>0.26</td>
<td></td>
<td>95% Cr</td>
<td>8</td>
<td>112</td>
<td></td>
</tr>
<tr>
<td>866</td>
<td>0.29</td>
<td></td>
<td>73% Ni</td>
<td>54</td>
<td>2049</td>
<td></td>
</tr>
</tbody>
</table>
Table 10. Corrosion Data of Graphite-Melted Tin Alloys as Extruded

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Reduction Ratio</th>
<th>%C</th>
<th>%Sn</th>
<th>Corrosion Rate (mg/cm²/mo)</th>
<th>Total No. of Hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>823</td>
<td>16:1</td>
<td>.19</td>
<td>2.43</td>
<td>0.095</td>
<td>5715</td>
</tr>
<tr>
<td>959</td>
<td>16:1</td>
<td>.19</td>
<td>2.97</td>
<td>Low</td>
<td>322</td>
</tr>
<tr>
<td>902</td>
<td>16:1</td>
<td>.17</td>
<td>1.99</td>
<td>Negligible</td>
<td>1279</td>
</tr>
<tr>
<td>965</td>
<td>16:1</td>
<td>.17</td>
<td>2.84</td>
<td>Low</td>
<td>158</td>
</tr>
<tr>
<td>961</td>
<td>16:1</td>
<td>.16</td>
<td>2.80</td>
<td>Low</td>
<td>322</td>
</tr>
<tr>
<td>965</td>
<td>40:1</td>
<td>.14</td>
<td>3.01</td>
<td>Negligible</td>
<td>3392</td>
</tr>
<tr>
<td>911</td>
<td>16:1</td>
<td>.12</td>
<td>2.23</td>
<td>Negligible</td>
<td>1065</td>
</tr>
<tr>
<td>863</td>
<td>40:1</td>
<td>.12</td>
<td>2.66</td>
<td>Negligible</td>
<td>3409</td>
</tr>
</tbody>
</table>

Setting an upper limit for carbon at this time would be meaningless since it has been shown that this depends largely on the distribution of the carbides which in turn is affected by the melting operation and the amount of subsequent working.

Table 11 shows that extruded, graphite-melted nickel alloys give about the same corrosion resistance as the extruded tin alloys.

Table 11. Corrosion Data of Graphite-Melted Tin and Nickel Alloys as Extruded (Reduction Ratio - 16:1)

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>%C</th>
<th>%Ni</th>
<th>%Sn</th>
<th>Corrosion Rate (mg/cm²/mo)</th>
<th>Total No. of Hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>908</td>
<td>.26</td>
<td>.51</td>
<td>None</td>
<td>.27</td>
<td>1,065</td>
</tr>
<tr>
<td>907</td>
<td>.17</td>
<td>.66</td>
<td>.25</td>
<td>.05</td>
<td>1,279</td>
</tr>
<tr>
<td>910</td>
<td>.16</td>
<td>.40</td>
<td>2.24</td>
<td>Negligible</td>
<td>1,065</td>
</tr>
<tr>
<td>906</td>
<td>.11</td>
<td>1.0</td>
<td>None</td>
<td>.09</td>
<td>1,279</td>
</tr>
</tbody>
</table>

Additional study is needed on graphite-melted zirconium alloys, but the indications are that the carbon pickup can be kept low enough so that corrosion resistant metal can be obtained. More work is needed to fill gaps in the data but the indications are that iron, nickel, and possibly chromium, will give corrosion resistant metal which is comparable to the tin alloy. In addition, the iron and nickel alloy is superior to the tin alloy in corrosion resistance in steam.
References

CORROSION RESISTANCE OF ZIRCONIUM ALLOYS

B. A. Rogers and J. T. Williams

Introduction

The resistance of zirconium and its alloys to corrosion by hot distilled water has been of interest for some time. The high degree of resistance of good iodide zirconium and of some of the zirconium-tin alloys is well known. However, as more information on the subject is needed, some additional data are presented in this report. The alloys on which results are given were not made by the authors but by other members of the Ames Laboratory Staff to whom acknowledgment is made herewith. Not all of the data are reported but a selection has been made of the results that appear to be the most valuable.

Apparatus and Procedure

As the tests were made at 315°C, at which temperature the pressure is approximately 1500 pounds per square inch, small autoclaves were necessary for holding the samples. These vessels are very similar to equipment used in other laboratories. The body of the autoclave is made by machining a 1 3/8 inch diameter hole in a 2 1/2 inch diameter bar of No. 347 stainless steel. The end is closed by a plug of similar steel that bears on a silver gasket and is held in place by a carbon steel cap screwed onto threads on the exterior of the autoclave body.

The vessels are heated in an air-circulating furnace large enough to hold sixteen of them in one test. The furnace is essentially a large, metal, doughnut-shaped enclosure through which air is circulated by a fan. Heat is supplied by electric heating units set at the vertical portions of the vertically set doughnut. Screens in these heated regions support the autoclaves. The temperature is controlled by a Brown "Electronik" strip-chart recorder-controller.

Samples are ground to the desired shape for testing. They are finished on 600 grit silicon carbide paper discs. After a sample has been wiped clean, its dimensions are measured with a micrometer caliper. Next it is scrubbed with soap and water, rinsed with distilled water, rinsed again with acetone and dried in air.
The cleaned and weighed specimen - usually with several other specimens - is placed in a clean autoclave which is then filled about one third full of water, capped, and placed in the furnace. After the autoclave has been held at 315°C for the required length of time, the specimens are removed, rinsed with acetone, air-dried and weighed. Occasionally, deposits of silver are found on the walls of the enclosure and on the surfaces of samples. In such cases, rinsing with acetone is preceded by immersion for one minute in a solution of one part concentrated nitric acid to one part distilled water.

The grinding, scrubbing, and measuring operations are omitted when previously exposed specimens are to be given additional exposure.

Experimental Results

Both zirconium-tin and zirconium-antimony alloys have shown good corrosion resistance in 315°C distilled water. Table 1 shows some of the results obtained on graphite-melted, zirconium-tin alloys. The first column under

Table 1

The Corrosion of Graphite-Melted Zirconium-Tin Alloys
Held in 315°C Distilled Water for 1672 Hours

<table>
<thead>
<tr>
<th>Tin per cent</th>
<th>Corrosion rate in mg/cm²/mo for</th>
<th>Coreduc.</th>
<th>Iodide</th>
<th>Ames</th>
<th>Bur. Min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>5</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>1</td>
<td>7</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>0.7</td>
<td>7</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>0.1</td>
<td>9</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>0.2</td>
<td>5</td>
<td>6</td>
<td></td>
</tr>
</tbody>
</table>

corrosion rate gives results for alloys made by coreduction in a bomb and melted in a graphite crucible afterwards. In the next three columns are the results for alloys that were made by melting a mixture of tin and the indicated kind of zirconium in a graphite crucible. The coreduced alloys were melted in a resistance furnace with a graphite heating element. The others were melted by induction heating. The data suggest that addition of the tin in the reduction step
rather than during melting is the most effective way of producing a corrosion resistant alloy.

More detailed information on the effect of tin content on the corrosion rate of coreduced alloys is presented in Table 2. Obviously, the optimum amount of tin is about 5 per cent, yet unexplainable results are sometimes obtained as is evident from the high corrosion rate of the 4.25 per cent alloy. If unalloyed zirconium is made by bomb reduction and tin added afterwards as part of the crucible charge, the resulting alloys have a higher rate of corrosion than coreduced and remelted alloys of the same composition. For

<table>
<thead>
<tr>
<th>Tin per cent</th>
<th>Corrosion rate after 1065 hours mg/cm²/mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.78</td>
<td>0.4</td>
</tr>
<tr>
<td>3.00</td>
<td>0.3</td>
</tr>
<tr>
<td>3.27</td>
<td>0.2</td>
</tr>
<tr>
<td>3.32</td>
<td>0.2</td>
</tr>
<tr>
<td>3.56</td>
<td>0.1</td>
</tr>
<tr>
<td>3.58</td>
<td>0.2</td>
</tr>
<tr>
<td>3.90</td>
<td>0.1</td>
</tr>
<tr>
<td>3.95</td>
<td>0.2</td>
</tr>
<tr>
<td>4.25</td>
<td>0.2</td>
</tr>
<tr>
<td>5.31</td>
<td>0.2</td>
</tr>
<tr>
<td>5.57</td>
<td>0.07</td>
</tr>
<tr>
<td>9.25</td>
<td>0.4</td>
</tr>
</tbody>
</table>

example, five alloys made up in this way with intended compositions of 5 per cent tin had corrosion rates of 2, 10, 22, 4 and 2 milligrams per square centimeter per month after 213 hours at 315°C. One difference that may be mentioned is that the coreduced alloys were melted in a resistance furnace whereas the others were melted by induction heating. However, other experiments have indicated that the kind of furnace is unlikely to have so large an effect on the corrosion rate.
Usually, zirconium-tin alloys appear to be most resistant when in the cast state. Heating the cast material or fabricating it reduces its resistance to attack by distilled water. An illustration of this behavior is given in Table 3 for two nominally 5 per cent tin alloys made from iodide zirconium. Both of the alloys were melted in graphite crucibles by induction heating.

Table 3

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Corrosion rate after 450 hours</th>
<th>mg/cm²/mo</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As-cast</td>
<td>Cast and</td>
</tr>
<tr>
<td></td>
<td></td>
<td>annealed</td>
</tr>
<tr>
<td>JR-3-14</td>
<td>13</td>
<td>62</td>
</tr>
<tr>
<td>JR-3-16</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>

The considerable variation in rates of corrosion of zirconium-tin alloys melted in graphite crucibles suggests that the carbon content of these alloys has a marked effect on their behavior. Such an inference would be drawn from Table 4 which shows the comparative resistance of some

Table 4

<table>
<thead>
<tr>
<th>Tin per cent</th>
<th>Corrosion rate after 753 hours</th>
<th>mg/cm²/mo</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cold-rolled</td>
<td>Recast in graphite and annealed</td>
</tr>
<tr>
<td>1</td>
<td>0.07</td>
<td>23</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
<td>21</td>
</tr>
<tr>
<td>3</td>
<td>0.1</td>
<td>20</td>
</tr>
<tr>
<td>4</td>
<td>0.03</td>
<td>22</td>
</tr>
<tr>
<td>5</td>
<td>0.1</td>
<td>22</td>
</tr>
</tbody>
</table>

DECLASSIFIED
alloys before and after they were melted in graphite. The alloys were melted originally in the direct current arc furnace from iodide zirconium and ordinary chemical grade tin. Even in the cold-rolled condition their resistance is fairly good. However, remelting them in graphite crucibles and reheating pieces of ingot resulted in the relatively high values shown in the last column of the table.

As has been stated above, good resistance to corrosion has been obtained in alloys melted in graphite so that the effect of carbon is still uncertain. A complicating factor is the nitrogen content. The effect of both elements is uncertain as resistant alloys have been obtained with either element high - carbon up to 5000 ppm and nitrogen up to 500 ppm. About the only statement that can be made is that if both carbon and nitrogen are high, the alloy almost certainly will have poor resistance.

Table 5

The Corrosion of Coreduced, Graphite-Melted Zirconium-Antimony Alloys in 315°C Distilled Water

<table>
<thead>
<tr>
<th>Antimony per cent</th>
<th>Exposure hours</th>
<th>Corrosion rate mg/cm²/mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.04</td>
<td>243</td>
<td>8</td>
</tr>
<tr>
<td>0.06</td>
<td>305</td>
<td>14</td>
</tr>
<tr>
<td>0.07</td>
<td>274</td>
<td>5</td>
</tr>
<tr>
<td>0.15</td>
<td>274</td>
<td>0.3</td>
</tr>
<tr>
<td>0.2</td>
<td>243</td>
<td>0.4</td>
</tr>
<tr>
<td>0.3</td>
<td>305</td>
<td>2</td>
</tr>
<tr>
<td>0.44</td>
<td>274</td>
<td>0.2</td>
</tr>
<tr>
<td>1.1</td>
<td>305</td>
<td>1.0</td>
</tr>
<tr>
<td>1.6</td>
<td>293</td>
<td>0.8</td>
</tr>
<tr>
<td>1.9</td>
<td>293</td>
<td>7</td>
</tr>
<tr>
<td>2.7</td>
<td>305</td>
<td>7</td>
</tr>
<tr>
<td>4.3</td>
<td>305</td>
<td>1</td>
</tr>
</tbody>
</table>

Antimony also has a beneficial effect on the resistance to corrosion of alloys melted in graphite crucibles. Apparently, both tin and antimony counteract the bad effect of carbon on unalloyed zirconium. Only fractional percentages of antimony are needed as may be noted from Table 5 which
gives the results for a series of coreduced alloys melted in graphite crucibles heated in a graphite resistor furnace.

Tin and antimony together also produce resistant alloys as indicated in Table 6. These alloys were prepared by reduction of the zirconium fluoride in a bomb with tin and antimony added to the charge in the usual way. They were melted afterwards in graphite crucibles in a graphite resistor furnace. The intended compositions in Table 6 are to be taken as approximate; analysis of alloys produced by the bomb method invariably shows considerably less tin and antimony than were introduced into the charge.

**Summary**

Graphite-melted alloys of zirconium containing from 0.2 to 1.5 per cent antimony or two to five per cent tin have been found to have good corrosion resistance in 315°C distilled water. Some zirconium-tin-antimony alloys also have shown good corrosion resistance in similar tests. The

<table>
<thead>
<tr>
<th>Tin per cent</th>
<th>Antimony per cent</th>
<th>Corrosion rate after 1060 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.46</td>
<td>1.3</td>
<td>0.2 mg/cm²/mo</td>
</tr>
<tr>
<td>0.55</td>
<td>0.2</td>
<td>0.4</td>
</tr>
<tr>
<td>0.65</td>
<td>0.14</td>
<td>0.6</td>
</tr>
<tr>
<td>0.77</td>
<td>a</td>
<td>0.8</td>
</tr>
<tr>
<td>1b</td>
<td>0.2b</td>
<td>39</td>
</tr>
<tr>
<td>1b</td>
<td>0.5b</td>
<td>13</td>
</tr>
<tr>
<td>2b</td>
<td>1b</td>
<td>0.2</td>
</tr>
<tr>
<td>3b</td>
<td>2b</td>
<td>0.5</td>
</tr>
<tr>
<td>4b</td>
<td>3b</td>
<td>0.3</td>
</tr>
<tr>
<td>5b</td>
<td></td>
<td>0.1</td>
</tr>
</tbody>
</table>

*a* Antimony added in bomb charge, none found by analysis.

*b* Calculated composition.
corrosion rates of these alloys appear to be sensitive to other factors besides the content of major constituents. Two factors believed to be important are carbon and nitrogen but positive evidence has not been obtained yet.
SESSION IV

SYMPOSIUM ON THE FABRICATION OF URANIUM

(NO PAPERS)
SESSION V-A

THE METALLURGY OF THORIUM

Chairman - J. H. Frye, Jr.
THE FABRICATION OF THORIUM

H. A. Saller and J. R. Keeler

Battelle Memorial Institute

Report No. BMI-738

Introduction

The fabrication of thorium has been studied from the standpoint of developing satisfactory methods of converting the castings received from Ames into sheet, rod, wire, tubing, and other useful shapes. Some work was also done on the cladding of thorium to improve the corrosion resistance in water. The welding of thorium was also investigated.

Forging

The castings received from Ames varied from 3 inches to 4-3/4 inches in diameter and weighed up to 90 pounds. These castings were too large to roll directly in the Battelle 8-x 12-inch mill, and it was necessary to forge to a size suitable for rolling. For rolling sheet, a 1-1/2-inch-thick by 5- to 6-inch-wide plate was forged by alternately flattening and edging the billet. Square forgings were made for rolling into bar stock.

The billets were heated to 1500 F in an electric muffle furnace in a helium atmosphere and were forged with flat dies on an air-operated hammer which had a rated blow of 6930 foot-pounds. Several reheats were usually necessary to obtain the desired size.

Several requests were made for 3-inch-diameter forgings to be made from the 4-3/4-inch castings. These were made by drawing down the billet as a square and finally finishing as an octagon. Efforts to round the octagon on the flat dies were unsuccessful and usually resulted in cracking at the center of the ends.

Some billets also cracked at the ends during the forging of the plates and squares, but some forged without cracking. Data on the analyses of the billets are incomplete, but where available, no correlation could be found between the amount of impurity and the tendency to crack. On metallographic examination of the cracked ends, however, it was observed that there was a grain-boundary precipitate outlining the cast-grain structure and the cracks appeared to follow this intergranular network.

Fig. 1 shows a section taken at one end of a forged three-inch octagon adjacent to a crack. Fig. 2 shows the base of a crack which appears to be following the grain boundary.
Fig. 1. End of Forged Billet Adjacent to Crack. Note Intergranular Precipitate.

Fig. 2. Section at Base of Crack in End of Forged Billet.
The cracking usually occurred at the top end of the casting and may be the result of segregation during solidification. Analyses for carbon, however, at the center and outer edge of the billets showed no segregation of this element.

In addition to forging the large Ames castings, some drop-hammer tests were made at temperatures between 1000°F and 1800°F. Cylindrical specimens 5/8 inch in diameter by 1-1/2 inches long were machined from hot-rolled bars. These specimens were hit one blow by a falling weight, and the decrease in length measured. The temperature was varied by 100°F increments, and tests were made with both 25-pound and 100-pound weights dropped from heights of 44 and 60 inches, respectively.

The deformation increased with increasing temperatures up to 1200°F; but between 1200 and 1500°F, the amount of deformation was slightly less than at 1200°F. Above 1500°F, the amount of deformation again increased with increasing temperatures.

Fig. 3 shows the appearance of the forged cylinders. Deformations up to 47 per cent were obtained at 1800°F with the 500-foot-pound blow, but there was no evidence of cracking on any of the specimens.

The hot hardness of thorium showed a fairly linear decrease from 32 VHN at 1000°F to 9 VHN at 1500°F, and no explanation for the anomalous behavior during the forging tests is evident.

Cylindrical specimens similar to those used for the drop-hammer tests were also forged on the large air hammer from 1 inch to 1/4 inch in length, a reduction of 75 per cent in two blows. Samples were forged at 1000, 1200, 1400, 1600, and 1800°F. There was only slight cracking at the circumference of the pancake, and the samples forged at 1200°F showed the least cracking.

**Hot Rolling**

After forging, the billets were hot rolled at 1550°F to sheet or rod as required. In rolling sheet from the 1-1/2-inch-thick plate, reductions up to 25 per cent per pass have been made and larger reductions are probably feasible. Our usual practice is to make reductions of 0.080 to 0.100 inch per pass until the plate has been reduced to 0.4 inch thick. The reduction is then limited to 25 per cent per pass until the desired thickness is reached. Two to three passes are usually made before reheating the sheet.

Rods of various sizes were rolled in open passes designed for rolling steel. Diamond-oval-round and hand-rounding rolls have been used to roll round rod, and both yielded satisfactory rods from the forged billet.

Round bars also have been rolled directly from the casting. Several months ago, thorium bars 1-7/16 inch in diameter were rolled at the Simmons Saw and Steel Company (1). The cast billets were roughed down in diamond grooves from either 3-inch or 4-7/8-inch-diameter castings to a 1-3/4-inch square. This square was entered in hand-rounding rolls and rolled to 1-7/16-inch-diameter rod.
Fig. 3. Appearance of Thorium Cylinders After Drop-Hammer Tests With 25-Pound Hammer. (145 Foot Pounds)

<table>
<thead>
<tr>
<th>Forging Temp., °F.</th>
<th>1000</th>
<th>1100</th>
<th>1200</th>
<th>1200</th>
<th>1300</th>
<th>1400</th>
<th>1600</th>
<th>1800</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deformation, Per Cent</td>
<td>13.4</td>
<td>15.1</td>
<td>19.5</td>
<td>19.2</td>
<td>18.7</td>
<td>17.9</td>
<td>17.4</td>
<td>17.5</td>
</tr>
</tbody>
</table>
The billets were heated to 1550-1600 F in a gas-fired furnace with no protective atmosphere other than the products of combustion. They were rolled without intermediate reheating to the final size and finished at a temperature of 900 to 1000 F.

The lot of metal to be rolled contained both virgin metal and remelted chips. Both types of metal rolled without difficulty. There was practically no cracking and no end splits in the bars rolled according to schedule. The surface quality of the rolled rods appeared to be excellent with the exception of one or two rods rolled from billets which had large areas of surface porosity and numerous cold shuts. After rolling, the bars were straightened in a Medart straightener and machined to Hanford-size slugs.

Oxidation losses were approximately two per cent, and the recovery of finished slugs was 75 per cent of the total weight. Most of the machining losses occurred in the bars rolled from castings which had poor surfaces and from a bar which was badly seamed by inadvertently entering the wrong groove in the hand-rounding rolls.

The structures of the rolled bars varied considerably. Some bars had only slightly cold-worked structures while others were severely cold worked. The differences in the number of inclusions were striking.

Figs. 4, 5, and 6 show the inclusions in rods rolled from two different billets of virgin metal as well as those in a rod made from remelted chips.

The large gray inclusions are oxide. The smaller, lighter colored particles may be caused by carbon, nitrogen, iron, aluminum, beryllium, chromium, or nickel, which are present in quantities greater than 50 ppm. The variation in the number of inclusions in the virgin metal is indicated in Figs. 4 and 5. All of the remelted scrap metal contained large numbers of oxide inclusions.

Cold Rolling

The hot-worked metal has good ductility and can be cold rolled to reductions of 80 to 90 per cent without serious cracking. The hot-rolled metal has a hardness of about 85 VHN and increases to about 135 VHN after 90 per cent reduction. Most of the work-hardening occurs in the first ten per cent reduction, after which little increase in hardness is observed. Thorium foil 0.001 inch thick was rolled from 0.020-inch-thick hot-rolled sheet with only slight edge cracking.

Wire Drawing

Wire is another form of metal which was desired for experimental work by the physicists who, of course, thought nothing of asking for 0.003-0.005-inch-diameter wire as a starter.

Initial attempts to draw the metal were unsuccessful. The thorium seized to the Carboloy dies, and none of the commercial lubricants available
Fig. 4. Virgin Metal Rod A-228-B.

Fig. 5. Virgin Metal Rod A-118.

Fig. 6. Remelted Chips, Rod MX-312-A.
prevented this difficulty. After considerable experimenting, a lubricant was found which was satisfactory, and wire down to 0.045 inch was drawn from 1/4-inch hot-rolled rods of Ames metal. Further reductions were not made because smaller swaging dies were not available for pointing the wire.

The lubricant consisted of 100 cc of thinned Duco lacquer, No. 246-2048, thinned 3:1 with lacquer thinner and mixed with 30 grams of Molykote, which is molybdenum disulfide, and 10 grams of fumed lead-zinc oxide. This lubricant was also found to be a satisfactory lubricant for drawing titanium, zirconium, and uranium.

Wire down to 0.003 inch was made from arc-melted iodide thorium by another technique. This consisted of jacketing a 1/4-inch-diameter rod in a copper tube and drawing the composite. Pointing was accomplished by swaging and, in the smaller sizes, by pickling in nitric acid. The copper acted as a lubricant and was stripped from the wire in nitric acid when the desired size was reached. Ames thorium was also drawn by this technique, but the minimum size that could be made from 1/4-inch-diameter rod without annealing was 0.008 inch.

Tubes

Thorium tubes were made to investigate the difficulties to be expected in this operation. Tubes down to 0.115 x 0.020-inch wall were made from 1/2-inch-diameter drilled rod, and some drawing was also done on extruded tubes produced at Oak Ridge. The drawing was done at the Superior Tube Company using a proprietary lubricant developed by this company for drawing titanium. The drawing was done on steel mandrels rather than by plug drawing, since previous experience at Superior on titanium indicated that plug drawing would probably not be feasible. Some difficulty was experienced in removing the steel mandrel, but by careful rolling in hand rolls with light pressure, the tube could be expanded enough to remove the mandrel. Power rolling, swaging, and Medart rolling all tended to crack the thorium tubes. Initial reductions up to 35 per cent in cross-sectional area could be made and total reductions of 85 per cent were made before the tubes cracked and annealing was necessary. The flaring and flattening characteristics of the drawn tubes were poor.

Welding

Considerable work has been done on the welding of thorium. Satisfactory spot welds could be made in 1/16-inch-thick sheet, but cracks were a major problem in the shielded-tungsten-arc process. Single-pass welds could be made if special precautions were taken, but cracking invariably occurred if a second pass was made on a joint. Alloying with 2-1/2-atomic per cent of molybdenum, tungsten, and columbium improved the welding characteristics of the metal.
Cladding

Thorium has poor corrosion resistance in water, and an attempt was made to clad thorium with zirconium, titanium, and stainless steel. Thus far, only the zirconium cladding looks promising. Stainless steel reacts with thorium to form a brittle diffusion product at the interface. This, coupled with a large difference in the coefficients of thermal expansion of the two metals, has resulted in poor bonding.

Thorium tubes were drawn with stainless steel and titanium on both outside diameter and inside diameter. In neither case were good bonds obtained on drawing or after diffusion annealing. Roll cladding of thorium with titanium by the picture-frame technique was also unsuccessful. The interfaces appeared dirty and no bonding was obtained.

In the case of zirconium, good bonds were obtained on roll cladding by the picture-frame technique. The thorium core in a zirconium picture frame and outer welded steel jacket was rolled to 66 per cent reduction in four equal passes at 1650 F.

Several methods of preparing the thorium surface were investigated, but only a pickled surface yielded satisfactory bonds. This bond could be bent double, twisted, or chiseled without breaking the bond. The results on duplicate samples have been erratic, however, and additional work on the cladding of thorium is in progress.

Conclusion

Samples of the various shapes and sizes that we have fabricated are on the stage at the front of the auditorium and may be examined at the close of this session. On the whole, the mechanical working characteristics of the currently produced Ames castings are good. The metal is soft and ductile and can be worked by most of the standard metal-working procedures with only a few special precautions.

BIBLIOGRAPHY

EFFECT OF IMPURITIES AND ALLOY ADDITIONS ON THE MECHANICAL PROPERTIES OF THORIUM

D. E. Hamby*, J. A. Milko*, E. J. Boyle*

Introduction

Considerable interest has been shown in metallic thorium in the past few years because of its use as breeder material in reactors. The Metallurgy Division of the Oak Ridge National Laboratory embarked on a study of the mechanical and physical properties of thorium and thorium alloys in July, 1949. Considerable data have been obtained from this study (1) concerning the following properties: tensile properties including strength, ductility, modulus of elasticity, Poisson's ratio, shear modulus, impact strength, etc.

At the present time an extensive program of alloy development is being carried out. In order to obtain accurate, quantitative data for the effect of individual alloying elements, it is highly desirable to know the effects of the usual impurities found in thorium. These include oxygen, carbon, beryllium, and nitrogen. The present work is concerned with the effects of the first three. Data are also presented for the effect of one alloying element, i.e., chromium, on the mechanical properties of thorium.

Experimental Procedure

The alloys described in the present work were prepared by two techniques, as follows:

1. Arc Melting

The non-consumable electrode, arc-melting furnace is shown in Fig. 1. The alloy charge was placed in one of the cavities in the water-cooled, copper melting plate; the furnace was sealed and evacuated to one micron pressure. The furnace was flushed with purified argon, was evacuated again, and, finally, filled with argon to an absolute pressure of five psi. Direct current was employed and was furnished from an arc-welding unit. Approximately 380 amperes at about 50 volts were required to melt a charge of about 90 grams.

