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Title: **Some Studies on the Uranium - Thorium - Zirconium Ternary Alloy System**

Author: **Oscar Norman Carlson**

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UNCLASSIFIED

SOME STUDIES ON THE URANIUM - THORIUM - ZIRCONIUM TERNARY ALLOY SYSTEM

by

Oscar Norman Carlson

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State College
1950

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INTRODUCTION

Before proceeding far with the ternary studied it was essential, first, to acquire an understanding of the three binary systems. This the author has attempted to accomplish. Only a preliminary survey of the three component system has been conducted but the binary systems have been studied in considerable detail.

For systems of three components there is a maximum of four degrees of freedom possible, temperature, pressure and the concentrations of two components. By considering pressure as a constant a three dimensional construction will describe the system completely. With three component systems it is customary to plot composition on an equilateral triangle with the pure components at the three corners. It can be shown by simple geometry that if a point is taken inside an equilateral triangle the sum of the distances from the point to the sides of the triangle along lines parallel to the three opposite sides is always the same and equal to a side of the triangle. Taking the length of the side as unity and expressing the amounts of each component as fractions of the total, the composition of any ternary system can be described by a single point. Temperature can then be plotted along the vertical axis perpendicular to the base. The three walls of such a construction represent the binary systems.

By considering temperature as a constant the graphical representation can be simplified. Where solid models are impractical a series of isothermal binodal curves can be plotted in a single plane within the triangular composition diagram.

In this investigation insufficient data were obtained for a three dimensional diagram but the binary regions have been explored and a few ternary alloys have been examined with the intent of determining the nature of the liquidus surface.

The metallurgy of all three of the pure components, thorium, uranium and zirconium, is a relatively recent development so that their physical properties are not fully known.

Uranium is a dense, bright metal which tarnishes very readily upon contact with air taking on a dull, dark brown oxide coat. A rather complete knowledge of the physical and chemical properties of uranium has been accumulated within the past ten years because of its importance in the atomic energy program. The Project Handbook (1), a recent compilation of this information, gives the melting point of uranium as 1132° C., the boiling point as 3900° C. by extrapolation, and the observed density as 18.9 - 19.0 grams per cubic centimeter. There are three crystalline modifications known. The high temperature (gamma) form is body-centered cubic with a lattice constant, a = 3.48 Angstroms (Å). Gamma transforms to beta uranium on cooling at 770 - 760° C. The exact structure of the beta form has not been determined although a cubic type structure has been reported. Beta transforms to alpha, the room temperature form, on cooling at 650 - 640° C. Alpha uranium is ortho rhombic with a:b:c = 2.852:5.865:4.945. Å.

Thorium is a soft, silver-white metal with an atomic number of 90, an atomic weight of 232.12, and an atomic radius of 1.80 Å. The melting point of thorium has not been definitely established principally because the heat of fusion is so small that distinct heating and cooling breaks are not observed. A number of early investigators reported melting points varying from 1450 to 1842° C. In 1933 Thompson (2) reported a value of approximately 1730° C. for calcium reduced metal and 1680° C. for electrolytically reduced metal. Experience in this laboratory corroborates the lower of these results.

The structure of thorium at room temperature is face-centered cubic. Thompson reported a lattice constant, $a = 5.09$ Å. The Project Handbook gives values for the lattice constant of thorium ranging from 5.074 to 5.091 Å increasing with the oxygen content. No allotropic modifications of thorium have been established.

The density values range from 11.1 to 11.7 grams per cubic centimeter depending upon the method of preparation and fabrication treatment of the metal. The value calculated from X-ray data is 11.61 while the average of the observed values is about 11.5.

Zirconium is a silver-white metal the atomic number of which is 40 and the atomic weight 91.22. Its atomic radius is 1.60 Å. Melting points of zirconium have been reported from 1700 to 1900° C. with 1830 ± 25° C. the value appearing most often in the literature. Its density is 6.5 grams per cubic centimeter at room temperature.

Zirconium has two allotropic forms. Burgers (3) has described the high temperature form, beta, as body-centered cubic with the lattice constant $a = 3.61$ Å. Beta transforms to alpha zirconium upon cooling at 862° C. The alpha form is hexagonal closest packed with lattice constants as follows (4); $a = 3.228$ Å and $c = 5.140$ Å.

Both thorium and zirconium show a strong tendency to dissolve oxides and nitrides resulting in an increase in hardness of the metals and a decrease in their ductility. Zirconium dissolves up to 40 atomic per cent oxygen, and up to 20 atomic per cent nitrogen. The dissolved oxygen raises the transition point of zirconium, causing it to appear sluggish.

II. BINARY SYSTEMS

A. Uranium - Thorium System

1. Historical

There has been nothing found reported in the general literature which could be directly related to alloy studies of this system.

The present thorium-uranium binary investigation was begun by A. H. Daane and the author five years ago and a summary paper (5) was published in the project literature at that time. In this paper the system was reported as a simple eutectic system with the eutectic composition estimated at 5 weight per cent thorium.

At about the same time a study was made by the University of Chicago Metallurgical Laboratory and the results were likewise published as classified project reports (6) (7). Here a simple eutectic system was reported with the eutectic composition at less than 3.4 weight per cent thorium. A strong tendency for the small thorium particles within the interdendritic material to agglomerate was noted. A preliminary series of heat treatment experiments was conducted on a 50 weight per cent thorium alloy to locate approximately the eutectic temperature. The specimen when quenched from 1100° centigrade showed no melting of the specimen whereas when quenched from 1200° C., melting of the interdendritic material was observed. No determination of the thorium liquidus was reported and no evidence for liquid immiscibility was presented.

The hardness of the alloys was found to decrease with increasing thorium content as follows:

% Thorium	1	3.4	6.8	20	30	40	50	60	90	95	100
Hardness R"C"	91	93	95	95	90	86	90	77	75	70	27

The result of X-ray studies of 50, 90 and 95 per cent thorium samples quenched from 1000° C. showed the phases present to be face-centered cubic thorium and alpha uranium.

2. Experimental

a. Preparation of alloys

Some of the early studies were made on alloys prepared by the co-reduction of the mixed fluorides of thorium and uranium. This was carried out in a bomb, consisting of an iron pipe one end of which was welded closed and the other end of which was fitted with a screw cap. The charge consisted of thorium fluoride and uranium fluoride in the desired proportion, calcium reductant and a booster. This was thoroughly mixed and poured into the bomb liner, the bomb closed by screwing the cap tightly in place, and the reaction started by heating in a gas fired furnace. Good yields were obtained in the uranium-rich alloys by this method.

As soon as pure massive thorium became readily available the alloys were prepared by a more direct method. The pure metals in the desired weight ratio were heated self-inductively under vacuum to a temperature of 1300° to 1800° C. depending upon the alloy composition. The uranium used was produced by the Ames process and was of very high purity. The thorium was also produced by the Ames process and had a correspondingly high purity.

After testing several refractories it was found that beryllium oxide or zirconium oxide were most suitable refractories for use in casting of alloys.

The stirring action of the self-inductive method of heating gave a vigorous mixing of the molten alloy and usually resulted in a homogeneous alloy.

b. Thermal analysis

Preparatory to thermal analysis a thermocouple well was drilled into each casting and the drillings analyzed chemically. The sample was then annealed just below the eutectic temperature for 24 hours to insure equilibrium. The apparatus used for obtaining cooling curve data consisted of a graphite heater crucible packed with Norblack insulation (a special grade of lamp black) in a quartz vacuum tube. This was heated in an induction coil to the desired temperature and allowed to cool uncontrolled. This gave a smooth reproducible curve with an average cooling rate of six to eight degrees per minute. The eutectic and transformation breaks were obtained with a chromel-alumel thermocouple. Time-temperature curves were taken on a Micromax automatic recorder. Tungsten-molybdenum and platinum - platinum + 13% rhodium thermocouples were also used with this apparatus in an attempt to study the temperature region about the chromel-alumel range.

c. Determination of liquidus and immiscibility limits

The failure to pick up liquidus breaks on the cooling curves made it necessary to resort to a method of solubility studies. In this method the lower melting uranium was held in contact with excess solid thorium at a fixed regulated temperature until an equilibrium amount of thorium was dissolved. Chemical analysis of the sample gave a point on the liquidus for the given temperature.

In the region of liquid immiscibility the same methods were used. The sample was maintained at a fixed temperature allowing the two layers to separate completely, and rapid cooling of the sample then followed. Samples were taken from each layer by drilling or turning off on a lathe and the drillings were analyzed chemically. The composition of each layer then determined the limits of immiscibility at a given temperature. A number of points were thus obtained for various temperatures between the eutectic at 1085° and the melting point of thorium.

Special measures were taken in preparing the samples before starting an experiment. A small hole, 3/8 to 1/2 inch in diameter, was drilled in a one inch diameter bar of thorium to an approximate depth of one inch. A cylinder of uranium was machined on a lathe to fit snugly into the hole. This was done to reduce oxidation of the freshly machined surfaces upon heating since an oxide surface would tend to slow down the solution rate of thorium in the molten uranium. This also assures a maximum amount of liquid in the hole.

At temperatures of 1400° C or above the uranium showed a peculiar tendency to creep up the walls of the thorium, over the top, and into the containing refractory crucible. To eliminate this a variation of the above method was used. A rod of uranium which fit snugly inside of a BeO crucible was drilled with a 3/8 inch hole. Through this was inserted a 3/8 inch cylinder of thorium with a larger diameter thorium disc at each end to keep the thorium rod supported upright in the molten uranium. The added weight also kept the thorium from floating upward in the more dense liquid thus maintaining solid thorium in contact with the liquid from bottom to top.

Another method which was used in a few experiments consisted simply of placing pieces of thorium and uranium in a crucible and holding them in contact at a certain temperature. The thorium dissolved until molten uranium became saturated and the undissolved thorium being less dense would float to the surface. This allowed sufficient separation for chemical and microscopic study of the uranium rich phase.

Finding a method of heating the samples and holding them at the required temperatures was the first big problem, since the temperature region to be studied lay between 1100 and 1700° C. Furthermore, heating had to be done in a good vacuum at these relatively high temperatures.

The furnace that was first tried consisted of a 6 KVA Ajax converter and a small 2 1/2 inch diameter induction coil. The thorium "crucible" containing the uranium cylinder was put in a beryllia crucible and this was placed in a 2 1/2 inch quartz vacuum tube. The temperature was controlled by adjusting the converter manually. By setting the apparatus at a constant power output the temperature leveled off after a few minutes and was controllable to no observed variation in the optical pyrometer readings.

This method had certain disadvantages, however, which made it desirable to design a more satisfactory furnace. The vigorous agitation produced by self inductive heating could mechanically break off small pieces of thorium, holding them in suspension, and thus introduce error. The temperature readings by an optical pyrometer are greatly affected by film on the sight glass or an oxide crust which often forms on the metal surface. Furthermore, it is difficult to avoid sudden fluctuations in temperature when heating by an induction furnace over prolonged periods.

To overcome these difficulties, a high temperature resistance furnace was designed specifically for the temperature range to be studied (Fig. 1). It was constructed to operate inside an evacuated quartz tube. The heating element (A) was 70 mil molybdenum wire wound on a grooved alundum core. Concentric with this was a secondary 20 gauge Kanthal winding (B), on a beryllia tube, connected in parallel with the primary winding. A single pair of leads was introduced through the vacuum head. Calculations were made as to proper wire sizes and lengths for each winding so that the Kanthal winding would not burn out as the high temperatures were reached. Kanthal A-1 is recommended for furnace temperatures of 1350° C. and molybdenum for above 2000° C. As long as heating was done under a good vacuum the molybdenum winding stood up very well with repeated runs.

The stainless steel reflectors (C) were selected rather than the conventional furnace insulators such as dicalite or powdered graphite because a better vacuum could be maintained on the furnace if no gas adsorbing powdered insulation materials were present, and the lower heat capacity of the furnace with the reflectors would allow it to heat up and cool off much more rapidly. Since a rapid cooling rate was desirable in many of the experiments this was quite essential.

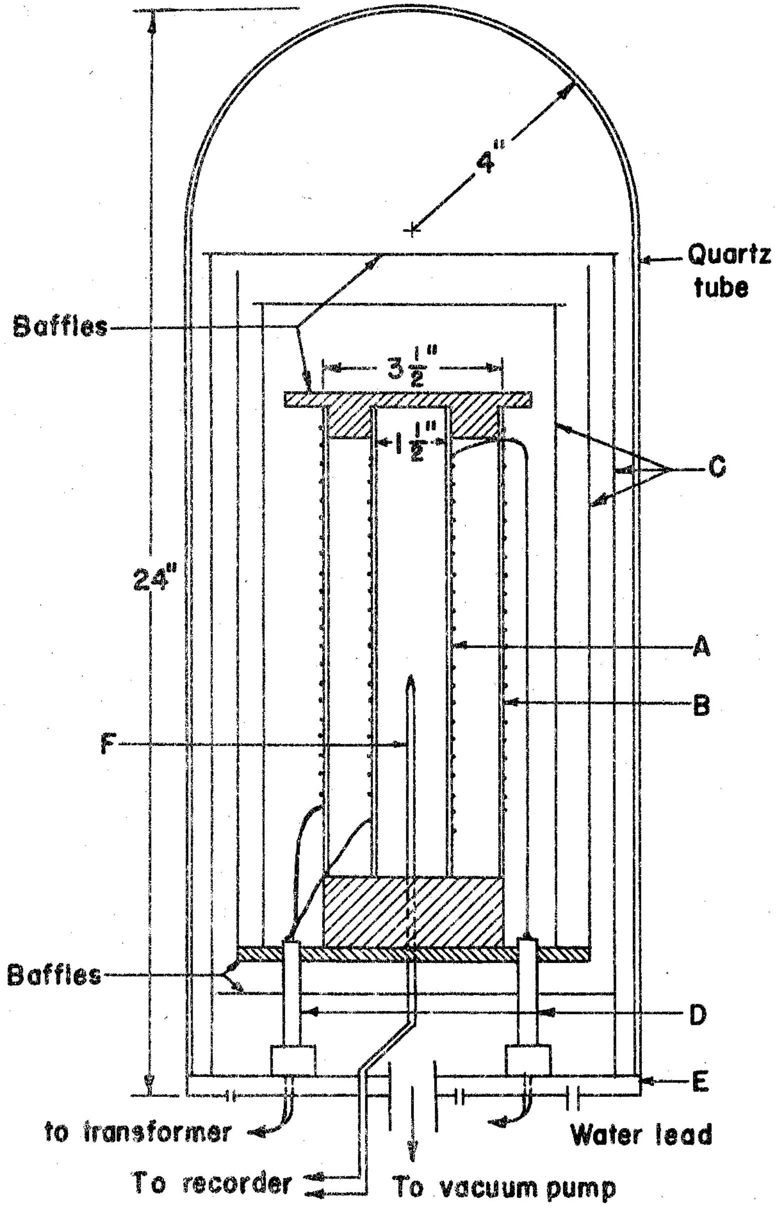


Fig. 1 - High Temperature Resistance Furnace.

The elctrical leads (D) were cooled by passage of water through them. The brass vacuum head (E) likewise was cooled by a stream of water through it.

The temperature was recorded on a Micromax recorder using a tungsten-columbium thermocouple (F) which had been calibrated against a platinum-platinum + 13% rhodium thermocouple (8). The latter type of couple could not be used for more than a short period of time without deteriorating but the tungsten-columbium couple lasted almost indefinitely at high temperatures. The tungsten becomes very brittle, however, and any disturbance makes it necessary to form a new junction.

A 110 volt 40 ampere capacity adjustable transformer served as the power source for the furnace. The power required to maintain a temperature of 1500° C. was 3.5-4 KVA. The temperature was controlled merely by setting the transformer at a given position. At no time was the fluctuation over a 20 hour run greater than ± 15° C. and with a minimum of attention was regulated to ± 5° C.

A rubber gasket between the quartz tube and the vacuum head sealed the system so that it could be evacuated. Using a Hypervac "23" pump a pressure of 3 to 5 microns was sustained on the furnace at a temperature of 1500° C. Pressure readings were taken with a Stokes McLeod gauge. Under these conditions little oxidation of the sample took place. By placing uranium turnings as a "getter" in a crucible above the sample, additional insurance against oxidation was provided.

d. Microscopic examination

Following either thermal analysis or solubility studies the sample was sectioned for microscopic examination. The specimen was ground to a flat surface on a rough grinding wheel and abraded on papers of decreasing grit size. Polishing was done on a felt covered wheel using 600 mesh carborundum suspended in soap solution as the abrasive. This was usually followed by an electrolytic polish in a bath consisting of 8 parts ethyl alcohol, 5 parts ethylene glycol and 5 parts phosphoric acid. The current density was not found to be particularly critical although 1 ampere per square centimeter of 20 seconds was generally used. Usually no additional etching was required although an electrolytic etch with 10 per cent oxalic acid or immersion in dilute nitric acid produced a greater contrast between the uranium and thorium phases.

e. X-ray analysis

X-ray diffraction patterns were taken on powdered samples in a Debye-Scherrer camera with filtered copper K alpha radiation.

f. Chemical analysis

For chemical analysis the sample was dissolved in hydrochloric and perchloric acid. The uranium was reduced in a Jones reductor to tetravalent and trivalent uranium, air oxidized completely to the tetravalent state and titrated with ceric sulfate to uranyl sulfate. The titration was performed at room temperature with ferroin as indicator.

Taking a separate aliquot, thorium was precipitated as the oxalate from a 4 per cent perchloric acid solution by the addition of excess oxalic acid. This was filtered and washed in dilute hydrochloric plus oxalic acid, ignited to the oxide at 800-950° C. and weighed.

