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PHASE STUDIES IN THE URANIUM-HAFNIUM SYSTEM

by

Donald Joseph Beerntsen

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.

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I. INTRODUCTION

The investigation of the uranium-hafnium alloy system was undertaken to establish the binary equilibrium phase diagram. The metallurgy of uranium is important and basic to the whole atomic energy program since either uranium or plutonium, which is made from uranium, is used in every nuclear reactor. Interest in the alloying properties of uranium has been enhanced by the fact that the metal has poor aqueous corrosion resistance, is subject to dimensional changes during thermal cycling and exposure in nuclear reactors and has low strength at high temperatures.

A further point of interest was the fact that hafnium and zirconium, which are usually very similar in their chemical and metallurgical properties, form quite dissimilar systems with thorium (1, 2). This study presented an opportunity to determine whether the complete high temperature solid solution and the low temperature intermediate phase found in the uranium-zirconium system also occur in uranium-hafnium alloys.

Metallic uranium exists in three allotropic modifications between room temperature and its melting point. Duwez (3) has summarized the results reported by six different investigators for the temperatures of these transformations. The averaged values are 662°C . for the alpha to beta transformation and 772°C . for the beta to gamma transformation.

Klepfer and Chiotti (4) report $662 \pm 3^{\circ}\text{C}$. and $774 \pm 4^{\circ}\text{C}$. in excellent agreement with these averages. The melting point as determined by Dahl and Cleaves (5) is $1132 \pm 1^{\circ}\text{C}$.

The structure of the alpha phase was first determined by Jacob and Warren (6) in 1937. It is orthorhombic with four atoms per unit cell. The lattice constants of this phase have been examined as a function of temperature by Bridge et al. (7) and Klepfer and Chiotti (4). The room temperature values are $a = 2.854 \text{ \AA}$., $b = 5.868 \text{ \AA}$. and $c = 4.956 \text{ \AA}$. In alpha uranium there are two groups of interatomic distances of about 2.8 and 3.3 \AA . (6). The structure may be regarded as being composed of corrugated sheets of atoms. In these sheets the atoms are tightly bound as indicated by four neighbors at approximately 2.8 \AA . The bonding between the sheets is much weaker as indicated by interatomic distances of 3.3 \AA . The anisotropic nature of the atomic arrangement in alpha uranium suggests appreciable covalent bonding analogous to that occurring in arsenic, antimony and bismuth (8). The bonding cannot be explained in terms of covalent bonding utilizing the simple atomic orbitals directly as in the case of arsenic, antimony and bismuth. By hybridization of available atomic orbitals, equivalent, covalent bond orbitals can be formed which are directed to the corners of a trigonal bipyramid. There is a close similarity between the alpha uranium atomic arrangement and this configuration (8, 9).

The beta form of uranium is a complex tetragonal struc-

ture containing 30 atoms per unit cell and is stable between 662°C. and 772°C. The lattice constants are $a = 10.759$ A. and $c = 5.656$ A. (4, 10). The exact space group and precise atomic positions have been the subjects of considerable debate, the status of which has been discussed by Tucker et al. (11).

The high temperature, gamma modification of uranium was established as body-centered cubic with two atoms per unit cell by Wilson and Rundle (12). The lattice constant at 800°C. is 3.534 A. (4).

Hafnium occupies a close-packed hexagonal lattice at room temperature. The lattice constants are $a = 3.197$ A. and $c = 5.057$ A. (2, 13, 14, 15). At high temperature, hafnium transforms to a body-centered cubic lattice for which Duwez (16) has determined an approximate lattice constant of 3.50 A. He obtained this value by extrapolating the lattice constant versus atomic percent columbium curve for a series of columbium-hafnium alloys to zero percent columbium. The alpha-beta transformation temperature of hafnium has been reported as $1310 \pm 10^\circ\text{C}$. (16), as 1735°C . (2) and $1950 \pm 100^\circ\text{C}$. (14). Values given for the melting point include $2130 \pm 15^\circ\text{C}$. (15), 2150°C . (13) and $2222 \pm 30^\circ\text{C}$. (17).

Hume-Rothery and Raynor (18) have demonstrated that extensive solid solubility between metals is possible only when the difference in their atomic radii is less than 15 percent

and their electronegativities are similar. Large differences in electronegativity usually restrict solid solubility by the formation of stable intermediate phases. Complete solubility is possible only if the terminal structures are the same.

When discussing solid solubilities and atomic radii involving uranium, it is best to distinguish between uranium as the solvent and as the solute. Solute atoms in the alpha uranium lattice must occupy a position which is 2.76 Å. in its smallest dimension. Thus the most favorable solute radius for alpha uranium would be 1.38 Å. Since the exact atomic arrangement of beta uranium is not known, it is difficult to determine what radius should be used for it.

For the body-centered cubic gamma structure, it is simple to calculate an atomic radius from the closest approach of atoms. This value is 1.53 Å. at 800° C. The gamma uranium lattice constant extrapolated to 25° C. is 3.47 Å. (4) from which an atomic radius of 1.50 Å. can be calculated for room temperature. The volume per atom calculated from the extrapolated lattice constant is less than one percent larger than that calculated from the alpha uranium lattice constants at 25° C. It therefore seems reasonable to use a value of about 1.50 Å. for the atomic radius of uranium as a solute atom for either gamma or alpha as the saturating phase. Valences of approximately four, five and six have been suggested for the

alpha, beta and gamma uranium modifications, respectively (19). Haissinsky (20) gives 1.3 as the electronegativity of uranium.