*Metallurgy Division, Oak Ridge National Laboratory
Paper presented at Ames Metallurgy Information Meeting, March, 1952
Prior to the start of melting of the thorium alloy charge, a small getter sample of zirconium was melted in order to remove any contaminants remaining in the argon atmosphere. For some alloy compositions which showed inhomogeneity after a single melting, two additional remeltings were employed.

2. Induction Melting

The second technique used for preparation of the alloys was induction melting in vacuum. The equipment is shown in Fig. 2. A stabilized zirconia crucible, in the vertical position, is used. Casting is accomplished by tilting the entire furnace shell assembly through 90° and thereby pouring into a zircon mold, encased in graphite, which is set with its axis at 90° to the axis of the crucible. The tilting is accomplished through a rotating "O" ring seal which connects the furnace shell to the vacuum system. All melting is carried out at pressures below 50 microns. When outgassing causes pressure rises above this figure, heating is discontinued until the system is pumped down again to 50 microns or less.

Fabrication

The buttons prepared by arc melting were fabricated into test specimens by cold rolling to 85% reduction followed by annealing for 30 minutes at 650°C, in the case of iodide thorium alloys, or 30 minutes at 750°C, in the case of Ames thorium alloys. Cast ingots of approximate size, one-inch diameter by five-inch length prepared by induction melting were cold rolled or swaged to appropriate size for preparation of test specimens. All alloys prepared by this technique were made with Ames thorium as the starting material.

Results and Discussion

Effect of Carbon

Tests were performed to determine the effect of carbon on the hardness of iodide thorium as quenched from various temperatures. The alloys were prepared from iodide crystal bar and a thorium-carbon master alloy by arc melting. The arc-melted buttons were homogenized for 24 hours at 950°C, held at the test temperature for 15 minutes, and quenched into water. The results are plotted in Fig. 3. It will be noted that carbon has a very marked hardening effect in thorium, especially when quenched from the higher temperatures.

The effects of carbon on the mechanical properties of iodide thorium are shown in Fig. 4. These alloys were prepared by arc melting followed by cold rolling 85% and were annealed for one-half hour at 650°C. It
may be seen that carbon has a very marked strengthening effect and lowers ductility. The highest carbon alloy tested, however, still retains substantial ductility.

The effects of carbon on the mechanical properties of Ames thorium are shown in Fig. 5. These specimens were prepared from Ames material which had been extruded in the temperature range of 700--850°C at reduction ratios from 3 to 1 to 9 to 1. All tensile specimens were annealed for one hour at 850°C prior to testing. The strengths and ductilities observed are approximately the same as those of iodide thorium alloys of equivalent carbon contents.

Effect of Oxygen

Alloys of thorium and oxygen were prepared by arc melting iodide thorium and a thorium-oxygen master alloy. The arc-melted buttons were treated as before, i.e., homogenized at 950°C for 24 hours, held at the test temperature for 15 minutes, and were water-quenched. The results are shown in Fig. 6. It is apparent that oxygen has only a minor hardening effect as compared with carbon. In the range of oxygen contents normally found in Ames thorium, the effect of increasing oxygen content is negligible.

Effect of Beryllium

Iodide thorium-beryllium alloys were prepared by arc melting and cold rolling in the same manner as the thorium-oxygen and thorium-carbon alloys. The results of tensile tests on specimens annealed for one-half hour at 650°C are shown in Table No. 1. There appears to be little effect up to beryllium contents of 0.11%. Beyond this amount, there appears to be a slight strengthening effect.

The effect of varying beryllium content in Ames material was investigated by examination of the properties of normal Ames thorium which had been extruded at temperatures in the range, 700 to 850°C at reduction ratios of 3 to 1 to 9 to 1. The results, listed in Table No. 2, show no significant effect from beryllium contents ranging from 0.014% to 0.0345%.

Effect of Chromium

Data for the effect of chromium on the properties of iodide thorium are shown in Fig. 7. These alloys were prepared in the same manner as the previous iodide alloys. Chromium appears to have a significant hardening effect, showing a 100% increase in strength for a 3% addition. The most marked effect on properties in this series of alloys, however, was that produced by the 0.038% carbon content in the 0.75% chromium alloy. There is some possibility that the combined effects of carbon
and chromium are greater than would be expected from their individual effects.

A single chromium Ames thorium alloy was prepared by arc melting, followed by cold rolling 75% and annealing. The properties of this alloy, in comparison with unalloyed Ames material prepared in the same manner, are shown in Table No. 3. The strengths for this alloy are considerably higher than those of the equivalent iodide alloy probably because of the effect of the higher carbon content.

Conclusions

On the basis of the data obtained in the preliminary experimental work described above, the following conclusions appear to be justified:

1. The most marked hardening and strengthening effect of any of the impurity elements investigated appears to be that of carbon. It has been shown that carbon contents in the range normally found in Ames thorium can produce increases of approximately 100% in strength and hardness as compared with unalloyed iodide thorium.

2. Oxygen and beryllium, in the range normally found in Ames thorium, do not produce significant hardening effects.

3. Chromium has been shown to be a potent hardening element in thorium. There is some possibility that combined carbon and chromium additions can result in larger increases in strength than would be expected from their individual effects.

References

1. ORNL-1090 Interim Report on Metallurgy of Thorium and Thorium Alloys--D. E. Hamby
Fig. 2. Induction Melting Furnace
Fig. 3.

EFFECT OF QUenchING TEMPERATURE ON THE HARDNESS OF THORIUM-CARBON ALLOYS
EFFECT OF C ON PROPERTIES OF IODIDE THORIUM

VICKERS HARDNESS NO.

YIELD STRENGTH, 1000 PSI

TENSILE STRENGTH, 1000 PSI

EFFECT OF C ON PROPERTIES OF IODIDE THORIUM
EFFECT OF C ON PROPERTIES OF AMES THORIUM

ALL SPECIMENS ANNEALED 1 HOUR AT 850 °C SECRET Y-6362

[Graph showing the relationship between tensile strength and yield strength in psi, and elongation in %, as a function of WGT. % C.]
EFFECT OF QUENCHING TEMPERATURE ON THE HARDNESS OF THORIUM-OXYGEN ALLOYS

Fig. 6.
EFFECT OF CR ON PROPERTIES OF IODIDE THORIUM

TENSILE STRENGTH AND YIELD STRENGTH (1000 PSI)

ELONGATION %

0.038% C
0.015% C
0.006% C

TENSILE STRENGTH

VICKERS HARDNESS NO.

% ELONGATION

YIELD STRENGTH (0.2% offset)

WGT. % Cr

0 0.5 1.0 1.5 2.0 2.5 3.0

0 10 20 30 40 50 60 70 80 90

VICKERS HARDNESS NO.
Table 1

Effect of Beryllium Content on the Properties of Iodide Thorium

(All samples were cold rolled approximately 85% into sheet form and annealed at 650°C for one-half hour)

<table>
<thead>
<tr>
<th>Alloy No.</th>
<th>% Be</th>
<th>% C</th>
<th>% W(1)</th>
<th>% Cu(1)</th>
<th>Tensile Strength psi</th>
<th>Yield Strength at 0.2% Offset psi</th>
<th>Prop. Limit psi</th>
<th>Mod. of Elast. (4) 10^6 psi</th>
<th>Elong. in 2&quot; %</th>
<th>Reduct. of Area %</th>
<th>Rockwell-H</th>
<th>Vickers Hardness</th>
<th>1360 D.P.H.</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-54</td>
<td>&lt; 0.01</td>
<td>0.015</td>
<td>0.15</td>
<td>0.02</td>
<td>18,000</td>
<td>7,600</td>
<td>2,100</td>
<td>12.8</td>
<td>27.0</td>
<td>69.0</td>
<td>74</td>
<td>10</td>
<td>54</td>
</tr>
<tr>
<td>F-56</td>
<td>0.02</td>
<td>0.018</td>
<td>0.10</td>
<td>0.03</td>
<td>19,500</td>
<td>6,700</td>
<td>4,000</td>
<td>8.0</td>
<td>36.0</td>
<td>71.0</td>
<td>60</td>
<td>37</td>
<td>11</td>
</tr>
<tr>
<td>F-55</td>
<td>0.03</td>
<td>0.008</td>
<td>0.20</td>
<td>0.02</td>
<td>18,600</td>
<td>7,000</td>
<td>5,000</td>
<td>10.0</td>
<td>11.0</td>
<td>57.0</td>
<td>65</td>
<td>36</td>
<td>17</td>
</tr>
<tr>
<td>F-58</td>
<td>0.04</td>
<td>0.022</td>
<td>0.01</td>
<td>0.03</td>
<td>19,900</td>
<td>6,300</td>
<td>3,600</td>
<td>8.2</td>
<td>29.0</td>
<td>76.0</td>
<td>63</td>
<td>37</td>
<td>16</td>
</tr>
<tr>
<td>F-59</td>
<td>0.11</td>
<td>0.017</td>
<td>0.07</td>
<td>0.03</td>
<td>21,700</td>
<td>7,800</td>
<td>1,800</td>
<td>7.7</td>
<td>38.0</td>
<td>67.0</td>
<td>71</td>
<td>40</td>
<td>52</td>
</tr>
<tr>
<td>F-86</td>
<td>0.32</td>
<td>0.02</td>
<td>&lt; 0.001</td>
<td>0.03</td>
<td>18,500</td>
<td>10,700</td>
<td>6,100</td>
<td>---</td>
<td>4.0</td>
<td>11.0</td>
<td>78</td>
<td>53</td>
<td>62</td>
</tr>
<tr>
<td>F-84</td>
<td>0.50</td>
<td>0.027</td>
<td>&lt; 0.001</td>
<td>0.03</td>
<td>21,100</td>
<td>12,200</td>
<td>8,200</td>
<td>13.1</td>
<td>29.0</td>
<td>36.0</td>
<td>75</td>
<td>48</td>
<td>57</td>
</tr>
<tr>
<td>F-85</td>
<td>0.69</td>
<td>0.01</td>
<td>&lt; 0.001</td>
<td>0.03</td>
<td>31,600</td>
<td>16,900</td>
<td>10,300</td>
<td>8.2</td>
<td>25.0</td>
<td>34.0</td>
<td>84</td>
<td>57</td>
<td>72</td>
</tr>
</tbody>
</table>

(1)Probably introduced during arc melting.
(2)10-kg. load, 2/3" objective
(3)10-kg. load, 16-mm. objective
(4)Value not determined with precision
Table 2

Effect of Carbon and Beryllium on the Properties of Extruded Ames Thorium

<table>
<thead>
<tr>
<th>Billet No.</th>
<th>Chemical Composition</th>
<th>Tensile Strength</th>
<th>Yield Point in 2&quot;</th>
<th>Elong.</th>
<th>Reduction of Area</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% C</td>
<td>% Be</td>
<td>% Si</td>
<td>psi</td>
<td>psi</td>
</tr>
<tr>
<td>A223A</td>
<td>0.045</td>
<td>0.017</td>
<td>0.27</td>
<td>30,500</td>
<td>22,100</td>
</tr>
<tr>
<td>A222C</td>
<td>0.053</td>
<td>0.017</td>
<td>0.35</td>
<td>30,300</td>
<td>20,800</td>
</tr>
<tr>
<td>A227A</td>
<td>0.051</td>
<td>0.022</td>
<td>0.18</td>
<td>29,600</td>
<td>21,100</td>
</tr>
<tr>
<td>A234A</td>
<td>0.050</td>
<td>0.014</td>
<td>0.11</td>
<td>31,100</td>
<td>22,700</td>
</tr>
<tr>
<td>Aver.</td>
<td>0.050</td>
<td>0.017</td>
<td>0.28</td>
<td>30,400</td>
<td>21,600</td>
</tr>
<tr>
<td>A231A</td>
<td>0.070</td>
<td>0.021</td>
<td>0.14</td>
<td>34,200</td>
<td>28,000</td>
</tr>
<tr>
<td>A231B</td>
<td>0.076</td>
<td>0.021</td>
<td>0.19</td>
<td>34,800</td>
<td>27,500</td>
</tr>
<tr>
<td>A231C-1</td>
<td>0.074</td>
<td>0.018</td>
<td>0.20</td>
<td>34,300</td>
<td>27,600</td>
</tr>
<tr>
<td>A231C-2</td>
<td>0.062</td>
<td>0.034</td>
<td>0.20</td>
<td>34,500</td>
<td>27,400</td>
</tr>
<tr>
<td>Aver.</td>
<td>0.071</td>
<td>0.024</td>
<td>0.18</td>
<td>34,900</td>
<td>27,600</td>
</tr>
<tr>
<td>A239C-1</td>
<td>0.095</td>
<td>0.029</td>
<td>0.26</td>
<td>38,200</td>
<td>33,100</td>
</tr>
<tr>
<td>A239D-2</td>
<td>0.084</td>
<td>0.028</td>
<td>0.22</td>
<td>38,900</td>
<td>31,900</td>
</tr>
<tr>
<td>A239D</td>
<td>0.085</td>
<td>0.031</td>
<td>0.30</td>
<td>37,800</td>
<td>31,400</td>
</tr>
<tr>
<td>A239B</td>
<td>0.088</td>
<td>0.029</td>
<td>0.12</td>
<td>38,800</td>
<td>32,100</td>
</tr>
<tr>
<td>A239A</td>
<td>0.098</td>
<td>0.016</td>
<td>0.37</td>
<td>39,000</td>
<td>31,300</td>
</tr>
<tr>
<td>Aver.</td>
<td>0.090</td>
<td>0.026</td>
<td>0.25</td>
<td>38,500</td>
<td>31,900</td>
</tr>
</tbody>
</table>
Table 3

Effect of Chromium Content on the Properties of Ames Thorium

<table>
<thead>
<tr>
<th>Specimen No.</th>
<th>Chromium Content %</th>
<th>Tensile Strength psi</th>
<th>Prop. Limit psi</th>
<th>Elongation in 2&quot; %</th>
<th>Reduction of Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ames Th</td>
<td>0</td>
<td>32,200</td>
<td>22,000</td>
<td>44</td>
<td>64</td>
</tr>
<tr>
<td>&quot;</td>
<td>0</td>
<td>32,000</td>
<td>23,600</td>
<td>47</td>
<td>40</td>
</tr>
<tr>
<td>&quot;</td>
<td>0</td>
<td>32,300</td>
<td>23,000</td>
<td>50</td>
<td>42</td>
</tr>
<tr>
<td>Average</td>
<td>0</td>
<td>32,200</td>
<td>22,900</td>
<td>47</td>
<td>49</td>
</tr>
<tr>
<td>Al72A</td>
<td>2.0</td>
<td>47,400</td>
<td>35,200</td>
<td>25</td>
<td>35</td>
</tr>
<tr>
<td>Al72E</td>
<td>2.0</td>
<td>52,200</td>
<td>38,100</td>
<td>25</td>
<td>31</td>
</tr>
<tr>
<td>Al72C</td>
<td>2.0</td>
<td>53,300</td>
<td>40,500</td>
<td>22</td>
<td>10</td>
</tr>
<tr>
<td>Average</td>
<td>2.0</td>
<td>51,000</td>
<td>37,900</td>
<td>24</td>
<td>25</td>
</tr>
</tbody>
</table>
MECHANICAL PROPERTIES OF AMES THORIUM

Glenn Murphy, R. T. Othmer and R. E. Uhrig

Summary

This paper constitutes a progress report on the mechanical properties of the thorium being produced at the Ames Laboratory. The tests were undertaken with the following objectives:

1. To evaluate the important mechanical properties, for use in engineering design, of the metal as produced.
2. To determine the effect of shaping operations and of ambient temperature on the properties.
3. To determine whether or not correlations existed between pairs of properties so that simple quality control tests could be used to check the acceptability of the metal as produced.
4. To determine the effect of impurities on the mechanical properties.

Tests are reported on specimens from 188 billets. The mechanical properties presented include the ultimate tensile strength, yield strength (0.2% offset), percentage elongation, percentage reduction in area, modulus of elasticity, endurance limit, and impact strength. A decrease in modulus of elasticity and yield strength and an increase in impact strength with an increase in temperature up to 600 degrees Centigrade is shown. An increase in carbon content results in a decrease in impact strength and an increase in yield strength. Strain hardening of thorium is indicated in creep tests.

Creep Tests

Creep tests at room temperature were performed in Baldwin Constant Load Creep Testing Machines using specimens either 0.505 in. or 0.252 in. in diameter with threaded ends. Two methods of strain measurement were used: an A-1, SR-4 strain gage with a Baldwin L-type strain indicator, and a mechanical extensometer which is part of the testing machine. Both methods gave approximately the same results.

The results are summarized in Table 1. There are very definite indications of strain hardening. The "settling down" period following loading or increasing load, during which the strain rate decreases from an extremely high value during loading to a constant value hundreds of
Table 1
Results of Creep Tests

<table>
<thead>
<tr>
<th>Specimen No.</th>
<th>Condition</th>
<th>Stress psi</th>
<th>Temp. Deg. C</th>
<th>Duration hr*</th>
<th>Creep rate after initial stretch per cent per hr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>cold rolled</td>
<td>24000</td>
<td>25</td>
<td>50+1150</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>32000</td>
<td></td>
<td>50+2150</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>36000</td>
<td>300+700</td>
<td>0.2 x 10^{-4}</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1700</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40000</td>
<td></td>
<td>45</td>
<td>Failed</td>
</tr>
<tr>
<td>2</td>
<td>cast</td>
<td>20000</td>
<td>25</td>
<td>500+1100</td>
<td>2.7 x 10^{-4}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25000</td>
<td></td>
<td>100+1300</td>
<td>0.5 x 10^{-4}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>500+2400</td>
<td></td>
<td>10.9 x 10^{-4}</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>900+2000</td>
<td>5.1 x 10^{-4}</td>
</tr>
<tr>
<td>3***</td>
<td>cast</td>
<td>15000</td>
<td>300</td>
<td>300+900</td>
<td>0.76 x 10^{-4}</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>500</td>
<td>0.35 x 10^{-4}</td>
</tr>
</tbody>
</table>

* First number is time of initial adjustment with gradually decreasing rate. Second number is time of approximately constant creep rate.

** Specimen No. 1 was from Billet A-238 and had a diameter of 0.252 in. Specimen No. 2 was from Billet A-238 and had a diameter of 0.505 in. Specimen No. 3 was from Billet A-283 and had a diameter of 0.505 in.

***Tested in a modified creep machine in which a vacuum of 0.6 microns was maintained.

hours later is probably the best indication. Another is the change of creep rate, sometimes abruptly, sometimes gradually, to another constant value after being constant for many hundreds of hours.

Tensile Tests

All tensile tests have been performed on a Baldwin Southwark 60,000-lb. Hydraulic Universal Testing Machine. Speed of testing to a strain of approximately 0.010 in. per
in. was 0.002 in. per in. per minute, and for those tests
carried to fracture the cross-head speed for strains above
0.010 in. per in. was 0.040 in. per minute which was a
speed of straining of approximately 0.027 in. per in. per
minute.

Specimens from billets A-238 and A-283 were standard
ASTM 0.505 in. diameter threaded end specimens. For the
high temperature series, a furnace-type Baldwin microformer
extensometer was used. A 16-in. Marshall furnace was
supported around the specimen during test, and a chromel-
alumel thermocouple was located at the center of the gage
length for temperature observation and control. The speci-
mens tested at elevated temperatures had a layer of silver
approximately 0.0015 in. thick electrodeposited over their
surface for protection against corrosion.1 Fig. 1 shows the
variation in modulus of elasticity of "as cast", cold rolled
(60% reduction of area), and forged (at 600 degrees Centi-
grade) thorium specimens from billet A-283 between 25 and
700 degrees Centigrade. The forged specimens appear to
have the lowest modulus through the entire temperature range.

Fig. 2 shows the decrease in yield strength (0.2% offset)
of thorium with an increase in temperature. The yield
strength of the cast thorium is, of course, much less than
the forged or cold-rolled thorium, and although the forged
and cold-rolled yield strength decreases by a larger value
than the cast, there is a larger percentage decrease in the
yield strength of the cast thorium. The maximum rate of
yield strength decrease with respect to temperature for the
cast thorium occurs within the first 200 degrees of tempera-
ture increase, whereas for the cold rolled it occurs roughly
the same throughout, and for the forged it occurs within
the last (or highest) 200 degrees of temperature increase.

Specimens tested from billet A-238 in the "as cast"
condition gave results similar to the "as cast" of billet
A-283 but with slightly higher values throughout the entire
temperature range.

In order to investigate the range of tensile properties
of commercial thorium and the effect of impurities, a supple-
mentary series of tests using a smaller specimen was initiated.
With the use of the smaller specimen, one tensile specimen
and sometimes more could be obtained from the cropping of
each billet of thorium produced. Most of the croppings are
between two and four inches in length, so that a 0.252 in.
diameter specimen was decided upon with an overall length
of approximately 2½ in. which includes a turned down section
approximately 1½ in. long with the remaining length con-
sisting of 3/8 in. diameter threaded ends.
FIG. 1 MODULI OF ELASTICITY OF COMMERCIAL THORIUM

- CAST
- COLD ROLLED
- FORGED 600° C
FIG. 2 YIELD STRENGTH OF
AMES THORIUM
BILLET A-283

- CAST
- COLD ROLLED
- FORGED 600°C

![Graph showing yield strength against temperature for different processes.](image-url)
Tensile tests have been performed on 130 specimens representing 110 different billets. All tests of 0.252 in. diameter specimens have been carried to fracture and very few specimens have fractured due to visible flaws existing in the ruptured cross-section.

Fig. 3 shows the relationship between the ultimate tensile strength, yield strength, and Rockwell hardness number. It is evident that the two groups of points representing the relationships between the ultimate strength and hardness number, and the yield strength and hardness number are very nearly parallel. The relation between the yield strength ($S_y$) and the ultimate strength ($S_u$) can be expressed in an equation

$$S_y + 10,400 = S_u$$

where all quantities are expressed in pounds per square inch (psi).

In both Fig. 3 and 4 the solid circles represent specimens which after fracturing had a rough surface resembling the surface of an orange hence the designation "orange peel". Examination of an "orange peel" specimen showed larger grain size than a "non-orange peel" specimen. In general the "orange peel" specimens had lower strengths.

Fig. 4 shows the relationship between carbon content and yield strength which inherently includes the relationship between carbon content and ultimate strength. While the general trend is toward an increase in strength with an increase of carbon there is sufficient variation to indicate that other impurities have a definite influence on the strength of thorium. Correlation of chemical analysis and properties is continuing.

Table 2 presents some of the properties of thorium obtained from tensile tests.
Figure 3: Yield strength and ultimate strength of thorium versus hardness number of Ames peel versus rockwell E hardness number.
FIG. 4 YIELD STRENGTH VS. CARBON ANALYSIS

- "A" BILLETS
- "A" BILLETS - ORANGE PEEL
- "MX" BILLETS

YIELD STRENGTH (0.002) - KSI
CARBON ANALYSIS - PPM
Fatigue Tests

All fatigue tests have been run on a Krouse Rotating Beam Fatigue Testing Machine. Fatigue specimens used are circular in cross-section with a minimum diameter of 0.252 in. and an overall length of four inches. The tests were carried out at a speed of 5,000 rpm. In accordance with standard practice for non-ferrous materials the endurance limit was taken as the maximum completely reversed stress which the material could withstand 500,000,000 times without failure. Fig. 5 is a stress-number of cycles (S-N) diagram for thorium. The diagram shows the endurance limit for the cast and forged material to be approximately 12,000 psi, and the endurance limit for the cold rolled thorium to be approximately 15,000 psi.

Impact Tests

Impact tests have been performed on standard keyhole type Charpy impact specimens of cast, cold rolled, and forged thorium. A Sonntag Impact Testing Machine with a range of 0-120 ft-lb has been used. All points plotted in the accompanying graphs are averages of two to four specimens.

In order to determine whether or not a relationship existed between the impact strength and the ductility of a given specimen the impact strength was plotted against the angle of fracture as shown in Fig. 6. The angle of fracture was obtained by placing the two parts of a fractured specimen together and measuring the angular rotation in the direction of impact of one part with respect to the other part. A larger angular rotation indicates a greater ductility and in general is accompanied by a higher impact strength.

Tests were run to obtain the effect of the temperature of the test specimen on Charpy impact strength. The specimen to be tested was heated or cooled to the desired temperature in a furnace or in a container of dry ice located near the testing machine. When the specimen had been at the desired temperature for one-half hour the specimen was removed and tested; the overall time from removal to fracture was five seconds. Fig. 7 shows the increase in impact strength with an increase in temperature up to 600 degrees Centigrade. This effect corresponds to the increase in impact strength with ductility as indicated in Fig. 6, since the material becomes more ductile with an increase in temperature. However, it appears that the impact strength
FIG. 5  S-N DIAGRAM FOR AMES THORIUM
BILLET A-283
KROUSE ROTATING BEAM FATIGUE MACHINE

- CAST
- COLD ROLLED
- FORGED 600° C

STRESS - KSI.

CYCLES IN A KROUSE ROTATING BEAM FATIGUE MACHINE
FIG. 6 CHARPY IMPACT STRENGTH VS. ANGLE OF FRACTURE
AMES THORIUM - BILLETS A-396 TO A-565
(EXCEPT BILLETS A-443, A-451 TO A-453, A-458 TO A-478,
A-483, AND A-501)
CAST SPECIMENS - (KEYHOLE TYPE)
FIG. 7 EFFECT OF TEMPERATURE UPON CHARPY IMPACT STRENGTH OF AMES THORIUM (KEYHOLE SPECIMENS)

- BILLET A-226 CAST
- BILLET MX-557 CAST

CHARPY IMPACT STRENGTH - FT. LB.

TEMPERATURE - DEG. C
reaches, or is approaching, a maximum value near 600 degrees and would begin to decrease with higher temperatures. The "MX" billets indicated in Fig. 7 are billets containing scrap thorium and generally having a higher carbon content than "A" billets as indicated in Fig. 8.

Fig. 8 shows the relationship between carbon content and the Charpy impact strength. The general trend is toward a decrease in impact strength with an increase in carbon content, but, here again as in the carbon content vs. yield strength of Fig. 4, the scatter of points is great enough to indicate that some other impurity or impurities has a pronounced effect on the properties of thorium.

Conclusions

The mechanical properties of thorium are influenced by impurities, mechanical working, and heat treatment. An increase in carbon content from 300 to 900 parts per million will decrease the impact strength about 70% while almost doubling the yield strength (0.2% offset). The tensile strength of both cold worked and hot worked thorium is approximately 50% greater than cast thorium for the degrees of working investigated. Definite indication of strain hardening has been observed in creep tests.

Further work is in progress to determine the influence of impurities in addition to carbon on the strength of thorium and to interrelate the mechanical properties.

Reference

1. Othmer, R. T. and Murphy, Glenn, Protection of Thorium at Elevated Temperatures. ISC Report No. 214.
FIG. 8 CHARPY IMPACT STRENGTH VS. CARBON ANALYSIS FOR AMES THORIUM

○ "A" BILLETs
○ "MX" BILLETs

CHARPY IMPACT STRENGTH - FT. LB.

CARBON ANALYSIS - PPM.
THE EFFECT OF MINOR ADDITIONS ON THE MECHANICAL PROPERTIES OF AMES THORIUM

D. Peterson and R. F. Russi

An investigation of the effects of impurity amounts of carbon, oxygen, nitrogen, aluminum and beryllium on the physical and chemical properties of thorium was undertaken in an effort to improve the thorium production processes. Also this information would be useful in determining limits or specifications of the maximum content of these impurities consistent with the desired properties of the thorium metal.