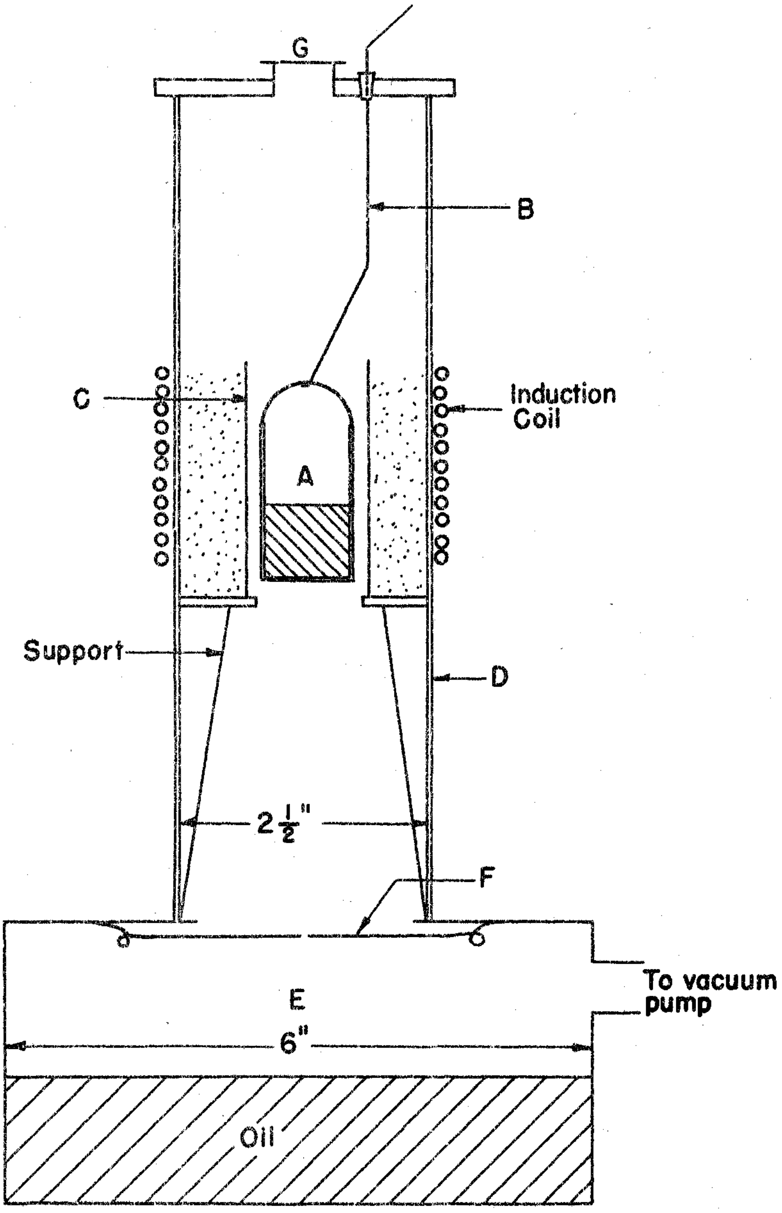


Fig. 2 - High Temperature Quenching Apparatus.

g. Quenching experiments

Quenches from below 1050° C. were carried out in an evacuated quartz tube. Prior to quenching the sample was annealed in a Kanthal wound resistance furnace. A helium atmosphere was then admitted and one end of the tube opened. Tilting the tube plunged the hot specimen into cold water.

Where higher quenching temperatures were desired a somewhat more elaborate type of equipment was used (Fig. 2). The sample (A) was suspended by a tantalum wire from a tantalum trip rod (B) that was admitted through the vacuum head through a rubber stopper. An open end tantalum tube (C) served as the heater and all of this was enclosed in a quartz vacuum tube (D). Heating was done in a small induction coil with a 6 KVA Ajax converter.

Quenching was done by dropping the crucible and sample into a large reservoir (E) containing a low vapor pressure oil the entire operation taking place under a vacuum of 10 microns. A trap door (F) which was closed by a spring helped prevent oil and vapors from splashing up into the tube as the sample was dropped. The temperature readings were made by means of an optical pyrometer through the sight glass (G).

3. Presentation and Interpretation of Data.

The phase diagram shown in Figure 3 is based on thermal data and solubility studies, information obtained from X-ray examination and microscopic evidence. The portions of the diagram about which a reasonable doubt exists have been dotted in. A plot of all thermal

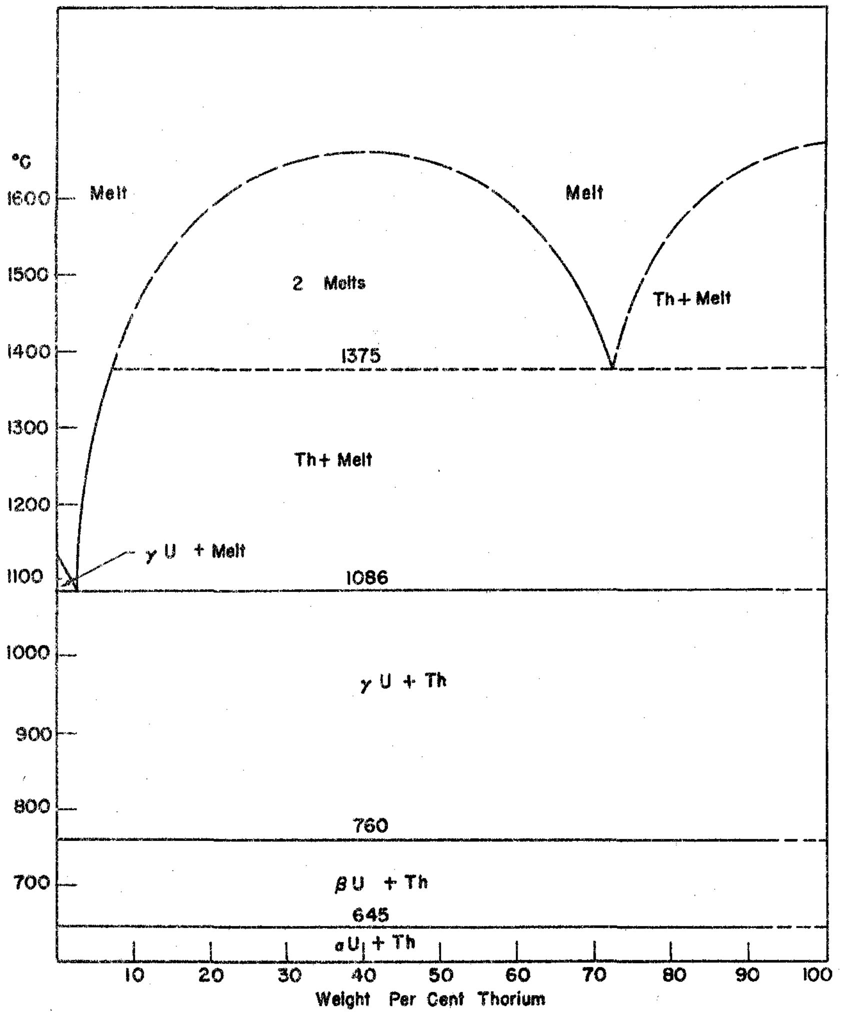


Fig. 3 - Uranium - Thorium Phase Diagram.

data and solubility points has been made in Figure 4.

Starting with pure uranium a eutectic is formed at 2.5 - 3.0 weight per cent thorium at a temperature of 1086° C. This eutectic composition is based primarily upon microscopic evidence. Figures 5, 6 and 7 are photomicrographs of alloys near the eutectic and on either side. The eutectic temperature was determined by cooling curves. The thermal arrest at 1086° C. has been observed in all compositions studied as is shown in Table 1. The intensity of the break diminishes as the thorium content increases so that the thermal effects become questionable in the high thorium region.

No changes in the transformation temperatures of uranium are brought about by the addition of thorium. From Figure 4 it is apparent that the gamma to beta transformation in uranium takes place at 760° C. across the entire system. The same is true of the beta to alpha transition at 650° C. with the exception of the high thorium region in which the transformation was not detected in cooling curves. This is not considered significant however; instead it is believed that the break is so weak that it escapes detection.

A property of the eutectic which made it somewhat difficult to locate its composition exactly was a tendency to spheroidize on slow cooling. This destroys the eutectic structure making its identification more difficult. Figures 8 and 9 illustrate this point showing a sample which has been cooled slowly so that all the fine eutectic structure has agglomerated, while the same sample quenched from the eutectic temperature has retained the eutectic structure.

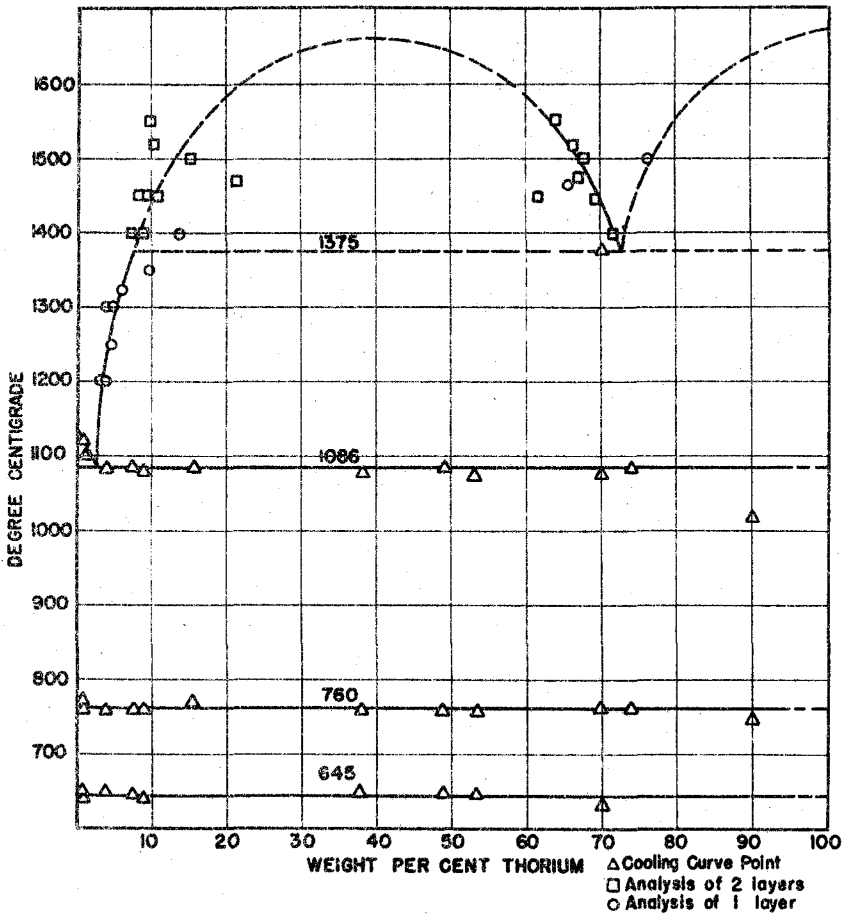
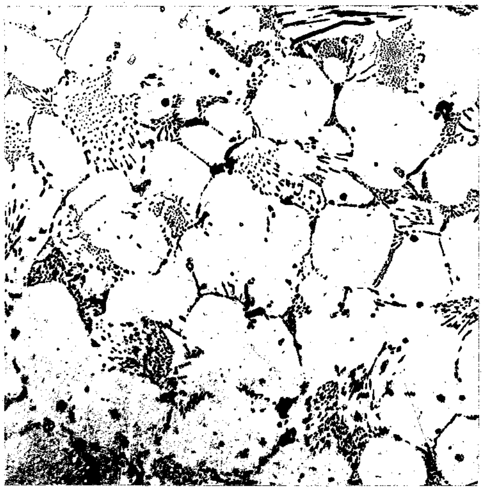


Fig. 4 - Thermal Data of Uranium - Thorium System.

Table I

Thermal Data

Composition wt% Th	Monotectic °C	Eutectic °C	Transformations °C	
pure U		1133	760	650
0.7		1123	773	651
1.0		1104	764	645
4.0		1086	761	649
4.3		1096	768	649
7.0		1080	764	645
7.2		1088	766	652
9.0		1080	760	640
15.5		1086	772	-
38.1		1080	759	645
49.0		1088	761	647
53.5		1072	759	645
70.0	1375	1078	764	633
74.0		1091	764	-
90.0		1020	750 735	-



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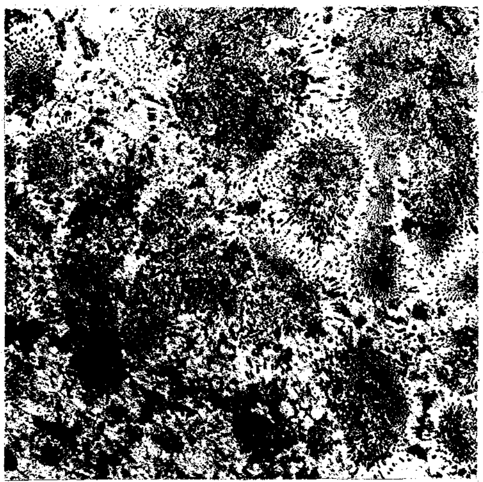

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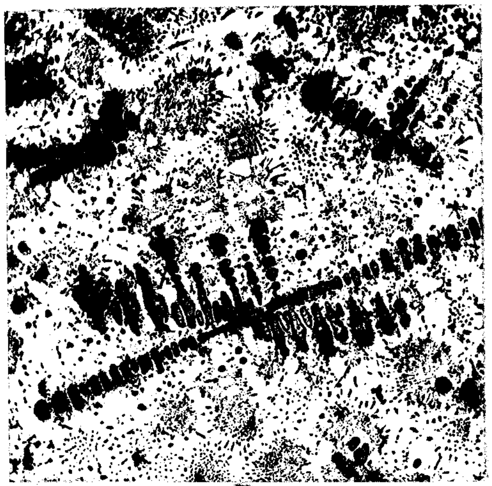

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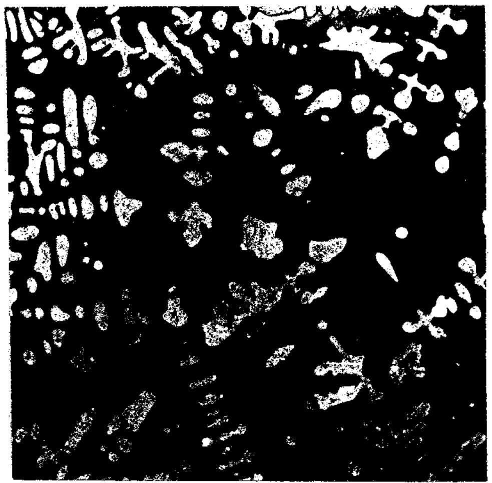

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Fig. 5 - 0.7% thorium. Contains excess uranium (clear phase) plus eutectic. Electrolytic polish. X 100.

Fig. 6 - 3.1% thorium. Eutectic. Elec. polish. X 100.

Fig. 7 - 4.6% thorium. Dendrites of thorium in eutectic matrix. Elec. polish. X 150.

Fig. 8 - 15.5% thorium. Thorium dendrites (light phase) on uranium background. Oxalic acid etch. X 100.

All of the above samples were cooled slowly.

The temperature range at which this spheroidization takes place was located by a series of quenches. A 4.0 per cent thorium cast alloy, shown in Figure 10, was then annealed at 1050° C for four hours and quenched. At this temperature complete spheroidization had taken place (Fig. 11). The same sample annealed at 780° C and quenched showed little or no tendency to agglomerate (Fig. 12).

The determination of the thorium liquidus proved to be a more difficult problem than was expected. The failure to pick up liquidus breaks on cooling curves was due either to the insensitivity of the thermocouples used in the high temperature ranges, i.e. tungsten-molybdenum, tungsten-columbium, and platinum-rhodium, or the extremely small heat of fusion of thorium. Solubility studies by the procedure described did give some reproducible results and thus has become the basis for the major portion of the diagram.