The atomic radius of hafnium calculated from the hexagonal lattice constants at room temperature is 1.56 Å. Using 3.50 Å. as the lattice constant for the body-centered cubic form of hafnium, an atomic radius of 1.52 Å. is obtained. A valence of four is usually attributed to hafnium (19) and Haissinsky (20) reports its electronegativity as approximately 1.3.

The crystal structure of alpha uranium is unique among metals. Since it is characterized by a considerable degree of covalent character, it is to be expected that the formation of solid solutions will be restricted even though the atomic size and valence of solute atoms are favorable. Based on the assumption that alpha uranium has a valence of about four, it might be expected that the quadrivalent elements such as titanium, zirconium and hafnium would stabilize the alpha phase relative to beta. This has been observed experimentally with titanium (21) and zirconium (22). Although these elements have a favorable size factor and similar electronegativities as well as the same valence, their maximum solubility in alpha uranium is less than two atomic percent. For all other elements for which information is available,

with one exception, solubility in alpha uranium is reported as negligible, limited or less than 1.5 atomic percent. Accurate measurement of the solid solubility in uranium is complicated because of the inclusions normally present in uranium and because measurement of the alpha uranium lattice parameters to high precision is difficult. In many cases the solubility may be considerably below the limit which has been reported.

The exception to the rule of low solubility in alpha uranium is plutonium for which a maximum solubility of about 15 atomic percent has been reported (22). Between room temperature and its melting point at 640°C ., plutonium has six allotropic modifications of varying complexity (23). The density over this range varies irregularly from 19.7 to 16.5 so that the volume per atom is in the same range as that of uranium. The atomic radius at 520°C . of the body-centered cubic epsilon phase, stable from 510°C . to the melting point, is 1.58 Å. This is 14.5 percent larger than half the distance of closest approach of atoms in alpha uranium and on the basis of the size factor, assuming a spherical plutonium atom, extensive solubility would not be expected. Probably the main reason for the high solubility of plutonium in alpha uranium is the similarity of their electronic structures. This similarity probably allows plutonium to participate in covalent bonding in much the same manner as uranium.

The complex tetragonal structure of beta uranium is also unique among pure metals. The hardness and low ductility suggest that this structure has some degree of nonmetallic bonding. Only very limited solubilities in beta uranium have been observed with the exception of plutonium for which a solubility of 20 atomic percent has been reported (22). Some elements showing solubilities of the order of one to three atomic percent are Cr, Au, Mo, Ni, Nb, Si, Ti, V, and Zr (22). With the exception of the Group IV A metals, solubility in beta uranium is greater than that in alpha uranium with the result that the alpha to beta transformation is either unchanged or slightly lowered.

The only elements which show appreciable solubility in the body-centered cubic gamma modification of uranium are those of Groups IV A, V A, VI A and plutonium. These are all elements which, on the basis of size, crystal structure, and valence, would be expected to form extensive solid solutions with gamma uranium. Of these, titanium (21), zirconium (22, 24), columbium (25), and plutonium (22) are soluble in all proportions. Molybdenum (26, 27, 28), vanadium (29) and chromium (30) are soluble to the extent of 40, 12 and 4 atomic percent respectively. Tantalum (31) which usually shows marked similarity to columbium in its chemical and metallurgical properties is soluble to only a very limited extent.

Tungsten (31) which is normally much like molybdenum also has very low solubility.

The solid solutions in the titanium, zirconium, molybdenum and plutonium systems transform on cooling to intermediate phases with rather broad composition limits. The plutonium system has two intermediate phases with unusually broad composition limits. The delta phase extends from 26-75 atomic percent plutonium and is stable up to about 590°C. It has a primitive tetragonal lattice with lattice constants $a = 10.57$ A. and $c = 10.76$ A. (22). The epsilon phase, stable between about 270°C. and 720°C. extends from 30-98 atomic percent plutonium. It is primitive cubic with a lattice constant equal to 10.664 A. (22). The structure of these phases has not been reported.

In the molybdenum system, recent work indicates that the intermediate phase is an ordered body-centered tetragonal structure of the M_3S_{12} type with lattice constants $a = 3.427$ A. and $c = 9.834$ A. (32). The intermediate phases in the titanium and zirconium systems have primitive hexagonal structures of the AlB_2 type with compositions around TiU_2 and UZr_2 . The TiU_2 phase is completely ordered (33) and the UZr_2 phase is either completely disordered or only slightly ordered (34, 35). Of course under conditions of complete equilibrium UZr_2 may also be found to be completely ordered. The lattice con-

stants of TiU_2 are $a = 4.828 \text{ \AA}$. and $c = 2.847 \text{ \AA}$. (33). Those reported for UZr_2 are $a = 5.03 \text{ \AA}$. and $c = 3.08 \text{ \AA}$. (34). Other uranium compounds having the AlB_2 structure are UHg_2 (36) and beta USi_2 (37). These do not form from solid solutions.

It is interesting that of the three intermediate phases, the two with the highest uranium content, MoU_2 and TiU_2 , are the ordered ones. They are layer structures in which each uranium atom has a group of uranium atoms as nearest neighbors at about 2.8 \AA . and a group of unlike atoms as second nearest neighbors at $3.0\text{-}3.1 \text{ \AA}$. The analogy with the alpha uranium structure is immediately apparent.

The delta phase of the uranium-zirconium system has been observed to be very sensitive to the oxygen concentration of the alloys. Saller et al. (38) have demonstrated that small quantities of oxygen decrease the activity of alpha zirconium so that the intermediate phase does not form at all. This is probably the reason a number of investigators had difficulty in forming the phase and came to the conclusion that it was not an equilibrium structure.

II. EXPERIMENTAL

A. Preparation of Alloys

The alloys for this investigation were prepared from biscuit uranium and crystal bar hafnium. Each metal was analyzed qualitatively by spectrographic methods and impurities which appeared to be present to a significant extent were determined quantitatively. The analytical results are given in Table 1.