Thorium prepared by bomb reduction and cast by the present Ames process always contains some impurities. The elements with high cross section for slow neutron capture are, of necessity kept low. Some are not allowed to be present in amounts of more than one part per million. Elements such as aluminum, beryllium, carbon, oxygen, and nitrogen are difficult to keep out of thorium in this process of producing the metal from its salts. These are tolerable impurities from the standpoint of cross section and the permissible limit of their occurrence in thorium would depend only on their effect on the chemical and mechanical properties of thorium metal.

It may be possible to improve the properties of thorium metal by raising or lowering the content of these elements. If some of these elements were found to have little harmful effect on thorium, significant decreases in production costs could be made without lowering the quality of the finished metal.

The samples used in this investigation were prepared by adding impurities to Ames thorium metal. A small scale casting furnace capable of casting two kilograms of thorium was designed. This amount of metal was sufficient to produce several impact and tensile bars and also an adequate sample for chemical analysis. The same dezinced biscuit was used for a series of up to twelve castings, thus eliminating the effect of variations in the starting metal. This small scale casting procedure parallels quite closely the production method and the results should be applicable to the regular production process. (Fig. 1 shows the apparatus used.)
The metal is melted in a beryllia crucible under vacuum using a 20 KW mercury arc convertor, and bottom poured into a graphite mold. The beryllia crucible is set in a cylindrical graphite heater. The heater is insulated thermally by powdered graphite held in place by a beryllia shield. A quartz tube is placed over this assembly to complete the vacuum chamber and provide electrical insulation from the induction coil.

The funnel shaped bottom of the beryllia crucible has a pouring hole, which is closed with a beryllia plug during the heating and melting portion of the operation. At the desired time, the graphite mold is raised by means of a shaft protruding through the water cooled bottom of the apparatus and a trip rod on the top of the mold dislodges the valve as the head of the mold seals against the bottom of the crucible. The valve floats to the top of the molten thorium and the metal pours into the graphite mold. The pressure is kept under ten microns during the melting and casting operation. While in the liquid state, the metal is self agitated rather vigorously which insures thorough mixing of the added impurities. It was found good castings were obtained when the metal was allowed to remain in the molten state for 20 minutes before pouring.

The cast thorium slug is two inches in diameter and ranges from 2 3/4 to 3 in length after the cropping which contains the solidification pipe has been removed. After casting, the metal is pickled in a solution of dilute nitric acid containing sodium fluosilicate. This frees the metal from the reactive thorium carbide coat formed by reaction with the graphite mold. The rough surface of the slug is then machined off and millings are cut from the top of the casting for chemical analysis.

Two parallel cuts are made along the length of the casting removing a little more than 1/4 inch of metal from each side. From these sections two impact bars and two tensile specimens are machined to obtain samples of the metal in the as cast condition. The rest of the casting is hot rolled at 600°C to approximately 0.4 inch giving a 40% reduction in cross sectional area. From this sheet sections are cut parallel and perpendicular to the direction of rolling. Two samples from each direction are machined into impact bars and a tensile specimen is also prepared from this rolled sheet. Some of the metal is further reduced in cross sectional area by hot swaging at 600°C to 3/8 inch diameter and from this tensile specimens are machined. The thorium is heated, for the hot working operations, by means of a lead bath. This was found necessary because when exposed to air at these...
elevated temperatures thorium is readily oxidized. When rolled or swaged this ThO₂ coating cracks off in the form of a fine dust which is a definite health hazard. When heated under molten lead very little oxide is formed and little attack by the lead was observed. Fabrication is easier by this method than by jacketing the thorium. The lead is easily dissolved off in the pickling bath before machining the thorium.

After machining, the samples were annealed at 800°C for fifteen hours under a vacuum. The samples were furnace cooled after annealing.

ASTM standard Charpy type impact tests were carried out on a Sonntag Universal Impact Machine. The simple beam notched-bar impact test specimen with keyhole notch was utilized to measure impact energy. The tests were conducted at room temperature.

The tensile tests were made on a Baldwin-Southwark, 60,000 pound testing machine. This is a hydraulic straining device. A Baldwin-Southwark microformer extensometer was used to measure the strain. A head speed of 0.003 inches/minute was used until after the yield point was reached. The rate was then increased to 0.040 inches per minute and the samples strained to fracture. The ASTM standard 1 inch test specimen with 1 inch gage length was used. The tensile tests were all made at room temperature.

As cast samples and samples that had been rolled and annealed were polished and etched. A 2 molar solution of nitric acid with 0.003 molar sodium fluosilicate was used as the electrolyte for the electroetching of these samples. A current density ranging from 20 to 90 milliamps per square centimeter was used and they were etched from 20 seconds to five minutes. Photomicrographs were taken and the grain size was measured by the Jefferies Planimetric Method.

Table 1 shows a typical analysis of a blank thorium sample prepared by this method and the magnitude of impurity additions. In the figures that follow the data will be identified by the chemical symbol of the element added and a superscript figure will designate the relative amounts of this impurity present.

All samples prepared in this investigation could be hot worked by rolling and swaging. The high aluminum sample cracked, however, when it was being flattened after rolling.

The grain size of the as cast metal ranges from 5 to 50 grains per square millimeter, with the exception of the high aluminum sample which contains approximately 150 grains per square millimeter. The size of the recrystallized
<table>
<thead>
<tr>
<th>Element Added</th>
<th>Parts per million added</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
</tr>
<tr>
<td>Blank</td>
<td>45</td>
</tr>
<tr>
<td>Aluminum₁</td>
<td>200</td>
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<tr>
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</tr>
<tr>
<td>Aluminum₃</td>
<td>1000</td>
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<tr>
<td>Beryllium₁</td>
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<td>Beryllium₂</td>
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<td>Beryllium₃</td>
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<tr>
<td>Carbon₅</td>
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</tr>
</tbody>
</table>

* estimated values
grains average between 200 and 250 grains/mm$^2$. Again aluminum additions increase the number of grains to approximately 2000.

The hardness of the castings varied from Rockwell E 61 to Rockwell E 90. In Figure 2 the hardness of these samples is plotted against carbon content and a good correlation is found. It appears that carbon alone is responsible for hardening the thorium in metal of this purity. The hardness of two of the high aluminum castings fell off the curve but this may have been due to the very small grain size of these samples.

The Charpy impact tests were carried out on samples in the as cast condition and on hot rolled samples that were cut both parallel and perpendicular to the direction of rolling. In both the as cast and rolled samples the impact strength varied inversely with the hardness of the metal. This is shown in Figure 3 in which the hardness of as cast thorium is plotted against its impact energy. There is considerable scatter in the points but the trend is quite pronounced. In the as cast condition the samples to which oxygen, nitrogen, and aluminum, were added fall to the left of the band indicating that these elements may cause a lowering of the impact strength. Figure 4 shows the hardness plotted against impact strength for bars fractured parallel to the direction of rolling. The impact resistance of the high carbon samples and of the very soft samples rise but slightly while the samples containing oxygen, aluminum or nitrogen now fall closer to this band. The impact strengths of rolled samples cut parallel to the rolling direction and thus broken perpendicular to it are shown in Figure 5. It may be seen that the entire curve has shifted to the right, reflecting the increased impact resistance of these samples. In every case, the impact strength of the rolled samples cut perpendicular to the direction of rolling was slightly higher than that of the as cast metal, while bars cut parallel to the direction of rolling and fractured perpendicular to it always showed considerably higher impact resistance. Thus, two conclusions may be drawn from the aforementioned figures. One, that the harder metal has lower impact strength, and since carbon can be directly related to hardness, an increase in carbon content brings about a decrease in impact resistance due to the increase in hardness. Two, impurities occurring as a second phase also lower the impact energy especially in the as cast metals. The distribution of the impurity then becomes important as well as the amount of it which is present.
Fig. 2

CARBON CONTENT VS HARDNESS

O - NO IMPURITIES ADDED

PARTS PER MILLION CARBON

HARDNESS ROCKWELL E

400 500 600 700 800 900 1000 1100 1200 1300

58 60 62 64 66 68 70 72 74 76 78 80 82 84 86 88 90 92 94

Al³ C¹ N² Be² N Al¹ O² Be¹ O¹ C² C³ C⁴
As cast impact energy vs. hardness
Test conducted at room temperature
O - No impurities added

Fig. 3
Fig. 4

IMPACT ENERGY VS. HARDNESS
BARS WERE BROKEN PARALLEL TO DIRECTION OF ROLLING
O - NO IMPURITIES ADDED

IMPACT, FOOT POUNDS
HARDNESS

0 2 4 6 8 10 12 14 16 18 20 22

0 60 62 64 66 68 70 72 74 76 78 80 85 90 94

$\text{IMPACT, FOOT POUNDS}$
$\text{HARDNESS}$

$\text{AL}_3$
$\text{Al}_2$
$\text{Al}_1$
$\text{Al}_0$
$\text{N}_2$
$\text{N}_1$
$\text{C}_1$
$\text{C}_0$
$\text{C}_2$
$\text{C}_3$
$\text{C}_5$
$\text{B}_0$

$\text{IMPACT ENERGY VS. HARDNESS}$
$\text{BARS WERE BROKEN PARALLEL TO}$
$\text{DIRECTION OF ROLLING}$
$\text{O - NO IMPURITIES ADDED}$
IMPACT ENERGY VS. HARDNESS

BARS WERE BROKEN PERPENDICULAR TO DIRECTION OF ROLLING

O-NO IMPURITIES ADDED

Fig. 5.
In the as cast condition the primary grain boundaries contain much of the second phase material present in the metal since it collected there on solidification. The bar usually fractures along these weakened grain boundaries and the result is low impact energies for the as cast specimens. On working the metal the impurities are disturbed and spread more throughout the sample. Examination of the microstructure showed these impurities to be elongated along the direction of rolling. Thus when a bar was cut perpendicular to the direction of rolling and fractured parallel to it the second phase impurities are distributed so that the metal offers less resistance to fracturing than a bar broken at right angles to this, but more resistance than an as cast sample.

Aluminum, oxygen, and nitrogen, appear to lower the impact strength by appearing as a second phase. Carbon lowers the impact resistance by hardening the metal. Beryllium, seems to increase the impact resistance. This effect cannot be explained at the present time.

Tensile tests were made on as cast, rolled and swaged samples. The fabrication method used did not result in any significant change in any of the measured tensile properties. The ultimate tensile strength was usually 10,000 to 14,000 psi greater than the yield strength at 0.1% offset. The 0.2% offset yield strength was equal to or slightly higher than the 0.1% offset. The proportional limit was very hard to determine and was not reproducible. A yield point was observed in all of the samples that had been swaged and annealed and most of the as cast samples.

The 0.1% offset yield strength varies directly with the hardness. Figure 6 shows that the points all fall quite close to the curve regardless of what impurity had been added to the metal.

In summary, it appears that oxygen and nitrogen, in the range which we have studied, do not affect the tensile properties of thorium but may cause a decrease in impact strength. Aluminum has little effect on the tensile properties but lowers the impact strength and possibly the room temperature ductility. Aluminum also acts as a grain refining addition but this grain refinement does not appear to improve the properties of thorium. Beryllium has no effect on tensile properties, and does not lower the impact strength, may indeed increase it.

Carbon increases the hardness and 0.1% offset strength of thorium in amounts up to at least 1300 ppm. The impact resistance of the high carbon samples is low but ductility
0.1% OFFSET VS HARDNESS
TESTS CONDUCTED AT ROOM TEMPERATURE
O - NO IMPURITIES ADDED

YIELD STRENGTH, 0.1% OFFSET

Fig. 6
as shown by per cent elongation and reduction in area of tensile samples is not decreased.

The impact strength of all samples was improved by hot working and possibly would be further improved by greater reductions in area.
A PRELIMINARY INVESTIGATION OF METHODS FOR ROLL-CLADDING THORIUM WITH ZIRCONIUM

J. J. Lawless

Introduction

During the past year a small-scale fabrication program was initiated at Oak Ridge National Laboratory, to develop suitable techniques for cladding thorium with zirconium by rolling. One possible application for such a plate product would be in the breeder type reactor for production of U\textsuperscript{233}. Since thorium, like uranium, exhibits poor resistance to water corrosion, it must be adequately protected to be serviceable in a water cooled reactor. As a cladding material, zirconium is most promising because of its combination of chemical, physical, and mechanical properties.

Essentially the production of a maximum strength bond between dissimilar metals requires that all foreign material that would prevent intimate contact of the mating surfaces must be removed. Such foreign material must be prevented from forming, or reforming, until the bonding process is completed. Although the zirconium-thorium phase diagram is favorable, several other factors complicate the problem of bonding these dissimilar metals by conventional hot working techniques. These are:

1. Thorium metal readily oxidizes at rolling temperatures, even in the presence of low concentrations of the nuisance gas oxygen. The product, ThO\textsubscript{2}, forms a plane of weakness.
2. Zirconium exhibits a high chemical affinity for both oxygen and nitrogen. Small quantities of nitrogen adversely affect the corrosion resistance of zirconium.
3. Both metals form objectionable low melting phases with the common canning materials and, hence, limit the temperature of rolling.
4. Diffusion between the metals is relatively slow at safe rolling temperatures.

Experimental Technique

Two methods of preparing billets were used in this investigation. The first method employed a billet of the type shown in Fig. 1. Indications were that the best available methods of preparation and evacuation used with this cylinder type of billet did not prevent reoxidation of the thorium bonding surface during heating for rolling. To overcome the effect of reoxidation would require that higher reductions and higher rolling temperatures be employed in the bonding process, and since flat billets permitted higher reductions within the limitations of the available rolling mill, a billet of the type shown in Fig. 2 was adopted. Both of these designs proved to be economical in terms of machining time required and consumption of zirconium.
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BILLET

STEEL

CAP

NICKEL BRAZE WIRE

CORE

STEEL CAN

JACKET

FIGURE 1

CYLINDER TYPE BILLET FOR ROLL-CLADDING

CLADDING

CORE

CLADDING

STEEL COVER

FIGURE 2

FLAT SANDWICH TYPE BILLET FOR ROLL-CLADDING;
CLADDING DOES NOT EXTEND AROUND EDGES

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A. Billet Design and Preparation

The method of preparing both cylinder and flat billets was varied from one billet to another. However, the general method of evacuation, sealing, and canning was as follows:

1. Cylinder Billet: After preparation of the surfaces the thorium core was assembled into the zirconium jacket which was capped, and a ring of nickel-zirconium alloy metal was brazed around the cap. The assembly was evacuated in a glass envelope to 0.1 microns. After evacuation, the billet was slowly heated with an induction coil and the pressure maintained at 0.1 microns in an attempt to outgas and remove adsorbed gases from the billet. When a temperature of approximately 1000°F had been attained and outgassing appeared to be completed, the braze metal was melted to seal the billet. The billet was then taken from the vacuum system and placed in a steel can which was plugged and welded on the ends.

2. Flat Billets: This type of billet required that the can be vacuum tight because any leak or failure would automatically oxidize the core elements during the heating and rolling operations. Canning material is an important factor in this problem and is worthy of considerable more study than it has thus far received. However, of the materials used to date, steel plate equal to ASTM A-285 was found to be suitable from the standpoint of weldability and rolling characteristics.

In preparing this type of billet, the initial operation was to weld the tubes and bottom cover plate to the steel frame. After cooling the steel to room temperature, the thorium core and zirconium cover plates were inserted. In order to minimize heating of the core elements and prevent their oxidation during the welding of the top steel cover plate, the assembly was placed in a try of water 1/2" deep and a gentle flow of helium passed through the billet.

Rolling technique for both flat and cylinder billets was varied with respect to temperature and reduction, but otherwise the practice was to preheat for one hour and reheat every second pass for long enough to regain temperature. The mill used was a Mesta two-high with 20" x 30" rolls. Kerosene was used as a lubricant and the mill speed was 22 revolutions per minute (115.5 feet per minute).

B. Effect of Variables

The starting points for the variables under consideration were selected arbitrarily. Main emphasis was placed upon study of the effects of reduction, rolling temperature, surface preparation, and internal billet atmosphere. However, the type of canning material apparently has a significant effect upon the internal billet atmosphere, and this variable is still being studied.
Metal Surface Preparation

In studying metal surface preparation it was found after examination of plates made from billets prepared in a number of ways, that several techniques might be acceptable. However, the importance of this variable, though minor in comparison to temperature, reduction, and atmosphere, may become more critical at some later date when better control of the other variables has been attained.

Machining, wire brushing, electropolishing, and shot blasting (zirconium only) were all found to be practical and effective procedures for cleaning the bonding surfaces. Electropolished thorium seems to have a degree of passivity, and somewhat resists reoxidation at lower temperatures.

Vacuum

The degree of vacuum within the billet was found to effect bonding. Some preliminary tests were made by heating thorium and zirconium at different vacuums. Indications from these tests were that the atmosphere within the billet should be in the range of one ppm of total active gases if contamination of the mating faces was to be avoided.

The bond shown in Fig. 3 was obtained by rolling a billet which had been evacuated only. Fig. 4 shows the bond in another plate which had been rolled from a billet which had been subjected to alternate evacuation and flushing with helium and outgassing at 1000°F, before sealing at a pressure below five microns. The results represented in Figs. 3 and 4 were confirmed in several tests. In each case the reductions and rolling temperatures were effectively the same.

Attempts to produce bonds by rolling plates in which the billet had been sealed in either air or helium atmospheres were failures.

Rolling Temperature

Rolling temperature in the roll-cladding problem might be considered for its effect upon plastic properties and the development of diffusion layers. Temperatures between 1000 and 1500°F in the case of thorium, however, result in release of adsorbed gasses, to a degree sufficient to promote reoxidation of the thorium if the gases are not removed immediately. Above a critical temperature in the range of 1800°F, the oxides of thorium apparently redissolve in the opposing zirconium, and in time disperse in the surrounding metal. The effects of temperature on outgassing and solution of oxides seem to be as important as the effect on plasticity.

No hot hardness nor similar data for the temperature range of interest were available; however, billets were rolled at temperatures from 1150°F to 1900°F without difficulty resulting from differences in plasticity of zirconium and thorium.
Fig. 3  Microstructure in the bond area of a plate rolled from a billet that had been simply evacuated before sealing. 1000x  Acetic and Perchloric

Fig. 4  Microstructure in the bond area of a plate rolled from a billet that had been evacuated, helium flushed, and re-evacuated before sealing. 1000x  Alcohol and Perchloric
Metallographic examination of rolled bonds indicated that diffusion layers between zirconium and thorium increased with both temperature and time at temperature. The thorium-zirconium phase system shows no compounds, and it is indicated that the presence of diffusion layers would not effect the ductility of clad plates significantly. Samples of the best plates produced in this investigation were bond around a 1/2" mandrel and straightened without apparent damage to the bond. At higher temperatures, in the range of 1700°F and higher, very thick diffusion layers were obtained in comparatively short heating times. The sharp increase in the rate of diffusion was thought to be related to the alpha to beta phase change in zirconium at about 1650°F.

In addition to the effect of diffusion, high temperatures tend to result in solution of thorium-oxide in the zirconium, and with time the oxides disperse to such a degree that they do not form a plane of weakness at the interface. Two ideas for utilizing high temperature to enhance bonding were investigated.

1. 1900°F Rolling. Fig. 5 shows the bond produced in a plate rolled partially at 1900°F. Tantalum was successfully used as a diffusion barrier between Zr and Fe at this high temperature. The tantalum, however, bonded also to zirconium. Rolling of zirconium in steel cans at 1650°F is not practical, due to the formation of a liquid iron-zirconium eutectic and attendant hazard. The lack of bond line voids is notable. The plate shown in Fig. 4, on the other hand, was characterized by the occurrence of oxides at the interface. The photomicrographs shown in Figs. 4 and 5 were obtained from plates made under identical conditions except for rolling temperature.

2. Heat-treat the Finished Plate at 1900°F after obtaining bonding at a lower temperature and stripping Fe jacket. This procedure was attempted on plates reduced 15 to 1 and 30 to 1. Fig. 6 is the macrostructure of a series of plates rolled 15 to 1 and heat treated in vacuum at various times and temperatures. The occurrence of voids and irregular diffusion is noted. Fig. 7 shows a similar series of tests made on a plate reduced 30 to 1 in rolling. The diffusion layer is noted to be more regular and less porous. It can be seen that the regularity and porosity of the diffusion layer seems to be related to time and temperature of heat treatment as well as the reduction history of the plate. The shorter time and lower temperature gives the best results.

The structure produced in a 15 to 1 reduced plate followed by heat treatment for two minutes at 1965°F is shown in Fig. 8. The original structure of the plate reduced 30 to 1 is shown in Fig. 9. The structures developed by heat treatment of this plate for two minutes at 1965°F is shown in Fig. 10, and the effect of heat treatment for six minutes at 2055°F is apparent in Fig. 11. It is felt that the results of these tests indicate one feasible method of producing a fairly satisfactory clad plate.
Fig. 5 Microstructure in the bond zone of a plate rolled at 1900°F.
1000x
HC104 and Acetic
Fig. 6 Macro-photo showing effect of vacuum-heat-treatments on a series of plates rolled with a reduction of 15 to 1.

8x No etch

Zr clad Th
Reduced 15-1

No Ht. Treat

Ht. Tr. 2 min. 1075°C
6 min. 1075°C
2 min. 1125°C
6 min. 1125°C
Fig. 7: Macro-photo showing effect of vacuum-heat-treatments on a series of plates rolled with a reduction of 30 to 11
(7x) No etch
Fig. 6. Microstructure of the plate rolled with a reduction of 75 to 1 after heat-treatment for 2 minutes at 1075°C in vacuum

Acetic and Perchloric

Fig. 7. Original microstructure of the unheat-treated plate shown in Fig. 7.

1000x

Acetic and Perchloric
Fig. 10  Microstructure of the plate rolled with a reduction of 30 to 1 after heat-treatment for 2 minutes at 1075°C in vacuum.  
1000x  Acetic and Perchloric

Fig. 11  Microstructure of the plate rolled with a reduction of 30 to 1 after heat-treatment for 6 minutes at 1125°C in vacuum.  
1000x  Acetic and Perchloric

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Reduction in Rolling

Reduction in rolling has the effect of spreading interface contamination and breaking it into islands that do not obstruct bonding except intermittently. The employment of high reductions to counteract reoxidation resulting from outgassing in the billet was found to be effective in improving bonds.

Conclusions

It is felt that at this time, one possible method may be used for obtaining thorium plates bonded to zirconium. The method consists of rolling an evacuated billet at 1500°F to a 30 to 1 reduction in area followed by a heat treatment at 1900°F. It seems likely also that improved methods for preventing reoxidation of the thorium during preheating and rolling may make lower reductions possible and/or may eliminate the need for heat treatment.
THORIUM-RICH ALLOYS

R. M. Goldhoff, H. R. Ogden, and R. I. Jaffee

Battelle Memorial Institute

Report No. BMI 739

The development of strong, dilute, binary thorium alloys was the primary objective of the work reported. Alloying was to provide a minimum thorium dilution and minimum increase in thermal neutron absorption cross section. During the course of the work, practically all feasible alloying elements were added to Ames thorium and evaluated for their effect on mechanical properties, weldability, flow properties, response to cold work and heat treatment, and hardness at 300 C. The alloying elements were screened and classified into several series according to a number of criteria. Thus the initial additions were chosen on the basis of interstitial or substitutional size fit, nuclear properties, volatility, and reactivity.

Interstitial alloying appeared to be good from the size-fit criterion because thorium has a large atom. However, because of high reactivity, many of the interstitial elements form compounds with thorium rather than enter interstitial solid solution. From the size-fit criterion of an atomic diameter ratio less than 0.59, corresponding to Hagg's rule, the potential interstitially dissolving elements, in order of decreasing diameter ratio, are: sulfur, boron, carbon, nitrogen, oxygen, and hydrogen. Of these, carbon appeared best because of its lesser electronegativity and low cross section. Hydrogen was not considered because of the thermal instability of thorium hydride.

Initial substitutional solid solution alloying additions were chosen to fit the following requirements: (1) an atomic size difference of less than 15 per cent that of thorium, (2) less than one barn per atom cross section, and (3) a boiling point of 1500 C or higher. Subsequent additions were chosen in the order of increasing deviation from these requirements.

All alloying additions were added at the one and five atom per cent levels, and whenever the five per cent additions could not be fabricated, an additional alloy at the 2.5 per cent level was made. All alloys were prepared by arc melting on a water-cooled copper hearth under a partial pressure of argon using a tungsten electrode.

Ames Thorium

Base Properties

The properties of the base metal were determined under the same conditions as would be used for testing the alloys. The following fabrication and
annealing schedule was set up: forge and hot roll at 700°C in air, cold roll to 50 per cent reduction, and anneal two hours at 850°C. Table 1 shows the average mechanical properties of the Ames metal strip after this fabrication:

Table 1. Average Mechanical Properties of Ames Thorium

(Annealed two hours at 850°C)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2 per cent offset yield strength</td>
<td>19,400 psi</td>
</tr>
<tr>
<td>Ultimate strength</td>
<td>31,700 psi</td>
</tr>
<tr>
<td>Elongation in one inch</td>
<td>46 per cent</td>
</tr>
<tr>
<td>Reduction in area</td>
<td>50 per cent</td>
</tr>
<tr>
<td>Vickers Hardness number</td>
<td>79</td>
</tr>
</tbody>
</table>

Flow properties for all alloys were determined in order to predict the yield strength for any given amount of cold reduction. Initially, however, it was necessary to test the validity of the prediction of yield strengths from these flow curves. To do this, samples of unalloyed thorium were cold rolled 20 and 50 per cent after annealing and were then tested. Table 2 compares the data obtained experimentally with that predicted from the flow curve.

Table 2. Flow Data Yield-Strength Values of Cold Worked Thorium

<table>
<thead>
<tr>
<th>Condition</th>
<th>0.2 Per Cent Offset Yield Strength, psi</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>From Tensile Test</td>
</tr>
<tr>
<td>Annealed one hour at 750°C</td>
<td>29,000</td>
</tr>
<tr>
<td>Cold rolled 25 per cent</td>
<td>55,000</td>
</tr>
<tr>
<td>Cold rolled 50 per cent</td>
<td>62,000</td>
</tr>
</tbody>
</table>

From the data shown, it appears that the prediction of cold worked yield strengths from the flow curve is valid.

Alloys

After the preliminary work on the unalloyed metal, the screening program for alloys was undertaken. Table 3 presents the mechanical properties of the best dilute alloys investigated, as compared with unalloyed Ames thorium.
Table 3. Mechanical Properties of the Best Dilute Ames Thorium Alloys

(Annealed two hours at 850 °C)

<table>
<thead>
<tr>
<th>Element</th>
<th>0.2% Offset Yield Strength, psi</th>
<th>Ultimate Strength, psi</th>
<th>Elongation % in 1 inch</th>
<th>Reduction of Area, %</th>
<th>Vickers Hardness Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>None</td>
<td>19,400</td>
<td>31,700</td>
<td>46</td>
<td>50</td>
</tr>
<tr>
<td>0.20C*</td>
<td>3.72C</td>
<td>57,600</td>
<td>58,600</td>
<td>-</td>
<td>19</td>
</tr>
<tr>
<td>0.13C</td>
<td>2.45C</td>
<td>29,400</td>
<td>42,000</td>
<td>35</td>
<td>36</td>
</tr>
<tr>
<td>2.49In</td>
<td>4.91In</td>
<td>35,600</td>
<td>49,800</td>
<td>23</td>
<td>40</td>
</tr>
<tr>
<td>0.55In</td>
<td>1.10In</td>
<td>22,500</td>
<td>36,100</td>
<td>31</td>
<td>38</td>
</tr>
<tr>
<td>1.23Sn</td>
<td>2.36Sn</td>
<td>24,000</td>
<td>40,500</td>
<td>31</td>
<td>43</td>
</tr>
<tr>
<td>1.00U</td>
<td>0.97U</td>
<td>25,600</td>
<td>38,400</td>
<td>37</td>
<td>51</td>
</tr>
<tr>
<td>5.08U</td>
<td>4.94U</td>
<td>27,400</td>
<td>42,300</td>
<td>38</td>
<td>44</td>
</tr>
</tbody>
</table>

*Annealed one hour at 750 °C
Carbon and indium, at the upper addition levels shown, (approximately five atom per cent) about double the yield strength while maintaining good ductility.