In order to determine the time required to establish equilibrium between the liquid and excess solid thorium at different temperatures, a series of experiments was run in which the time of heating was varied. A series at 1200° C. showed a definite tendency to reach a constant value in 4 to 5 hours as indicated in Table 2 (Runs 1, 2 and 3). A similar determination was made at 1300° C (Runs 4 and 5). Here again a time of about 4 hours was required to reach a maximum solubility. It was concluded that equilibrium should be established between solid and liquid in a maximum time of four hours. As the temperature is increased the rate of solution should be more rapid due to increased molecular activity so that equilibrium between two

Table 2

Solubility Determinations of Thorium Liquidus

Run	Temp. °C	Annealing time in hours	Analysis of lower layer wt% Th	Analysis of lower layer wt% U	Analysis of upper layer wt% Th	Analysis of upper layer wt% U
1	1200 ±5	3	2.50	97.75		
2	1200	4	3.35	96.60		
3	1200	10	4.0			
4	1300	3	4.60	95.00		
5	1300	8.5	4.85	94.90		
6	1250	3	4.55	90.0		
7	1400	2.25	13.70	85.80		
8	1100	8	1.55	98.40		
9	1500	3	No lower layer		76.60	22.50
10	1450	1	8.10	91.85	68.90	31.06
11	1500	1 - 2	15.05	83.90	67.60	32.40
12	1520	1	10.00	90.75	66.20	32.45
13	1470	1	21.33	77.95	66.80	32.80
14	1550 ±15	4 1/2	9.40	90.70	64.15	35.15
15	1450	6	10.45	89.60	62.80	39.0
16	1450	5 1/2	7.15	92.80	Not analyzed	
17	1400 ±10	7	6.95	93.80	71.50	28.50
18	1400	7	8.80	90.84	Not analyzed	
19	1325	24	5.80	94.25	No 2nd. layer	
20	1465 ±10°	1 hr (ajax)			65.5	34.5
21	1350	3/4 hr (ajax)	9.60	88.3		

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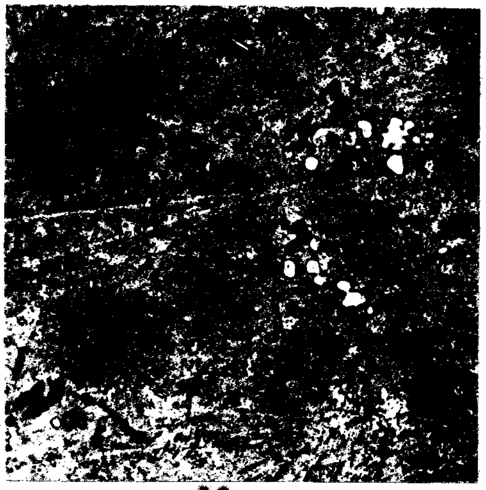

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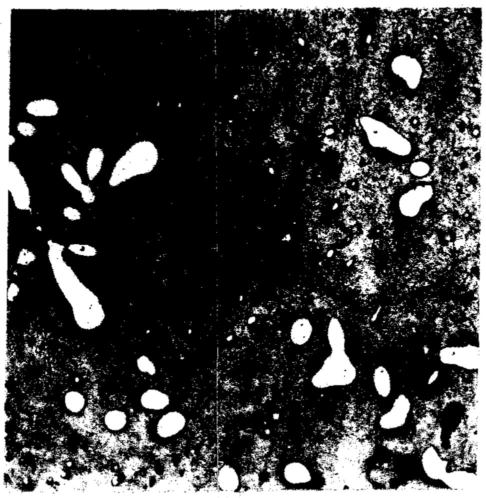

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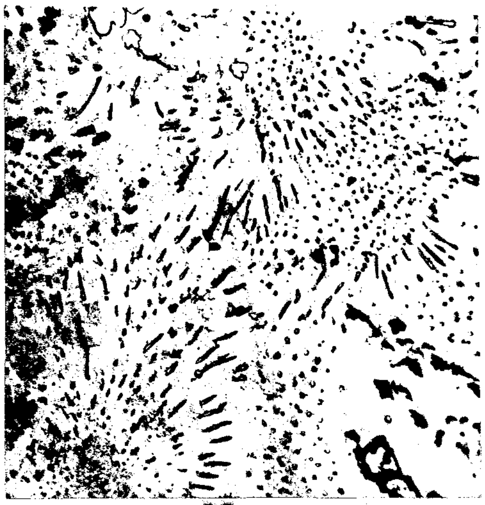

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Fig. 9 - 15.5% thorium. Quenched from 1090° C. Thorium dendrites on eutectic background. X 100.

Fig. 10 - 4.0% thorium. Cooled slowly. Eutectic structure.

Fig. 11 - 4.0% thorium. Quenched from 1050° C. Shows spheroidization of eutectic.

Fig. 12 - 4.0% thorium. Quenched from 780° C. Same structure as slowly cooled sample.

Above samples oxalic acid etch. X 250.

liquids in the region of immiscibility should be reached in an even shorter time.

A series of points was thus obtained at 1100°, 1200°, 1250°, 1300°, 1325°, 1350° C. as tabulated in Table 2 and plotted in Figure 4. These points lie on a smooth curve except for the 1100° C. point which is too low in thorium to fall on the thorium liquidus. It does fall on the corresponding uranium liquidus although this was hardly expected. The low result may be due to incomplete solution.

To check the method of sampling, drillings were taken from the center portion of a specimen and compared with drillings taken from near the outer edge. From the data in Table 3 (Runs 7 and 8) no concentration gradient was found from outer surface to core. Likewise the homogeneity from top to bottom was checked on a specimen heated self-inductively. Samples were taken from near the upper and lower surfaces for chemical analysis (Run 20). A slight tendency toward segregation was found.

The data indicate that the thorium liquidus rises sharply from the eutectic and begins to level off around 1300° C. As the thorium content is increased beyond about 8 per cent and above 1375° C. a region of liquid immiscibility occurs. Figure 13 is a macrophotograph of a sample which had been held at 1470° C. (Table 2, Run 13). Clearly evident are three distinct homogeneous layers; a uranium-rich layer at the bottom, a thorium-rich layer in the middle and a cap of pure thorium on top. Actually had this been given a long enough annealing period this excess thorium should have dissolved, but since it has no direct

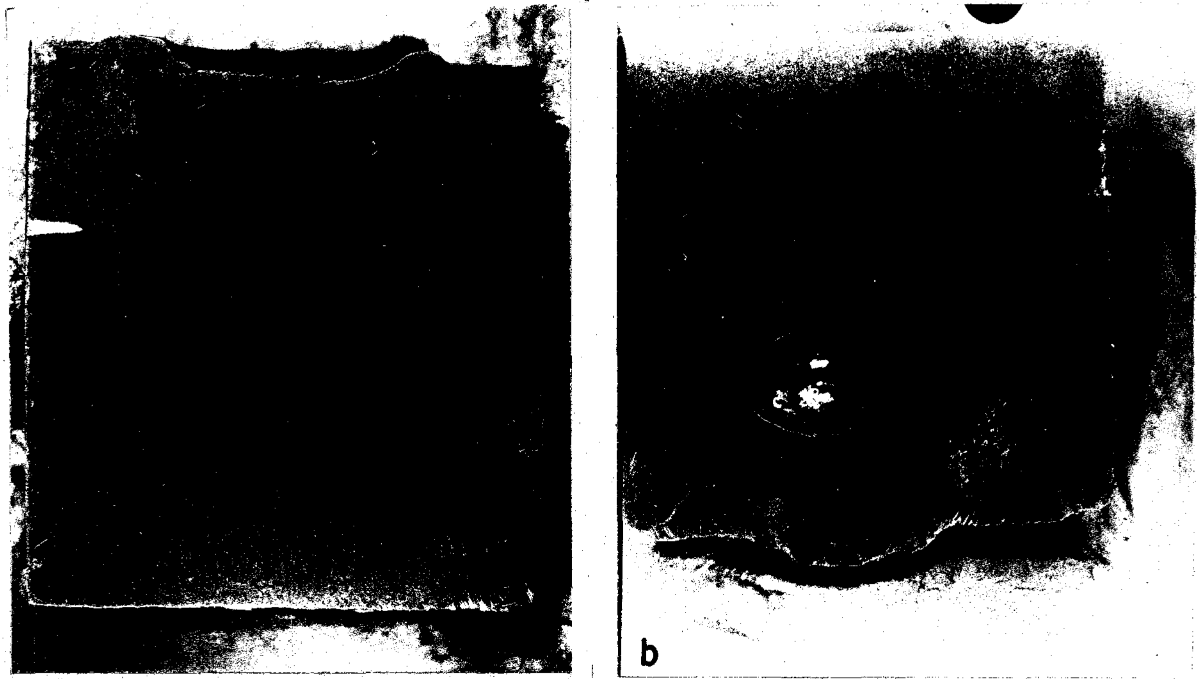


Fig. 13 - Macrophotographs showing liquid immiscibility. (a). Upper half of alloy prepared at 1470° C. Pure thorium cap in thorium rich layer. (b). Lower half of same alloy. Two distinct layers can be seen. Air etch. X 3.5.

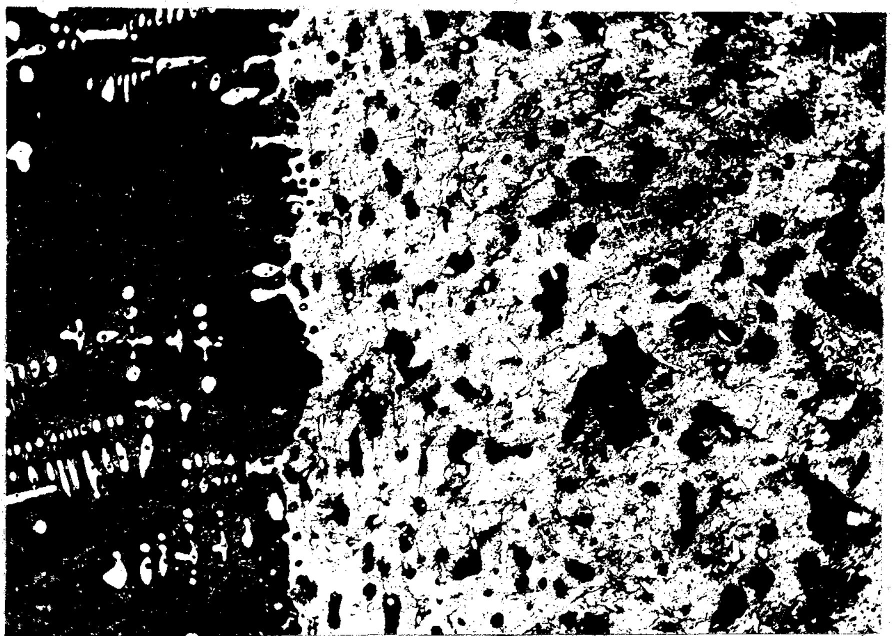


Fig. 14 - Photomicrograph of boundary between two liquid layers of above alloy. Oxalic acid etch. X 150.

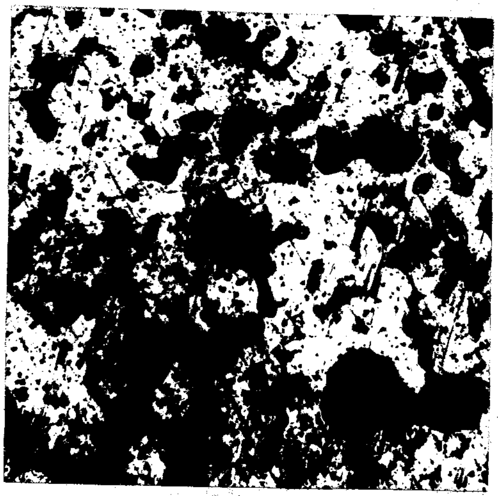
Table 3

Homogeneity of Samples

No. of run	Portion sampled	Wt% Th	Wt% U
$7A_1$	1/8" Center Portion of Sample	2.49	97.74
$7A_2$	1/4-1/8" Outer Portion	2.39	97.92
$8A_1$	1/4" Center Portion	3.33	96.59
$8A_2$	3/8"-1/4" Outer Portion	3.39	96.66
$20A_1$	Upper Half	66.9	33.6
$20A_2$	Lower Half	65.6	34.4

contact with the uranium layer in which it is most readily soluble this might have required a much longer time. A photomicrograph of the boundary between the two liquid layers (Fig. 14) shows a sharp discontinuity at the interface. Photomicrographs of the upper layer and also of the bottom layer are shown in Figures 15 and 16.

Further evidence for this immiscibility are Figures 17 and 18 showing a 15 and a 20 per cent thorium alloy which have been prepared by heating the metals by self-induction and cooling rapidly (100-200 degrees per minute). The round globular areas when enlarged (Fig. 19) appear thorium-rich and resemble in the relative amounts of the phases present, the upper layer that is found in the solubility experiments. The surrounding area contains thorium dendrites and a uranium-rich eutectic similar in appearance to the lower layers found in other studies. While there are a large number of the globules in the 20 per cent thorium alloy, only a few were observed in the 15 per cent sample. On the basis of this



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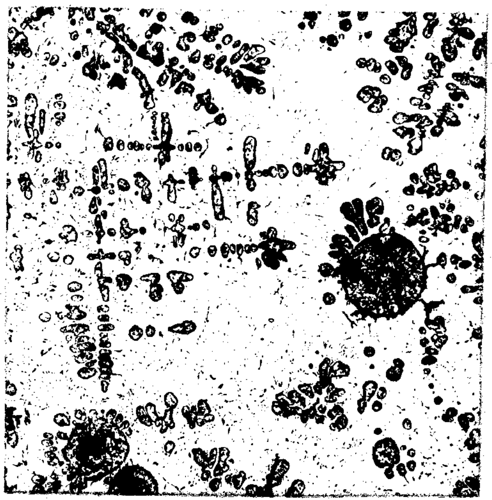

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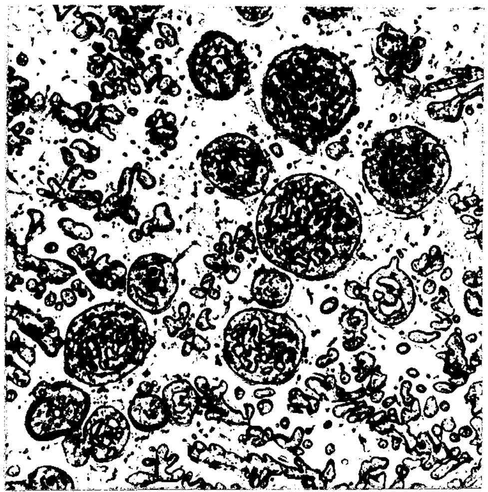

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Fig. 15 - Upper layer showing dark uranium-rich regions in thorium phase.

Fig. 16 - Lower layer showing thorium dendrites in eutectic matrix.

Fig. 17 - 15% thorium. Cooled rapidly. Globules are immiscible areas of thorium-rich liquid.

Fig. 18 - 22% thorium. Thorium-rich globular areas on uranium-rich background.

Above samples electrolytic polish. X 150.

evidence one might estimate the limit of immiscibility to be somewhat higher than 8 per cent probably closer to 12 per cent.

On the thorium-rich side of the immiscibility gap the precision is much better. The points lie on a smooth curve and indicate a low flat immiscibility loop.

The temperature at which immiscibility begins has been determined by two methods. The experimental evidence that one layer only is obtained at 1325° C. even after a 24 hour anneal but that two layers are readily formed at 1400° C. places the temperature somewhere between these two limits. A cooling curve run on a 70 per cent thorium alloy, at which composition any thermal breaks should be nearly maximum, showed a small reproducible break both on heating and cooling between 1350 and 1375 degrees centigrade.

The question of the actual existence of liquid immiscibility might be discussed at this point. The early investigations of the author and also of the Chicago group failed to show any two liquid region. For example a 50 weight per cent alloy prepared by self-induction heating in which a thorough stirring had taken place produced the homogeneous alloy shown in Figure 20. A tendency toward segregation was observed from top to bottom but there was no evidence of liquid immiscibility. Other alloys in the two liquid region were found to have similar appearances.

A possible explanation for this anomalous result is that in preparing the alloys they were heated to a temperature about the two liquid region and then cooling took place so rapidly that the layers did not separate. Present data indicate that the immiscibility loop is a low flat area so that a continuous single liquid region may exist above 1650° C.

To test this theory a 50% alloy was prepared by self-induction heating and brought to a homogeneous condition. The sample was then annealed in the resistance furnace at 1520° C., a temperature at which two liquid layers should form. Two distinct layers were observed (Table 2 run 12). Similar results were obtained when annealed at 1400, 1450 and 1500° C.

One other inconsistency appears here which requires some explanation. As was shown in Figure 8, a 15.5 per cent thorium alloy was prepared in which no immiscible layers or globules were observed. Either the limits of immiscibility are wrong or something peculiar has happened. Contrasting this alloy with the 15 per cent alloy shown in Fig. 17 the question arises as to which structure is the true equilibrium structure of the alloy.

The author believes that both structures are truly representative depending upon the previous treatment of the sample. The 15.5 per cent alloy was prepared by heating self-inductively to 1800° C. which according to the diagram as constructed is a one liquid region. This was followed by rapid cooling to room temperature. The 15 per cent alloy (Fig. 17), on the other hand, was prepared by heating self inductively to 1400° C. in the two liquid region and cooled rapidly from there. Upon annealing below the two liquid region these immiscible areas disappear and the alloys show only thorium dendrites in a eutectic matrix.

From this one can conclude that while the true equilibrium is described by a liquid immiscibility loop, rapid cooling through the shallow region does not allow a separation into liquid layers and a non equilibrium structure often results.

Beyond the monotectic point at 72 per cent thorium and 1375° centigrade the liquidus rises to the melting point of thorium at approximately 1675° C. A solubility study at 1500° (Run 9) was made in which an excess of thorium was maintained in contact with both top and bottom layers so as to cause the complete disappearance of the lower layer. The liquid phase that existed in contact with excess thorium when analyzed chemically gave the liquidus point shown at the extreme right of Figure 4. This has been interpreted as a thorium liquidus point.

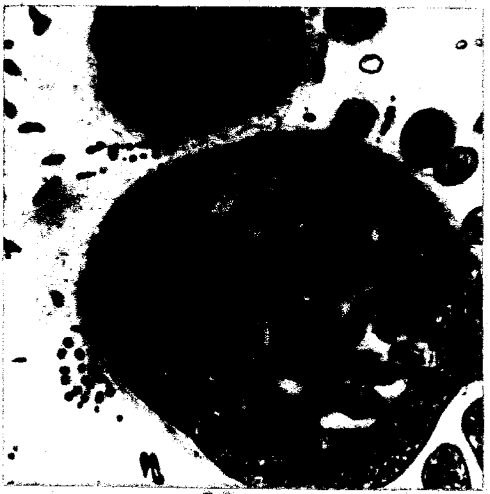
The microstructures of alloys beyond the two layer region appear completely homogeneous. As an alloy in this region, for example 80 per cent thorium, is cooled from the liquid the following occurs; as the thorium liquidus is crossed solid thorium solidifies and continues to freeze out on further cooling until at 1375° C. the liquid remaining has the composition of the monotectic (72 per cent). At the monotectic, this being a univariant point, the composition of the liquid shifts to liquid of 8 per cent thorium by rejecting more solid thorium. It then follows the normal liquidus curve on further cooling to the eutectic where complete solidification takes place.

The solid solubility was estimated mostly from microstructures although the fact that there is no depression or raising of the uranium transformations provides good evidence that there is very little solid solubility of thorium in uranium. Microscopic study of the 0.7 thorium alloy (See Fig. 5) shows a considerable amount of eutectic present. Quenching from 800° C. in the region of beta uranium did not produce any change in the microstructure (Fig. 21a) indicative of no increased solubility of thorium in beta uranium.