Table 1. Analysis of biscuit uranium and crystal bar hafnium

Impurity	Composition (ppm)	
	Biscuit uranium	Crystal bar hafnium
C	90	190
O	16	208
N	58	210
Fe	50	660
Zr	--	300

All of the alloys were prepared by arc-melting under an atmosphere of purified helium. In the arc-melting furnace, a D.C. arc was struck between a tungsten electrode and the sample which was resting in a water-cooled copper crucible. To insure homogeneity, the alloys were melted six times. After each melting, the metal button was turned over and placed against the edge of the crucible so that on subsequent melting

the metal would run down into the crucible and be mixed well. Analysis of the alloy buttons indicated that only about 13 ppm of copper were introduced in the melting operation.

All alloys used for thermal analysis or metallographic examinations below 1000°C . were homogenized for 48 hours at 1075°C - 1100°C . This was done under argon in tantalum crucibles encased in stainless steel. Samples used for experiments above 1000°C . were homogenized individually prior to the heat treatment to be given. This involved heating for a short time in the region of complete solid solubility. As a check on the homogeneity of the as-prepared alloys, samples were taken from opposite sides of the arc-melted buttons and analyzed for uranium and hafnium. The values listed in Table 2 are the averaged analyses of these samples. The average deviation of a particular analysis from the overall alloy average was 3.5 percent of the amount present.

B. Chemical Analysis

The uranium and hafnium used for this investigation were analyzed quantitatively for carbon, oxygen, nitrogen, and iron and in addition the crystal bar hafnium was analyzed spectrographically for zirconium. Spectrographic analysis indicated that the uranium was as pure as the standard with which it was compared. Since conventional spectrographic

techniques do not detect carbon, nitrogen, and oxygen, these elements plus iron were determined by chemical means.

The samples analyzed for uranium and hafnium were single pieces which were dissolved in a mixture of nitric acid and hydrofluoric acid. These acids were then removed by adding sulfuric acid and evaporating almost to dryness. The solution was cooled and diluted with water in a volumetric flask.

An aliquot of this solution containing 0.1-0.3 grams of uranium was made three normal in hydrochloric acid and passed through a lead reductor into a flask containing an excess of ferric chloride. The lead reduced the uranium to a quadrivalent species which was oxidized to the hexavalent state by ferric ion. The resulting ferrous ion was titrated with ceric sulfate using ferroin indicator to complete the uranium determination.

For the determination of hafnium, an aliquot containing 0.1-0.2 grams of hafnium was taken. This was evaporated to dryness to remove sulfuric acid, which causes low results if present in more than small amounts. Ten ml. of concentrated hydrochloric acid were added and the solution was diluted to 100 ml. After the addition of 30 grams of mandelic acid, this solution was heated to boiling for 30 minutes. The precipitate was filtered, ignited and finally weighed as hafnium dioxide.

Table 2. Alloys prepared and their chemical analysis

Alloy No.	Nominal composition	Chemical analysis	
	(at. % Hf)	(at. % Hf)	(at. % U)
DJB-3-14	0.27	0.24	-
DJB-3-9	0.56	0.47	-
DJB-3-15	1.00	0.80	-
DJB-3-10	1.50	1.17	-
DJB-3-16	2.26	2.02	-
DJB-3-11	3.10	2.99	-
DJB-3-17	4.30	3.92	-
DJB-3-12	6.08	6.37	-
DJB-3-13	9.07	9.57	-
DJB-3-1	13.0	13.70	89.29
DJB-3-2	24.7	23.83	75.31
DJB-3-3	36.2	-	66.45
DJB-0-1 ^a	37.7	-	-
DJB-0-2 ^b	37.0	-	-
DJB-3-4	52.5	52.87	48.20
DJB-3-19	59.0	58.00	40.58
DJB-3-20	65.2	64.53	32.78
DJB-3-5	72.5	72.35	27.80
DJB-3-6	92.9	-	7.64
DJB-3-18	94.4	-	6.30
DJB-3-7	97.1	-	2.30
DJB-3-8	98.4	-	1.98
DJB-3-21	99.2	-	0.63
DJB-3-22	99.6	-	0.30

^aAlloy also contained 0.19 at. % oxygen added as U_3O_8 .

^bAlloy also contained 0.44 at. % oxygen added as U_3O_8 .

The amount of iron was determined by a colorimetric method using 1,10 phenanthroline. The sample was dissolved in hydrofluoric acid in a platinum dish and fumed with sulfuric acid for one-half hour to remove all the fluoride ion. The solution was diluted to volume, an aliquot was taken and the iron reduced to ferrous iron by hydroxylamine hydrochloride. The 1,10 phenanthroline reagent and a solution of tartaric acid were added and the pH raised to 5-7 with ammonium hydroxide. The light absorbance at 510 millimicrons was determined with a Beckman Model DU spectrophotometer. The amount of iron was determined from a standard curve. A portion of the original solution was used as a reference solution since uranium forms colored solutions which would otherwise interfere in the determination.

The determination of nitrogen was done by a modified micro Kjeldahl method. The sample was dissolved in hydrofluoric acid and fumed with sulfuric acid. The standard micro Kjeldahl procedure was then followed to complete the analysis.

The standard combustion method of determining carbon was used. The determination was done by burning the sample in oxygen, absorbing the carbon dioxide in an ascarite tube and observing the gain in weight. The uranium samples were small bars while the hafnium sample was a coarse powder.