Several general conclusions were drawn in the comprehensive topical report (1) regarding the dilute binary alloys. First, the majority of the alloy additions made to thorium have little strengthening effect. Some of the additions cause a perceptible softening of the Ames metal. These additions are five atom per cent zirconium, vanadium, columbium, and, particularly, titanium. This effect is probably due to scavenging of strengthening impurities in Ames thorium. The only consistently potent strengtheners in dilute amounts when added to Ames thorium are carbon, indium, and uranium. Secondly, it has been shown that the strength of Ames thorium shows a good response to cold work, and, further, that the dilute alloys are even more responsive to cold work. For a given percentage cold reduction, the yield strength increase of the alloys is greater than that for unalloyed Ames thorium. Also, since the recrystallization temperatures of thorium and its alloys are high, cold work strength benefits are maintained up to moderately elevated temperatures for long periods of time. The best recommendation for developing the highest strength in a dilute thorium-rich alloy for service at moderately elevated temperature, at about 300°C, is to use carbon as the alloying element and to supplement its solid solution strengthening effect by cold work.

Age-hardening tests were performed on all alloys using the following treatment: solution treat one hour at 850°C, quench, and age for two hours at 400°C. In general there was no response to age hardening for any of these alloys. Hot hardness values at 300°C were obtained on all specimens. As reported in the topical report (1) the hardness differential between the unalloyed metal and the alloys at room temperature is generally maintained at 300°C. There are several exceptions, however. The most outstanding of these is the alloy made with a five atom per cent magnesium addition. Very little of the magnesium addition was retained, but this alloy had good room-temperature hardness and it maintained its hardness very well at elevated temperature. At 300°C the hardness of this alloy was greater than that of the Ames metal at room temperature. The room temperature tensile properties of the thorium-magnesium alloy are only slightly higher than that of Ames metal, however. Another alloy that showed good retention of hardness at 300°C was the alloy with a five atom per cent indium addition.

A welding test using arc-welding techniques was applied to all specimens. This test was exclusively for screening purposes, and did no more than classify each alloy as inferior or superior to the Ames metal. The test consisted of determining the number of arc-welding passes a sample would take without showing
weld cracks. From this test, a 2.5 atom per cent molybdenum alloy was developed, which showed good arc-welding characteristics when tested as full-size weldments.

Binary alloys of thorium containing up to 50 atom per cent uranium were investigated. At the lower concentrations uranium is one of the most effective strengtheners for thorium. At the higher concentrations of uranium the alloys become progressively stronger, and possess adequate ductility for structural use. Fig. 1 shows the effect of uranium additions on the mechanical properties of Ames thorium. These alloys also show good strengthening responses to cold working.

**Iodide Thorium**

To gain basic information about the mechanism of strengthening thorium by alloying, a program using iodide metal was started. As a result of the prior work with Ames thorium, where carbon was shown to be the most effective strengthener, there was immediate interest in carbon as an alloying addition to iodide thorium. Oxygen and nitrogen were also of interest as potential interstitial solutes and, further, are present as impurities in Ames thorium. Alloys containing up to five atom per cent of each of these elements were prepared and analyzed by the best available chemical analysis methods. Test results confirmed the fact that carbon is a very potent strengthener for thorium and that it is probably the most influential impurity in the Ames metal. In fact, iodide thorium and Ames thorium with comparable amounts of carbon between 0.06 and 0.10 weight per cent, have about the same strength and ductility, while the iodide-base alloys containing nitrogen and oxygen in the amounts usually found in Ames metal show very negligible strength increases. Fig. 2 shows the effect of oxygen on the mechanical properties of iodide thorium. Iodide thorium with an addition of 0.18 weight per cent oxygen analyzed 0.08 weight per cent. This is the same amount of oxygen obtained by an analysis of the unalloyed iodide-thorium base using the same analytical techniques. The points plotted represent the analyzed composition with respect to oxygen, the unalloyed base being the stronger and more ductile of the two. We have considerable doubt concerning the accuracy of these oxygen figures, however. Up to 0.45 weight per cent oxygen the strength increase is nil to small. Since the oxygen content of Ames thorium is about 0.15 weight per cent, it seems safe to say from these results that oxygen contributes little to the strength of the Ames metal. In the microstructure of Ames thorium the predominant insoluble phase is undoubtedly an oxide of thorium. An 0.08 weight per cent oxygen iodide-thorium alloy had considerable amounts of this phase present in
its microstructure. This indicates that oxygen solubility in thorium is below 0.08 per cent, and consequently little interstitial solid solution strengthening due to oxygen is to be expected. This correlates well with the experimental findings. Fig. 3 shows the effect of nitrogen on the mechanical properties of iodide thorium. There is moderate strengthening up to 0.17 weight per cent nitrogen after which increases are small and tend to level off. The microstructure of the alloy containing 0.41 weight per cent nitrogen had large quantities of an insoluble, gold-colored constituent which is assumed to be a nitride. At the 0.17 per cent addition level, much less of this phase was evident. Under these conditions, the interstitial solubility of nitrogen in thorium can be said to be less than 0.17 per cent but sufficient to give the strength increases noted. The nitrogen content of Ames thorium is quite low, less than 100 parts per million, and, on this basis, practically none of the strength of Ames thorium should be attributed to nitrogen. Fig. 4 shows the effect of carbon on the mechanical properties of iodide thorium. Carbon, in very dilute amounts, is an excellent strengthener. It appears from metallographic work that carbon solubility in thorium is greater than 0.10 per cent but less than 0.24 per cent. Fig. 5 compares carbon, oxygen, and nitrogen as to their effect on the strength and ductility of iodide thorium. In order to compare the effects of these elements on the same basis, the analyzed amounts of each in the iodide base were subtracted from the analyzed amounts in the alloys. From this graph it can be seen that carbon is by far the better strengthener of the three, and if consideration is given to the amounts of each, normally present in Ames metal, it is obvious that carbon is responsible for the major portion of the strength differential between Ames and iodide thorium.

To check the scavenging effect of titanium, an alloy containing five atom per cent was prepared using iodide metal. This alloy had a mild strengthening effect on the base. Previously an alloy with the same amount of titanium added to Ames metal had shown properties roughly equivalent to the unalloyed iodide metal. Evidently then, titanium does exert a scavenging effect on Ames metal. Since carbon seems to be the strengthener, the inference is that carbon is the element being scavenged. This effect is being checked.

References

1. R. M. Goldhoff, H. R. Ogden, and R. I. Jaffee, "A Study of Thorium-Base Alloys", Battelle Memorial Institute, Report BMI 720 (see Fig. 7, 8, 11, and 12).
FIGURE 1. THE MECHANICAL PROPERTIES OF THORIUM-URANIUM ALLOYS UP TO 50 PER CENT URANIUM.
Elongation and Reduction of Area, per cent

Ultimate and 0.2 Per Cent Offset Yield Strength, psi \( \times 10^{-3} \)

Figure 2. The Mechanical Properties of Iodide Base Thorium-Oxygen Alloys

- Elongation
- Reduction of area
- Ultimate strength
- Yield strength
- Annealed 2 hours at 850°C

Weight Per Cent Oxygen

Atomic Per Cent Oxygen
FIGURE 3. THE MECHANICAL PROPERTIES OF IODIDE-BASE THORIUM-NITROGEN ALLOYS
FIGURE 4. MECHANICAL PROPERTIES OF IODIDE-BASE THORIUM-CARBON ALLOYS
FIGURE 5. THE EFFECT OF CARBON, OXYGEN, AND NITROGEN ON THE STRENGTH AND DUCTILITY OF IODIDE THORIUM.
METALLOGRAPHIC EXAMINATION OF THORIUM AND THORIUM ALLOYS

R. J. Gray, J. A. Milko, and F. H. Eckert

Introduction

The problem of preparing thorium and thorium alloys for metallographic examination has been quite difficult. Mechanical polishing resulted in preservation of the inclusions present; but, unless grain boundaries were outlined by some precipitate, grain boundary delineation was almost impossible unless severe etchants were used, and then only for macroscopic examination.

Polishing Procedure

Our efforts have been concentrated on the preparation of specimens by electrolytic methods because of the usual short time involved and the resulting undisturbed metal surface. One popular electrolyte, the ten-to-one glacial acetic acid-perchloric acid mixture, was used for some time. A suitable surface was obtained except for the poorly revealed grain boundaries for recrystallization and grain-growth studies.

Best results have been achieved with an electrolyte of 15 parts absolute ethyl alcohol and one part perchloric acid.

Specimens are ground to about a 400-grit paper and then polished with a four-to-eight micron diamond paste on an airplane cloth. Electrolytic polishing follows at 35 volts with the electrolyte maintained at room temperature and turbulently agitated. A bakelite mounted specimen can be used making contact with the specimen through the back of the mount. The time for the electrolytic polishing period is about 10 to 15 seconds.

After removing the specimen from the electrolytic cell, an alcohol rinse is given; and the specimen is ready for examination. A chemical etch is sometimes necessary with alloys to show the structure to better advantage.

A transverse view of the Battelle iodide crystal bar thorium is shown in Fig. 1. The base wire is on the left with the deposited thorium as the radial shaped grains.

The structure of arc-melted crystal bar is shown in Fig. 2. Here one problem which has been encountered in the electrolytic polishing of thorium and also in mechanical polishing to some degree is the "peppered finish" of the specimen. This pseudo-precipitate is also present in other metals, such as tantalum, prepared by electrolytic polishing. The possibility of this being only a polishing texture is not positive, but indications are favorable to this explanation. The presence of such a finish is not too objectionable except in dilute alloy additions where a small amount of precipitate is difficult to isolate and identify.

Recrystallization Studies

Recrystallization in its early stages was divulged by the previously described method of polishing.
For a series of recrystallization studies, the crystal bar was arc melted by a non-consumable electrode method using a positive pressure of purified argon. The as-cast button was 80 per cent cold worked and recrystallized for various times and temperatures. Examinations were made on longitudinal sections.

Recrystallization at 530°C for 5, 10, 20, 40, and 60 minutes is shown in Fig. 3. The 80 per cent cold-worked structure with a hardness of D.P.H. 76 (diamond pyramid hardness, 10 Kg. load) is shown at top left in the panel for comparison. One hour at 530°C resulted in a D.P.H. of 51. Recrystallization was just visible at 10 minutes. Some thorium dioxide was present as shown by the scattered dark patches.

Recrystallization at 550°C for 1, 5, 10, 20, and 60 minutes is shown in Fig. 4 as compared to the cold-worked structure. Recrystallization was apparent after five minutes, and 60 minutes at 550°C gave a D.P.H. of 50.

For comparison, the Ames thorium was recrystallized at 550°C after the same per cent of cold work and for the same periods in Fig. 5 as shown in the previous figure. The cold-worked structure had a D.P.H. of 110, and the specimen annealed for 60 minutes had a D.P.H. of 91. Recrystallization was apparent at five minutes with a small grain size after 60 minutes.

Some grains were visible in the cold-worked crystal bar after one minute at 580°C, as shown in Fig. 6. Complete recrystallization with a hardness of D.P.H. 38 was present after 60 minutes.

The anneal at 600°C for the same indicated times, as shown in Fig. 7, had grains visible after one minute and a non-uniform grain size after 60 minutes with a D.P.H. of 39.

A comparison was made again, using Ames thorium, in Fig. 8 with the previous figure at 600°C. Small grains were visible after one minute; however, as would be expected, the grain size was much smaller after 60 minutes. The D.P.H. value after 60 minutes was 71.

An anneal at 650°C with the crystal bar thorium, as shown in Fig. 9, had only a slight difference in uniformity of grain size after five minutes or 60 minutes. The hardness was D.P.H. 38 after 60 minutes.

**Thorium Alloys**

Two thorium-beryllium alloys of .04 weight per cent and .11 weight per cent beryllium additions are shown in Figs. 10 and 11 after having been arc melted, cold worked 85 per cent, and annealed at 650°C for one-half hour. Based on the present tentative thorium-beryllium diagram which shows a eutectic of α thorium and a compound of ThBe₁₃ at 1.75 weight per cent
ELECTROLYTIC POLISH-ETCH
RECRYSTALLIZATION OF CRYSTAL BAR THORIUM ARC MELTED-80% COLD WORKED-ANNEALED AT 530°C

Fig. 3
Fig. 5

RECRYSTALLIZATION OF Ames Thorium
80% COLD WORKED-ANNEALED AT 550°C

ELECTROLYTIC POLISH-ETCH

250X
ELECTROLYTIC POLISH-ETCH
RECRYSTALLIZATION OF CRYSTAL BAR THORIUM ARG MELTED-80% COLD WORKED-ANNEALED AT 580°C

Fig. 6
Electrolytic polish-etch, recrystallization of crystal bar thorium, arc melted 80% cold worked annealed at 600°C. 250X

Fig. 7
Fig. 8

Recrystallization of Ames Thorium
80% Cold Worked-Annealed at 600°C
ELECTROLYTIC POLISH-ETCH
RECRYSTALLIZATION OF CRYSTAL BAR THORIUM
ARC MELTED-80% COLD WORKED-ANNEALED AT 650°C 250X
**Thorium-Beryllium Alloys**

Fig. 10
.04 wt. per cent beryllium

Fig. 11
.11 wt. per cent beryllium

Fig. 12
.32 wt. per cent beryllium

Fig. 13
.69 wt. per cent beryllium

Electrolytic Polish
Etch: 1% HF

1000x
beryllium, the globular areas are the eutectic. This eutectic was very fine and required high magnification for resolution.

Increased amounts of eutectic were present in Figs. 12 and 13 which were additions of .32 and .69 weight per cent beryllium. The ThBe$_{13}$ appears as a clear precipitate. These are structures which have been cold worked 85 per cent and annealed at 650°C for 60 minutes.

Two thorium-chromium alloys of five and seven weight per cent addition are shown in Figs. 14 and 15 after cold working 85 per cent and annealing for 30 minutes at 740°C. The tentative thorium-chromium diagram shows a eutectic at about 23 weight per cent chromium with no solid solubility of chromium in thorium. Judging from the structures obtained in this early investigation, the eutectic appears to be at a lower chromium addition as indicated by the amount of chromium present.

A study of the solubility of thorium carbide at various temperatures is shown in Figs. 16 to 19 with .50 weight per cent carbon addition. The arc-melted structure after homogenization at 950°C is compared with the degree of solubility of the thorium carbide after holding at 400°C, 800°C, and 1200°C for 15 minutes and water quenching. The higher solubility is apparent after heating at the higher temperatures.

An increase in the carbon addition to 2.50 weight per cent is shown in Figs. 20 to 23. A grain structure which has been homogenized at 950°C is the basis for comparison. The decrease in the lamellar thorium carbide is evident after a heat treatment at 1300°C, 1400°C, and 1500°C.

All the photomicrographs were prepared by the described method of polishing. Although this method has been found to be quite satisfactory with the alloy shown, it has not been very successful with the thorium-oxygen alloys without loss of the oxide precipitate.
Fig. 16. Arc Melted - Homogenized at 950°C for 24 hours.

Fig. 17. Arc Melted - Homogenized at 950°C, Heated at 1050°C for 15 min. and water quenched.

Fig. 18. Arc Melted - Homogenized at 950°C, Heated at 800°C for 15 min. and water quenched.

Fig. 19. Arc Melted - Homogenized at 950°C, Heated at 1200°C for 15 min. and water quenched.

Thorium-Carbon Alloys 0.50 wt. per cent carbon.

Electrolytic Polish

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530 x
Fig. 20
Arc Melted - Homogenized at 950°C for 24 hours.

Fig. 21
Arc Melted - Homogenized at 950°C, Heated at 1400°C for 15 min. and water quenched.

Fig. 22
Arc Melted - Homogenized at 950°C, Heated at 1400°C for 15 min. and water quenched.

Fig. 23
Arc Melted - Homogenized at 950°C, Heated at 1500°C for 15 min. and water quenched.

Thorium-Carbon Alloys
Electrolytic Polish
2.50 wt. per cent carbon.

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DECLASSIFIED
THE COMPOUNDS OF THORIUM WITH THE TRANSITION METALS
OF THE FIRST PERIOD

John V. Florio, N. C. Baenziger, A. I. Snow
and R. E. Rundle

Summary of Compounds Stable at Room Temperature

The binary alloy systems of thorium with manganese, iron, cobalt and nickel have been investigated by x-ray diffraction methods for the presence of room temperature stable intermetallic compounds. It has been found (Table 1) that thorium forms three compounds with manganese, ThMn2, Th6Mn23 and ThMn12, four with iron, ThFe3, ThFe3, ThFe5 and Th2Fe17, five with cobalt, Th7Co3, ThCo, ThCo2-3, ThCo5 and Th2Co17, five with nickel, Th7Ni3, ThNi, ThNi2, ThNi15 and Th2Ni17, and two with copper, Th2Cu and ThCu2.

The structures, ThMn2, Th6Mn23, ThMn12, ThFe3, Th7Co3, ThCo, ThCo5, Th7Ni3, ThNi, ThNi2, ThNi15, Th2Cu and ThCu2, have been completely determined. Though not completely verified the structures, ThFe5, Th2Fe17, Th2Co17 and Th2Ni17, are fairly well established. The structures of ThFe3 and ThCo2-3 are still unknown.

The compounds, Th6Mn23, ThMn12, ThFe3, Th2Fe17, ThCo, ThNi and Th2Ni17, represent new structural types. The compounds, Th7Co3 and Th7Ni3, are isomorphous with Th7Fe3, Th2Co17 with Th2Fe17, ThFe5 and ThCo5 with ThNi5, and ThNi2 with ThCu2.

Table 1. Compounds of Thorium with First Period Transition Metals

<table>
<thead>
<tr>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Th7Fe3a,b</td>
<td>Th7Co3a,b</td>
<td>Th7Ni3a,b</td>
<td>Th2Cu(CuAl2)d</td>
</tr>
<tr>
<td>(None)</td>
<td>ThMn2(MgZn2)</td>
<td>ThFe3b,c</td>
<td>ThCo b</td>
<td>ThCo2-3b,c</td>
<td>ThNi b</td>
</tr>
<tr>
<td></td>
<td>Th6Mn23</td>
<td>Th2Co17b</td>
<td>Th2Co17b</td>
<td>Th2Ni17b</td>
<td>Th2Cu(AlB2)e</td>
</tr>
<tr>
<td></td>
<td>ThMn12b</td>
<td>Th2Fe17b</td>
<td>ThCo5(CaZn5)</td>
<td>ThNi15(CaZn5)</td>
<td>ThCu4f</td>
</tr>
</tbody>
</table>

a Structure determined by Baenziger2.
b New structural type.
c Structure not yet fully known.
d Structure reported by Rundle3.
e Structure reported by Rundle4.
f Compound reported by Grube and Boltzenhardt5.
Electron Compounds and the Thorium-manganese System

It has been pointed out by Hume-Rothery\(^6\) that certain intermetallic compounds, electron compounds, with closely related structures but different chemical composition can be considered to have the same electron to atom ratio. There are three general types of electron compounds, \(\alpha\), \(\gamma\) and \(\varepsilon\) phases corresponding to the electron to atom ratios of 1.5, 1.615 and 1.75. The valences generally assumed by Hume-Rothery for some of the elements forming these compounds are listed in Table 2.

Some question as to the correctness of these metallic valences of the transition elements has been raised by Pauling\(^7,8,9\). In Pauling's treatment of the metallic state, the five d-orbitals are partitioned into 2.44 non-bonding or atomic d-orbitals while the remaining 2.55 d-orbitals hybridize with the one s and three p orbitals to give 5.78 orbitals used for bonding and 0.78 unused, or 'metallic', orbitals which are regarded as characteristic of the metallic state.

Table 2. Metallic Valences of Some Metals Which Form Electron Compounds

<table>
<thead>
<tr>
<th></th>
<th>Hume-Rothery</th>
<th>Pauling</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>1</td>
<td>5.44</td>
</tr>
<tr>
<td>Zn</td>
<td>2</td>
<td>4.44</td>
</tr>
<tr>
<td>Ga</td>
<td>3</td>
<td>3.44</td>
</tr>
<tr>
<td>Ni</td>
<td>0</td>
<td>5.78</td>
</tr>
<tr>
<td>Co</td>
<td>0</td>
<td>5.78</td>
</tr>
<tr>
<td>Fe</td>
<td>0</td>
<td>5.78</td>
</tr>
<tr>
<td>Mn</td>
<td></td>
<td>4.16</td>
</tr>
<tr>
<td>Th</td>
<td>4</td>
<td>4.16</td>
</tr>
<tr>
<td>Al</td>
<td>3</td>
<td>3</td>
</tr>
</tbody>
</table>

Using Pauling's values\(^8\) of metallic valences, listed in Table 2, one finds the electron to atom ratios of 4.94, 4.82 and 4.69 for the \(\alpha\), \(\gamma\) and \(\varepsilon\) phases. However, it can be shown that constant electron to atom ratios for elements forming these phases result if the valences change in an arithmetical progression as one goes across the periodic table\(^10\).

In most of the previously reported electron compounds, either Pauling's or Hume-Rothery's valences will give consistent electron to atom ratios. It appears that the three compounds ThMn\(_2\), Th\(_6\)Mn\(_2\) and ThMn\(_2\) might be related to the \(\alpha\), \(\gamma\) and \(\varepsilon\) phases. The \(\alpha\) phase is body-centered cubic whereas ThMn\(_2\) is body-centered tetragonal; the \(\gamma\) phase and Th\(_6\)Mn\(_2\) are complex face-centered cubic structures; and both the \(\varepsilon\) phase and ThMn\(_2\) form close-packed hexagonal structures. Both Pauling and Hume-Rothery agree on the thorium valence being four so that by assuming the three intermetallic compounds to be electron compounds it is possible to calculate the manganese valence for each. The values obtained are listed in Table 3.
Table 3. Manganese Valences in ThMn$_2$, Th$_6$Mn$_{23}$ and ThMn$_{12}$.

<table>
<thead>
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<th>Using Hume-Rothery's Ratios</th>
<th>Using Pauling's Ratios</th>
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<tr>
<td>ThMn$_2$</td>
<td>5.02</td>
<td>5.04</td>
</tr>
<tr>
<td>Th$<em>6$Mn$</em>{23}$</td>
<td>5.02</td>
<td>5.04</td>
</tr>
<tr>
<td>ThMn$_{12}$</td>
<td>5.04</td>
<td>5.04</td>
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</table>

It is thus apparent that only the Pauling valences give consistent results. The valence of five is in good agreement with the average value of the two valences, 4.16 and 5.78, given to manganese by Pauling.

Relation Between ThMn$_{12}$, Th$_2$Fe$_{17}$, Th$_2$Co$_{17}$, Th$_2$Ni$_{17}$ and the MgZn$_5$ Lattice

The compounds with high transition element composition, ThMn$_{12}$, Th$_2$Fe$_{17}$, Th$_2$Co$_{17}$ and Th$_2$Ni$_{17}$, are all related even though the compounds belong to different crystal classes. The structures are based on the MgZn$_5$ lattice in which thorium now replaces magnesium and the transition element replaces zinc. By systematically replacing particular thorium atoms in the MgZn$_5$ lattice with pairs of transition element, the superlattices of hexagonal ThMn$_{12}$, monoclinic Th$_2$Fe$_{17}$ and Th$_2$Co$_{17}$, and body-centered tetragonal ThMn$_{12}$ can be derived.

The projection of the atoms along the $c_0$ axis onto the (001) plane of the MgZn$_5$ lattice is shown in Fig. 1. In order to obtain the superlattice of the compounds with high transition element content we replace the following thorium atoms by pairs of the corresponding transition element parallel to the $c_0$ axis of the MgZn$_5$ lattice:

- **ThMn$_{12}$**
  - first layer, $B_1$, $B_2$, $B_3$, ..., $D_1$, $D_2$, ...
  - second layer, $A_1$, $A_2$, $A_3$, ..., $C_1$, $C_2$, ...

- **Th$_2$Fe$_{17}$ and Th$_2$Co$_{17}$**
  - first layer, $B_2$, $B_5$, ..., $D_2$, $D_5$, ...
  - second layer, $B_3$, $B_6$, ..., $D_3$, $D_6$, ...
  - third layer, $A_3$, $A_6$, ..., $C_3$, $C_6$, ...

- **Th$_2$Ni$_{17}$**
  - first layer, $B_2$, $B_5$, ..., $D_2$, $D_5$, ...
  - second layer, $B_3$, $B_6$, ..., $D_3$, $D_6$, ...

Though it is interesting to note the similarities between these structures, the reasons for the different methods of substitution are still not understood.
Fig. 1. Projection of MgZn₅ type lattice onto (001) plane; thorium atoms, large circles; transition element atoms with z=0, small unshaded circles; transition element atoms with z=1/2, small shaded circles; MgZn₅ type unit cell, solid line; ThMn₁₂ unit cell, dash-dot line; Th₂Fe₁₇ or Th₂Co₁₇ unit cell, short dashes; Th₂Ni₁₇ unit cell, long dashes.

Bibliography

SESSION V-B

STRUCTURE OF METALS

Chairman - C. S. Smith
A METHOD FOR THE QUANTITATIVE DETERMINATION OF
PREFERRED ORIENTATION IN METALS

L. K. Jetter and B. S. Borie, Jr.

Introduction

The quantitative study of preferred orientation has been made practical by the recent development of several Geiger counter spectrometer techniques. Among the new methods are those of Decker, Asp, and Harker; Field and Merchant; Schulz; and Norton. Each of them employs a special sample holder mounted on a conventional focusing spectrometer table. In each case the specimen orientation is varied while the Geiger counter, stationary at the appropriate Bragg angle, measures an intensity which may be related to the fraction of the irradiated volume of the specimen properly oriented to diffract.

With the exception of the technique proposed by Norton, flat specimens are used. This requires either that the primary beam intensity be severely limited or that complicated corrections for geometry variation with orientation be used. Norton's method is characterized by the use of a cylindrical specimen. For orientation changes by rotation about the cylinder axis, no geometry correction is necessary.

For any of these methods, complete exploration of the pole figure requires the use of a number of such specimens cut at various angles with respect to, for example, the rolling direction of a sheet.

The unique feature of the method to be described here is that a spherical diffraction specimen is employed. For orientation changes by rotation about any axis through the center of the sphere, the spectrometer geometry does not change, hence no intensity correction is needed. Complete pole figure data are available with only one specimen; and, since the diffracted beam is not transmitted through the sample, the method may be used satisfactorily regardless of the absorption coefficient of the metal to be studied.