The solid solubility of uranium in thorium, likewise, appears to be very low. No significant change in the lattice constant of thorium was observed as would be predicted if there were extensive solid solubility. X-ray examination of the 50 per cent alloy showed the following:

Phases Present	Lattice Constant	Intensity
f.c.c. Thorium metal	5.09 ±.02 Å	very strong
Alpha uranium		medium to strong
f.c.c. ThO_2	5.59 ±.02 Å	weak

The microstructures of high percentage thorium alloys do not indicate extensive solubility. A 90 per cent alloy (Fig. 21b) contains areas of uranium along the grain boundaries. A photomicrograph of a 95 per cent alloy in the Chicago laboratory report (2) shows uranium along the grain boundaries. Estimating from the amount of uranium present at 95 per cent thorium, the solubility of uranium in thorium at room temperature appears almost negligible.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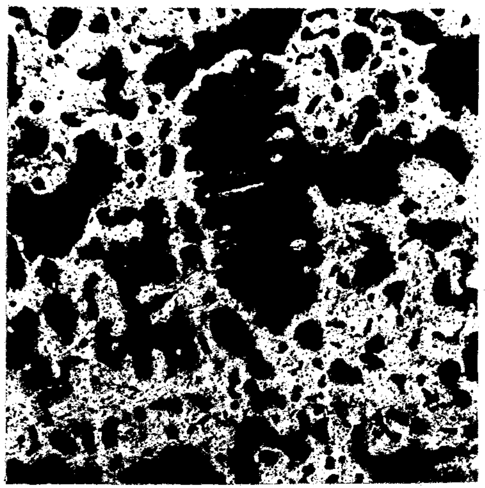
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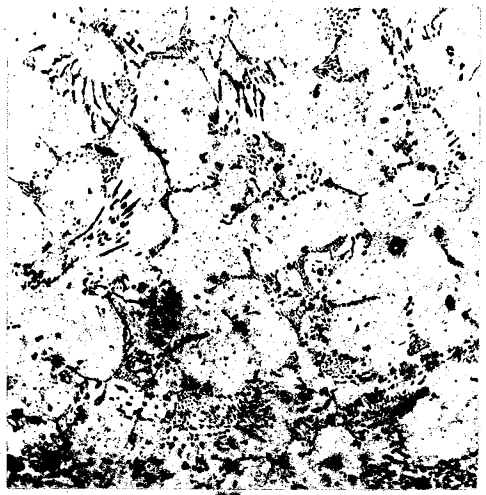
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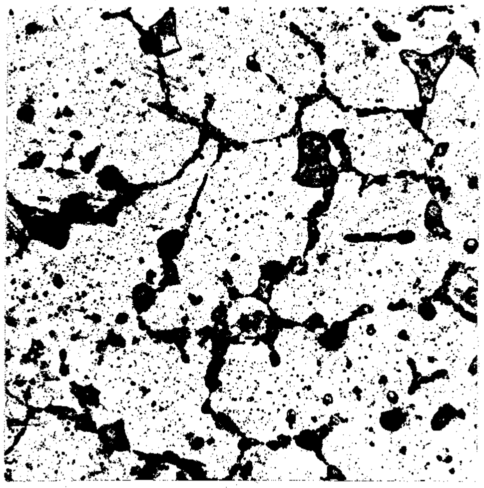

21b

Fig. 19 - Globular area enlarged. Shows thorium (dark phase in this picture) and uranium. Elec. polish plus nitric acid etch. X 500.

Fig. 20 - 49% thorium. Alloy heated by self-induction. Uranium-rich areas (dark) surrounded by thorium. Oxalic acid etch. X 100.

Fig. 21a- 0.7% thorium. 800° C. quench. Elec. polish. X 100.

Fig. 21b- 90 % thorium. Cooled slowly. Small amount of uranium (dark areas) on thorium background. Oxalic etch. X 100.

B. Thorium - Zirconium System

1. Historical

No previous investigation of this system has been reported in either the general or project literature. Freeman (9) did some of the preliminary work in this laboratory. His efforts to alloy zirconium and thorium by heating the massive metals directly were unsuccessful due to the formation of an oxide surface on the zirconium which prevented thorough mixing even in the liquid state. Some evidence that the two metals do alloy was found however.

2. Experimental

a. Preparation of alloys

The method of preparing the alloys has been related directly to the zirconium production program. As purer zirconium salts were obtained and as better methods of reducing zirconium metal were developed the purity and quality of the alloys improved.

Since the zirconium metal most readily available commercially at the time the studies were begun was metal powder, a supply was purchased from Foote Mineral Co. This was quite free from other metal impurities, but the powder being extremely fine oxidized readily so that several per cent of zirconium oxide was unavoidably present. Because of its pyrophoric nature all handling operations were performed under carbon dioxide atomosphere. The use of dry ice was found most convenient in mixing and transferring since in addition to maintaining an inert atmosphere over the powdered metal the low temperature reduced the danger of burning.

Thorium metal powder was prepared from cast thorium by the hydride process (10). In this process pieces of thorium or thorium turnings are heated in a hydrogen atmosphere at approximately 600° C. until no more hydrogen is absorbed, thus forming the dihydride. Then further reaction takes place at 325 to 200° C. forming a higher hydride which causes the product to disintegrate into a finely divided product. This is then decomposed to the metal by heating to 500° and then to 700° C. under vacuum. A finely divided powder still containing a little hydrogen is thus obtained.

In preparing the alloys the powders were mixed in the desired proportion in a mortar under a dry ice atmosphere. It was then transferred to a special die and pressed into a bar one fourth inch by one fourth by four inches long. These particular dimensions were chosen for the melting point determinations as will be described later.

Before weighing out the powders in the preparation of the pressed compacts, the amounts of metal powder required to give a pressed volume of $\frac{1}{4}$ x $\frac{1}{4}$ x 4 inches was calculated. Assuming the density of the compressed powders to be eight-tenths the density of the metals in the cast state, the amounts necessary to occupy a volume of $\frac{1}{4}$ cubic inches (4.12 cubic centimeters) were determined for each composition to be studied.

Since a massive metal alloy was considered preferable to the sintered powder early attempts were made at preparing the massive alloy. Thorium-rich alloys were prepared successfully by a bomb co-reduction of thorium tetrafluoride, ThF_4, and potassium fluozirconate, K_2ZrF_6, using calcium and a booster.

Since the supply of potassium fluozirconate was somewhat limited, this was later replaced with zirconium chloride, $ZrCl_4$. The commercial source of the latter was Titanium Alloy Manufacturing Company. The major impurities in this material are iron (0.2 per cent) and titanium (0.02 per cent). The chloride is very hygroscopic and so zirconium tetrafluoride was substituted for it as soon as a supply of this became available (11). The fluoride being non-hygroscopic could be handled conveniently in air without picking up water.

The best results were obtained with mixed fluorides although alloys containing more than 60 per cent zirconium were obtained in poor yields. They were extremely hard and their microstructures showed quite a few impurities. Hence, all zirconium-rich alloys were made by another step. Bureau of Mines sponge zirconium (12) was added to a bomb reduced thorium-zirconium alloy in a graphite crucible and heated under vacuum in an induction furnace to a temperature at which the sponge zirconium dissolved in the lower melting alloy. The porous sponge was found to dissolve readily whereas difficulty was encountered when a massive piece of zirconium was used due to the aforementioned oxide coat. Apparently the greater surface of the sponge material facilitates its solution. Samples prepared by this method were much softer and could be easily sawed, drilled, or machined on a lathe.

The casting of the alloys has been a problem just as it has been with the pure zirconium. Thorium could be cast in beryllia but zirconium was observed to react with beryllia above 1600° C. The thorium-rich alloys and those alloys which melt below 1600° C. could be cast in beryllia. This sufficed for all alloys containing up to 50 per cent zirconium. For the higher melting alloys graphite was first tried since in the Bureau of Mines process casting is done in graphite. Kaufmann(13) reported the formation of a carbide skin on the surface of the metal when zirconium was melted in graphite but only a small amount of carbide inclusions was observed in the microstructure of the casting.

To determine how much carbon was picked up in preparing the zirconium-rich alloys chemical analyses were made in this laboratory on three of the alloys which had been cast in graphite. It was observed that about 0.10 per cent carbon was dissolved at 1500° C., 0.17 per cent carbon was introduced by heating to 1700° C. and about 0.2 per cent when casting at 1800° C. Since thorium has been found to dissolve only very small amounts of carbon below 1750° C. (14) graphite was agreed upon as the best of a number of not too satisfactory refractories.

b. Thermal analysis

Because of the high melting point of the pure metals, the use of thermocouples for taking cooling curves did not offer much promise for obtaining solidus or liquidus data.

For determination of the melting points of high melting materials, P. Chiotti has constructed an apparatus for heating samples by passage of high current through the specimen and observing the temperature at which liquid was first sighted. A hole 0.039 inch in diameter and 0.15 inch deep was drilled in the specimen in order to approach black body conditions. The specimen, a $\frac{1}{4}$ inch by $\frac{1}{4}$ inch bar from 2 to 4 inches in length, was clamped between two water cooled copper electrodes and heated under vacuum or inert atmosphere. The high current required to heat the bar was provided by an 8 KVA transformer operating on a 220 volt single phase line, giving an output of 2, 4 or 8 volts at 4000, 2000 or 1000 amperes respectively. The output was controlled by an auto-transformer in the input circuit which gave continuous variation from zero to maximum output.

The temperature was read by means of a disappearing filament type optical pyrometer. Calibrations were made using pressed compacts of nickel and of molybdenum. On two runs the melting point of nickel was observed as 1427° C. and 1435° C. Readings were taken through a pyrex sight glass and had to be corrected for the absorption by the glass window. Using the relation developed by Foote et al (15) $1/T - 1/T_a =$

-0.0000046 where T is the absolute temperature and T_a the apparent or observed temperature in degrees absolute these corrected readings become 1440° and 1448° C. respectively as compared with the true melting point of 1452° C. for nickel.

In the calibrations with molybdenum the corrected melting points obtained were 2597° C. and 2580° C. as compared with the literature value of 2622 ± 10° centigrade.

In the case of the powdered compacts presintering was necessary in order to lower the resistance sufficiently to allow passage of high currents with the low potential available. This was accomplished by placing the pressed compact inside a molybdenum tube furnace connected between the two high current electrodes which brought the sample to a sintering temperature of 1000 - 1200° C. A small hole was then drilled in the sample for melting observations and the melting points were determined.

In solid transformation studies cooling curves were taken by means of the apparatus shown schematically in Figure 22a. This is the familiar neutral body type of differential cooling curve and has the advantage of being able to pick up breaks that by other methods might be very doubtful. Two small holes were drilled through the specimen (A) using a number 50 drill. Adjacent to this but not touching was a neutral body (B) such as pure thorium or nickel containing one hole. The differential thermocouple was made by butt welding two long pieces of chromel thermocouple wire (C) to a short piece (2 inches) of alumel (D). The wires

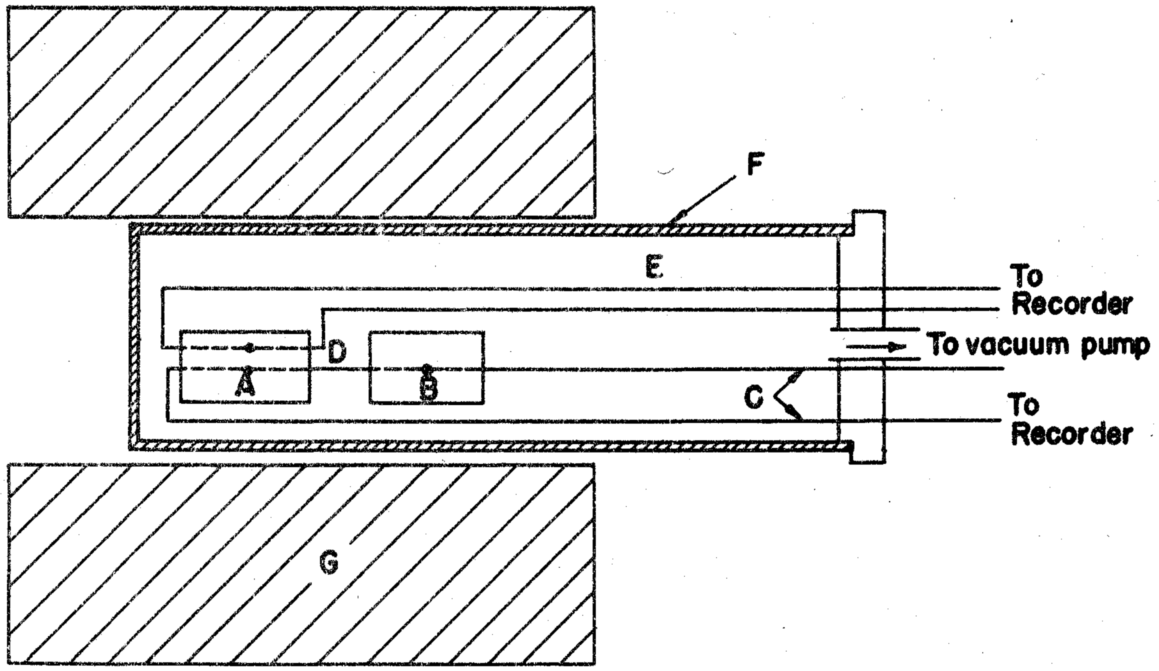


Fig. 22a - Differential Cooling Curve Apparatus.

were then insulated with small one-hole refractory spaghetti and connected so that one junction was in the center of the neutral body and the other in the specimen. The potential as measured by the recorder was that due only to temperature differences between specimen and neutral body. The recorder was a Brown Electronik instrument with a full scale range of 0-20 millivolts. A second thermocouple also located in the specimen measured the sample temperature directly and was recorded on another Brown Electronik. The sample was placed in a quartz tube (F) with the thermocouple leads emerging through a rubber stopper and the system was evacuated by a Welch Duo-Seal vacuum pump to pressures of 3 microns.

The tube was heated by a Kanthal wound resistance furnace (G) to a maximum temperature of 1050° C. The power was then turned off and the furnace allowed to cool slowly. As the specimen came to a thermal break its cooling rate was slowed up and the temperature difference between specimen and neutral body changed abruptly. Such a method proved useful especially in studying the extreme ends of the diagram where the eutectoid breaks became almost indistinguishable, or in detecting any slight heat effects.

A particular disadvantage of this apparatus is that as a break appears on the differential curve the specimen temperature must be read simultaneously from the other instrument. This requires careful attention while the curve is being run.

One special cooling curve was run on an alloy of composition corresponding to the minimum in the solidus-liquidus curve to compare if possible the accuracy of the optical pyrometer method with the generally preferred cooling curve method. Since the minimum was found to fall within the chromel-alumel thermocouple range this type of couple was employed. Heating of the sample was done in the molybdenum wound resistance furnace described in part A 1c. By adjusting the power input the furnace heating or cooling rate was controlled almost linearly over a narrow temperature range.

c. Microscopic examination

The same grinding and polishing techniques as described in part A 1d were applied to these alloys. Fortunately none of the alloys of this system were reactive with air or with water which made them easy to handle but this same non-reactivity made them extremely troublesome to etch. Almost completely different etching solutions and conditions had to be worked out for each composition studied and frequently for different heat treated samples of the same alloy. This made metallographic studies laborious at times and often cast doubt on the validity of results since a standard method of etching samples could not always be used.

In general three standard etchants were used. In the thorium rich alloys, i.e. those containing 0 to 40 per cent zirconium, the sample was immersed in or swabbed with 10 per cent hydroflouric acid in ethyl alcohol. The etching time varied from one second to thirty seconds depending primarily on the previous heat treatment of the sample.

The slow cooled samples were found to etch readily while the samples which were quenched from high temperature onephase regions etched more slowly. Alloys in the middle portion of the system (40 to 60 per cent zirconium) were etched most readily by an electrolytic etchant described by A. H. Roberson (16) consiting of 3 parts ethyl alcohol and 1 part concentrated hydrochloric acid applied for 20 seconds at a current density of 1 ampere per square centimeter.

The high zirconium alloys were etched with a 1 per cent hydrofluoric in nitric acid solution by swabbing for 1 to 10 seconds depending again upon the reactivity of the samples.

d. Chemical analysis

The alloy was dissolved in hydrofluoric and nitric acid with heat applied. Sulfuric acid was added and evaporated to remove all fluoride ions. The residue was then redissolved in dilute acid. An aliquot was taken and ammonium hydroxide added to precipitate thorium and zirconium hydroxides and thus removing the sulfate ion which interferes in the determination. The hydroxides were redissolved in nitric acid and thorium precipitated as the oxalate by addition of oxalic acid. The precipitate was filtered and washed, ignited to thorium oxide, ThO_2, and weighed.

To another aliquot enough hydrochloric acid was added to make the solution 0.1 to 0.8 molar in hydrochloric acid. Mandelic acid was added and zirconium precipitated as the zirconyl salt of mandelic acid. This was then ignited at 900° C. to zirconium oxide, ZrO_2, and weighed.

e. X-ray studies

All of the X-ray diffraction patterns were taken on powder samples with either a 57.3 or 114.3 millimeter diameter Debye-Scherrer powder camera which had been calibrated with pure uranium dioxide. The studies consisted principally of phase identification and of the approximation of lattice constants. The determination of the latter could be made to an accuracy of ± 0.01 Angstroms so that any appreciable distortions of the unit cell were readily detected. Copper K alpha radiation, nickel filtered, was used for these studies. Exposure times of from 3 to 8 hours were required for all samples.

Powder samples were prepared by filing from the massive alloys with a small clean file. The filings were then stuck onto a fine glass fiber coated with petrolatum and mounted in the camera for exposure.

When it was felt that the amount of cold work produced by the filing operation might introduce enough strain to interfere with accurate lattice measurements, the powders were annealed prior to diffraction studies. This was carried out in the following manner. The filings were heated in a small diameter sealed quartz capillary above the recrystallization temperature of the metal and cooled slowly to room temperature. The powder was then transferred to a very fine, thin walled glass capillary and this was mounted in the camera.