Oxygen was determined by the vacuum fusion method. The same procedure was used for uranium, hafnium and the alloys which were analyzed. Samples were dropped into a carbon-saturated platinum bath at about 1900°C. The samples dissolved in this bath and any oxides were reduced and carbon monoxide was evolved. The evolved gas, which contained nitrogen and hydrogen in addition to carbon monoxide, was collected in a known volume where the pressure was measured. Then, by oxidation and selective condensation of the resulting gases, the amount of carbon monoxide in the original gas mixture was determined.

C. Thermal Analysis

Thermal analysis studies were made on uranium and uranium-hafnium alloys between room temperature and 900°C. with the differential controlled thermal analysis apparatus shown in Fig. 1. The samples used for these measurements consisted of two pieces of alloy measuring approximately 1 x 1/4 x 1/8 inches. These were notched lengthwise so that a butt-welded thermocouple junction, protected by thermocouple insulation, could be inserted between them. Short lengths of thermocouple insulation were used to separate the sample from the short sections of wire used to bind the pieces of alloy in position over the thermocouple junction. This arrangement plus appropriate radiation shields was heated under vacuum in

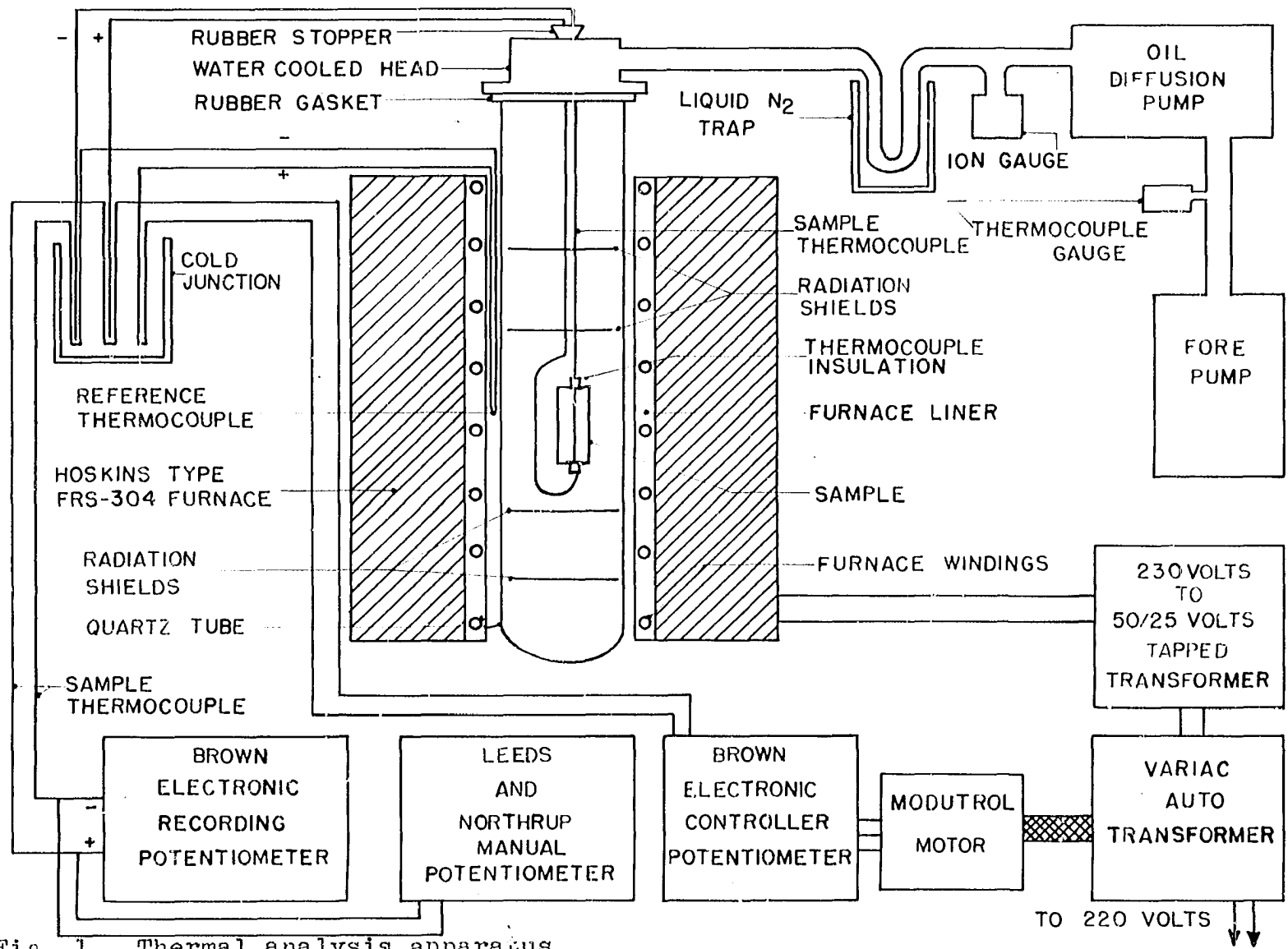


Fig. 1. Thermal analysis apparatus.

a 1-3/4 inch O.D. quartz tube by a Hoskins Type FHS-304 resistance tube furnace. A reference thermocouple was placed between the furnace liner and the quartz tube at the vertical position of the sample. The cold junctions of both thermocouples were placed in glass tubes containing mercury in an ice bath. The E.M.F. from the sample thermocouple was recorded by a Brown Electronik recording potentiometer. This instrument was checked at critical points with a Leeds and Northrup No. 8657-C manual potentiometer. The negative lead of the reference thermocouple was connected to the negative lead of the sample thermocouple. The reference thermocouple positive lead and the sample thermocouple positive lead were connected to a Brown Electronik controller potentiometer which maintained a constant temperature difference by regulating the power to the furnace. By thus maintaining a constant temperature difference between the furnace and the sample, it was possible to obtain quite constant rates of heating and sharper thermal arrests than by heating without control.