Principle of the Method

The spherical diffraction specimen is prepared so that there is appended to it a cylindrical stem by which the specimen is mounted on the x-ray spectrometer. The stem axis may be used to define some principal direction; reference marks on the stem surface may be used to identify other directions of importance. By means of a special goniometer the specimen is mounted on the spectrometer so that the stem axis is in the plane of the incident and diffracted beams--the plane of the spectrometer. The goniometer provides for rotation of the sphere about the stem axis through an angle $\alpha$ and for rotation of the sphere about an axis normal to the spectrometer plane through an angle $\phi$. Both axes pass through the center of the...
sphere. The motion of the specimen relative to the spectrometer plane caused by rotation through $\phi$ and $\alpha$ are illustrated in Fig. 1. When the angle $\phi$ is zero, the stem axis bisects the angle between the incident and diffracted beams. In this position only grains in the specimen oriented such that their plane normals are parallel to the stem axis will diffract. If the intensity observed by the Geiger counter for this orientation be plotted at the pole of a Wulff net, then the intensity observed after rotations through $\phi$ and $\alpha$, as shown in Fig. 1, would be plotted at the point whose latitude is $\phi$ and longitude $\alpha$. It is clear that this intensity is directly comparable to that observed at $\phi = 0$ since the geometry of diffraction remains unchanged upon rotation through $\phi$ and $\alpha$. It is also evident that the only limitation on $\phi$ is that it may not become so large that the specimen stem (actually the stem support) moves into the diffracted beam. Since this maximum $\phi$ is always greater than 90°, and since rotation through $\alpha$ about the stem is unlimited, complete data for at least a hemisphere of the pole figure may be obtained.

Description of the Method

A photograph of the special goniometer together with the diffraction specimen mounted on a horizontal x-ray spectrometer is shown in Fig. 2. The goniometer consists of a multiple base the upper section of which is dovetailed into the lower and which can be moved linearly with respect to the lower section by means of a micrometer screw. The lower section is rigidly attached to the goniometer bushing of the spectrometer. The upper section supports an arm which can be rotated about a vertical axis; this arm in turn supports a horizontal spindle to which the specimen is attached by means of a chuck. The specimen is positioned with the aid of a toolmaker's microscope so that the center of the sphere lies on the vertical rotation axis of the arm. A horizontally-mounted Bodine synchronous motor with accessory gearing provides for automatic rotation of the arm about its vertical axis through the angle $\phi$. Another Bodine motor, mounted vertically, provides for automatic rotation of the spindle about its horizontal axis through the angle $\alpha$. By means of an eccentric the latter motor also provides for an oscillatory motion superimposed on the scan through $\phi$. Such a motion is sometimes desirable statistically when specimens of large grain size are under examination.

Thus, preliminary to measurement of the orientation texture, the specimen may be made to undergo three independent motions for its alignment:

1. It moves through an angle $\theta$ about the vertical spectrometer axis as the Geiger counter arm moves through 28, the scattering angle associated with the family of planes to be studied.
2. Sliding the specimen in the chuck moves it linearly in the direction of the axis of the specimen stem. This motion positions the sphere on the vertical rotation axis of the arm.

3. The sphere may be translated linearly in the direction of the diffracting plane normal by rotation of the micrometer screw which slides the upper section of the base over the lower. This causes the specimen to move into the primary beam, aligning it for optimum diffraction geometry.

To observe the preferred orientation the Geiger counter is fixed at the proper $2\theta$, and the specimen is aligned in the primary beam. Then, with $\alpha$ held constant, the intensity of the diffracted beam is recorded on a Brown potentiometer recorder as the specimen is automatically rotated through $\phi$. This procedure is repeated for other values of $\alpha$ sufficient to scan at least a hemisphere. For materials exhibiting a fiber texture parallel to the specimen stem axis, the specimen may be rotated rapidly through $\alpha$ while it is rotated slowly through $\phi$.

It has been found that the principal effect of small specimen misalignments is to cause small changes in the observed $2\theta$ for different $\phi$. Misalignment, if it is not large, seems to have a negligible effect on the observed intensity as one scans through $\phi$. Hence, whenever possible, wide slits are used at the Geiger counter. This causes a broad, relatively slowly changing diffraction maximum. The observed count rate, then, is essentially independent of small shifts in $2\theta$ caused by misalignment.

When such a wide Geiger counter slit is used, it has been found convenient to use a set of Soller slits at the Geiger counter to keep the background down to a reasonable level. Soller slits are shown mounted on the face of the counter tube housing in the photograph of Fig. 2. Though the lines of face-centered cubic metals are usually spaced such that wide slits may be used, for metals such as uranium it is often necessary to use narrow slits to resolve a set of closely spaced lines. In such a case, careful specimen preparation and alignment are required.

Specimen Preparation

Accurately spherical diffraction specimens may be obtained by the use of a vertical milling machine equipped with an eccentric boring head and a dividing head, as shown in Fig. 3. The stem of desired diameter is first machined on a lathe. By means of the stem the specimen is then mounted in the dividing head of the milling machine. The angle of inclination $\theta$ of the dividing head and the eccentricity $e$ of the boring head are related to the specimen radius $r$ and the stem diameter $x$ as follows:
The sphere is machined by rapidly rotating the eccentric cutter while slowly rotating the dividing head and slowly elevating the table of the milling machine. When the cutter just contacts the stem, the specimen is fully formed.

The machined sphere is lapped to smoothness with diamond grit on a hollowed-out block of cast iron and then electroetched to remove the surface layer deformed by machining and lapping. The sphere is reduced in diameter approximately 0.010 inch by an electroetching technique employing a cathode of stainless steel in the form of a hollow sphere 4 inches in diameter. Conditions are adjusted so that etching occurs slowly and sphericity of the specimen is maintained until nearly the desired amount of metal is removed. Then a rapid finishing etch is used to remove pitting and to polish the sphere. With this technique specimens spherical to within 0.001 inch are obtained consistently. Spheres ranging down to 0.2 inch in diameter have been prepared in this manner.

**Deformation and Recrystallization Textures in Extruded Thorium**

The method described here has been used to observe the textures developed in extruded thorium rod. The fabricating conditions and the results of examination are summarized in Table I. The degree of recrystallization indicated for each specimen in this table was determined both by noting the spottiness of the lines in an x-ray Debye-Scherrer photograph and by metallographic examination. The textures found for each specimen are indicated in the last three columns. These were determined from the intensity vs. $\theta$ plots of the various lines (hkl) of the thorium spectrum. $\phi$ plots for three of the specimens of Table I for the (111), (200), (220), and (311) planes are shown in Figs. 4-7. The positions marked on the horizontal lines at the top of each figure indicate the values of $\phi$ at which intensity maxima should be observed for the textures indicated at the left of each line. The number beside each mark gives the multiplicity of planes for that position.

These results indicate that extruded thorium rod develops a deformation texture similar to that developed by other face-centered cubic metals, i.e., $\{111\}/\{100\}$. The $\{111\}$ recrystallization texture, however, is somewhat different; other metals either retain one or both of the components of the deformation texture upon recrystallization or else develop a $\{112\}$ fiber texture. It is presumed that the $\{100\}$ component in the nearly completely recrystallized thorium rod represents the unrecrystallized portion since this texture is
not present in the completely recrystallized sample. Apparently, the growing recrystallized grains selectively absorb those deformed regions composing the [111] texture.

Deformation and Recrystallization Textures in Extruded Uranium

The results of a similar investigation of extruded uranium rod are summarized in Table II. Figs. 8-25 are some of the φ plots from which the textures listed in Table II were determined. All samples, as extruded, exhibited a duplex [410]/[010] fiber texture. Increasing the extrusion ratio resulted in an increase in the strength of the [410] relative to that of the [010] component with an increase in sharpness of both. From the front to the back of the extruded length of rod given the greatest reduction, there was an increase in the strength of the [010] relative to that of the [410] component.

Metallographic examination, as well as the lines of Debye-Scherrer photographs, showed that the degree of recrystallization increased with increase in extrusion ratio; and, for the rod given the greatest reduction, that the degree of recrystallization decreased from the front to the back end of the extruded length.

It would appear from this that the preferred orientation is related to the microstructure, in that the strength of the [410] increases relative to that of the [010] component with increasing degree of recrystallization.

Upon deliberate annealing after extrusion, a specimen initially showing a high degree of recrystallization showed essentially no texture change, as expected. However, an annealed specimen initially having a deformed structure was found to have a major [431] texture instead of [410]. It would seem, then, that two recrystallization textures are possible, the manner in which recrystallization is induced determining which of them is developed.

BIBLIOGRAPHY


### TABLE I

<table>
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<tr>
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<th>Extrusion Sample No.</th>
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<th>Extrusion Rate (ft/min)</th>
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<th>Major</th>
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Diameter of extruded rod - 1 in.
Extrusion ratio - 9.0
Extrusions water quenched at die.
Samples taken 18 in. from front end of extruded length.
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Diameter of billet - 3-1/8 in.
Billet temperature - 500°C
Die - 25° conical
Extrusions water quenched at die
Annealed - 1 hr. at 550°C

Front = 1/4, middle = 1/2, back = 3/4 distance along extruded length.
Fig. 1 - Relationship between specimen orientation and coordinates on stereographic net.
Fig. 2 - View of specimen mounted on x-ray diffraction goniometer.
Fig. 3 - Arrangement for machining spherical x-ray diffraction specimens.
FIG. 4

FIG. 5

CONIDENTIAL

031432111110
PREFERRED ORIENTATION PLOT—(220) — EXTRUDED THORIUM ROD

PREFERRED ORIENTATION PLOT—(311) — EXTRUDED THORIUM ROD
Figs. 8 - 10
Figs. 11 - 13
Prefereed orientation plot - O(001) - Extruded uranium rod

Figs. 17 - 19

Declassified
Figs. 23 - 25
THE STRUCTURE OF LIQUID BISMUTH AND LIQUID LEAD

C. P. Smith and P. C. Sharrah

The purpose of the research to be reported in this talk was to determine the structure of liquid lead and liquid bismuth each at two temperatures. These structures were determined from an analysis of the patterns obtained by the diffraction of neutrons by the liquid metals.

There were two reasons for conducting this research. First, only one other study has been made of the diffraction of neutrons by liquids. In this study the structures of liquid lead, liquid bismuth and liquid sulfur were obtained. In the case of liquid lead the structure obtained does not show some of the important details given by x-ray diffraction methods. Intrinsically, neutron diffraction should be more suitable for the study of liquid lead than x-ray diffraction. This is because the relative magnitudes of the scattering and absorption coefficients for lead are more favorable in the case of neutron diffraction than in the case of x-ray diffraction. It was hoped that the neutron spectrometer available at the Oak Ridge National Laboratory would be capable of giving better results for liquid lead because of its intense monochromatic beam.

A second reason for conducting this research was to determine what effect a change in temperature might have on the structures of liquid lead and liquid bismuth. Previous studies both with x-rays and neutrons have all been made in the neighborhood of the same temperatures for these liquids.

The apparatus used in this work consisted of a neutron spectrometer and recording system similar to that previously described by Wollan and Shull. and a special furnace with accessories to hold the metal in the liquid state at a controlled temperature. The liquid metals were contained in quartz tubes which were a little over one centimeter in diameter and which had a wall thickness of about one-half millimeter.

A wave length of 1.16 A was used for most of the work except one run which was made using a value of 0.71 A. This latter run gave experimental intensity data out to larger values of (sin θ)/A but the graph was essentially constant beyond (sin θ)/A equal to 0.7. For this reason data beyond (sin θ)/A equal to 0.7 was not used in this work.

\[ 4\pi R^2 \rho(R) = 4\pi R^2 \rho_0 + \frac{2R}{|\pi|} \int_0^{S_0} S i(s) \sin (RS) \, ds \quad \ldots \quad 1 \]

or

\[ 4\pi R^2 \rho(R) = 4\pi R^2 \rho_0 + \frac{2R}{|\pi|} \int_0^{S_0} S i(s) \sin (RS) \, ds \quad \ldots \quad 1 \]
Equations 1 through 4 give the relations by which the structure of the liquid metals may be obtained from the experimental results. In these equations $R$ is the distance measured from any atom chosen as the origin in the liquid. $\rho(R)$ is the atomic density as a function of $R$. Hence, $4\pi R^2\rho(R)$, given on the left hand side of the first two equations, is an atomic distribution function. This distribution function has the following property: If the function is plotted against $R$, the area under the curve out to any value of $R$ is equal to the number of atoms contained in a spherical shell of radius $R$ about the central atom.

Equation 1 is the form customarily used in x-ray work for the calculation of the atomic distribution function. Equation 2 is the form which has been used previously for neutron diffraction work. Equations 3 and 4 serve to define symbols used in the first two equations.

In order to use the second equation it is necessary to make an absolute measurement of the intensities of the incident and diffracted beams. The first equation avoids the necessity for these absolute measurements and was used in the work reported here. Because of the limited time available the second equation will not be discussed further.

In the first equation, $\rho_0$ is the average density of the atoms in the liquid given in atoms per cubic Angstrom and determined from the density and the atomic weight. The variable $S$ is given by Equation 3 where $\theta$ is the scattering angle and $\lambda$ is the neutron wave length. The function $i(S)$ is given by Equation 4. In this equation, $I$ is the experimentally determined diffraction curve which has been corrected for sample holder scattering, background, incoherent scattering, absorption and multiple scattering. $K$ is the coherent scattering intensity which would be expected if no interference effects were present. Hence, it is seen that the function $i(S)$ contains all of the neutron diffraction data.

Figs. 1 and 2 give the experimentally determined neutron diffraction curves corrected for scattering by the quartz sample holder.

Fig. 3 shows the atomic distribution curves for liquid lead which were calculated from the neutron diffraction curves. The smooth lines which do not have experimental points give the distribution functions which would have been obtained if the liquid had been a structureless homogeneous fluid. The peaks on the experimental curves represent clusters of lead atoms in the liquid. The area under any peak gives the number of atoms in the cluster associated.
with that peak. The first pronounced peak represents a shell of atoms clustering closely about the central atom. Hence, the area under this peak gives the coordination number for the atoms in the liquid.

The position of the second pronounced peak occurs at 6.6 A for both curves. Previous x-ray diffraction data gives 6.5 A and the previous neutron diffraction data gives 6.4 A.

In between the two major peaks is a very small peak which is defined more clearly at the lower temperature. This peak was observed in previous x-ray diffraction work but was not observed in previous neutron diffraction work.

The coordination number for liquid lead obtained from these curves is approximately 9.5 atoms for both temperatures. Previous x-ray diffraction results give 8 atoms and previous neutron diffraction results give 12 atoms. The large value obtained in the previous neutron diffraction study may be accounted for if it is assumed that since the small second peak was not resolved, the atoms associated with this peak have been counted in the coordination shell.

The effect of increasing the temperature, as might have been expected, was to produce an increasing disorder in the liquid. However, it will be noted that this effect was small for the two temperatures studied.

Fig. 4 gives the atomic distribution curves for liquid bismuth. The positions of the peaks and the coordination number are essentially those obtained in the previous x-ray and neutron diffraction experiments. The coordination number given by the curves shown is approximately 7.5. The coordination number previously obtained was approximately 8.

It will be noted that the curve shown for 300°C shows the second major peak partially resolved into two peaks. This has not previously been reported for liquid bismuth although similar increase in the fine structure of liquid state order with decreasing temperature has previously been observed for liquid tin.

A detailed comparison of the curves obtained in this study with those given in previous investigations shows that there is a marked improvement in the agreement between the x-ray results and this neutron study over that given in the previous neutron investigation.

It is concluded that neutron diffraction techniques are reliable for giving the general features of liquid metal structure. In addition neutron diffraction techniques offer certain advantages over x-ray diffraction techniques for liquid structure studies. First, in neutron diffraction studies of the elements of high atomic number large samples of simple geometry may be used; whereas in x-ray work it is usually necessary to study very small samples of awkward geometry such as individual drops. Second, neutron diffraction data can be obtained out to larger values of (sin θ)/λ than is possible with x-ray diffraction. This is because of the nature of the form factor for neutron scattering for slow neutrons. For these reasons neutron diffraction appears to be a promising tool for studying the structures of liquid metals.
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(2) Made available by H. A. Levy and S. W. Peterson.
(3) E. O. Wollan and C. G. Shull, Phys. Rev. 73, 830 (1948).
Fig. 1 - Neutron Diffraction Curves for Liquid Lead
Fig. 2 - Neutron Diffraction Curves for Liquid Bismuth
Fig. 3 Atomic Distribution Curves for Liquid Lead
Fig. 4 - Atomic Distribution Curves for Liquid Bismuth
DIFFUSION STUDIES BY CATHODIC SPUTTERING AND PHASE BOUNDARY MIGRATION

D. D. Van Horn

In this paper I should like to present some of the methods which have been developed at the Knolls Atomic Power Laboratory for the study of diffusion in the solid state. We hope to study in the near future the effect of pile irradiation on diffusion in both fissionable and non-fissionable materials. In order to accomplish this, we have developed a method of obtaining diffusion penetration curves from small, highly radioactive specimens. With very small diffusion couples both the total activity is reduced and the problem of maintaining a uniform temperature in the specimen is simplified.

The specimens which we shall use are small cylinders one-half inch long and 80 mils in diameter. A method of removing thin layers of uniform thickness by cathodic sputtering has been developed in our laboratory by T. F. Fisher and C. E. Weber. Fig. 1 shows the essential features of the sputtering apparatus without the glass envelope and associated vacuum equipment. The specimen (c) acts as the cathode and is centered in a cylindrical anode about one inch long and an inch in diameter. The system is evacuated and then krypton is introduced into the system at a pressure of about 200 microns. A potential of 1400 volts is maintained between anode and cathode, giving a current of about one milliampere. Under these conditions about 0.04 mils are removed from the radius of the specimen per milliampere-hour of integrated current in the gaseous discharge. The inner surface of the anode is lined with aluminum foil which collects 80 to 90% of the material sputtered from the specimen. This foil is replaced after the desired amount of materials has been sputtered from the cathode and chemically analyzed. The sample weight is less than ten milligrams per mil removed from the radius so that appropriate micro-methods of analysis must be used to determine the composition of the material removed by sputtering. Various blanks of single phase and two-phase binary alloys of uniform composition have been run and no difference between the composition of the material collected on the foil and the original sample composition have been detected (within the errors in chemical analysis for such small quantities).

As a test of the method, we have studied diffusion in a copper-nickel couple and compared the results with the values of the diffusion constants obtained by other investigators. Since it has been found that in copper-rich binary alloys of copper and nickel the diffusion rates vary quite rapidly with composition, we studied the diffusion of copper from a Ni - 55% Cu alloy onto pure nickel. The specimen was prepared by electroplating a layer of nickel onto an alloy wire core. The core diameter was approximately 60 mils and the nickel layer was about seven mils thick. A one-half inch section of the wire was sealed in an evacuated tube and heated for seven days at 977°C.
diameter of the wire was measured microscopically before and after plating and, on the diffused specimen, before and after each layer was removed by sputtering.

Fig. 2 shows the results of the analysis of the diffused specimen. \( \beta \) is the initial outer radius of the plated wire and the copper concentrations are expressed in terms of the fraction of the initial core concentration. The heavy line shows the concentration distribution in the undiffused specimen. The large scatter of the results in the region of high copper concentration is due to dilution errors in the chemical analysis. A colorimetric method was used which was highly sensitive to small amounts of copper, and hence was not too well adapted to higher copper concentrations. Since this figure was drawn, these specimens have been re-analyzed by another method and this scatter has been almost entirely eliminated. The diffusion rate can be determined, however, from the shape and position of the toe of the penetration curve, so even this scatter affects but little the determination of the diffusion coefficient D.

The solution of the diffusion equation for cylindrical geometry is a convergent infinite series whose terms involve Bessel functions. For the amount of diffusion shown in Fig. 2, ten terms would be required in the series to attain sufficient accuracy to match the experimental curve. For this small amount of diffusion, however, the cylindrical solution can be approximated very closely in the region of the initial interface by the solution for diffusion in one dimension from a finite layer into an infinite bar. Fig. 3 shows the experimental results using this approximation, where d is the thickness of the finite layer. The solid curve is the theoretical curve \(^2\) for \( K = \sqrt{Dd} = 2.0 \).

This gives a value \( D = 6.7 \times 10^{-11} \text{ cm}^2/\text{sec.} \) at 977°C. Using the values of \( D_0 \) and Q for this temperature range found by Matano (as reported by Smithells), we get \( D_{977} = 6.35 \times 10^{-11} \text{ cm}^2/\text{sec.} \). While da Silva and Mehl, for the same composition range, report a value \( D_{977} = 5.5 \times 10^{-11} \text{ cm}^2/\text{sec.} \). The value which we obtained agrees with the results of other investigators quite well, so we feel confident that the method of cathodic sputtering will yield valuable results in the analysis of diffusion in other systems. We are working at present on collecting more data for the copper-nickel system, and will obtain diffusion coefficients at other temperatures and hence be able to get a value for the activation energy for the diffusion process in this material.

As was mentioned previously, the advantage of the sputtering method is that it can be used on radioactive specimens without having to worry about the spread of contamination inherent in the machining operation more customarily used in the determination of penetration curves. Our laboratory has used the sputtering method with remote handling operation in the examination of pin-type fuel samples which have been irradiated at Hanford and Chalk River. We are now fabricating pins with uranium or uranium alloy cores with stainless steel or zirconium pin walls so that the effect of irradiation on diffusion in
Fissionable materials may be studied. Another aspect of the problem of solid state diffusion which is under investigation is the relationship between diffusion rates and phase boundary migration. Most measurements of diffusion rates are in binary alloys in regions of continuous solubility. Unfortunately, many systems of practical interest, particularly binary or higher order alloys of uranium, do not satisfy these ideal conditions, nor has there been a satisfactory theory developed by which these problems can be handled. I should like to mention briefly some approaches to this problem, both theoretical and experimental, which we have made and in which further work is in progress.

One of the problems in the observation of the motion of phase boundaries or diffusion layers is that of determining the origin of the position coordinates. This problem may be solved by making the diffusion couple in a symmetrical form and using the plane of symmetry as the origin. We have developed a method of producing diffusion bonds by hot pressing techniques which eliminate the necessity of a vacuum furnace. Fig. 4 shows the method by which diffusion "sandwiches" are produced. In this case, a five mil uranium disk is to be bonded between one-eighth inch copper disks. The molybdenum disks and collar are to prevent the "sandwich" from bonding to the mild steel container. After all the parts are cleaned, they are assembled as shown in two cups of 16 mil mild steel. The whole assembly is placed in a cylindrical glass flask and evacuated. The evacuated flask is placed in a close-fitting, single-turn coil of an induction welder and the container is welded closed around the flange. The bonding of the sandwich is performed by pressing between graphite dies in a graphite cored tube furnace. When the furnace has reached the desired temperature, the container is placed between the dies and the pressure applied by a dead-weight loaded arbor press with a total force of about 400 pounds. Figs. 5 through 7 show some of the welds which can be obtained by this method. After welding, the sandwiches are cut into six or eight small pieces, which are sealed in evacuated quartz tubes for the diffusion anneal. The motion of the phase boundaries can be measured by a travelling microscope or by a filar eyepiece.

Before any sort of fundamental information can be obtained from the observed motion of phase boundaries, we must know what the relationship is between diffusion rates and the boundary motion. An approach which has been made is to consider coordinate systems which move relative to the initial interface. This method has not been attempted for a system with more than one phase boundary, in fact, it would seem to lead to all sorts of difficulties if attempted in a finite system of any sort. A more basic weakness of this approach is that it applies the diffusion equation \( \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \) in the moving coordinate system. If one attempts to translate back to a stationary system, the form of the equation is entirely changed. It seems necessary that any solution to the problem of diffusion with a phase boundary should be such as to obey the diffusion equation in a stationary coordinate system.
A means of obtaining such a solution is shown in Fig. 8. The position of the initial interface is $x_{00}$ and the position of the phase boundary at some later time is $x_0$. Initially we have phase 1 (the concentration of one constituent being $C_1$) in contact with phase 2 (the concentration of the same constituent being $C_2$). $c_{10}$ and $c_{20}$ are the equilibrium concentrations of the two phases for the temperature at which diffusion has taken place. Suppose that the diffusion coefficients $D_1$ and $D_2$ for the two phases are different. Then the solutions for $x > x_0$ and $x < x_0$ must satisfy the equation

$$\left[ -D_2 \left( \frac{\partial \phi}{\partial x} \right) \right]_{x_0} - \left[ -D_1 \left( \frac{\partial \phi}{\partial x} \right) \right] = \left( c_{20} - c_{10} \right) \frac{dx_0}{dt}$$  \hspace{1cm} (1)

That is, the difference between the diffusion flux up to and away from the phase boundary must be equal to the concentration difference across the miscibility gap times the velocity of the phase boundary. Other conditions which the solutions must satisfy are the following:

$$c_1(x_0, t) = c_{10}$$  \hspace{1cm} (2)

and

$$c_2(x_0, t) = c_{20}$$  \hspace{1cm} (3)

It has been found that these conditions can be satisfied if we assume that the solution in phase 1 (that is, $c_1$) behaves as though it were but a portion of a continuous diffusion curve from some "phantom" concentration to the left, without any discontinuity existing at the concentration $c_{10}$. Similarly, the concentration in the second phase behaves as though there were diffusion to some "phantom" concentration to the right of $x_0$.

The exact solutions for the two branches of the concentration curve are

$$c_1 = c_1 + \lambda_1 \left[ 1 - \text{erf} \left( 2^{-\frac{1}{2}} Y_1 \right) \right]^{-1} \left\{ 1 - \text{erf} \left[ (x-x_{00})(4D_1 t)^{-\frac{1}{2}} \right] \right\}$$  \hspace{1cm} (4)

and

$$c_2 = c_2 - \lambda_2 \left[ 1 + \text{erf} \left( 2^{\frac{1}{2}} Y_2 \right) \right]^{-1} \left\{ 1 + \text{erf} \left[ (x-x_{00})(4D_2 t)^{-\frac{1}{2}} \right] \right\}$$  \hspace{1cm} (5)

where $Y_1$ and $Y_2$ are parameters which determine the positions of the phantom concentrations, and which may be determined from the conditions of the problem. The values for $Y_1$ and $Y_2$ must be determined by solving simultaneously the equations

$$Y_1 D_1 \frac{d^2}{dt^2} = Y_2 D_2 \frac{d^2}{dt^2} = K \text{ (const.)}$$  \hspace{1cm} (6)

and

$$\lambda_2 f_2(Y_2) - \lambda_1 f_1(Y_1) = \xi$$  \hspace{1cm} (7)
where $K$ is determined from the motion of the phase boundary by the relationship

$$d = K(2t)^{\frac{1}{2}}$$

(8)

and where the function $f_1(Y_1)$ and $f_2(Y_2)$ involve exponential functions and error functions of the $Y$'s as shown in Fig. 9.

A nomograph for the solution of equations (6) and (7) is given in Fig. 9. For any problem the quantities $\lambda_1$, $\lambda_2$, and $S$ must be known. The ratio between $\lambda_2$ and $\lambda_1$ is found on the diagonal scale and a vertical line drawn which shall have the length $S/(\lambda_1 + \lambda_2)$ in the units of the $y$-scales. Then any line through the point so determined shall intersect the $x$- and $y$-scales in solutions of equation (7). We can now solve the following two important problems.

I) Given the diffusion coefficient in one phase and the motion of the phase boundary, determine the diffusion coefficient for the second phase. Equations (6) and (8) determine the value of $Y_1$. Knowing the phase diagram, $Y_2$ can then be determined from Fig. 9.