Since no high temperature camera was available, X-ray studies of the higher temperature regions were limited to samples quenched from the region to be examined. Filings were then taken from the quenched alloy and powder diagrams were taken as was done with the slowly cooled samples. An alternate technique was to anneal the filings in a sealed quartz capillary and to quench the capillary containing the powdered specimen in water prior to X-ray examination. In this way any disturbance of the quenched structure introduced by filing would be eliminated.

Unfortunately the powdered alloys appeared to react rather badly with the quartz capillary above 900° C. so that the latter technique was not found too successful in the temperature region in which it would have been most useful.

f. Quenching experiments

Most of the quenches were carried out by annealing in vacuum, admitting helium prior to quenching and plunging the samples into water as was described in part A 1f.

However, for a few experiments in which the quenching temperature was critical, a more elaborate apparatus was designed (Fig. 22b). The specimens were mounted on a disc (A) which was pivoted on a stainless steel rod (B) suspended from the vacuum head (C). The disc was kept horizontal by the weight of the soft iron core (D) of a solenoid. The entire unit fit inside a quartz vacuum tube (E) and was heated from the outside by a Kanthal resistance furnace. The quench was carried out by activating the solenoid which lifted the iron core enough to allow the disc to turn releasing the sample. The quenching medium (F) was a Woods metal bath (liquid at 60° C.) in a reservoir beneath the specimen. The Woods metal contains Cd, Bi, Pb and Sn none of which have an appreciable

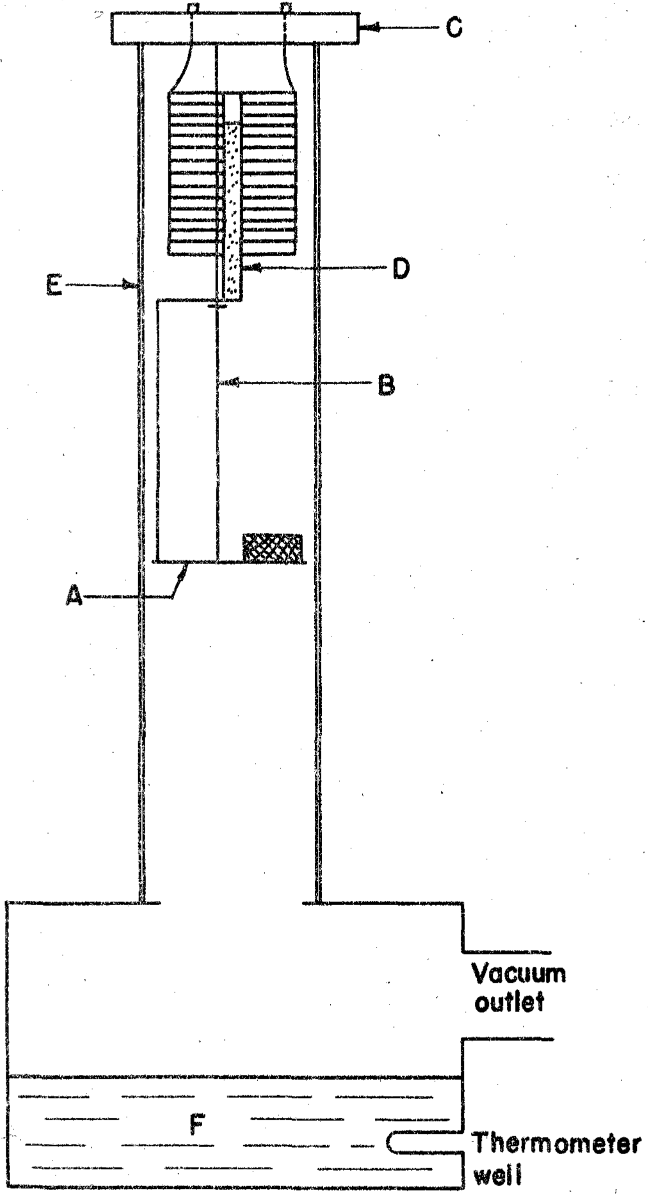


Fig. 22b- Apparatus for Quenching from Critical Temperatures.

vapor pressures at room temperature. The entire annealing and quenching operation was carried out under a vacuum of less than one micron. With this apparatus the temperature from which quenching had taken place could be controlled to an accuracy of ± 2° C.

3. Presentation and Interpretation of Data

On the basis of the data obtained from thermal, microscopic, and X-ray investigations, the phase diagram shown in Figure 23 has been constructed.

As stated previously the early work was done with samples prepared from the metal powders. The melting points of pressed compacts of several different compositions are shown below in Table 4.

Table 4

Melting Points of Pressed Powder Samples

Composition wt% Zr	Melting point (°C)
5	1620
5	1600
10	1510
20	1490
30	1430
35	1375
35	1390
40	1445
50	1545
Zr powder	1890

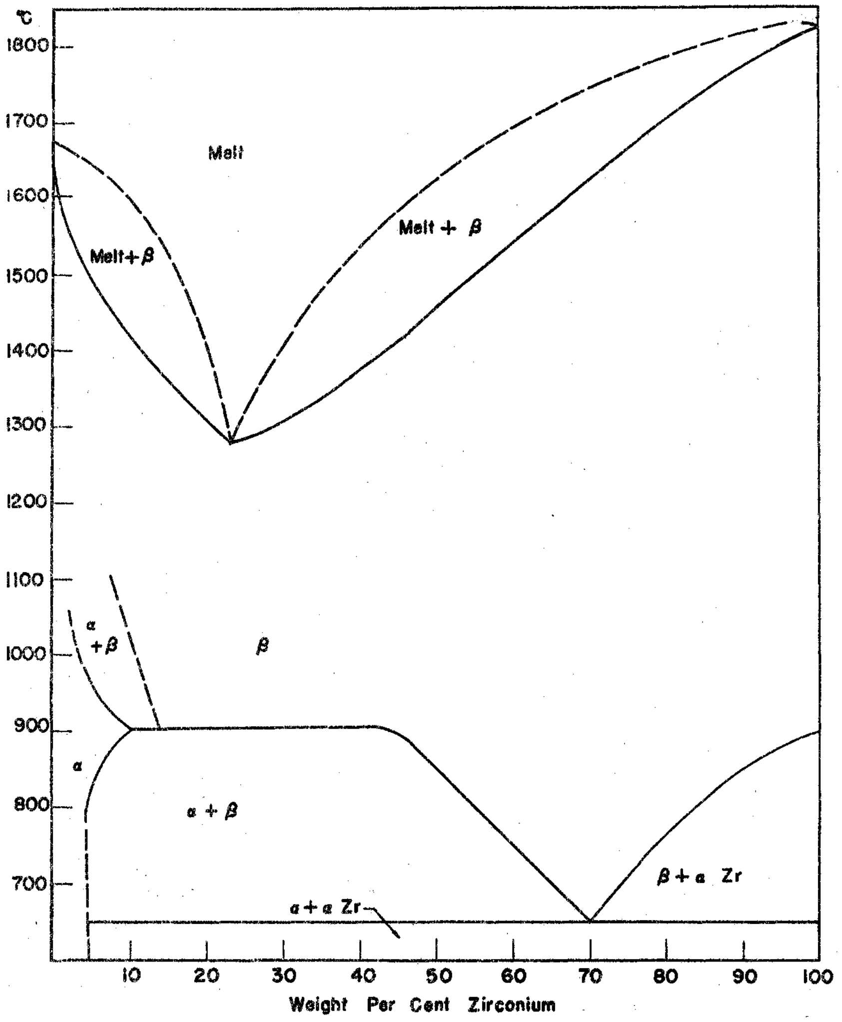


Fig. 23 - Thorium - Zirconium Phase Diagram.

The melting point as determined by the optical pyrometer method is considered to be a point on the solidus curve since it represents the temperature at which liquid first appears. The above series of runs gave a qualitative picture of the phase diagram indicating that a minimum in the solidus-liquidus curves occurs at a temperature of 1375° C. at a composition somewhere around 35 weight per cent zirconium.

Continuing the investigation using cast samples, the melting points and also the solid transformation were studied. All thermal data obtained from massive samples have been compiled in Table 5. All the solidus breaks there recorded were determined by the optical pyrometer method with the exception of the two points (see footnote in table) which were obtained from heating and cooling curves in which a thermocouple was used to measure the temperature. The cooling curve breaks occur 20 to 50 degrees lower than the corresponding optical pyrometer points. This is not too surprising since the optical pyrometer method requires that sufficient liquid be present in order to flow into the hole. In this system where melting takes place over a wide temperature range this discrepancy might be expected.

The solid transformation points were obtained from cooling curves in which the differential thermocouple and neutral body method described in B 2b was used.

All the data in Table 5 have been plotted in Figure 24 showing more completely the basis on which the diagram has been constructed.

Beginning at the melting point of thorium (1675°) the solidus curve

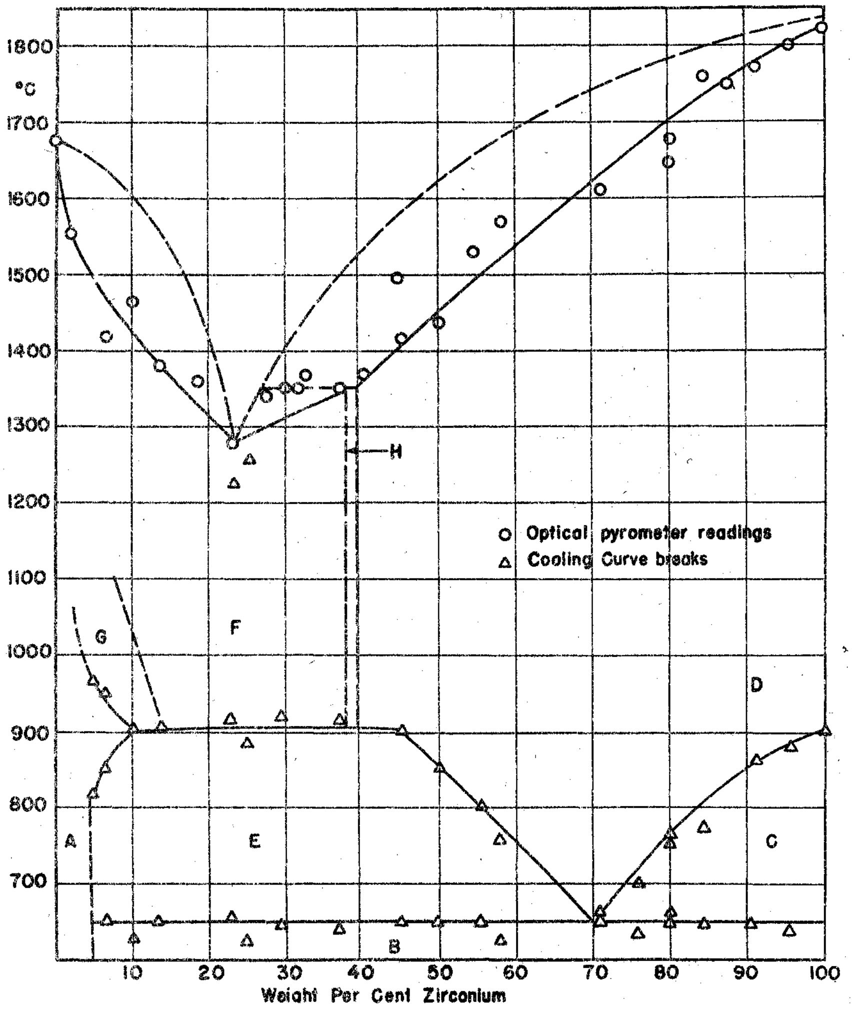


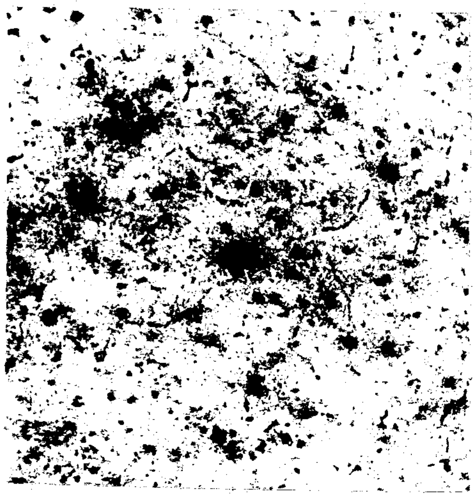
Fig. 24 - Thermal Data of Thorium - Zirconium System.

Table 5

Thermal Data for Th-Zr System

Composition wt%Zr	 wt%Th	Liquidus or solidus breaks °C.	Eutectoid or other transformations °C.	
Cast thorium		1675		no breaks
2.0	97.6	1555		no breaks
5	95		967, 817	no breaks
6.4	93.5	1420	951, 850	653
10	90	1465	906	626
13.5	84.5	1380	907	653
18.5	80.5	1360		
23.2	75.9	1275	918	656
25	75	1344, 1225* 1255†	886	626
27.5	60.0	1340		
29.5	71.5		920	646
30.0	69.0	1353		
31.5	66.5	1352		
32.5	66.0	1370		
37	73	1350	915	638
40.0	55.5	1370		
44.5	52.5	1495		
45	55	1415	896	652
50.0	47.0	1435	852	649
54.3	44.5	1530		
55.6	42.1		802	649
58.1	41.0	1570	761	623
71.0	29.4	1610		650 640
76	24			702 635
80.1	19.5	1645		760 663
80.2	19.0	1675		750 650
84.5	16.0	1760		771 646
87.6	8.6	1750		
91.2	7.7	1770		862 644
95.6	4.7	1800		881 638
Bureau of Mines Zr		1820		900
Crystal bar Zr		1782		877

*Obtained from cooling curve with Pt-Pt+13% Rh thermocouple.
†Obtained from cooling curve with chromel-alumel thermocouple.



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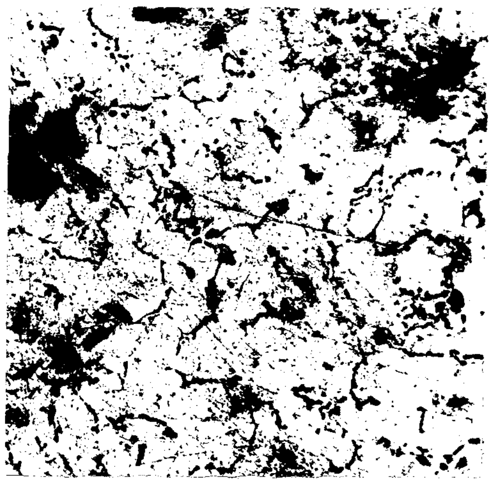

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Fig. 25 - Cast thorium.

Fig. 26 - 5% zirconium. As cast.

Fig. 27 - 6.4% zirconium. As cast. Second phase along grain boundaries.

All samples 10% HF in ethyl alcohol etch. X 250.

drops smoothly to a minimum of 1250 - 1275° C. at somewhere around 25 per cent zirconium. From this point it rises almost linearly, except for a scatter around 30 per cent, to the melting point of zirconium (1820° C.). The liquidus curve has not been established by experiment but it most likely follows the general course indicated by the dashed line.

The one phase region (A) in Figure 24 is based upon a number of observations. The fact that the thermal break at 640° C. was not observed in alloys containing 2 and 5 per cent zirconium whereas it did appear at 6.5 per cent would place the limits of solubility around 5 per cent zirconium. It is possible of course that the 640° C. break was present in the lower zirconium alloys but too weak to be detected even with the extremely sensitive differential method.

The microstructures of alloys in this region likewise indicate the presence of a one phase area. All the alloys examined from pure thorium (Fig. 25) to 5 per cent zirconium (Fig. 26) appear one phase but at 6.5 per cent a small amount of second phase begins to show up along the grain boundaries (Fig. 27).