The thermocouples were made of 22 gauge chromel and alumel thermocouple wire. Thermocouples from this lot of wire were standardized against a U. S. Bureau of Standards aluminum sample and against a sample of coulometer grade silver using U. S. Bureau of Standards procedures as outlined by Roeser and Wensel (39). The thermocouples consistently agreed at

both these temperatures with the E.M.F. values given in the table for chromelalumel thermocouples in the National Bureau of Standards Circular 561.

A Distillation Products, Inc. Type VMF-20-04 oil diffusion pump and a Welch Duo-Seal Type 1400-B mechanical pump were used to evacuate the system. Pressures were measured by a Type 507 ionization gauge and a Type 501 thermocouple gauge, both manufactured by National Research Corporation. The pressure was usually between 5×10^{-4} and 1×10^{-5} mm. of Hg throughout a thermal analysis run.

D. Microscopic Examination

1. Heat treatment of alloys

The samples which were heat treated at temperatures below 900°C . were enclosed in quartz capsules to protect them from oxidation. Three to eight samples were prepared at one time in a quartz tube such as is shown in Fig. 2. Approximately one inch square pieces of 0.005 inch tantalum foil were folded around 0.5-2.0 gram samples and the corners were spot-welded together. These were placed around a thermocouple well in the closed end of a 25 mm. diameter quartz tube. Zirconium turnings resting on a stainless steel screen were next inserted into the quartz tube which was then drawn down so that an eight mm. diameter tube could be attached. This

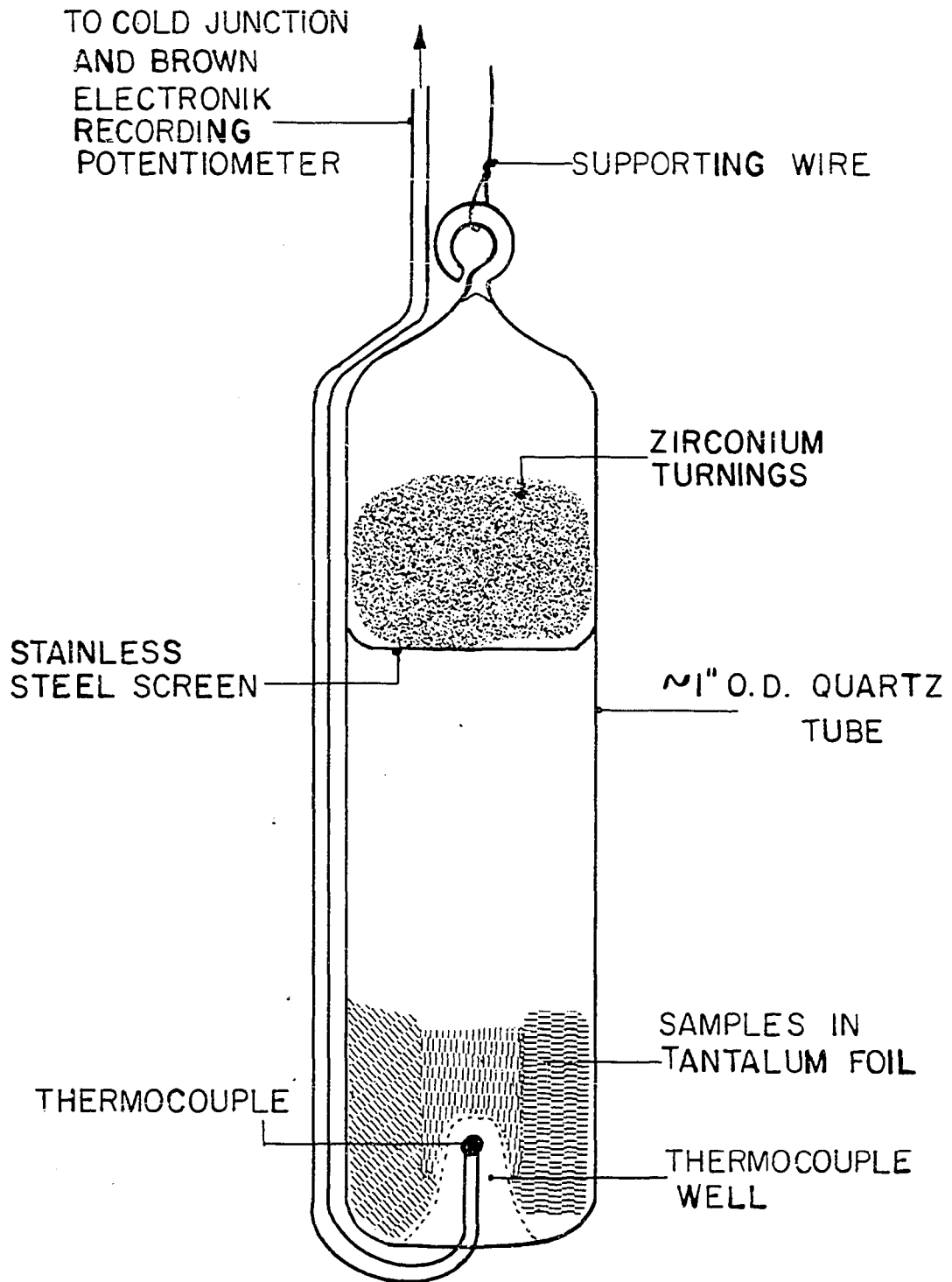


Fig. 2. Quartz sample preparation capsule.

tube was used to evacuate the quartz tube and fill it with argon before being sealed off. The region of the tube containing the zirconium turnings was heated to get rid of any remaining reactive gases.