II) Given the diffusion coefficients for the two phases, determine what the motion of the phase boundary shall be. In this case, equation (6) determines the ratio between $Y_1$ and $Y_2$. The slope of the dashed line in Fig. 9 is adjusted until the desired ratio is found and the resulting $Y$'s give, in equation (6), the value of $K$, thus determining the phase boundary motion.

At the present time, work is being done to extend the above method to cases with finite geometry and to cases where more than one phase boundary exists, such as in cases with formation of one or more intermetallic compounds.
REFERENCES

1. Since this paper was presented, a detailed description of the sputtering method has appeared in the open literature. Those readers desiring more specific information on the method are referred to this paper.


2. The solution for the finite case is

   \[
   \frac{c}{c_0} = 1 - 1/2 \left[ \text{erf} \left( \frac{x + d}{\sqrt{4Dt}} \right) - \text{erf} \left( \frac{x - d}{\sqrt{4Dt}} \right) \right]
   \]

   or

   \[
   \frac{c}{c_0} = 1 - 1/2 \left[ \text{erf} \left( \frac{s + 1}{2K} \right) - \text{erf} \left( \frac{s - 1}{2K} \right) \right]
   \]

   where \( K = \frac{\sqrt{dt}}{d} \) and \( s = \frac{x}{d} \)


Fig. 1 - Cathodic Sputtering Apparatus
Fig. 2 - Diffusion of Copper in Nickel, Cylindrical Specimen. Diffused 7 Days at 977°C
Fig. 5
Zr-U-Zr Sandwich
Pressure weld: 15 min. at 900°C; 100X; polarized light.

Fig. 6
Zr-347 stainless-Zr
Pressure weld: 15 min. at 920°C; 100X; polarized light.

Fig. 7
347 stainless-Be-347 stainless
Pressure weld: 20 min at 950°C
Slow cooled at 4°C/min. 150X
Fig. 8 - Diffusion in Infinite Specimen with Presence of Phase Boundary

\[ C_2 - c_{20} = \lambda_2 \]
\[ c_{10} - C_1 = \lambda_1 \]
\[ -c_{10} + c_{20} = \delta \]
\[ x_0 - x_{00} = d \]
\[ \lambda_2 f_2(y_2) - \lambda_1 f_1(y_1) = \delta \]

\[ f_1(y_1) = \left( \frac{2}{\pi} \right)^{\frac{1}{2}} \frac{\exp(-y_1^2/2)}{y_1 \left[ 1 - \text{erf}(y_1/\sqrt{2}) \right]} \]

\[ f_2(y_2) = \left( \frac{2}{\pi} \right)^{\frac{1}{2}} \frac{\exp(-y_2^2/2)}{y_2 \left[ 1 + \text{erf}(y_2/\sqrt{2}) \right]} \]

\[ y_1 \sqrt{D_1} = y_2 \sqrt{D_2} = K \]

\[ d = K (2t)^{\frac{1}{2}} \]

Fig. 9 - Nomograph for Calculation of Phase Boundary Migration and Diffusion Rates
CREEP AND STRESS-RUPTURE FACILITIES
AT OAK RIDGE NATIONAL LABORATORY

R. B. Oliver and W. D. Manly

In general there is a scarcity of creep and stress-rupture data and this is particularly true at the higher temperatures, for the rarer metals and for tests conducted in special atmospheres or environments. The reactor engineers are interested in such data for uranium and thorium tested in vacuum and various atmospheres.

For these reasons the Metallurgy Division of the Oak Ridge National Laboratory has designed, and is operating, a laboratory for creep and stress-rupture testing in high vacuum, argon, or other controlled atmospheres.

The following design criteria were selected for the chambers to be used for testing in vacuum, inert atmospheres, or other controlled atmospheres.

1. A uniform temperature over the central four inches of the furnace chamber.
2. The temperature of the furnace to be controlled from the surface of the test specimen with a temperature cycle of less than plus or minus one degree Fahrenheit.
3. Capable of being evacuated to a pressure of less than 0.10 micron.
4. Equipped with viewing windows to allow for optical measurement of the elongation and for inspection of the specimen during test.
5. The sealing system for the test chamber to have a minimum side thrust.

Fig. 1 is a cut-away view of the test chamber used in this laboratory, showing the relation of component parts and the placement of accessories. The central tube, side arms, and water cooled heads are of 316 stainless steel with all joints heliarc welded. The thermocouples are shown coming in through seals at the very top. An ion type vacuum gage is located at the top of the chamber while a thermocouple gage is located on the connection to the diffusion pump. The windings of the furnace are tapered to give a flat gradient and ten shunt terminals are provided for adjustment of the
gradient should the need arise. This design gives a minimum surface to hold gases that may later interfere with the evacuation of the chamber or that may provide contaminants for inert or controlled atmospheres.

Fig. 2 is an exploded view of the same furnace showing the pull rod assembly for both 0.505 inch round bar specimens and for sheet specimens. This view also shows the placement of the thermocouples—one at each end of the test section and two couples at the middle of the test section. The beads are covered with asbestos tape to prevent the bead from "seeing" the chamber wall which is hotter than the specimen surface.

Fig. 3 is a view of four of the eight chambers operating at 300° and 500°C with a vacuum of less than 0.05 micron. The diffusion pumps can be seen to the right of each furnace and the mechanical fore pumps are located immediately to the rear of each diffusion pump.

Fig. 4 is a view of six of these chambers being used with an argon atmosphere instead of vacuum. The only changes are in the external "plumbing", the inert gas being introduced at the top left of the chamber and flowing out of the chamber at the bottom left. In place of the connection to the diffusion pump a valve and hose connection is provided so that the chamber can be evacuated and purged prior to the introduction of the purified argon.

The centralized temperature and vacuum control panel is shown in Fig. 5. The rear panels carry the meters for vacuum gages and the vacuum pump controls. Eight of the remaining panels each carry two Speedomax - D.A.T. temperature controllers. The panel near the center has a twelve point Speedomax recorder and a 75 point precision indicator, thus all thermocouples in the laboratory can be read on the precision indicator and with a patch-board arrangement any 12 couples can be fed into the recorder. The Speedomax - D.A.T. controller combination controls the temperature from the surface of the specimen with no detectable temperature cycling, except for a drift of about plus or minus one-half degree over a 24 hour period.

Chromel-Alumel thermocouples are used in this laboratory, this selection being made on the basis of a 1000 hour stability test of Chromel-Alumel, platinum-10% rhodium, and iron-Constantan couples in vacuum.

The bellows employed to seal the chamber have two effects on the loading of the specimen. If there is a pressure difference across the bellows they will function as a piston; however, in most cases the pressure difference will be constant during a test, and thus will be a constant correction and easy to apply. The second bellows effect is one of spring loading, and as the specimen elongates the spring load of the bellows....
decreases. Fig. 6 illustrates diagrammatically how this spring load
effect may be compensated by placing the center of gravity of the lever-
arm counterweight above the plane of the lever-arm knife edges. The
counterweight can be so positioned that, through the small angle traveled
by the lever-arm, the decrease in the moment of the counterweight will
approximate the decrease of the bellows spring load. This same principle
could be used to approximate a constant stress test condition.

After studying the problems of using the commercially available types
of extension measuring devices in an enclosed chamber, an optical measure-
ment of extension was selected. A continuous, automatic, recording type
of extensometer would be very desirable but there are many problems
involved in operating them in an enclosed chamber and their complexity
detracts from their reliability for long time operation. Fig. 7 shows
the type of platinum alloy strip (2-1/2X) selected and the enlarged
insert is at 20 diameters, showing the strip as it appears in the measuring
microscope. For extension measurement the points are selected on either
of the outside surfaces and on the center surface. The distance between
these points is measured with a micrometer microscope having a least
division of 25 micro-inches, though the best measurement is about 50
micro-inches. In a three inch gage length this allows an accuracy of at
least 30 micro-inches per inch.

Essentially leak free chambers are imperative for long time testing
in vacuum or inert atmosphere; hence, a rigorous leak detection schedule
is employed. First, all potential leak sources are surveyed with acetone
on a small brush; any leak will appear as a change of the vacuum in the
chamber. After taking remedial measure for any leaks thus detected a
helium leak detector is tied into the system and the joints are again
surveyed with a fine jet of helium.

For such a testing program the cost of the large number of specimens
required becomes quite high, particularly if the materials being tested
are difficult to machine; also reproducibility of specimens is very
desirable. For these reasons, unusual methods of machining both the round
and sheet specimens are employed. In both cases a vertical milling machine
is used. Fig. 8 shows the drilling jig, the milling templates, the formed
tool end mill, the specimen blanks, and the finished sheet specimens.
Fig. 9 is a close-up view showing the method of jigging and machining the
sheet specimens. Fig. 10 is a close-up view of the method of machining
round bar specimens in a vertical milling machine using a sharp tooth end
mill cutter. The chatter that is seen in the picture results from the
light cut being made; when a heavy cut is taken this chatter does not occur.
Fig. 11 is a general view of the method of turning the round bars on the
milling machine showing the dividing head which rotates the specimen at
about one rpm while the cutter is rotating 250 to 300 rpm. Not only do these methods result in a time savings of about 25 percent per specimen but they give a more uniform cross section than the conventional methods without the hand finishing, also a smaller amount of cold work is given to the machined surfaces.

Since the time allotted is not sufficient to present much of the data gathered during the life of this laboratory only the data shown in Fig. 12 and Fig. 13 will be presented to illustrate the flexibility of operation allowed by this design. Fig. 12 presents the data from an experiment to determine the effect of hydrogen on the creep rate of uranium. It is interesting to note that the presence of hydrogen increases the creep rate but that this effect is reversible, when the chamber is re-evacuated the curve closely parallels the curve for a test conducted in vacuum only. Fig. 13 presents the results of a similar experiment with thorium as the metal in test. In this case the overall result is a marked decrease in the creep rate, the effect not being reversible. The difference noted between thorium at 300°C and uranium at 500°C may be related to the stability of the hydrides at their respective temperatures.
Fig. 2 - ORNL Vacuum Creep Test Furnace Showing Assembly of Both Bar and Sheet Specimens
GEOMETRY OF A LEVER ARM SYSTEM WITH THE COUNTER WEIGHT ABOVE THE KNIFE EDGES

Fig. 6 - Lever-Arm System to Correct for Changing Bellows Spring Load
Fig. 7 - Platinum Alloy Strip for Optical Extension Measurement (2.5X and 20X)
Fig. 8 - Jigs and Tools to Fabricate Sheet Test Specimens on a Vertical Milling Machine
Fig. 10 - Turning a Round Bar Test Specimen with a Sharp Tooth End Mill Cutter
Fig. 11 - Vertical Milling Machine Used to Turn Round Test Specimens
Fig. 12 - Effect of Hydrogen on the Creep Rate of Uranium
THORIUM (EXTRUDED)
TESTED AT 300°C

CURVE 1: AS EXTRUDED-DEFORMED 5% IN TENSION PRIOR TO TESTING IN VACUUM (0.05 MICRONS) 16,000 PSI
CURVE 2: AS EXTRUDED-TESTED IN VACUUM (0.05 MICRONS) 16,000 PSI
CURVE 3: AS EXTRUDED-TESTED IN ALTERNATE VACUUM (0.05 MICRONS) & HYDROGEN ATMOSPHERE (3,000 MICRONS) 17,000 PSI
CURVE 4: AS EXTRUDED- SILVER PLATED & TESTED IN ARGON ATMOSPHERE (ATMOSPHERIC PRESSURE) 16,000 PSI

Fig. 13 - Effects of Atmosphere on the Creep Rate of Thorium
LIQUID METAL CORROSION BY SODIUM, LITHIUM, AND LEAD AT ELEVATED TEMPERATURES

A. deS. Brasunas

Because of the scope of this paper, the restricted time available for presentation, and the nature of our data, this paper will give only a superficial coverage of certain aspects of liquid metal-solid metal interaction observed in molten sodium, lithium, and lead at 1000°C (1832°F).

If one were to consider the nature and extent of interaction possible between a pure liquid and a pure solid metal at some given temperature, an equilibrium diagram of the binary system would be useful as a first approximation. Unfortunately, such diagrams are either non-existent or incorrect for many systems which are currently of great interest.

As an illustration, let us consider the tin-nickel system shown in Fig. 1. At 1000°C, it may be seen that tin is soluble in nickel up to 19%, and that nickel is soluble in tin to 20%. In spite of the tendency to form intermetallic layers of Ni_2Sn and Ni_2Sn, this system would probably not be satisfactory for high temperature service. One should be cautioned, however, that in addition to the maximum extent of reaction possible, the kinetics involved may be equally important.

In the tin-silicon system shown in Fig. 2, one sees the type of equilibrium diagram which may have good possibilities for high temperature use. At 1000°C, the solubility of tin in silicon is indicated to be practically nil, whereas the solubility of silicon in tin is about 2%. Here the surface-(of the solid metal) to-volume-(of the liquid metal) ratio is extremely important. One should emphasize that such information may indicate that little corrosion may be anticipated under strictly isothermal conditions, but it is definitely not indicative of behavior under conditions where a thermal gradient exists.

Testing Technique

A logical method of corrosion testing would be to insert a solid metal specimen into an inert container, add a liquid metal to the capsule and seal it under vacuum. After a suitable time interval at a selected temperature, the capsule may be opened to observe the extent of interaction. The problem encountered was the selection of a truly "inert" container. There was none.

As an illustration, nickel was found to have negligible interaction with sodium, and iron was found to be quite non-reactive with lithium and lead. The logical step was taken; nickel containers were designed for sodium tests and iron containers were prepared for lithium and lead tests. Unexpected difficulties were encountered in a number of instances; for instance, a silicon
specimen appeared to have completely dissolved in lithium at 1000°C in four hours! However, a section of the iron capsule indicated, as shown in Fig. 3, that silicon deposited on the iron capsule in a manner resembling electroplating. This phenomenon would obviously not have occurred if iron were truly inert. A testing technique was therefore developed in which such mass transfer cannot occur. This is illustrated in Fig. 4.

Tubular metal stock is required. It serves both as specimen and container. Both ends are crimped and heliarc welded after partially filling the tube with the liquid metal and evacuating the tube. This technique was found to be very satisfactory, although an objection may be raised that not all metals are available in tubular form, nor can all metals be crimped and welded easily.

**Tests with Sodium**

Sodium was found to be least corrosive of the liquid metals investigated at 1000°C. Tests were made under static conditions for 100 to 400-hour periods. The following metals showed no evidence of interactions and are rated very good: nickel, cobalt, tungsten, and 80 Ni - 20 Cr alloy.

In the 'fairly good' category (these indicate, on the basis of static isothermal tests, that such metals can be used for short periods of time at 1000°C or for long periods of time at lower temperatures), the following metals are placed: chromium, Inconel, N-155, carbon-steel, molybdenum, the 300 series stainless steels, and the 400 stainless steels. Niobium alone showed sufficient weight loss to be classed 'poor'.

Fig. 5 illustrates the surface of nickel after a 100-hour exposure to sodium at 1000°C. No evidence of interaction is apparent. Fig. 6 shows decarburization of Inconel—a type of surface instability which is not very damaging and occurs only in the case of certain alloys. A more damaging type of surface instability is depicted on 304 stainless steel in Fig. 7. Here the precipitation of some unknown phase, possibly sigma, may have been caused by an inward diffusion of sodium. Fig. 8 shows a deposit of nickel from the "inert" container on a molybdenum test specimen. Such action illustrates the need for the elimination of "third components" in corrosion testing and the invalidation of the results of such test data is obvious.

**Tests with Lithium**

Lithium differs appreciably from sodium in its corrosive behavior. The relatively high solubility of nickel in lithium is an illustration. Because of this fact, nickel base alloys and the nickel-bearing stainless steels are subject to appreciable corrosion.

In static corrosion tests at 1000°C for 100 hours, iron alone showed no evidence of interaction. Metals which have fairly good resistance to reaction
include titanium, niobium, zirconium, molybdenum, tantalum, tungsten, carbon steels, and the 400 series stainless steels. The following metals were attacked severely by lithium: nickel, cobalt, beryllium, nickel base alloys, cobalt base alloys, and the 300 series stainless steels.

Figs. 9 and 10 illustrate the type and extent of corrosion observed in 430 stainless steel and 304 stainless steel respectively. The ferritic steel shows a shallow reaction zone, whereas the austenitic steel shows grain boundary penetration and transformation to a b.c.c. structure presumably because of nickel leaching. Such corrosion may have very detrimental effects on mechanical properties far beyond what one may be inclined to predict from dimensional or weight change measurements.

Tests with Lead

Lead is surprisingly similar to lithium in corrosion behavior. Static corrosion tests at 1000°C have indicated that the following metals showed very good resistance to corrosion: iron, tungsten, zirconium, and molybdenum. In the category 'fairly good' are tantalum, columbium, vanadium, and the 400 series stainless steels. Very severe attack was noted for nickel, cobalt, titanium, beryllium, the 300 series stainless steel, Inconel, and other nickel (and cobalt) base alloys.

The surface zones of several elements are shown in Figs. 11 to 14. Molybdenum (Fig. 11) shows absolutely no evidence of any interaction after a 100 hour test. Beryllium (Fig. 12) was partially dissolved leaving a saw-tooth surface caused by preferential solution along certain crystallographic planes. Nickel was also found to be quite soluble and intergranular penetration is quite severe as shown in Fig. 13. Vanadium developed an intermetallic compound at the V-Pb interface. The high hardness of this phase is evident in Fig. 14 from the hardness impressions shown. Such layers can impede liquid metal-solid metal interaction considerably.

Fig. 15 illustrates severe grain boundary penetration and phase transformation in 304 stainless steel. This is quite similar to the attack on 304 stainless steel by lithium. In addition to grain boundary penetration and transformation, Fig. 16 also shows the presence of a new intermetallic phase in the grain boundary in the surface region of a 316 stainless steel. Numerous unknown grey metallic particles were also detected below the surface of 410 stainless steel as is shown in Fig. 17.

A peculiar surface phenomenon, shown in Fig. 18, was noted on a nickel specimen exposed to lead. Subsurface grain boundary penetration was observed as expected, but a layer of nickel crystals above the original metal surface was quite unexpected. This is now attributed to the presence of a thermal gradient in the furnace which resulted in a similar gradient on the specimen. As may be seen in the Pb-Ni diagram illustrated in Fig. 19, a thermal coefficient of solubility could explain this phenomenon; that is, nickel may dissolve at hotter areas and deposit at colder areas. This would obviously result in
abnormal solution at the hot area. Such solution-deposition phenomena, sometimes called mass transfer, are presently being studied quite intensively in several laboratories using several different types of apparatus.

Thermal Gradient Corrosion Tests

The apparatus used to study corrosion under the added influence of a thermal gradient include thermal convection loops, forced circulation loops, toroids, cold fingers, chimney units, etc. A "seesaw" test was developed at ORNL which has the advantage of using a simple apparatus and test specimen; the latter is illustrated in Fig. 20. The tube which also acts as the specimen is prepared, filled, and sealed in a manner similar to that used to prepare static corrosion test specimens previously illustrated in Fig. 4. One end is inserted into a furnace maintained at some suitable high temperature, and the other projects from the furnace. As the specimen and furnace tilt in a manner resembling a seesaw, the liquid (or any other fluid) flows by gravity to either end of the tube. Thermocouples welded to ends of the tube give an indication of the hot and cold zone temperatures. After a suitable number of cycles, the specimen may be opened for inspection. The sectioned tubular metal specimen shown in Fig. 21 illustrates the crystal deposition frequently observed at the cold end of specimen. The puncture at the hot end resulted from very severe localized solution.

Although some progress is being made by various investigations in the field of liquid metal corrosion, many challenging problems remain to be resolved.
Fig. 1 - The Sn-Ni equilibrium diagram.

Fig. 2 - The Sn-Si equilibrium diagram.
Fig. 3: Sectioned view of lithium-filled iron capsule which contained a silicon specimen; exposed for 4 hours at 1000°C. Note heavy silicon deposit on capsule wall; silicon specimen was entirely consumed.
Fig. 4 - Tabulating technique used in making corrosion tests.
Fig. 5 - No evidence of interaction found on nickel after 100-hour exposure to sodium at 1000°C.

Fig. 6 - Inconel susceptible to decarburization by sodium in 100-hour test at 1000°C.
Fig. 7 - Precipitation of unknown phase, possibly sigma, in surface region of 304 stainless steel specimen exposed to sodium at 1000°C for 100 hours.

250X

Fig. 8 - Nickel-rich phase formed on molybdenum surface during corrosion test at 1000°C using obsolete testing technique which utilized "inert" nickel container.

1000X
Fig. 9 - Corrosion of 430 stainless steel by lithium is relatively shallow in comparison with austenitic stainless steels.

250X

Fig. 10 - Severe grain boundary attack is encountered at 1000°C with 304 stainless steel when in contact with lithium.

250X

DECLASSIFIED
Fig. 11 - Molybdenum specimen is apparently unattacked by molten lead at 1000°C in 100 hours.

Fig. 12 - Beryllium is dissolved primarily along certain crystallographic planes by molten lead at 1000°C.
Fig. 13 - Severe grain boundary penetration, as well as appreciable solution, occurs when nickel contacts lead at 1000°C.

Fig. 14 - A hard (note hardness impressions) intermetallic layer forms at vanadium (lower) when in contact with molten lead (upper) at 1000°C in a 100-hour test.
Fig. 15 - Severe grain boundary attack noted on 304 stainless steel. This is very similar to the attack by lithium shown previously as Fig. 10.

100x

Fig. 16 - In certain cases, intermetallic phases are observed at sub-surface grain boundaries. The 316 stainless steel specimen shown in the above photo shows only slight austenite to ferrite transformation.

250x
Fig. 17 - Grey subsurface precipitates beneath the surface of 410 stainless steel are believed to be lead-containing intermetallic phases; 100-hour test at 1000°C in molten lead.

Fig. 18 - Coherent layer of crystalline nickel was noted on part of the surface of an attacked nickel specimen submerged in lead at 1000°C. This is attributed to a slight temperature gradient in the system.
Fig. 19 - The Pb - Ni equilibrium diagram (M. Hansen).
Fig. 20 - Sketch of Seesaw test specimen in furnace showing positions during cycling.
Fig. 21 - Sectional view of seesaw test specimen after failure because of dissolution at hot zone; note build-up of metal crystals at cold zone (at left).
THE STUDY OF CONSTITUTIONAL DIAGRAMS

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Report No. BMI-740

Introduction

This paper constitutes a preliminary report on alloy work in progress at Battelle. Some details of the work on zirconium-tin, thorium-zirconium, thorium-aluminum, and columbium-uranium will be discussed.

Zirconium-Tin Alloys

Work on the zirconium-tin diagram has been done on binary arc-melted alloys. Starting materials for this work were Grade I Foote crystal bar and chemically pure tin. In presenting a completed diagram, there have been incorporated a few temperatures and compositions from work at Armour Institute,1,2,3,4,5 and Ames Laboratory6,7,8,9,10 in order to present what is believed to be the most accurate complete diagram, or one on which the majority agree. The diagram, Fig. 1, is characterized by three compounds: Zr3Sn, a second compound, Zr2Sn or Zr3Sn2, and a third compound which is probably ZrSn or in that range of composition. Other compounds have been reported, but these are attributable to the difficulty of preparing alloys of uniform, known composition in the high-tin range. The melting point of Zr2Sn is about 1985 C. The compound at about 50 atomic per cent tin forms by a peritectic reaction at 1145 C and little zirconium is soluble in tin.

In the high-zirconium alloys, a eutectic occurs at 19 atomic per cent and 1590 C. The solubility of tin in beta-zirconium is 14 or 15 per cent at the eutectic temperature. At 1325 C, Zr3Sn forms by a peritectoid reaction. A second peritectoid occurs at about 1020 C or lower where alpha-zirconium forms. The solubility of tin in alpha-zirconium at 1020 C is about six or seven atomic per cent. This decreases rapidly and at 700 C a solubility of about two per cent tin has been observed as shown by micrographs in Fig. 2. The alloys for this series were hot rolled, then cold worked to speed the approach to equilibrium and were annealed and quenched from 700 C. When the samples were etched, a precipitate was observed in the 2.3 and 3.8 per cent samples which was not present in the 0 and 1.5 per cent samples. From this, it is estimated that the solubility is about two atomic per cent at 700 C. At lower temperatures the solubility is expected to decrease further, and, since equilibrium may be extremely slow in this range, methods of study should be sensitive to small amounts of precipitate.
FIGURE 1. ZIRCONIUM-TIN EQUILIBRIUM DIAGRAM
Fig. 2. Microstructures of Heat Treated Zirconium-Tin Alloys. The Alloys were Hot Rolled, Cold Worked 35 Per Cent, and Heat Treated 15 Hours at 700 C and Quenched.
Thorium-Zirconium Alloys

Dr. Carlson of Ames presented the thorium-zirconium diagram at the metallurgical conference last year. At that time, we were just beginning our study of the system to check primarily the high-thorium alloys. Brief checks also of high-zirconium alloys confirmed the previous report and showed a eutectoid at about 650 °C and 14 atomic per cent thorium as shown in Fig. 3. The data on this region include both thermal data, the black points, and a few metallographic checks.

At the thorium end, arc-melted alloys were prepared at the intervals shown in the diagram. Metallographic examination traced the beta-plus-thorium region clearly to 1100 °C. At 1200 °C, metallographic examination was questionable, and for this reason high-temperature resistivity is being used to determine whether the two-phase region goes over to an allotropic modification in thorium. This is being done with high-purity iodide thorium. If a transformation exists, the diagram is probably as given in Fig. 3. If not, it may be as shown in Fig. 4.

Thorium-Aluminum Alloys

Our interpretation of the thorium-aluminum diagram is shown in Fig. 5. A eutectic occurs at 3.7 atomic per cent thorium and 632 °C. The solubility of thorium in aluminum is a maximum of 0.3 atomic per cent. The first compound is ThAl₃. Three additional compounds were also observed and correspond roughly to stoichiometrical ratios of Th₂Al₃, Th₃Al₂, and Th₂Al. These were all identifiable by X-ray analysis, but difficulty in accurate chemical analysis prevented precise structure studies.

The compound labeled "X" was shown to have a transformation when heat treated and examined. For this reason, it has been shown with some width. In general, the compounds were brittle and tended to decompose in time, if exposed to the air, so that the system was a rather difficult one to study. The diagram as shown is not complete in all details, but is believed to be correct generally. The high-aluminum end is believed to be accurate.

Columbium-Uranium Alloys

A limited amount of work has been done on columbium-uranium alloys, since last year's report. Additional studies indicate that complete solubility exists between gamma-uranium and columbium. No compounds nor intermediate phases occur in the system. Further work is now in progress to complete the detailed diagram.
FIGURE 3. THORIUM-ZIRCONIUM EQUILIBRIUM DIAGRAM
THERMAL EFFECT AT THIS TEMPERATURE

■ TWO PHASE AS QUENCHED FROM THIS POINT

○ SINGLE PHASE AS QUENCHED FROM THIS POINT

△ TRANSFORMED DURING QUENCHING FROM THIS POINT

FIGURE 4. THORIUM-ZIRCONIUM EQUILIBRIUM DIAGRAM
FIGURE 5. THORIUM–ALUMINUM CONSTITUTIONAL DIAGRAM
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THE TITANIUM-VANADIUM SYSTEM

Harley A. Wilhelm and Richard M. Powers

Introduction

Since both titanium and vanadium have been considered as desirable materials for use in certain reactors, it was thought that a study of alloys between these two might lead to materials with even more desirable properties than either metal alone. Consequently, a systematic investigation of the alloys of the titanium-vanadium system was undertaken.