The final and most conclusive evidence for solid solubility at room temperature is based on X-ray diffraction studies. Figure 28 shows graphically the behaviour of the lattice constant of thorium as zirconium is added. The value drops sharply from 5.09 Å for cast thorium to 5.05 Å as zirconium content increases. Estimating from these lattice constants maximum solubility has not been reached at 2.5 per cent but that a

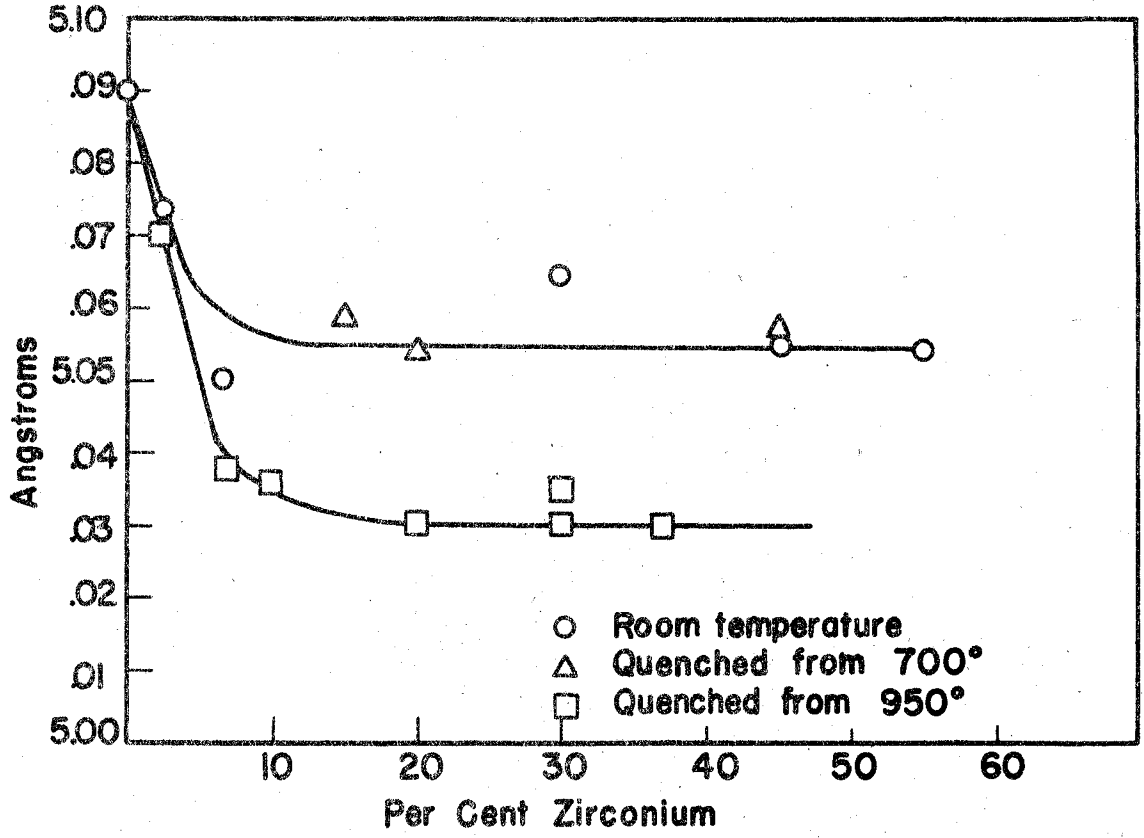


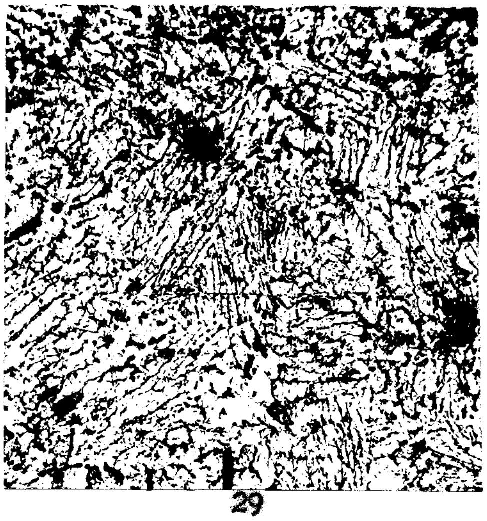
Fig. 28 - Plot of Lattice Constants of Thorium Alloys versus Zirconium Contents.

maximum has been reached at 6.5 per cent. On the basis of two samples quenched from 700° C., a 20 and a 45 per cent alloy, the same distortion of the lattice takes place at 700° C. as occurs at room temperature. From this the solubility limits at 700° C. have likewise been estimated to be near 5 per cent. The rather bad scatter of points on the room temperature curve fall within the limits of accuracy of lattice determinations since only a small diameter (57.3 millimeter) powder camera was used. In order to establish the lattice constants of thorium at room temperature to a greater degree of accuracy a diffraction pattern was taken of a 55 per cent zirconium alloy on a large diameter (114.3 millimeter) powder camera. The powder had been annealed at 650° C. after filing. From the X-ray diagram the following phases were identified:

Phase	Lattice constant	Intensity
f.c.c. thorium	5.054 ± .005 Å	strong
h.c.p. zirconium	a = 3.22 ± .01 Å c = 5.13 ± .01 Å	medium
thorium dioxide		weak

From the comparative radii of the two atoms one would expect a substitutional type of solid solution where the smaller zirconium atoms replace the larger thorium atoms at random within the face-centered structure. This would result in a decrease in the mean unit cell dimensions and a shrinkage of the lattice constant. This is apparently what happens.

As the zirconium content is increased beyond 5 per cent the amount of second phase increases (Figs. 29, 30, 31 and 32) with a typical



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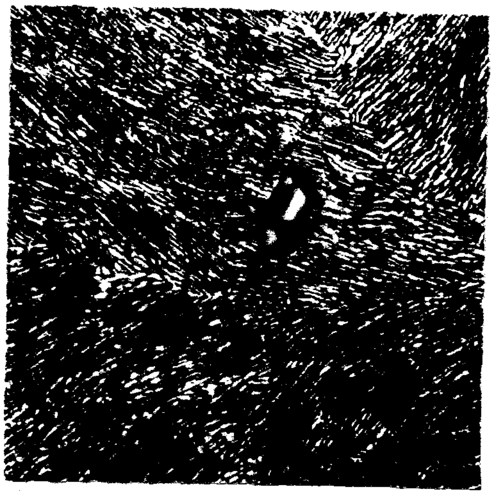

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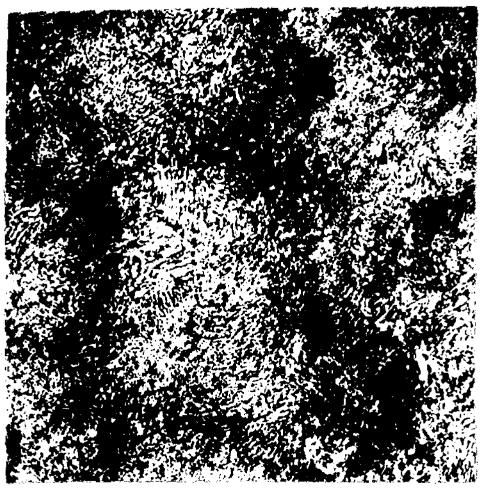

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Fig. 29 - 10% zirconium. Two phase structure.

Fig. 30 - 30% zirconium. Typical eutectoid structure. X 1000.

Fig. 31 - 37% zirconium. Eutectoid structure.

Fig. 32 - 60% zirconium. Eutectoid-type structure.

All samples cooled slowly to room temperature. 10% HF in ethyl alcohol etch. X 250.

eutectic or eutectoid-like structure appearing in all slowly cooled alloys between 10 and 70 per cent zirconium. The appearance of the eutectoid differs from alloy to alloy but all of them possess a laminated structure usually associated with eutectoid decomposition, most familiar in the pearlite form of steel. The X-ray powder diagrams of 30, 45 and the aforementioned 55 per cent zirconium alloys show the only phases existing at room temperature in the region (B) in Figure 24 are face-centered cubic thorium and hexagonal zirconium. No intermetallic compounds have been found to exist at room temperature in this system.

Thermal arrests were found at 640° C. in all alloys from 5 to 95 per cent reaching a maximum intensity between 70 and 80 per cent zirconium. The arrests locate a horizontal line which is the lower boundary for a region that originates in a eutectoid reaction. Microstructures would place the eutectoid composition at 70 per cent zirconium since primary needles begin to appear in the eutectic-like matrix of the 71 per cent alloy (Fig. 33). As the zirconium content is further increased the needles become larger and more predominant (Figs. 34, 35, 36, 37, and 38) until at 95 per cent the sample appears almost one phase and assumes the appearance of cast zirconium.

The thermal data plot in Figure 24 indicates that the alpha-beta transition in zirconium is lowered by the addition of thorium dropping almost linearly to the eutectoid temperature of 640° at 70 per cent. The two phase region (C) in Figure 24 was shown conclusively to exist by a series of quenches of alloys in that region. Figures 39, 40, 41,

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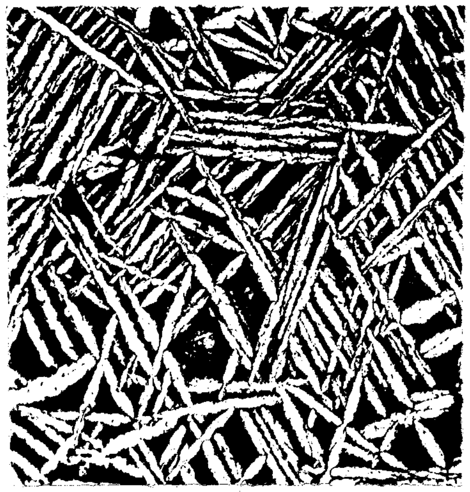

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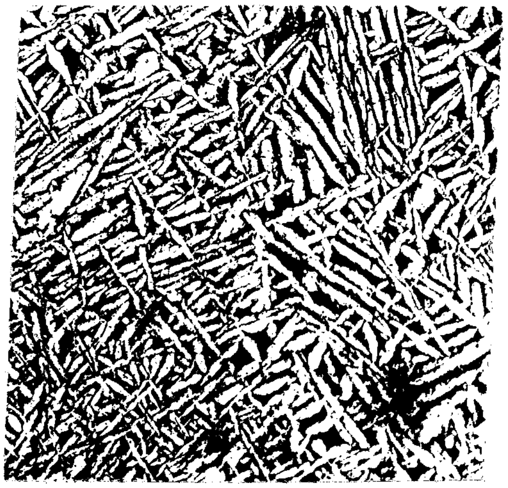

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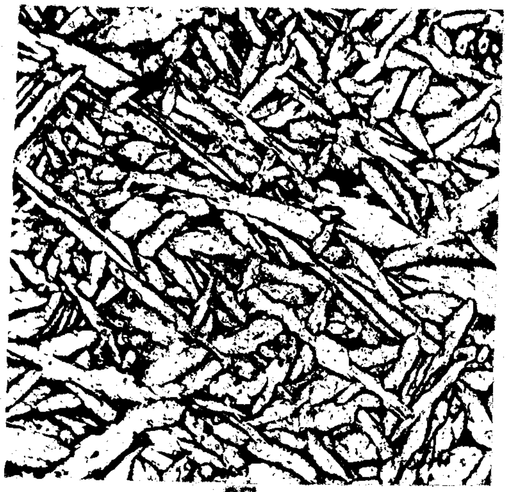
Fig. 33 - 71% zirconium. Eutectoid plus a few primary needles.

Fig. 34 - 76% zirconium. Primary zirconium plus eutectoid (dark phase).

Fig. 35 - 80% zirconium. Same two phases.

Fig. 36 - 85% zirconium. Note increase in zirconium (light phase).

Above samples cooled slowly. 1% HF in HNO_3 etch. X 250.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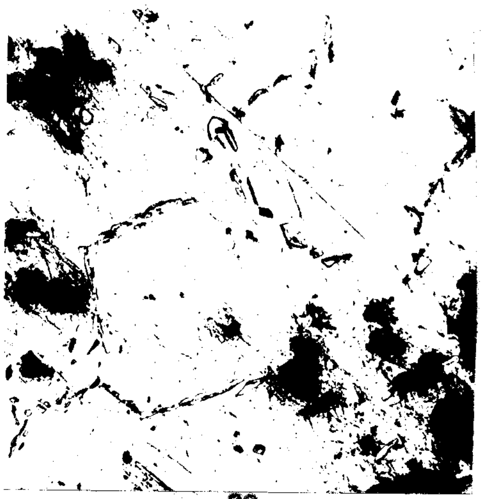
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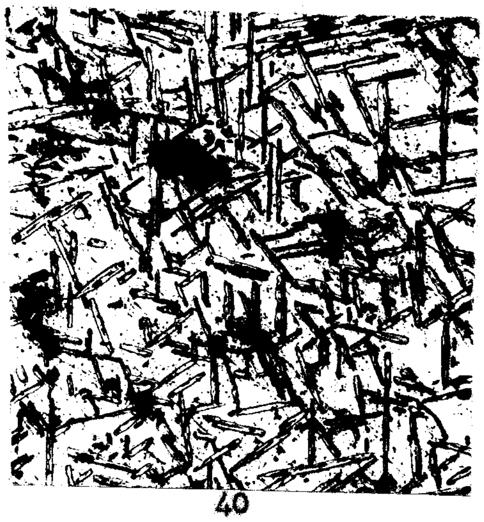
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Fig. 37 - 91% zirconium. Room temperature. Primarily alpha zirconium.

Fig. 38 - 95% zirconium. Same as above.

Fig. 39 - 71% zirconium. 695° quench. One phase structure.

Fig. 40 - 76% zirconium. 695° quench. Alpha zirconium plus solid solution.

Above specimens etched by 1% HF in HNO_3. X 250.

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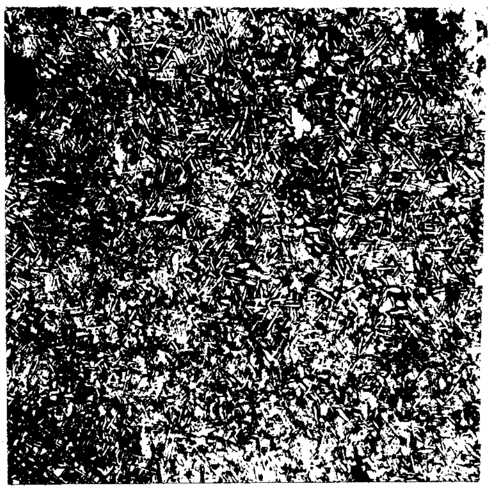

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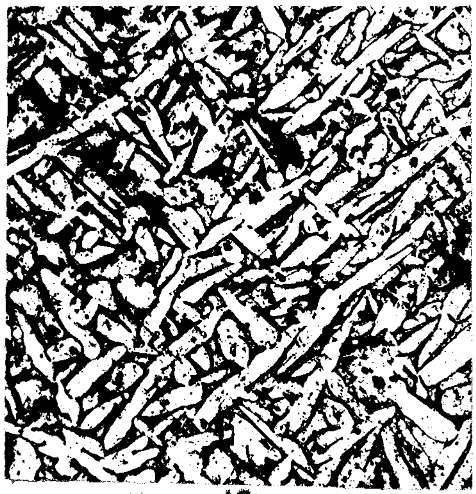

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Fig. 41 - 80% zirconium. Zirconium needles on background of solid solution phase.

Fig. 42 - 85% zirconium. Same two phases in about equal amounts.

Fig. 43 - 91% zirconium. Predominantly alpha zirconium (light phase).

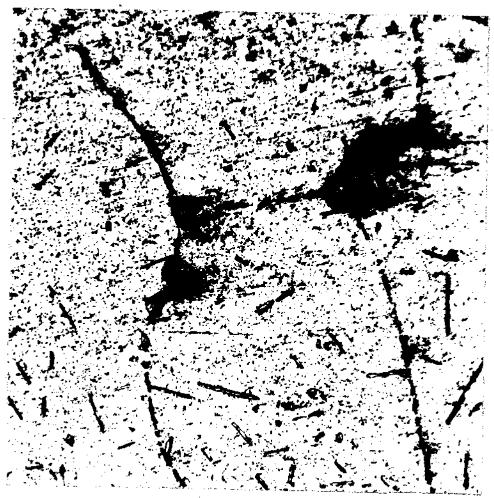
Fig. 44 - 95% zirconium. Second phase appears along grain boundaries of zirconium.

Series quenched from 700° C. 1% HF in HNO_3 etch. X 250.

42, 43 and 44 are photomicrographs of the 71, 76, 80, 85, 91 and 95 per cent zirconium alloys respectively quenched from 700° C. From this series it is readily apparent that the 71 per cent alloy, which is very close to the eutectoid composition, was quenched from a one phase region while the others which contain two distinct phases were quenched from within the region (C). The relative amounts of the two phases vary with increasing zirconium content. An important change from the structures of the same alloys at room temperature is the absence of a phase which has undergone eutectoid decomposition since quenching from above 640° C. retains this as a single phase.

The same series when quenched from 800° C. (Figs. 45, 46, 47, 48, and 49) show that the 71, 76, 80 and possibly the 85 per cent alloys were one phase at the time of quenching. However, the 91 and 95 per cent alloys appear to have been quenched from a two phase region although the relative amounts of each phase present in the alloys have changed considerably from the amounts present at 700° C. By applying the "lever principle" to estimate the relative amounts of each phase present one can readily explain these changes.

Continuing the quenching experiments on the same series of alloys, all of them indicate the presence of a one phase region (D) in Figure 24 above 900° C. The 80 per cent alloy when quenched from 1100° appears completely one phase (Fig. 50). The 91 and 95 per cent alloys when quenched from 1100° C. show a fine precipitation within the grains (Fig. 51). This appears to the author to have been one phase at the



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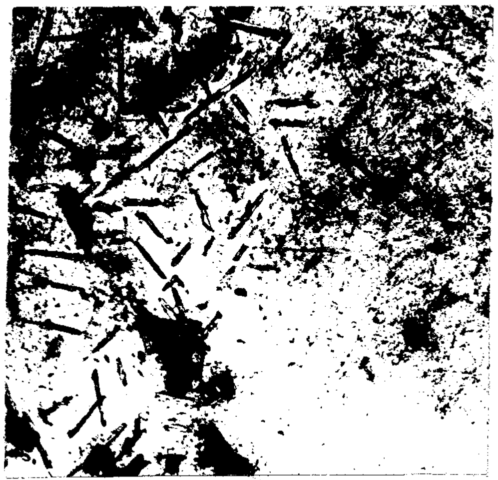

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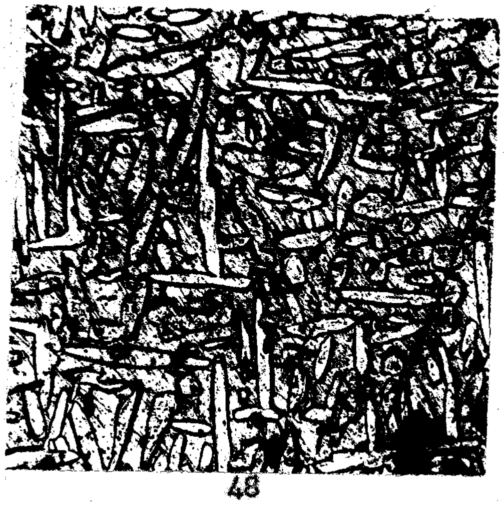

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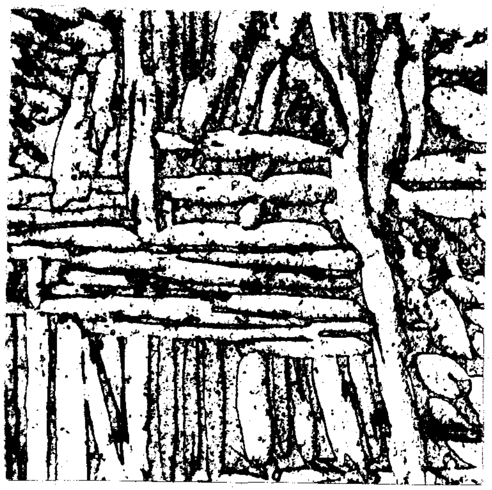
Fig. 45 - 76% zirconium. Quenched from 745°. One phase.