The heating, recording and controlling devices shown in Fig. 1 were used except that the sample thermocouple E.M.F. actuated the controller as well as the recorder. The vacuum system was not used and the ends of the furnace were closed with fitted blocks of firebrick. The samples were heated at 850-900°C. for 1/2-16 hours depending on the composition - samples of high hafnium content were heated for longer times - and the temperature was then lowered to that from which the samples were to be quenched. The samples were held at temperature for 24-72 hours. The temperature was constant to about $\pm 2^{\circ}\text{C}$. To quench the samples, the bottom firebrick was removed from the furnace, the quartz tube support wire was cut and the tube was caught on a wire screen held over a bucket of water. The tube was quickly broken with a hammer and the samples immersed in the water.

A few uranium-rich samples were heat treated in a thermal gradient so that the quenched sample contained microstructures representative of all the phase fields within the temperature range produced in the sample. This was very useful in locating phase boundaries and small phase fields. The sample

and thermocouple arrangement is shown in Fig. 3. The samples, approximately $1 \times 1/4 \times 1/8$ inches, had a thermocouple pressed firmly against each end and were held in position against the insulation of the lower thermocouple by wires.

Each sample was heated at 800° - 900° C. for 1/2-1 hour before the temperature was lowered to the desired range. The gradients, which varied from 16° - 47° C., were established by partially withdrawing the quartz tube containing the sample assembly from the furnace. The furnace was controlled to maintain the hot end of the bar at a constant temperature. The rubber stopper was removed from the quartz tube and the sample assembly was plunged quickly into cold water to quench the sample. Since the temperature gradients were not large, the temperature was assumed to vary linearly along the sample length.

Samples to be heat treated above 900° C. could not be protected in quartz capsules and were heated in a resistance tube furnace and quenched with a blast of room temperature helium. The furnace is shown in Fig. 4. A three inch long, one-half inch diameter, seamless tube of 0.015 inch tantalum served as a resistance element. A Superior Electric Co. Stabiline Voltage Regulator Type 1E55205 was used to provide a constant voltage which was controlled by an autotransformer and was stepped down to 12 volts with a water cooled trans-

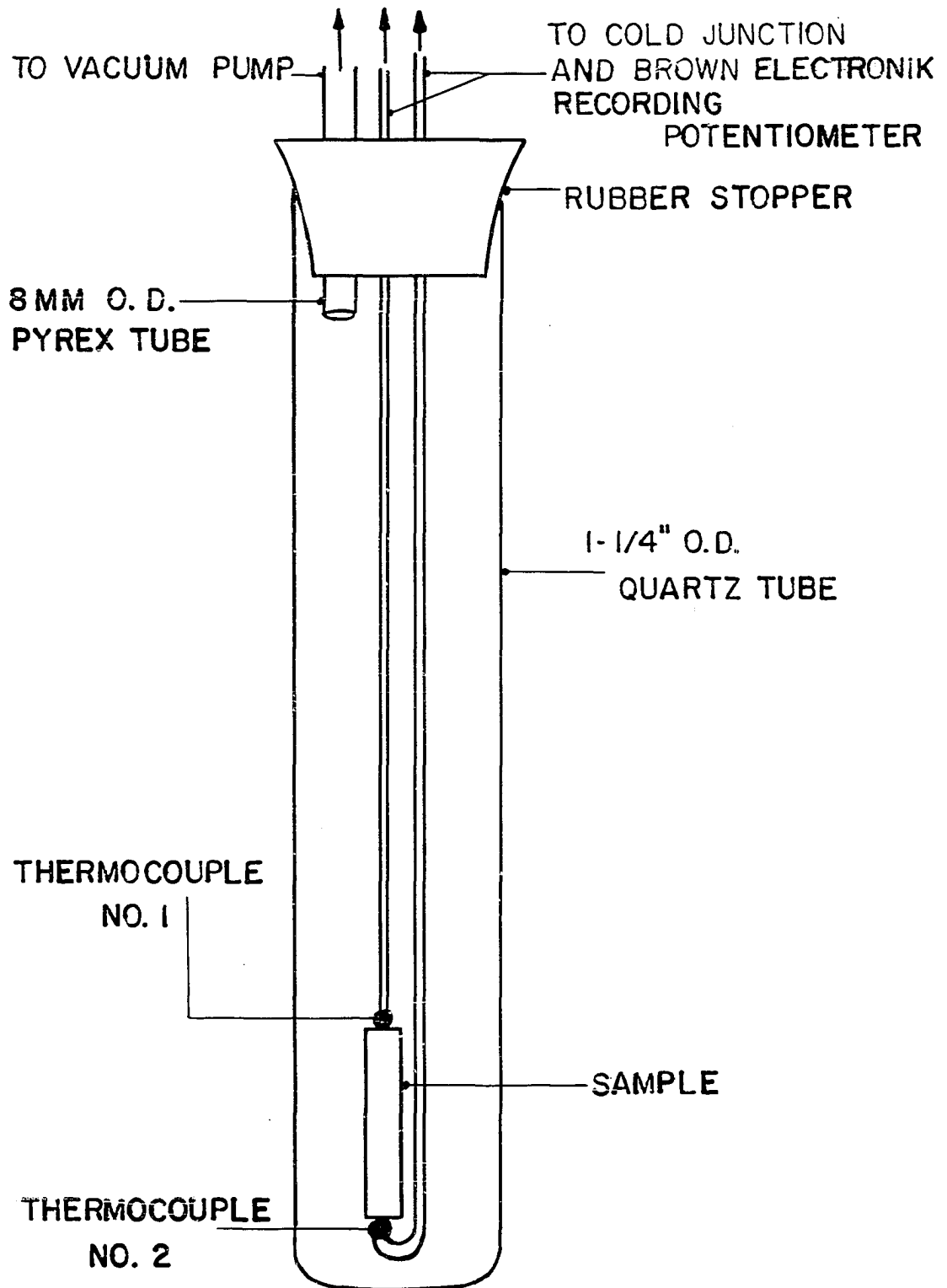


Fig. 3. Thermal gradient sample preparation tube.