Preparation of the Alloys

Some effort was spent in attempting to use electrolytic methods\(^1\) to obtain titanium and vanadium powders for alloy preparation by powder metallurgical techniques. Because of the difficulties encountered in preparation of vanadium electrolytically, however, the method was discontinued. A second method, that of coreduction of the mixed oxides by calcium, was not too successful in the low vanadium range so was employed on a limited scale in these studies.

Most of the alloys employed for the study of the titanium-vanadium system, were prepared by arc melting together the weighed component metals. The vanadium metal was prepared by bomb reduction of the pentoxides according to the procedures developed in this Laboratory\(^2\) and elsewhere.\(^3\) The analysis of the massive vanadium obtained by the bomb reduction processes in which sulfur and iodine were employed separately as boosters were 99.55% and 99.06% respectively.

The titanium employed was obtained from two commercial sources in the form of sponge. One grade of sponge analysed 98.2% titanium as received. The other grade of sponge yielded a 99.6% titanium after heating for 10 hours at 1000°C in a vacuum.

Two series of alloys were prepared by arc melting vanadium and titanium sponge in an argon atmosphere. Series I alloys were made using the vacuum treated titanium with the sulfur boosted vanadium. Series II alloys were made using the untreated titanium and the iodine boosted vanadium.
Melting Point Determinations

The melting point method used for these determinations has been used successfully by P. Chiotti and others in this Laboratory. It involves heating a bar of the metal to melting by passing a current through the bar. An optical pyrometer is employed to determine the temperature in a black-body hole drilled in the specimen. The method was tested and the equipment calibrated against electrolytic nickel, giving a mean value for that melting point of 1452 ± 7°C.

Melting point specimens for the titanium-vanadium study were cut directly from arc melted buttons and heated gradually to the melting point under a 0.1 micron vacuum. Fogging of the sight glass was reduced by surrounding the specimen with a cylindrical molybdenum shield with sufficient opening for viewing the black-body hole. Corrections were applied to the observed melting points for the optical pyrometer and sight glass fogging. The transmission of the sight glass was determined by Beckman spectrophotometer after each determination and corrections applied from the Forsythe tables. The fogging was indicated to be due to vanadium and not to impurities in the metal since repeated melting points on the same specimen in the 0.1 micron vacuum range continued to produce fogging. When the metal was melted under a 1.1 micron vacuum, however, the fogging was negligible but the character of the metal had changed radically.

The melting point of calcium-reduced vanadium by this method was 1860° ± 15°C. Increase in hardness as a result of melting under the 0.1 micron vacuum was negligible, and the oxygen content after melting, as estimated from hardness readings was indicated to be less than .04% (by weight). When melted under a 1.1 micron vacuum, however, the hardness of the vanadium increased markedly and corresponded to an oxygen content of about 1.4%. At the same time, the melting point was elevated at least 20°C. The melting point of titanium by the same method was found to be 1673°C for commercial sponge metal and 1677°C for crystal bar metal. On repeated redetermination of the melting point of a sample of crystal bar metal in a 0.1 micron vacuum, the values progressively dropped to as low as 1631°C.

Alloys of titanium with vanadium exhibit a minimum in the liquidus curve at about 30% vanadium and at a temperature around 1570°C, as seen from Fig. 1. In the case of alloys containing 51.7% and 69.5% vanadium, it was found that the melting points were increased by 86°C and 40°C respectively.
Fig. 1 Phase diagram of the titanium-vanadium system.
if a pressure of 1.1 microns was employed instead of the pressure of 0.1 micron. These observations illustrate the importance of relatively good vacua in determining the melting points of these reactive metals and alloys. A pressure of 0.1 micron or less was employed in the determination of most of the melting points of Fig. 1.

Metallography

The change in the transition temperature of titanium by addition of vanadium was first studied by a combination of heat treatments and microscopic observation.

The as-arc-melted Series I alloys employed in an approximate location of the transition line were given an abbreviated homogenization at 910°C for 30 hours in a vacuum of less than 0.001 micron. The temperature was then dropped slowly to the desired quenching temperature and then held for some time before quenching. Series II alloys, which were used to cover the transition area of the system more completely, were heated for 16 hours between 1150°C and 1250°C under a 0.1 micron vacuum after hot rolling at 800°C. The hardness of a titanium control sample increased during this homogenization; the increase corresponding to an oxygen content change from about 0.05% to about 0.25%.

The metallographic specimens were polished by standard procedures. After polishing the quenched alloys, they were etched with a mixture of concentrated nitric acid, 48% hydrofluoric acid and glycerol in the volume proportions of 1:1:3. Proportions of nitric acid were increased above this for etching the higher vanadium alloys.

The results of metallographic examination of the heat treated alloys show that the transition temperature is progressively lowered with increasing vanadium (see Fig. 1). A single phase beta solid solution was found to exist in all alloys between this transition line and pure vanadium and up to the solidus for the system. The body centered cubic vanadium and the high temperature form of titanium are therefore miscible in all proportions in the solid state at elevated temperatures. There is slight evidence from resistivity measurements that alloys of about 50% exhibit an order-disorder transformation somewhere below 800°C.

The extent of solid solubility of vanadium in alpha titanium was tested with samples containing 1.2% and 2.5% vanadium. Both of these samples were annealed for several hours at 500°C and quenched. The microstructure differed sufficiently from that of similarity treated titanium to indicate that at 500°C, the solid solubility of vanadium in alpha titanium is less than 1.2%.
X-Ray Studies

X-ray diffraction studies were employed in the further determination of the variation of the transition temperature with vanadium content. Preliminary diffraction studies were made on massive samples of as-arc-melted alloys. These specimens were placed on a Phillips X-ray unit and scanned with a spectrometer. Lattice constants corresponding to the prominent peaks were calculated and extrapolated against \( \cos^2 \theta \) values to determine the limiting value for each alloy. Compositions versus these lattice constants are plotted in the upper curve of Fig. 2. An almost linear relationship between lattice constant and composition from pure vanadium to the 20% vanadium alloy is apparent.

For the determination of the beta phase boundary, filings from the alloys were used. These finely divided samples were first placed in zirconium "gettered" silica tubes and given quenching treatments. Debye patterns were then taken of each on a 11.43 cm diameter camera. After correcting for film shrinkage, lattice parameters were calculated and plotted against the \( \theta \) function of Nelson and Riley. The relationship between lattice constant and the \( \theta \) function was linear in almost all cases. The extrapolated values of the lattice parameters for the one phase alloys were plotted against compositions and are shown in the lower curve of Fig. 2. Once the plot of lattice constant against composition had been established with the powdered alloys, the two phase alloys obtained on the various quenching treatments were examined in order to fix the phase boundaries. For a given quenching temperature, the lattice constant for the beta phase was found for each of several alloy compositions in the two phase region and the average value obtained. By using these average values and referring to the lattice parameter versus composition curve, the terminal solubility of titanium in vanadium was found for each temperature. These are indicated at the points of the arrows on the lower curve of Fig. 2 and are used in support of the phase diagram in Fig. 1.

The solubility of vanadium in the alpha form of titanium appears to be quite small as observed in the homogenized alloys containing approximately 0.25% oxygen. This was seen from the persistence of the X-ray lines of the beta solid solution in the quenched 1.2% vanadium alloys.

Density

The density variation with composition for titanium-vanadium alloys is shown graphically in Fig. 3. This regular
LATTICE CONSTANTS OF THE BETA PHASE
OF THE TITANIUM-VANADIUM SYSTEM
VS COMPOSITION

ATOMIC PERCENT VANADIUM

3.25
3.20
3.15
3.10
3.05
3.00

WEIGHT PERCENT VANADIUM

0 10 20 30 40 50 60 70 80 90 100

LATTICE CONSTANTS OF THE BETA PHASE (Å)

USING MASSIVE
AS-ARC MELTED ALLOYS

COMPOSITION DETERMINED FROM
DENSITY VS COMPOSITION CURVE

USING ANNEALED AND QUENCHED ALLOY
POWERS

SOLUBILITY LIMITS OF TITANIUM IN
VANADIUM (BETA PHASE) AT INDICATED
TEMPERATURE

Fig. 2 Lattice constant vs. composition.
Fig. 3 Density of the titanium-vanadium system.
variation of density was occasionally employed as a check on the unknown alloy compositions. However, a very satisfactory chemical method for determination of vanadium in titanium was developed by the Analytical Group of this Laboratory and employed in the analysis of most of the samples studied for this report. The density values were determined by water displacement.

Hardness

The hardness trends on the basis of limited data on some Series I alloys are shown in Fig. 4 and indicate two maxima, the higher maximum corresponding to the two phase high titanium region. Hardness measurements on some Series II alloys gave similar results. However, one of these alloys containing 2.5% vanadium exhibited much greater hardness which substantiates the hardness peak found by Raymer et al. at 2% vanadium.

Tensile Properties

Tensile properties and resistivities were determined on the same specimens. Arc melted buttons were hot rolled up to 90% at 800°C into strips 0.02" to 0.05" in thickness, 0.25" wide, and 2" long. After shaping, they were pulled between the jaws of a Dillon Dynamometer until they broke. The stress was plotted against strain as read on a Baldwin strain indicator and the desired quantities determined from this curve.

The plot of tensile strength, yield strength, and proportional limit as a function of composition is shown in Fig. 5. These approximately parallel each other as well as the hardness curve shown earlier. The same two principal maxima appear, the higher in the low vanadium range where primary alpha exists with partly transformed beta, the lower near the center of the beta solid solution.

Young's modulus appears to increase steadily for the hot rolled alloys in the beta region from about 25% vanadium to pure vanadium as shown in Fig. 6. It is seen to be higher for vanadium than for titanium with comparable amounts of hot work. The several maxima that occur in the curve of per cent elongation against composition in Fig. 6 may, or may not be of significance.
Fig. 4 Hardness of series I alloys vs. composition.
Fig. 5 Tensile properties vs. composition.
Fig. 6 Per cent elongation and modulus of elasticity vs. composition.
Rolling Characteristics

Most alloys of titanium and vanadium can be cold rolled satisfactorily in the as-arc-melted condition employing approximately 10% reduction in area per pass. Alloys in the high titanium range that show a maximum in the hardness values do not cold roll satisfactorily.

Hot rolling at 800°C was successful for most of the alloys, however the sizes of the samples were small and the quenching effect of the rolls was probably a factor in causing some of the low vanadium alloys to rupture during the rolling. The samples were brought to temperature in an argon atmosphere then removed from the furnace and rolled in air.

Rate of Oxidation in Air

Oxidation tests were carried out on various titanium-vanadium alloys in air at 775°C and 600°C. Metal samples were rolled out to increase the surface, then weighed and transferred to a muffle furnace. When heated for the desired time, they were removed from the muffle, cooled and weighed. The specimens were again replaced in the muffle and the cycle repeated a number of times. Curves of weight gain against time were plotted for each sample in order to obtain the rate of air oxidation at the test temperature. Figure 7 shows the resulting rates plotted against composition of the alloys for 775°C and 600°C. At either temperature, additions of up to about 30% vanadium to titanium increase the oxidation rate markedly. Additions of vanadium of around 50% reduce the air oxidation rate at both temperatures. The melting point of V₂O₅, one of the products of air oxidation of these alloys, is between the two temperatures employed. This probably explains the exceedingly high rate of oxidation observed for pure vanadium at 775°C. The dark purple liquid V₂O₅ formed at this temperature was observed to actually flow from the sample. At the lower temperatures, the brownish yellow solid V₂O₅ forms somewhat of a protective coating on the pure vanadium.

315°C Steam Corrosion Test

High temperature steam corrosion tests were made on alloys of titanium and vanadium. The alloys were found to have good resistance to this type of corrosion, the maximum rate being 2.2 mg/cm²/mo for the 26.1% vanadium alloy. The average for the compositions tested between pure titanium and the 75% vanadium alloy was 0.5 mg/cm²/mo for an exposure of 125 hours at 315°C in H₂O.
Fig. 7 Rate of oxidation of Ti-V alloys vs. composition.
References


MATERIALS FOR HIGH TEMPERATURE APPLICATION

E. J. Hassell

The metallurgical research program of the Flight Research Laboratory, Research Division, Wright Air Development Center, includes five projects directed toward the improvement of materials for use at elevated temperatures.

1. Research on Flash Sintering

The S-K-C Research Associates, Paterson, New Jersey, are investigating the possibilities of producing ceramic-metallic alloys and compounds (ceramets) having superior strength properties by means of the flash sintering or resistance heating process. The machine used in this work was constructed from press welding equipment. It has provision for independently varying the voltage applied to the specimen, the phase relationship of voltage and current, the magnitude of applied pressure, and the duration of application of the current and pressure cycles. In addition, two independently controlled current impulses, separated by a predetermined time interval, can be automatically applied. Instrumentation is not available for determining the magnitude of heating current. This is controlled and can be duplicated by means of the secondary voltage tap setting on a 150 KVA, $160/110$ volt transformer. The specimen and electrodes are electrically insulated from the compact holding assembly by ceramic die liners.

Recent work has concentrated on the flash sintering of titanium carbide bonded with nickel as a matrix. One composition ($80\%$ carbide-$20\%$ nickel) only was used to allow comparison of results with the properties of the same material subjected to conventional powder metallurgy processing techniques. Maximum density and hardness are produced by a combination of flash sintering conditions just short of those which cause expulsion of molten material from the die assembly. High density and hardness values are usually secured when appreciable sintering occurs; however, when these values are high, it is not necessarily an indication that optimum sintering has taken place, since
low modulus of rupture values sometimes accompany high
density and hardness. It is, however, necessary for compacts
showing high strength to be dense and of high hardness.

By varying the conditions of power input, time, and
ram load relative to one another, several sets of operating
conditions can be found which will produce satisfactory
bodies.

Cylindrical compacts of the blended powders are pressed
at 50 tsi. In order to increase the conductivity, these are
presintered in hydrogen at 1100°C for 1 hour. After
cooling, they are placed in the ceramic liners for flash
sintering. The mechanical setup of the compact assembly
during flashing is most important since the tungsten contact
wafers between the electrodes and compact must fit well
enough to prevent escape of plastic material due to extrusion
and still be capable of movement as the porous specimen is
densified by the application of pressure and heat.

A number of flash sintered titanium carbide-nickel
compacts have shown modulus of rupture values between 100,000
and 173,000 psi. Actual densities approach 100% and Rock-
well "A" hardness values are between 30 and 90. In general,
a ram load of 6200 lbs. was used with a firing time of
about 15 cycles for each of two pulses separated by time
intervals up to 3.5 seconds.

2. Molybdenum Based Alloys by Powder Metallurgy Methods

At Battelle Memorial Institute, alloys are prepared by
conventional powder metallurgy methods, hot rolled at 1250°C
to strip form, annealed 1/2 hour at 1100°C and evaluated
for their suitability for service at elevated temperature.
Rather good hardening and strengthening effects were found
in some of the alloys when tested in the standard fibered
condition. These effects are sharply reduced when the
alloys are tested in the recrystallized condition. Ex-
tensive studies are carried out on recrystallization
characteristics. Additions which increase the re-
crystallization temperature are Cr, Al, Fe, Si, and
W. Those which have no effect are B, Be, Co, Mn and
Th. Nickel has a lowering effect. Pronounced grain-
refinement after recrystallization occurred with B, C,
Si, and Co. Thus silicon promotes the best recrystalli-
zation characteristics, since, in addition to the beneficial
effects noted above, it also broadens the range over which
recrystallization occurs.

Binary alloying additions have included Al, B, Zr, Be, C, Cb, Co, Cr, Fe, Mn, Si, Ta, Th, S, P, In, and Sn. With the exception of tungsten (and possibly Cb, Ta, and Th), the amount of useful alloying addition was generally less than 1 percent. Marked strengthening was obtained with Co, Si, Fe, Al, and Cr. Tungsten strengthens and hardens molybdenum; and, considering fabrication characteristics, the composition Mo-20W appears to have the best combination of strength and ductility.

For creep testing, alloys are clad with nickel and the test conducted in air at 1800°F under 20,000 psi stress on the alloy core. Outstanding results were obtained on a 0.15% Si alloy which had a rupture time of 263 hours and a total elongation of 5.6%. The second stage creep rate was 0.011% per hour. Under these test conditions, unalloyed molybdenum ruptures in less than 50 hours. Silicon is one of the best additions for strengthening molybdenum. A maximum strength of 130,000 psi was obtained with the 0.42% alloy. However, the elongation is low, about 3% in one inch. The best combination of strength and elongation was found in the 0.18% alloy, 110,000 psi and 12% respectively. Unalloyed molybdenum has an ultimate strength of 84,000 psi with a 23% elongation.

Sixty ternary alloys containing combinations of Al, B, Cr, Co, Fe, Si, and W have been prepared and testing is now underway. Several compositions having exceptionally high ultimate strengths (about 140,000 psi) are 1.0Al-20W, 1.0Al-0.15I, and 1.0 Cr-10W.

Before proceeding with creep tests, the recrystallization characteristics of ternary alloys will be investigated and correlated with fabrication methods.

3. Protective Coatings for Molybdenum

Research at the Climax-Molybdenum Corporation is directed toward the development of more satisfactory spray coatings for protecting molybdenum against oxidation at temperatures up to 1900°F. Upwards of 200 specimens have been prepared by spraying layers of various compositions on 2"x2"x0.05" molybdenum sheet. Numerous samples were tested with a single layer; none contained more than three layers, the thickness of each varying from 0.003" to 0.010".

Diffusion treatments prior to testing involve heating in
purified hydrogen at 1700°F to 1900°F for 0.5 to 2 hours.

The most important achievements to date are summarized as follows: (1) significant resistance to oxidation at 2400°F, (2) substantial ductility in coatings at 1700°F, and (3) uniformly good resistance to oxidation at 1700°F of coatings containing a chromium-silicon alloy.

A sample coated with a 0.006 inch-thick layer of Al-12%Si alloy and tested in the as-sprayed condition endured for 1.5 hours at 2400°F before the coating failed. A sample containing an undercoat and overcoat of Al-12% Si alloy with an intermediate layer of 33% Al plus 67% of Cr-Mo-Si in equal amounts was given a diffusion treatment in hydrogen at 1800°F for 2 hours. Failure had not yet occurred after 21 hours at 2400°F.

Tensile bars were sprayed in sequence with the three compositions described and the coatings tested for ductility at 1700°F. Elongations in 2 inches of 8.6 and 15.5% and reductions in area of 34.7% and 70.5% were obtained before the coatings failed in their protection as evidenced by the appearance of the first visible molybdenum oxide vapors.

Other samples were prepared with triple coatings having the Al-12% Si alloy in the first and third layers with an intermediate layer containing a mixture of 33% Al plus 67% Cr-Si alloy (55% Cr-41% Si) and were given a diffusion treatment in hydrogen at 1900°F for 2 hours. Three of these specimens were still under test after 500 hours at 1700°F without failure.

4. Titanium Nitride Cermets

Rutgers University is investigating TiN both as a pure material and as a major component in cermets. Specimens of each composition prepared are formed by hydrostatic pressing and cut into test bars about 1.6 inches long and 0.25 inches square. After firing, the modulus of rupture and apparent porosity are determined. Then, after an oxidizing treatment at 2000°F for 8 hours, the test bars are checked for weight gain and modulus of rupture.

Mixtures of TiN and TiC exhibit less oxidation resistance than either material alone. Chromium added to TiN up to 40% improves the strength. Mixtures of 15% and 20% Cr maintained the highest strength after the oxidation treatment. Comparative tests indicate a firing atmosphere of nitrogen is more beneficial for TiN bodies than one of argon.
Samples in the general form of nozzle diaphragm blades were tested for thermal shock resistance by successively heating 10 minutes at 2000°F and cooling 5 minutes in a controlled air flow of 77 feet per second and repeating the cycle. Under these test conditions, TiN has very poor thermal shock resistance and the addition of 15% Cr offers only slight improvement. 

The influence of particle size on the properties of TiN was studied by controlling grinding time as the only variable. However, iron pick-up from hardened steel balls was proportional to the grinding time with a 14.5% iron content after 96 hours. The modulus of rupture after firing greatly increased with grinding time, reaching 50,800 psi for the 96 hour grind - an increase of 1000% over the as received (-325 mesh) material. The oxidation resistance and strength after oxidation were poor and fairly constant for all grinding times. In order to obtain data on pure TiN, material from the 96 hour grind was leached with hydrochloric acid to remove iron. The strength of test pieces from this leached TiN - 17,300 psi - was much less than that of the 96 hour grind with the iron present.

An investigation is underway to determine the properties of TiN from the 96 hour grind with additions of Ni up to 35%. The amount of metal retained before evidence of sweating during firing and the room temperature strength both increased with increasing time of milling. The modulus of rupture of the TiN-Ni bodies reached a maximum value of 73,500 psi for 10% Ni against 50,800 psi for TiN. The addition of Ni increases the resistance to oxidation, but the strength after oxidation at 2000°F for 8 hours is reduced about 50%.

5. Plastic Deformation of Ceramic-Oxide

The objective of this research at the National Bureau of Standards is to determine the plastic deformation (stress-strain behavior) and related mechanical and optical properties of several ceramic oxide single crystals, and to compare these properties with those of polycrystalline specimens for the purpose of changing the undesirable brittle qualities at high temperatures by increasing the grain size.

Results of creep tests in bending of corundum single crystal rods at 800°C, and 1200°C, indicate a great in-
crease of ductility with increase of temperature. This was surprising in view of the use of densely sintered alumina shapes at much higher temperatures. These preliminary results are encouraging with respect to the ultimate objective since previous investigators, testing sintered alumina in torsion, have found only elastic behavior at temperatures up to 1550°C.

Sustained transverse loading on the corundum rods at room temperature causes rupture at a stress well below the instantaneous breaking stress. Small stresses exerted for a long time will shorten the time normally required for rupture at higher stresses when the load is subsequently increased.

It is planned to study this fatigue behavior at room temperature and higher temperatures in more detail by determining whether the presence of minute amounts of water or other liquids in the surface cracks affects the property. Specimens of quartz, periclase, and rutile will be included in future work.
AN X-RAY DIFFRACTION STUDY OF THE HAFNIUM-HYDROGEN SYSTEM

S. S. Sidhu and J. C. McGuire
Argonne National Laboratory, Chicago, Illinois

The hafnium-hydrogen system at room temperature consists of three phases. The lattice parameters of the hafnium metal used in this investigation and of the three phases are as follows: hafnium, \( a_0 = 3.200 \, \text{Å}, \) \( c_0 = 5.061 \, \text{Å}, \) and \( c = 1.58; \) deformed cubic phase, \( a_0 = 4.702 \pm 0.012 \, \text{Å}, \) \( c_0 = 4.678 \pm 0.012 \, \text{Å}, \) and \( c = 0.995; \) face-centered cubic phase, \( a_0 = 4.708 \pm 0.002 \, \text{Å}; \) and face-centered tetragonal phase, \( a_0 = 4.882 \pm 0.002 \, \text{Å}, \) \( c_0 = 4.384 \pm 0.002 \, \text{Å}, \) and \( c = 0.898. \) The deformed cubic phase extends up to \( \text{HfH}_1.53 \) and converts into the face-centered cubic phase between \( \text{HfH}_1.53 \) and \( \text{HfH}_1.70. \) The face-centered cubic phase transforms into the tetragonal phase between \( \text{HfH}_1.80 \) and \( \text{HfH}_1.87. \) The tetragonal phase extends up to \( \text{HfH}_1.98. \)

Introduction

This paper covers the study of the limit of solid solubility of hydrogen in hafnium, the number of hafnium-hydrogen phases formed and their crystalline structures.

Experimental Procedure

The samples were prepared from \( 1" \times \frac{3}{4}" \times 11 \) mil pieces of metallic hafnium. Each piece was polished, cleaned, weighed, and then placed in a quartz tube, which was connected by means of stop-cocks to a mercury diffusion pump and to a calibrated volume equipped with a manometer, as shown in Figure 1. Connections were also made so that any gas present in the quartz tube could be returned to the calibrated volume by means of an automatic Toeppler pump and measured.

The system was pumped down to approximately \( 10^{-6} \, \text{mm Hg} \) pressure and the metal was outgassed for four hours by heating it at \( 1100^\circ \text{C}. \) The temperature was then lowered to \( 1000^\circ \text{C} \) and a measured volume of carefully purified hydrogen gas was admitted into the tube at a known pressure. Most of the absorption of hydrogen took place at \( 700 - 800^\circ \text{C}. \) The sample was cooled to room temperature at a rate of about \( 4^\circ \text{C} \) per minute. The gas pressure in the tube at this point was \( 0.1 \, \text{mm Hg}. \) The excess hydrogen was pumped back into the calibrated volume and measured.

In the preparation of \( \text{HfH}_2 \) sample where \( 125.4 \) cc of \( \text{H}_2 \) were required for each gram of \( \text{Hf}, \) the volume of hydrogen admitted into the tube was 300 per cent in excess of the theoretical absorption. The sample was cooled to room temperature at a rate of \( 2.5^\circ \text{C} \) per minute. Hydrogen was then desorbed from the metal by heating and evacuating with the Toeppler pump. This cycle was repeated twice to obtain a thoroughly reacted sample.
A few samples of lower composition were made by removing the desired volume of hydrogen from the higher hydrides at about 750°C. Compositions of the samples were calculated from the weight of the metal and the volume of the absorbed hydrogen.

X-ray diffraction data for identification and structure determination of each phase formed were obtained from powder patterns made of annealed representative samples of hydrides. The annealing was done at 350°C for periods over 24 hours. The limit of solubility of hydrogen in hafnium, and the interphase boundaries were determined by employing both the X-ray diffraction and the microscopic techniques.

Results

X-ray diffraction data for hafnium metal used in this study are given in Table 1. The lattice parameters are: \( a_0 = 3.200 \text{ Å}, c_0 = 5.061 \text{ Å}, \) and \( c = 1.58 \). The measured density of the metal was 12.9 gm/cc and the calculated density 13.1. These data differ considerably from those given in the literature\(^1\). The lattice parameters and the density too are different\(^1,2\) except for some recent values reported by Russell\(^3\). It is possible that the earlier data were obtained with relatively impure metal.

X-ray diffraction patterns of a series of hafnium samples containing 2.25 to 46.0 atomic per cent hydrogen showed that diffraction lines of a hafnium-hydrogen phase began to appear in the pattern of a sample containing 21.4 atomic per cent hydrogen. As shown in Figure 2, no appreciable change was apparent in the diffraction lines of the hafnium metal itself. Photomicrographs of the same series of samples, given below, however, showed that this phase was present in the sample containing as little as 2.25 atomic per cent hydrogen, and it increased in amount with the increasing atomic per cent of hydrogen until it could be identified by the X-ray diffraction method. It seems, therefore, that the solubility of hydrogen in hafnium must be very small.

Diffraction study of the next series of samples containing 46.0 to 61.8 atomic per cent hydrogen revealed that the increase in the hafnium-hydrogen phase continued up to 60.5 atomic per cent hydrogen. Between 60.5 and 63.0 atomic per cent hydrogen the hafnium metal was completely converted into a single phase hydride. As shown in Figure 3, this phase extends to 64.3 per cent hydrogen. Its diffraction data are given in Table 2. It has a face-centered cubic structure with \( a_0 = 4.708 \pm 0.002 \text{ Å} \).