Fig. 46 - 80% zirconium. Quenched from 800°. One phase.

Fig. 47 - 85% zirconium. 800° quench. A few sharp needles of zirconium.

Fig. 48 - 91% zirconium. 800° quench. Two phases in equal amounts.

Samples etched by 1% HF in HNO_3. X 250.



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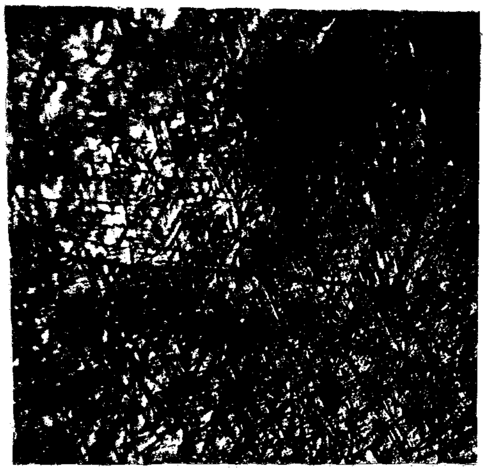

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Fig. 49 - 95% zirconium. Quenched from 900°. Solid solution (dark phase) plus zirconium.

Fig. 50 - 80% zirconium. 1100° quench. One phase.

Fig. 51 - 91% zirconium. 1100° quench. Precipitation within grains.

Samples etched by 1% HF in HNO_3. X 250.

time of quenching as indicated by the appearance of the large grains. The precipitation probably took place within the grains during quenching. Why a one phase appearance of the alloy could be retained on quenching a sample of one composition but could not be in the other is a little hard to explain. Such a phenomena, however, is not new in the field of metallurgy.

From the minimum point at 70 per cent the upper boundary line of the eutectoid region runs in one direction to the zirconium side of the diagram toward the alpha-beta transition point as has been described above. In the other direction the curve rises approximately linearly to a temperature of 900° C. at the composition of 45 per cent from where the line extends horizontally toward the thorium end of the diagram. This curve forms the upper boundary of the two phase region (E) in Figure 24. Samples quenched from within the two phase region have structures almost identical to those of the cast alloys (Figs. 52 and 53). X-ray diffraction patterns of alloys quenched from this region have identified a face-centered cubic thorium phase with a = 5.05 Å as was mentioned previously. No zirconium lines were detected however. It will be recalled that on the 45 per cent alloy which had been cooled slowly a strong zirconium phase appeared in the powder pattern.

According to the equilibrium diagram as constructed no pure zirconium phase should, of course, be present. The two phases which should exist at 700° C. are face-centered cubic thorium containing 5 per cent zirconium in solid solution plus a phase which corresponds to a solid solution of 65 per cent zirconium and 55 per cent thorium. Attempts to examine the nature of this phase have met with little success. The results will be discussed in greater detail a little later.

As higher quenching temperatures are approached the structure of the alloys suddenly changes. Quenching from above the horizontal line at 900° C. reveals the one phase region (F) in Figure 24. A series of quenches made on 19, 30, 37, 50 and 60 per cent zirconium alloys from 900° C. or higher all appear to have been entirely one phase at the time of quenching (Figs. 54, 55, 56, 57 and 58).

The exact significance of the 900° C. horizontal line is not fully understood at this writing. As was explained previously alloys of all compositions lying beneath the curve have similar eutectoid-like structures. While the individual grains of the slowly cooled samples are masked by the laminations, when examined under polarized light the separate grains become plainly visible (Fig. 59). Thus one must conclude that an intergranular precipitation takes place, invariantly, as the 900° C. solid transformation line is crossed.

The thermal data show that the 900° C. cooling curve break is of maximum intensity somewhere in the vicinity of 35 per cent and diminishes in intensity as the composition is shifted in either direction. Thus a solubility maximum or pseudo-compound must exist at this composition.

At 10 per cent the 900° C. break is still quite strong but at 5 and 6.4 per cent the breaks are barely discernible and occur about 50 to 65 degrees higher. Also occurring in the same alloys are small breaks

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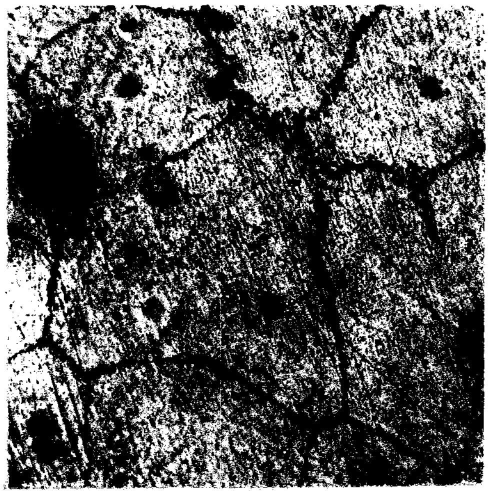

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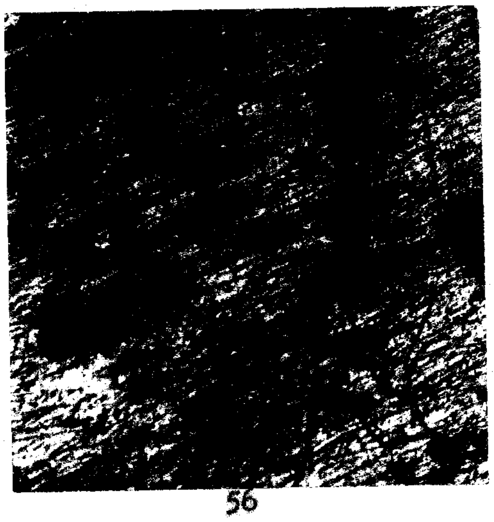
Fig. 52 - 60% zirconium. Quenched from 700°. Eutectoid type structure. HCl plus ethyl alcohol electrolytic etch.

Fig. 53 - 20% zirconium. 700° quench. Eutectoid structure. 10% HF in ethyl alcohol etch.

Fig. 54 - 20% zirconium. 900° quench. One phase. Same etch as above.

Fig. 55 - 30% zirconium. 1100° quench. One phase. Same etch. All X 250.



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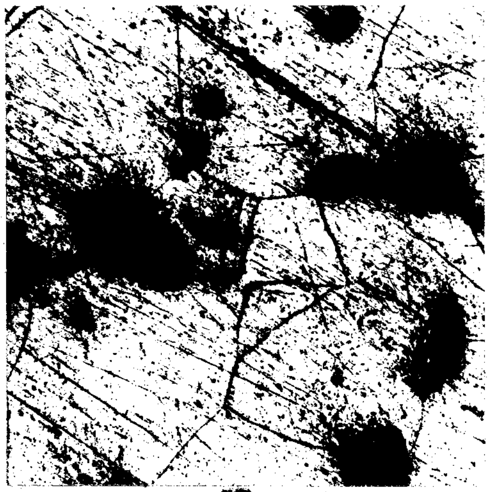

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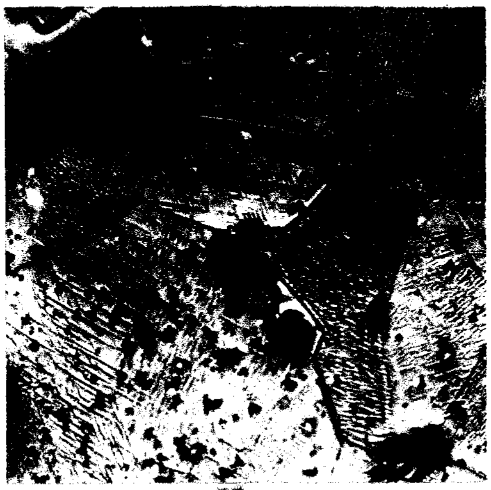

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Fig. 56 - 37% zirconium. One phase. 10% HF in ethyl alcohol etch.

Fig. 57 - 50% zirconium. One phase. Same etch as above.

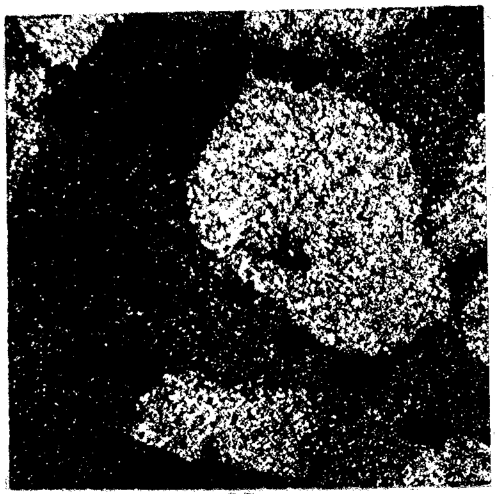
Fig. 58 - 60% zirconium. One phase. HCl in ethyl alcohol electrolytic etch.

Above series quenched from 950° C. X 250.

around 825 to 850° C. which has been interpreted as a change in slope as the lower solidus line is crossed in passing from the one phase region (A) into the two phase region (E).

A series of quenches from 900° C. conducted on 6.4, 10 and 13.4 per cent alloys (Fig. 60, 61 and 62) indicate the presence of a two phase region (G) in this vicinity. The microstructures of the above mentioned quenched alloys change from one phase at 6.4 per cent to two phases at 10 per cent and back to almost one phase at 13.4 per cent zirconium. In order to determine more exactly the boundary limits of the two phase region a series of 950° C. quenches was made (Figs. 63, 64 and 65). A 2.5 per cent alloy shows only one phase but the 6.4 and 10 per cent alloys contain two distinct phases. It is significant to note that the dark phase corresponding to the thorium-rich solid solution is the phase that disappears as the quenching temperature is increased. At 1000° C. the 6.4 per cent alloy still appears to have been quenched from a two phase region whereas the 10 and 13.4 per cent alloys are one phase at that temperature (Figs. 66, 67 and 68). A quench of the 6.4 per cent alloy from 1100° C. (Fig. 69) shows that this is not completely one phase but the thorium-rich phase (the dark region) has almost disappeared. It is on the basis of these microstructures that the two phase region (G) has been postulated.

The exact nature of this area and how it is related to pure thorium remains open to question. The existence of a transformation in thorium somewhere above 1200° C. would seem the simplest and most logical explanation. While no such transition has been formally reported there is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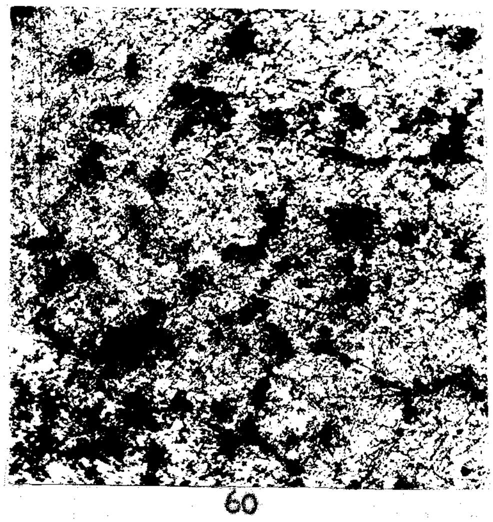
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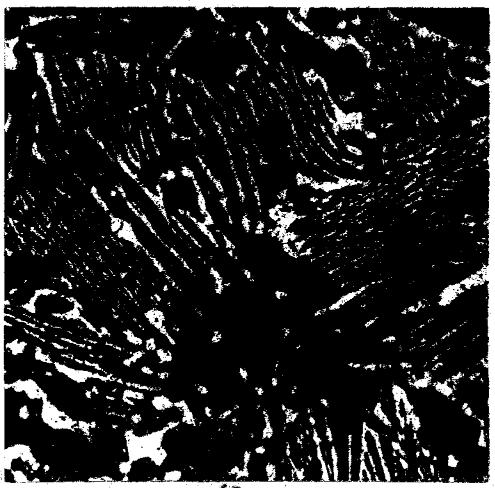
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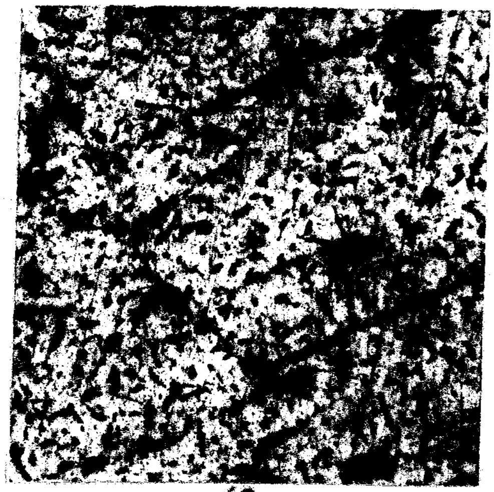
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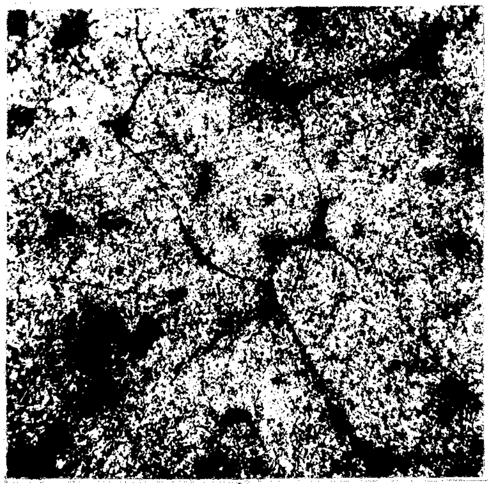
Fig. 59 - 45% zirconium. Slowly cooled. Photomicrograph taken with polarized light. Note distinct grain boundaries. 10% HF in ethyl alcohol etch. X 250.

Fig. 60 - 6.4% zirconium. Quenched from 900° C. One phase (all dark).

Fig. 61 - 10% zirconium. 900° C. quench. Two distinct phases.

Fig. 62 - 13.4% zirconium. 900° C. quench. Nearly one phase (light).

Samples etched by 10% HF in ethyl alcohol. X 250.



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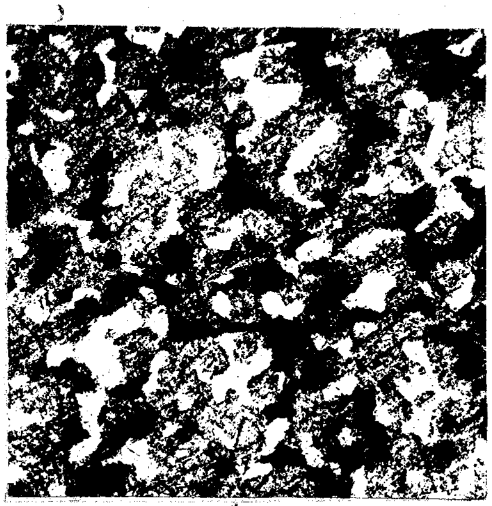

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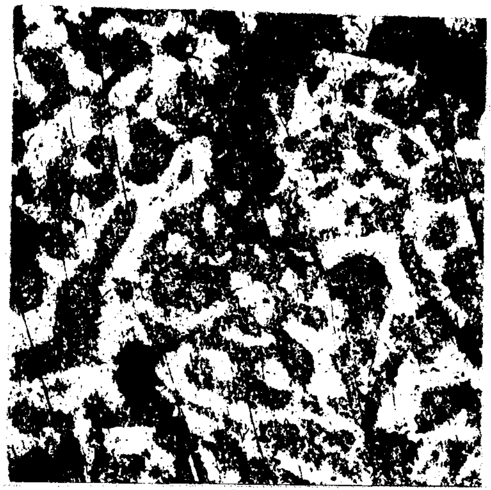

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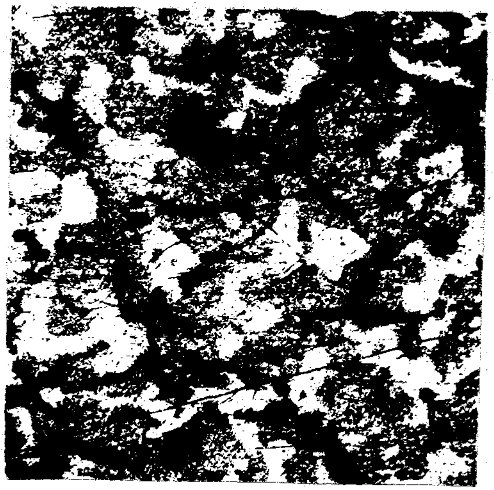
Fig. 63 - 2.5% zirconium. One phase (dark). X 250.

Fig. 64 - 6.4% zirconium. Small amount of light phase appearing. Black areas are impurities. X 100.

Fig. 65 - 10% zirconium. Equal amounts of two phases. X 250.

Above series quenched from 950° C. 10% HF in ethyl alcohol etch.