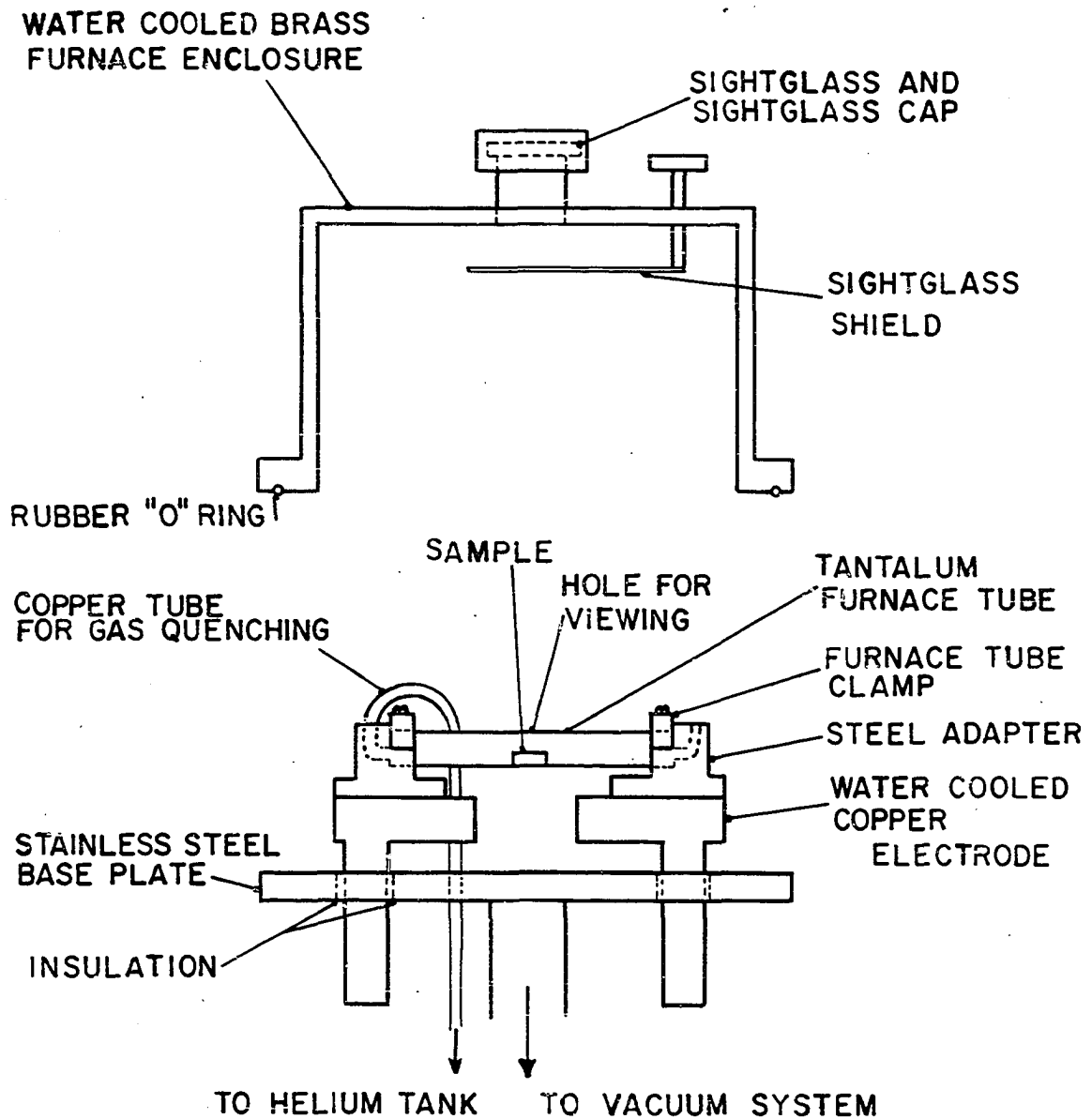


Fig. 4. High temperature tantalum tube vacuum furnace.

former. The furnace system was evacuated with a Distillation Products, Inc. Type MC-500-06 oil diffusion pump backed by a Kenney Model KC-15 mechanical pump. Pressures, which were measured with a Miller Laboratories Type 100-A cold cathode vacuum gauge, were kept below 5×10^{-5} mm. of Hg. The samples, which were about $3/16 \times 3/16 \times 1/16$ inches, rested on a small grid of tungsten wire to prevent reaction with the tantalum tube. The sample temperature was measured by a Leeds and Northrup optical pyrometer Type 8622-C. The samples were viewed through a one mm. diameter hole in the wall of the tantalum tube. The furnace tube was a black-body cavity and the temperature measurements were corrected only for the absorption of the sightglass.

For the quenching operation, the vacuum system was first isolated from the furnace chamber. Then the power to the furnace was shut off and simultaneously a valve was opened which allowed helium at 40-50 psi pressure to rush into the furnace tube. Helium was allowed to flow for about five seconds until the sample had cooled to room temperature.