As shown in Figure 4, the face-centered cubic phase transforms into a face-centered tetragonal phase between 64 and 65 atomic per cent hydrogen with lattice parameters, \( a_0 = 4.882 \pm 0.002 \text{ Å}, c_0 = 4.384 \pm 0.002 \text{ Å}, \) and \( c = 0.898 \). The diffraction data for this phase are given in Table 3.

FIG. 1 SYSTEM FOR PREPARING HAFNIUM-HYDRIDES
Table 1 - Interplanar Spacings (d), Estimated Relative Intensities (I/I₀) and the Miller Indices (hkl) of Hafnium

<table>
<thead>
<tr>
<th>d(A)</th>
<th>I/I₀*</th>
<th>hkl</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.77</td>
<td>s</td>
<td>100</td>
</tr>
<tr>
<td>2.53</td>
<td>s</td>
<td>002</td>
</tr>
<tr>
<td>2.43</td>
<td>v.s.</td>
<td>101</td>
</tr>
<tr>
<td>1.868</td>
<td>s</td>
<td>102</td>
</tr>
<tr>
<td>1.600</td>
<td>s</td>
<td>110</td>
</tr>
<tr>
<td>1.443</td>
<td>w</td>
<td>103</td>
</tr>
<tr>
<td>1.383</td>
<td>s</td>
<td>200</td>
</tr>
<tr>
<td>1.354</td>
<td>s</td>
<td>112</td>
</tr>
<tr>
<td>1.337</td>
<td>s</td>
<td>201</td>
</tr>
<tr>
<td>1.265</td>
<td>m+</td>
<td>004</td>
</tr>
<tr>
<td>1.216</td>
<td>m</td>
<td>202</td>
</tr>
<tr>
<td>1.152</td>
<td>m</td>
<td>104</td>
</tr>
<tr>
<td>1.065</td>
<td>s</td>
<td>203</td>
</tr>
<tr>
<td>1.049</td>
<td>w+</td>
<td>120</td>
</tr>
<tr>
<td>1.027</td>
<td>s</td>
<td>121</td>
</tr>
<tr>
<td>0.993</td>
<td>s</td>
<td>114</td>
</tr>
<tr>
<td>0.968</td>
<td>m</td>
<td>122</td>
</tr>
<tr>
<td>0.951</td>
<td>s</td>
<td>105</td>
</tr>
<tr>
<td>0.935</td>
<td>m</td>
<td>204</td>
</tr>
<tr>
<td>0.924</td>
<td>m</td>
<td>300</td>
</tr>
<tr>
<td>0.890</td>
<td>s</td>
<td>123</td>
</tr>
<tr>
<td>0.868</td>
<td>m</td>
<td>302</td>
</tr>
<tr>
<td>0.844</td>
<td>w</td>
<td>006</td>
</tr>
<tr>
<td>0.817</td>
<td>m</td>
<td>205</td>
</tr>
<tr>
<td>0.807</td>
<td>m</td>
<td>124,106</td>
</tr>
</tbody>
</table>

* V = Very; S = Strong; M = Medium; W = Weak
FIG 2: X-ray diffraction patterns of Hf-H alloys between 0-46.0 atomic % H.
(Cu Ka radiation, 114.6 mm diameter camera)
FIG. 3. X-ray diffraction patterns of Hf-H alloys between 46-63 atomic % H.
(Cu Kα radiation; 114.6 mm diameter camera)
Table 2 - Interplanar Spacings, Estimated Relative Intensities, and the Miller Indices of the Cubic Phase of Hafnium-Hydrogen System. Composition: 63.0 atomic per cent Hydrogen

<table>
<thead>
<tr>
<th>d(Å)</th>
<th>I/10</th>
<th>hkl</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.71</td>
<td>v.s.</td>
<td>111</td>
</tr>
<tr>
<td>2.35</td>
<td>s</td>
<td>200</td>
</tr>
<tr>
<td>1.665</td>
<td>s</td>
<td>220</td>
</tr>
<tr>
<td>1.419</td>
<td>m</td>
<td>311</td>
</tr>
<tr>
<td>1.360</td>
<td>m</td>
<td>222</td>
</tr>
<tr>
<td>1.177</td>
<td>w</td>
<td>400</td>
</tr>
<tr>
<td>1.081</td>
<td>m</td>
<td>331</td>
</tr>
<tr>
<td>1.053</td>
<td>m</td>
<td>420</td>
</tr>
<tr>
<td>0.962</td>
<td>m</td>
<td>422</td>
</tr>
<tr>
<td>0.906</td>
<td>m</td>
<td>(333,511)</td>
</tr>
<tr>
<td>0.832</td>
<td>w</td>
<td>440</td>
</tr>
<tr>
<td>0.796</td>
<td>m</td>
<td>531</td>
</tr>
<tr>
<td>0.784</td>
<td>m</td>
<td>(442,600)</td>
</tr>
</tbody>
</table>
FIG 4. X-ray diffraction patterns of Hf-H alloys between 63 - 66.4 atomic % H
(Cu Ka radiation; 114.6 mm diameter camera)
<table>
<thead>
<tr>
<th>d(Å)</th>
<th>I/I₀</th>
<th>hkl (F.C.T.)</th>
<th>hkl* (B.C.T.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.71</td>
<td>v.s.</td>
<td>111</td>
<td>101</td>
</tr>
<tr>
<td>2.44</td>
<td>s</td>
<td>200</td>
<td>110</td>
</tr>
<tr>
<td>2.197</td>
<td>m</td>
<td>002</td>
<td>002</td>
</tr>
<tr>
<td>1.727</td>
<td>m</td>
<td>220</td>
<td>200</td>
</tr>
<tr>
<td>1.631</td>
<td>s</td>
<td>202</td>
<td>112</td>
</tr>
<tr>
<td>1.555</td>
<td>s</td>
<td>311</td>
<td>211</td>
</tr>
<tr>
<td>1.356</td>
<td>m</td>
<td>222</td>
<td>202</td>
</tr>
<tr>
<td>1.348</td>
<td>m</td>
<td>113</td>
<td>103</td>
</tr>
<tr>
<td>1.219</td>
<td>w</td>
<td>400</td>
<td>220</td>
</tr>
<tr>
<td>1.113</td>
<td>m</td>
<td>331</td>
<td>301</td>
</tr>
<tr>
<td>1.091</td>
<td>m⁻</td>
<td>420</td>
<td>310</td>
</tr>
<tr>
<td>1.064</td>
<td>m⁺</td>
<td>313</td>
<td>213</td>
</tr>
<tr>
<td>1.002</td>
<td>w⁻</td>
<td>204</td>
<td>114</td>
</tr>
<tr>
<td>0.977</td>
<td>w⁺</td>
<td>422</td>
<td>312</td>
</tr>
<tr>
<td>0.935</td>
<td>w</td>
<td>511</td>
<td>321</td>
</tr>
<tr>
<td>0.928</td>
<td>w</td>
<td>224</td>
<td>204</td>
</tr>
<tr>
<td>0.905</td>
<td>w</td>
<td>333</td>
<td>303</td>
</tr>
<tr>
<td>0.863</td>
<td>w</td>
<td>410</td>
<td>400</td>
</tr>
<tr>
<td>0.853</td>
<td>w</td>
<td>115</td>
<td>105</td>
</tr>
<tr>
<td>0.822</td>
<td>m</td>
<td>531</td>
<td>411</td>
</tr>
<tr>
<td>0.817</td>
<td>w</td>
<td>404</td>
<td>224</td>
</tr>
<tr>
<td>0.802</td>
<td>m⁻</td>
<td>412</td>
<td>402</td>
</tr>
</tbody>
</table>

* hₜₜₜ = ½(h + k)F.C.T.; kₜₜₜ = ½(h - k)F.C.T.; lₜₜₜ = 1F.C.T.
The phases found at various hydrogen compositions may be summarized as in Table 1.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Atomic % H</th>
<th>Phases and Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>HfH0.023</td>
<td>2.25</td>
<td>Deformed cubic (v.v.w.) + Hf (s)</td>
</tr>
<tr>
<td>HfH0.27</td>
<td>21.4</td>
<td>Deformed cubic (v.w.) + Hf (s)</td>
</tr>
<tr>
<td>HfH0.55</td>
<td>35.0</td>
<td>Deformed cubic (w) + Hf (s)</td>
</tr>
<tr>
<td>HfH0.85</td>
<td>46.0</td>
<td>Deformed cubic (w+) + Hf (m+)</td>
</tr>
<tr>
<td>HfH0.995</td>
<td>49.9</td>
<td>Deformed cubic (m) + Hf (m)</td>
</tr>
<tr>
<td>HfH1.36</td>
<td>57.6</td>
<td>Deformed cubic (s) + Hf (w)</td>
</tr>
<tr>
<td>HfH1.53</td>
<td>60.5</td>
<td>Deformed cubic (s) + Hf (v.w.)</td>
</tr>
<tr>
<td>HfH1.70</td>
<td>63.0</td>
<td>Cubic (s)</td>
</tr>
<tr>
<td>HfH1.80</td>
<td>64.8</td>
<td>Cubic (s)</td>
</tr>
<tr>
<td>HfH1.78-1.86</td>
<td>64-65</td>
<td>Cubic (m) + tetragonal (m)</td>
</tr>
<tr>
<td>HfH1.87</td>
<td>65.3</td>
<td>Tetragonal (s)</td>
</tr>
<tr>
<td>HfH1.98</td>
<td>66.4</td>
<td>Tetragonal (s)</td>
</tr>
</tbody>
</table>

In working with these hydrides, it was observed that, in general, as the amount of hydrogen increased the ductility of the sample decreased. The sample containing 46.0 atomic per cent hydrogen was extremely hard. The hydrides with compositions HfH1.70-1.98 were very brittle and could be easily pulverized by crushing in mortar and pestal. Also, the metallic lustre of the hafnium metal in these hydrides was lost and the samples appeared gray-black. However, all the hydrides studied in this investigation were stable at room temperature.

Discussion

From the results obtained here it is seen that at room temperature hafnium-hydrogen system consists of three phases. The first phase forms at very low concentration of hydrogen, and increases with increasing amount of hydrogen as shown in Figures 5 - 7. It coexists with hafnium metal up to a composition of HfH1.53. X-ray diffraction patterns of samples between HfH and HfH1.53, as seen in Figure 3, have characteristic appearance of line splitting and groups of lines
where single reflection for cubic structure occurs. Diffraction data for HfH1.53 sample, as given in Table 5, are typical of these samples. The unit cell is slightly deformed and displays a degree of tetragonality with, \( a_0 = 4.702 \pm 0.012 \) \( \AA \), \( c_0 = 4.678 \pm 0.012 \) \( \AA \), and \( c = 0.995 \). However, it approaches a cubic symmetry, and converts to an ideal face-centered cubic structure between HfH1.53 and HfH1.7.

The structure of tetragonal phase with composition HfH1.58 appears isomorphous with those of ZrH2\(^{1,5}\) and ThH2\(^{5}\). For a body-centered tetragonal cell as transformed* from face-centered tetragonal:

\[
a_0 = 3.452 \pm 0.002 \, \AA, \quad c_0 = 4.384 \pm 0.002 \, \AA, \quad c = 1.27.
\]

The volume of the unit cell is \( 52.2 \times 10^{-24} \) cc, density 11.48 grams per cc, and there are 2 HfH2 per unit cell:

Hf: \( 0 \, 0 \, 0, \frac{1}{2} \, \frac{1}{2} \)

H: \( 0 \, \frac{1}{2} \, \frac{1}{2}, 0 \, \frac{1}{2} \, 3/4, \frac{1}{2} \, 0 \, \frac{1}{2}, \frac{1}{2} \, 0 \, 3/4 \).

The transformation of the tetragonal cell into the face-centered cubic cell at HfH1.8 produces only a slight contraction in the cell. It seems, therefore, that it may be a second order transformation. The mechanism of this transformation and the detailed structure of the face-centered cubic cell will be described elsewhere.

Our thanks are due to Mr. Maurice Odie and Dr. H. H. Chiswik for the metallographic examinations of the samples, to Mr. Daniel Zauberis for the X-ray diffraction patterns, and to Dr. Frank G. Foote for helpful discussions.

---

* \( a_0(B.C.T.) = \sqrt{2}(F.C.T.) \) and \( c_0(B.C.T.) = c_0(F.C.T.) \)

1. G. Hägg, Z. Phys. Chem. (B) 11, 433 (1930)
UNCLASSIFIED

Figure 5 (Negative No. 106-463 and 106-465) - Photomicrographs of HfH$_2$_0.023.
Magnifications (a) 150, (b) 500.
Figure 5 (Negative No. 106-463 and 106-465) - Photomicrographs of HfH$_2$O$_{0.023}$
Magnifications (a) 150, (b) 500.

HfH
0.023

500X

BRIGHT FIELD
Figure 6 (Negative No. 106-1641) - Photomicrograph of HfH₂O₂₇⁻
Magnification 150X
Figure 7 (Negative No. 106-162) - Photomicrograph of HfH₀.₅₅
Magnification 150.
Table 5 - X-ray Diffraction Data for a Deformed Cubic Phase of Hafnium-Hydrogen System: Composition 60.5 atomic per cent Hydrogen

<table>
<thead>
<tr>
<th>d(A)</th>
<th>I/Ip</th>
<th>hkl</th>
</tr>
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<tbody>
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<td>v&gt;s</td>
<td>111</td>
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<td>2.353</td>
<td>s</td>
<td>200</td>
</tr>
<tr>
<td>2.332</td>
<td>s</td>
<td>002</td>
</tr>
<tr>
<td>1.664</td>
<td>s</td>
<td>220</td>
</tr>
<tr>
<td>1.661</td>
<td>s</td>
<td>202</td>
</tr>
<tr>
<td>1.423</td>
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<td>1.411</td>
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<td>1.046</td>
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<td>0.960</td>
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<td>422</td>
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<td>0.956</td>
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<td>224</td>
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<td>0.909</td>
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<td>511</td>
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<td>0.904</td>
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<td>0.898</td>
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<td>w</td>
<td>440</td>
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<td>0.828</td>
<td>w</td>
<td>440</td>
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<td>0.796</td>
<td>m</td>
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</tr>
<tr>
<td>0.791</td>
<td>m</td>
<td>513</td>
</tr>
</tbody>
</table>
POWER IN ARC MELTING

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Introduction

In the various laboratories that arc melt zirconium, wide differences exist in the arc melting practice. The kind of atmosphere, the amount of power and the length of the arc vary considerably. The atmosphere used may be 100% argon, 80% argon-20% helium, 20% argon-80% helium, or 100% helium at a partial pressure. The power may be 50 to 100 KW and the arc length 3" to 5". It is true that good billets have been obtained under these different conditions but it is felt that optimum conditions should exist for each diameter of billet. The relative power developed in the billet will be taken as a measure of the effectiveness of any particular combination of atmosphere, power and arc length.

Description of Apparatus and Billets

The data for this report were obtained with D.C. generators, tungsten electrodes and zirconium billets. The tungsten tip is about 1-1/2" long and screwed into a water cooled copper electrode. The zirconium is melted in a water cooled copper crucible, 3" in diameter. The billet is molten at the top to a depth of 1/8" to 1/4" and into this molten pool small pieces of solid zirconium are dropped. As these pieces melt, the billet slowly increases in length. Three-inch billets are made at a rate of ten pounds per hour and 5" billets at sixteen pounds per hour. No shrinkage pipe has been found. The defects encountered are gas holes, pieces incompletely melted and tungsten contamination. Some of these defects have an embarrassing habit of persisting throughout the rolling and are found in the finished plate. The object of this investigation was to minimize these defects.

Effect of Atmosphere and Power on the Arc

The composition of the atmospheres used was 100% argon, 100% helium and four mixtures of argon and helium. In Fig. 1, the voltage across the arc is plotted against the current in the arc at a 3" arc length. The bottom curve is for an atmosphere of 100% argon, the next in 80% argon-20% helium, and so on to 100% helium - the top curve. The dashed curves connect points of equal power 10 KW, 20 KW, - to 80 KW. Argon is more easily ionized than helium and so requires less voltage across the arc. The argon rich curves flatten rapidly to almost a constant voltage. Even the 40% argon-60% helium curve is essentially flat above 40 KW. It may be noted that high power, 80 KW,
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may be obtained more easily in 100% helium at 1290 amps and 62 volts than in 100% argon in which 3200 amps would be required at a probable 25 volts. Argon rich atmospheres cannot be used if high power is desired and generator capacity is not to be exceeded.

In Fig. 2, a log log plot of power versus arc resistance per inch is shown. The arc resistance per inch is defined by the fraction-volts across the arc divided by arc length times the current in amps. The heavy lines are of constant slope while the dashed lines fit the points more closely. In this graph the data were obtained at a 3" arc length in a 3" diameter crucible. The resistance per inch may be found in any atmosphere at any power. After estimating the voltage from Fig. 1, the required current may be calculated.

The data shown in Fig. 2 fit a general equation of the form

\[ R = \frac{C}{(P)^n} \]

\[ R = \text{arc resistance, ohms/inch} \]
\[ P = \text{power in KW} \]
\[ n, C = \text{constants} \]

We use a particular equation that fits the solid lines which are at a constant slope of 49°.

\[ R = \frac{C'}{P^{0.87}} \]
\[ n = 0.87 \text{ for } 49° \text{ slope} \]

In Table 1, the values of \( C' \) are listed for each atmosphere. The method of calculation is shown by two examples.

Argon is inherently more conductive and the higher power forms more ions - an increase, then, in the argon fraction of the atmosphere or an increase in power serves to lower the resistance of the arc.

Variation in Power Distribution

It might be well to consider the distribution of this power. A certain amount is necessary to ionize the gas of the atmosphere. Some power will be lost to the copper crucible. We are interested mainly in that power which is absorbed in the billet and melts the metal. To measure relative amounts of this power under different melting conditions we imbedded thermocouples in the billet an inch below the top of the molten metal surface. One thermocouple was placed 3/16" from the side and the other at the center of the billet. This center thermocouple reached a temperature greater than 1350°C and gave non-reproducible readings after a few runs. The side thermocouple did not go over 1125°C and gave good readings throughout the tests. The following results were based on the readings of this thermocouple.

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In Fig. 3 the billet temperature is plotted against power. The high temperatures attained with large fractions of argon in the atmosphere indicate that a greater part of power is absorbed in the billet than with helium atmospheres. In Fig. 4 a log log plot of power versus billet temperature per KW of power is shown. The rapid decrease in degrees per KW with increased power is undoubtedly due to much greater heat losses by radiation and conduction at higher temperatures. More power may very well be lost in the crucible as a result of increased ionization. These points also fit parallel straight lines rather well.

In addition to this temperature effect there is a significant difference in the appearance of the molten pool in various atmospheres. Melting in a helium atmosphere results in a wide diameter shallow pool while in an argon atmosphere the pool is deep and of small diameter. For example, at 20 KW and 3" arc length, the pool in a helium atmosphere is 3" in diameter, while in argon it is only 1-1/2" in diameter. The temperature produced in the billet by the argon is about 20% greater. In argon the surface of the molten pool is quite agitated over 10 KW. To produce similar agitation in helium about 70 KW are required. The points marked "V" in Fig. 3 are those at which the pool is violently agitated. All points greater than 10 KW on the 80% A and 100% A curves have this violent agitation. This agitation may be taken as a measure of the depth of the molten pool and its fluidity (or temperature). The agitated surface is necessary to insure completely melted billets.

Tungsten Contamination

At this point the problem of good melting seems resolved. We need merely use high power in a high percent argon atmosphere and the billets will be good. The tungsten contamination of the billets has not been considered, however. The power or current used do not seem to have much effect on the amount of tungsten lost from the tip. The splashing of metal from the molten pool onto the tungsten tip is the major cause of tungsten loss. The weight of the charged pieces should be small - about 1 gram. If 5 gram pieces are used, the tungsten loss is excessive. The metal should not contain much hydrogen as this will cause more splashing. If the metal is pickled before melting, it should be degassed by heating at 1000°C for about 3 hours to a pressure of 5 x 10^-5 mm. The tungsten loss from the tip may be increased from 0.1 grams to 1.0 grams as a result of heavy pieces or large gas content. After corrosion testing, metal does not require degassing. The amount of free fall that the pieces have is another factor that is important. In our 3" castings the pieces bounce from the electrode to the wall and thus lose some of their momentum. In the 5" and 7-1/2" crucibles, the pieces fall directly into the melt. The tungsten loss on these castings has been 3.0 to 5.0 grams. It is necessary to have a deflector on the electrode that will absorb some of the pieces' momentum and change the direction of the pieces as they hit the molten pool. Another method of feeding the charge, such as using 5/8" rods around the circumference of the crucible, may also be effective.
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When pieces are charged into the three inch furnace the arc length is an important factor. If a 3" arc is used, the tungsten loss will be 0.2 grams instead of 0.1 grams when a 4" arc is used. The arc length is the third variable in the melting conditions to be considered. The voltage across the arc varies linearly with the arc length as shown in Fig. 5. It may be noted that the fluidity of the molten pool also depends upon arc length. The longer the arc the less the fluidity. On the curves for 100% helium and 20% argon arc points marked with a "V" to indicate the violent agitation previously discussed. At arc lengths less than 3" (20% argon curve) or 1-5/16" (100% helium curve), the proper fluidity is obtained. At all points on the 40% argon, 60% argon, 80% argon and 100% argon curves, the agitation is violent. The corona discharge from the electrode to the crucible increases with increasing arc length. At the points marked with a "C" on the 100%, 80%, 60% and 40% argon curves, the corona discharge is slight. This corona discharge is a visible indication of the power lost to the copper crucible. At the points marked with "C's", although the corona is slight, the temperature developed in the billets drops off about 70°C. In fact, so much power may be lost by corona discharge that the metal will be frozen solid if 100% argon, 3-3/16" arc length, 40 KW and 1500 amps are used. If the corona discharge is excessive, copper is sputtered off the electrode and should be avoided for this reason also. Corona is lessened by decreasing the arc length or the argon fraction in the atmosphere.

The resistance or current versus arc length plot as straight lines on log log graph paper up to a point at which the arc length equals about 80% of the crucible diameter (2-1/2" on 3" crucible or 4" on 5" crucible). This effect is shown in Fig. 6. More power is absorbed in the crucible at these points of change in slope although no relation with the corona discharge is noticed. The points marked "C" again refer to a slight corona discharge. The temperature developed in the billet, however, does begin to drop at these points. A longer arc length at constant power also decreases the diameter of the molten pool - another effect, when observable, that indicates less power in the billet at longer arc lengths.

Power Equipment for Arc Melting

Welding generators, welding rectifiers or constant potential generators may be used for arc melting. The advantages of the welding equipment are the current limiting control and lower cost. A disadvantage is that the rated maximum current is usually produced at 40 volts. At higher voltages, the maximum current is less. These machines are generally rated as constant power, i.e., 400 amps at 40 volts equals 267 amps at 60 volts. A point to be remembered is that welding equipment is NEMA rated for a 60% duty cycle (typical of the welding operation). For a 100% duty cycle (as in arc melting) the maximum current is 80% of the NEMA rated current. Thus a 400 amp generator will deliver 320 amps continuously. The constant potential generators cost about 15% more, for the same power output, and require a resistance box to start the arc. The resistance may be switched out after the arc is started. The voltage range is much greater and more variation can be obtained in melting. We have two 70 volt, 1500 amp constant potential generators that have proved very satisfactory in melting.
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Summary

For best melting, then, we want a high power, a high amperage, a high percent argon, no corona discharge and low tungsten contamination. The heating done in the billet does not bear a simple relation to these factors, however. If the power is held constant, more melting is produced if the current is increased. On the other hand, at constant current, more melting is produced by increasing the power. And finally, more melting is obtained at a 3" arc length than at a 4" arc length with higher power and amperage. The variations possible with a given billet diameter are not too numerous, however, if the factors of tungsten contamination, corona discharge and sufficient pool diameter are considered. In Table 2 are listed conditions suitable for certain crucible diameters. The arc length is at a minimum of 4" to reduce tungsten contamination by splashing. The atmosphere contains a large percentage of helium to eliminate corona. The economy in making large billets is twofold. Comparing the 3" and 5" sizes: we melt 2.78 times the area with a power increase of 1.43; the 5" size is made at 16 pounds per hour and the 3" size at 10 pounds per hour, then 6-1/4 KWH are used per pound in 5" diameter and 7 KWH are used per pound in the 3" diameter billets. The alternate value listed for the larger diameters should be used if very thin sections are to be made from the billets, and billets as free as possible from small holes are desired.

Table 1. Constants for Resistance Equations.

<table>
<thead>
<tr>
<th>Atmosphere</th>
<th>100% A</th>
<th>80% A</th>
<th>60% A</th>
<th>40% A</th>
<th>20% A</th>
<th>100% He</th>
</tr>
</thead>
<tbody>
<tr>
<td>C'</td>
<td>0.14</td>
<td>0.19</td>
<td>0.27</td>
<td>0.35</td>
<td>0.41</td>
<td>0.70</td>
</tr>
</tbody>
</table>

\[ R = \frac{C'}{p^{0.87}} \]

n = 0.87 at constant slope of 49°

At 20% A, 20 KW

\[ R = \frac{0.41}{20^{0.87}} = \frac{0.41}{13.5} = 0.0304 \]

At 40% A, 60 KW

\[ R = \frac{0.35}{60^{0.87}} = \frac{0.35}{35} = 0.10 \]

Table 2. Recommended Practices for Various Billet Diameters.

<table>
<thead>
<tr>
<th>Crucible Diameter</th>
<th>KW</th>
<th>Amp</th>
<th>Volts</th>
<th>Atmosphere</th>
<th>Arc Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>3&quot;</td>
<td>70</td>
<td>1320</td>
<td>53</td>
<td>20% A</td>
<td>4&quot;</td>
</tr>
<tr>
<td>4&quot;</td>
<td>85</td>
<td>1540</td>
<td>55</td>
<td>20% A</td>
<td>4&quot;</td>
</tr>
<tr>
<td>5&quot;</td>
<td>100</td>
<td>1930</td>
<td>44</td>
<td>40% A</td>
<td>4&quot;</td>
</tr>
<tr>
<td>7-1/2&quot;</td>
<td>120</td>
<td>2320</td>
<td>43</td>
<td>60% A</td>
<td>5&quot;</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>2700</td>
<td>45</td>
<td>60% A</td>
<td>5&quot;</td>
</tr>
</tbody>
</table>
FIG. 1

VOLTAGE AND CURRENT RELATIONS
IN VARIOUS ATMOSPHERES

CURRENTS, AMPS.

VOLTS

100% HE
20% A
40% A
60% A
80% A
100% A

10KW 20KW 30KW 40KW 50KW

80KW 70KW 60KW 50KW
FIG. 2

EFFECT OF POWER AND ATMOSPHERE ON ARC RESISTANCE

POWER, KW

100
80%
60%
40%
20%
100% A
100% A

RESISTANCE, OHMS/INCH

0.003
0.004
0.005
0.007
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.10
FIG. 4

EFFECT OF POWER AND ATMOSPHERE ON TEMPERATURE DEVELOPED PER KW

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POWER, KW

°C TEMP/KW
FIG. 5
ARC VOLTAGE VS. ARC LENGTH AT 40 KW IN 3" CRUCIBLE

ARC LENGTH, INCHES

100% A  80% A  60% A  40% A  20% A

VOLTS ACROSS ARC
FIG. 6
ARC LENGTH VS. ARC RESISTANCE PER INCH
AT 40 KW AND 3" CRUCIBLE

ARC LENGTH, INCHES

RESISTANCE, OHMS/INCH