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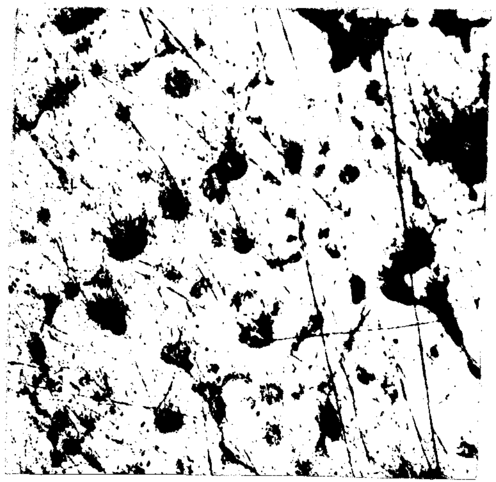

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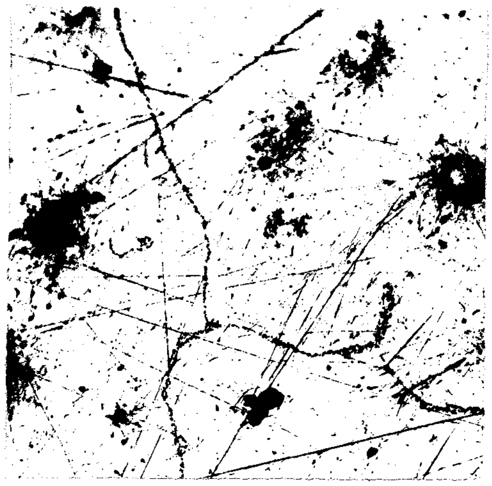

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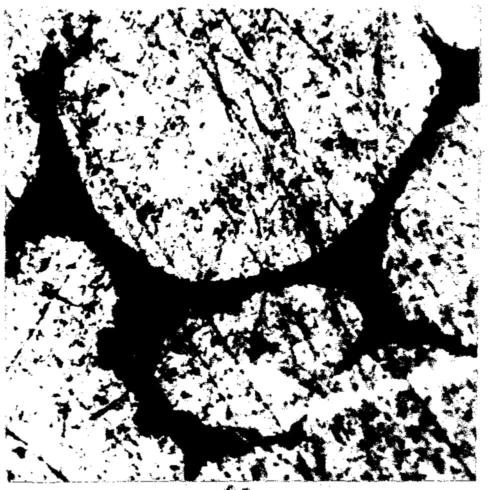

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Fig. 66 - 6.4% zirconium. 1000° C. quench. Two phases plus impurities. X 100.

Fig. 67 - 10% zirconium. 1000° C. quench. Nearly one phase (light).

Fig. 68 - 13.4% zirconium. 1000° C. quench. One phase (light).

Fig. 69 - 6.4% zirconium. 1100° C. quench. Small amount of thorium-rich (dark) phase on background of light phase.

Above samples etched with 10% HF in ethyl alcohol. X 250.

some evidence that one exists. P. Chiotti (17) has found from electrical resistance versus temperature curves that a sharp reproducible change in slope takes place at 1400° C. on both heating and cooling.

Other evidence to support the prediction of the transformation in thorium is found in thermal data taken on cast thorium. A distinct thermal arrest is detected at 1150° to 1175° C. The author carried out a detailed investigation of this break in the expectation of establishing a transformation. From these studies the conclusion was reached that the break was associated with the presence of oxide in the metal which is introduced on casting in amounts up to 0.1 weight per cent. However, the exact nature of the 1175° C. heat effect has never been fully understood. It may result from the formation of a thorium-thorium oxide eutectic or possibly through the lowering of a transformation. Cooling curves on the oxide free metal have failed to show any sharp thermal arrests although examination of heating curves obtained from casting several pound billets of thorium often show a weak break anywhere between 1300 and 1450° C.

One other bit of evidence which must be considered is the fact that the liquidus-solidus curves indicate that a continuous solid solution exists beneath the solidus line as is indicated in Figure 23. Likewise the quenching data support the view that a continuous solid solution exists above 900° C. and beneath the solidus curve.

In order for two metals to form a complete solid solution they must be isomorphous, have similar properties such as melting points and chemical affinities, and the size of the atoms must not differ by more than 15 per cent (18). Thorium and zirconium could not form a continuous solid solution unless they had similar crystal lattices. Zirconium assumes a body-centered cubic configuration above 900° C. while only a face-centered cubic structure of thorium is known. Reasoning from this a body-centered high temperature form of thorium might be predicted.

The author does not contend, however, that another allotropic form of thorium must exist. His position is that if one were to exist it would help resolve certain inconsistencies in this system which are difficult to explain on any other basis.

Quenching from above 900° C. produces still greater distortion of the face-centered thorium lattice. As was shown in Figure 28 the lattice parameter of thorium is decreased to 5.02 Å at 20 per cent zirconium upon quenching from 900° C. signifying greater solid solubility at that temperature. The fact that quenching retains a one phase microstructure without retaining a different crystal structure may appear to contradict the possibility of another crystal modification in thorium. This is not the case. Another allotropic form could exist above 900° C. since quenching need not necessarily prevent the transformation from taking place. Super-saturated alpha thorium would then be present. This type of quenching phenomenom is often observed in alloy systems.

At 30 per cent zirconium the lattice parameter is 5.02 Å as determined from filings taken from the quenched massive alloy. However, with alloys above 30 per cent the crystals apparently become so disordered that only the planes with the lower Miller indices reflect. The scattering at the higher angles and particularly in the back reflection region becomes so breat that only a few lines can be measured with any accuracy. If any confidence can be placed in calculations based on the measurement of five or six lines of a diffraction pattern, the lattice parameter of the face-centered cubic phase shifts suddenly from 5.02 Å at 37 per cent to 4.70 Å at 45 per cent. J. Florio (19) of this laboratory reports this observed change in both 45 and 55 per cent alloys. The shift is so large that it can be explained only by a phase change.

The author has attempted to confirm these results. The metal filings from a 55 per cent alloy were heated in an evacuated and sealed quartz capillary to 950° C. and quenched. From the X-ray diffraction pattern of the quenched powder a face-centered cubic lattice with a = 4.57 Å was identified plus a minor phase corresponding to thorium dioxide.

Since there was some visible evidence that a reaction between the quartz capillary and metal powder had occurred at 950° C., filings from the same 55 per cent alloy were quenched from 800° C. This was still in the one phase region (D) and yet a low enough temperature that the quartz remained unattacked. The predominant phase had a face-centered cubic structure with a = 5.04 Å plus weak phases corresponding to thorium dioxide and zirconium nitride, ZrN.

The possibility that this apparent new phase could be zirconium nitride must be considered. Zirconium has demonstrated its readiness to react with nitrogen and oxygen. The nitride structure is face-centered cubic, the sodium chloride structure, having a lattice constant of 4.61 Å. By comparison of relative intensities of the observed lines with those for the nitride, both the 4.57 and 4.70 phase could be zirconium nitride. It is of course difficult to explain why a nitride phase persists in showing up in the central portion of the system whereas the phase appears only weakly or not at all in the high thorium or high zirconium alloys.

Another observation which has been overlooked up to this point of the discussion is the flat series of points occurring on the solidus at 1350° C. between the compositions 30 and 40 per cent zirconium (see Fig. 24). This may be a normal experimental scattering or a tendency for the curve to flatten out at the minimum. The author has also considered the possibility of a peritectic reaction.

If the phase change described above actually happens, a two phase region must exist between the regions (D) and (F), according to the phase rule. Since quenches have failed to reveal such a two phase region if it exists it must exist as the very narrow region (H) in Figure 24. Such an area would help explain the horizontal series of points in the solidus curve, the apparent shift in lattice constant and the maximum in the intensity of the 900° C. thermal arrest which was observed at about 35 per cent.

The solid solubility of thorium in the room temperature (hexagonal) form of zirconium has also been studied. Microstructures and thermal data place the solubility limit definitely below 5 per cent thorium.

X-ray investigations of the zirconium-rich region showed no change in the zirconium lattice with increasing thorium content. The lattice constants of Bureau of Mines sponge zirconium were determined on the 114.3 mm powder camera as follows:

$a = 3.223 \pm .005$ Å

$c = 3.128 \pm .005$ Å

which are in good agreement with literature values. The lattice constant of the zirconium in the 91 per cent alloy was measured and the lattice constants were identical, within the limits of experimental error, with those of the pure zirconium. The solubility of thorium in alpha zirconium, therefore, is believed to be negligible.

A quench was carried out on the 91 per cent zirconium alloy from 950° C. above the alpha to beta transition in an attempt to retain the beta form of zirconium. The X-ray diffraction pattern of the quenched powder showed that the predominant phase was hexagonal closest packed zirconium with lattice constants identical with pure alpha zirconium. This is in agreement with microscopic evidence since the reader may recall that precipitation within the grains during quenching was observed in this same sample. The lattice constants for the 80 per cent sample quenched from 900° C. (in which a one phase microstructure was retained) showed considerable distortion. The cell dimensions, $a = 3.25$ Å and $c = 5.21$ Å are expanded considerably which could be interpreted as supersaturation alpha zirconium. This presents a consistent, although not entirely satisfactory picture.

It is well to note that not too much reliance should be placed on X-ray methods in estimating the solid solubility in zirconium. Oxygen which is readily introduced upon casting or even upon heat treating distorts the lattice as might also nitrogen.

One additional piece of information which corroborates much of the preceding data is a series of hardness values which are shown graphically in Figure 70. The curve for the quenched sample bears a close resemblance in its general shape to the solid transformation curves of the phase diagram. An extrapolation places a minimum in the curve at about 70 per cent which is close to the eutectoid composition.

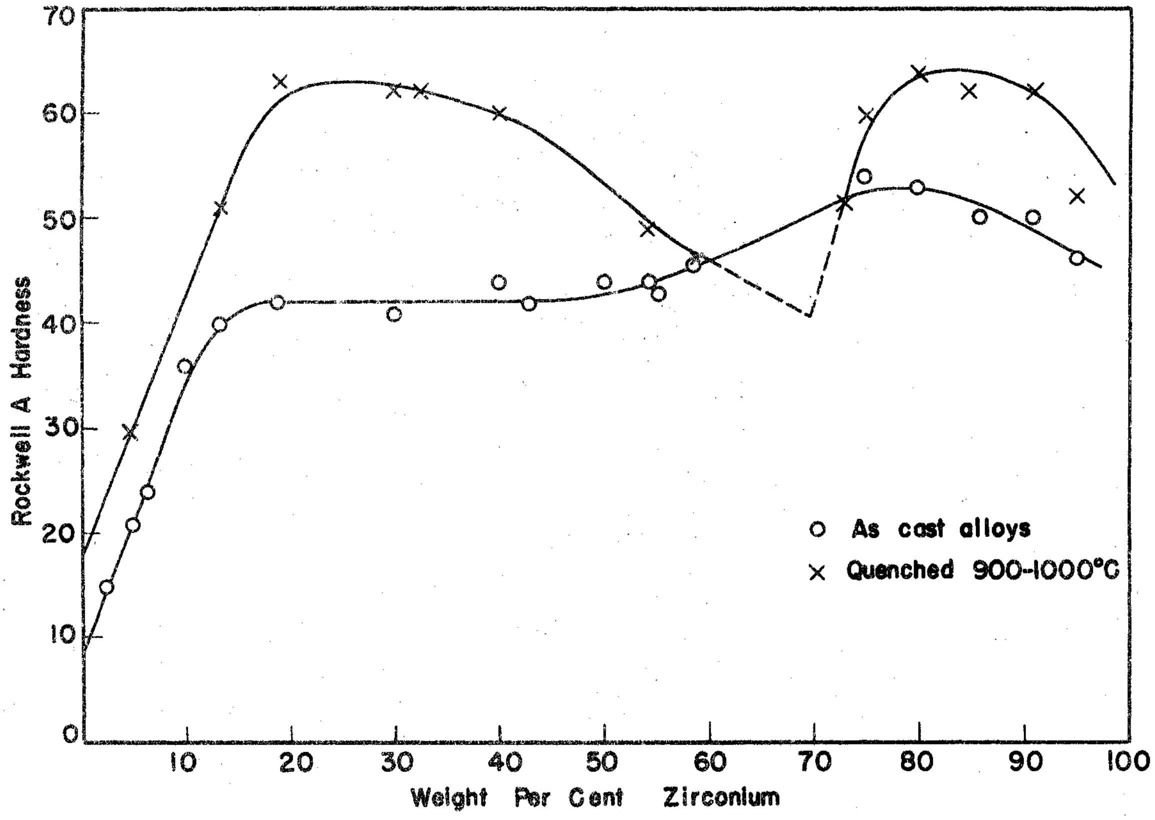

Fig. 70 - Hardness Curves of Thorium - Zirconium System.

C. Uranium - Zirconium System

The author has performed no experimental investigation of this system, since two or three independent studies of this system are now underway and have been intermittently for several years in the various cooperating laboratories of the Atomic Energy Commission.

Kaufmann (20) and co-workers reported in 1944 that the melting point of uranium is raised by the addition of zirconium. The melting point at 20 atomic per cent zirconium was determined to be 1225° C. At higher zirconium compositions, a peritectic was believed to exist at 1250° C. and 40 atomic per cent (21).

The one phase structure that resulted upon quenching 10 and 20 atomic per cent zirconium alloys from 925° C. indicates extensive solubility in gamma uranium. The gamma phase of uranium, however, was not retained upon quenching; instead super-saturated alpha uranium was believed to be present. This observation was based on X-ray diffraction findings. Above 10 atomic per cent zirconium one critical point was found in uranium, this is 710° C.

In 1949 Kaufmann and co-workers (22) reported a body-centered tetragonal phase which was found in 49 and 60 weight per cent zirconium alloys as cast. Upon annealing at 600° followed by a quench the same body-centered tetragonal phase was retained. The same two alloys were then annealed from 700° C. and also 1000° C. for 100 hours and quenched. By this treatment a body-centered cubic phase was retained. The lattice constant for the body-centered cubic phase was $a = 3.56$ Å. This value is intermediate between $a = 3.47$ Å for gamma uranium and 3.61 Å for beta zirconium.

D. Peterson (23) of this laboratory has carried out a detailed study of the system with the intent of establishing the phase diagram. According to his findings gamma uranium and beta zirconium form a continuous series of solid solutions. At 688° C. and a composition of 10 per cent zirconium a eutectoid decomposition has been observed. A lower break at 600° C. which extends horizontally across almost the entire system may also be due to a eutectoid.

Corrosion tests and additional microstudies have been conducted on uranium-zirconium alloys by the University of Chicago Metallurgical group (24) and also the Los Alamos Laboratory (25). One of the results of the tests was the observation that alloys quenched from the gamma region did not corrode nearly as badly (by a factor of ten) as the cast alloys.

At the present writing no phase diagram, complete or incomplete, has been published in the project literature.

III TERNARY ALLOY STUDIES

A. Experimental

The principles and practices applied in the binary studies were also used in the ternary studies. Alloys were prepared by adding the third component to one of the low melting binary mixtures. A master alloy consisting of 30 per cent zirconium in thorium melting at 1300° C. was prepared by co-reduction as described in part II B1. Uranium metal was added to portions of this and the metals were mixed by heating to 1400° to 1500° C. in an induction furnace.

One experimental reduction was tried in an attempt to prepare a ternary alloy of this system by co-reduction. The calculated amounts of the tetrafluorides of zirconium, thorium and uranium were mixed with calcium and a booster. The charge was packed into the bomb and fired. A ninety per cent yield was obtained on a 33.3 weight per cent thorium, 33.3 weight per cent zirconium and 33.3 weight per cent uranium alloy. The alloy was recast to remove any excess calcium.

Straight time versus temperature cooling curves were run on all of the samples. Heating was done in the Kanthal furnace described previously (Fig. 1) and a chromel-alumel thermocouple was used to measure temperature.

B. Results

One of the principle objectives of this investigation was to determine whether a ternary minimum occurs in the liquidus surface and if so its approximate composition. Janecke (26) in a detailed discussion of ternary and quaternary eutectics describes a method of locating such a minimum if all the binary eutectic compositions are known. Consider a triangular plot of the system in which the three binary minimum points are located on the sides of the equilateral triangle. The straight lines connecting these minima will enclose a smaller triangular area. Somewhere within this area the ternary minimum is located.

Since only two of the binary systems concerned here have eutectics or minima in the liquidus curves a direct application of this principle is impossible; but a valley extending almost linearly from one minimum to the other would be a logical prediction. With this picture in mind a series of alloys, whose compositions fall near the predicted valley, were prepared and their melting points determined by cooling curves. The thermal data recorded in Table 6 are insufficient for any definite conclusions to be drawn.

Table 6

Thermal Data for Ternary Alloys

Sample	Composition wt%U	wt%Th	wt%Zr	Solidus-liquidus °C.	Transformations °C.
1	90.0	4.25	3.86	1155-1123	671
2	11.0	61.4	27.6	1260,1150	928, 534,469,414
3	28.6	49.8	21.4	1235,1150	1010 602
4	16.9	58.1	25.0	1257,1150	967 553,464
5	33.3	33.3	33.3	1204,1084	1013,626,555,466,414

No distinct or pronounced liquidus minimum is apparent from the limited information presented here. The large number of solid transformation breaks indicate that this portion of the diagram is extremely complex and would require an extensive investigation before very much could be said about it.

IV. SUMMARY

The uranium-thorium-zirconium ternary alloy system has been investigated by thermal, microscopic and X-ray methods. The uranium-thorium binary system has been studied and a constitutional diagram proposed. There is a eutectic at 1086° C. and 3 weight per cent thorium. A region of liquid immiscibility exists above 1375° C. between the compositions 8 weight per cent and 72 weight per cent thorium. The boundary of the two liquid areas has been partially established with the upper limit believed to be about 1700° C. No intermetallic compounds or solid solubility have been observed.

The thorium-zirconium binary system has also been investigated and a phase diagram, likewise, has been proposed. A minimum in the solidus-liquidus curves has been found at about 1275° C. and 25 weight per cent zirconium. The solid solubility of zirconium in thorium at room temperature is approximately 5 weight per cent, but the solid solubility of thorium in alpha zirconium appears to be negligible. Above 900° C. in the beta zirconium region the solid solubility is extensive. Much of the data indicate a continuous solid solution region lying beneath the solidus curve. There is a eutectoid at 70 weight per cent zirconium and 645° C. There are no compounds which are stable at room temperature.

The literature of the uranium-zirconium system has been reviewed. Beta zirconium and gamma uranium are reported to exhibit extensive solid solubility in one another. Present investigations indicate that a eutectoid point exists at 687° C. and approximately 10 weight per cent zirconium.

A preliminary survey of the ternary system has failed to reveal a minimum in the liquidus of the three component system.

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