2. Polishing

All samples for microscopic examination were mounted in bakelite and ground on silicon carbide paper through 500 grit. The samples were polished on a Metcloth-covered wheel using

400 grit silicon carbide powder in water and then on a wheel covered with Microcloth using Linde A polishing compound in water. For alloys containing greater than 50 atomic percent hafnium alternate etching, and repolishing with Linde A were necessary for good results.

3. Etching

The etching methods used to reveal the microstructure varied considerably with the composition of the alloys. Electrolytic etching with an electrolyte consisting of equal parts by volume of ethylene glycol, ethyl alcohol and orthophosphoric acid was satisfactory for alloys containing less than 30 atomic percent hafnium. Current densities of 30-200 ma./cm.² were used for 20 seconds to three minutes. The current density and time necessary for good results varied with the heat treatment and composition and had to be determined for each sample.

For alloys containing more than 30 atomic percent hafnium, chemical etching methods were used. For alloys containing 30-90 percent hafnium, the etching reagent consisted of two parts water and one part nitric acid, saturated with sodium fluosilicate and sodium tartrate. More nitric acid was added to this reagent for high hafnium alloys and more water was added for alloys on the low hafnium end of the range. An etchant containing six parts by volume of glycerol, two parts

nitric acid and one part 48 percent hydrofluoric acid was used for alloys containing more than 90 atomic percent hafnium. Both of these etchants were applied by swabbing. After etching, all alloys were rinsed with distilled water and dried by a hot air blower. A Bausch and Lomb Optical Co. metallograph No. 42-31-36 was used for photomicrography.

E. Melting Temperature Determination

Melting temperatures were determined by measuring the temperature at which the first liquid was observed in samples which were heated by passage of an electric current. The melting bars were cut from arc-melted alloy buttons and measured approximately 1-1/2 x 1/4 x 1/4 inches. An optical pyrometer focused on the bottom of a black-body hole drilled in the center of the bar was used to determine the temperature at which the liquid phase was first observed. This portion of the bar was necked down to insure that melting would occur first in the region of the hole. The apparatus shown in Fig. 4, which was used for high temperature heat treatment, was also used for solidus point measurements. The tantalum tube furnace element and steel adapters were removed and the melting bar was clamped directly to the water cooled copper electrodes. The pressure in the furnace was kept below about 5×10^{-5} mm. of Hg and contamination of samples was slight.

F. Electrical Resistance Measurements

The electrical resistance data were obtained with an automatic recording apparatus which has been described in detail by Chiotti (40). The specimen bars were approximately seven cm. long with an elliptical cross-section of approximately 0.5 cm. by 0.7 cm. These bars were prepared by arc-melting the alloys in a mold of the given dimensions. A small radial black-body hole was drilled in the center of the bar to permit measurement of the sample temperature with an optical pyrometer. The specimen bar was clamped to water-cooled copper electrodes in a vacuum furnace much like that shown in Fig. 4. The sample was heated by an A.C. current from a step-down transformer.

To measure the resistance of the sample, the potential drop along the bar was compared to a potential which was proportional to the current through the bar. The potential drop along the bar was obtained from two tungsten probes placed in small indentations one half cm. on each side of the center of the bar. The current supply to the furnace developed a potential in current transformer which was proportional to the current. These potentials were balanced by a specially adapted Brown Elektronik recording potentiometer which had been calibrated to indicate directly the resistance of that portion of the sample between the potential drop probes.

G. X-Ray Diffraction Examination

All X-ray examinations were performed on polycrystalline samples using filtered copper radiation from a North American Phillips X-ray diffraction unit Type 12046. The X-ray diffraction patterns were recorded with a 11.4 cm. diameter Debye-Scherrer powder camera which was made by North American Phillips and used an unsymmetrical film mounting according to the Straumanis technique. The X-ray samples were cut from heat treated alloy bars. Rods measuring about $1-1/2 \times 1-1/2 \times 7$ mm. were formed by grinding the bars on a water cooled carborundum wheel. One end of these small rods was then clamped in the chuck of a high speed drill and abrasive paper was used to grind the other end to about 0.3 mm. diameter. The small end of the sample was etched to about 0.25 mm. diameter to remove cold worked metal by using nitric acid, or a mixture of nitric, hydrofluoric and tartaric acids. Massive samples from which the distorted or contaminated surface layer could be removed by etching were preferred to filings because of the danger of oxygen and nitrogen contamination during annealing. The spottiness of the diffraction lines due to the large grain size of the solid samples was considered a lesser hindrance to accurate identification than contamination which might cause the appearance or disappearance of a phase. All of the X-ray studies were conducted at room temperature on quenched, furnace-cooled or as arc-melted samples.

III. PRESENTATION AND DISCUSSION OF RESULTS

The uranium-hafnium equilibrium phase diagram is shown in Fig. 5 as it was determined by metallography, thermal analysis, X-ray diffraction identification, melting temperature observations and electrical resistance measurements. The portions which were not clearly established by experimental results are shown as dotted lines which have been drawn from consideration of the phase rule. The data pertaining to the peritectoid, the eutectoid and the monotectoid reactions, the solidus, and the solubility of uranium in hafnium will be presented separately in the following subsections.

A. Peritectoid Reaction

Solid state transition thermal analysis data were obtained from pure uranium and eleven uranium-hafnium alloys. The temperatures at which thermal arrests were observed are listed in Table 3. Although heating arrests are normally considered to be closer to the equilibrium values than cooling arrests, both are given in order to show how much hysteresis is involved. The thermal arrest temperatures on heating are plotted in Fig. 6. Most of the heating rates were between one and 8°C . per minute although rates as low as 0.5°C . per minute and as high as 20°C . per minute were occasionally used. With rates below about 5°C . per minute, the transformation temperatures showed no systematic variation with heating

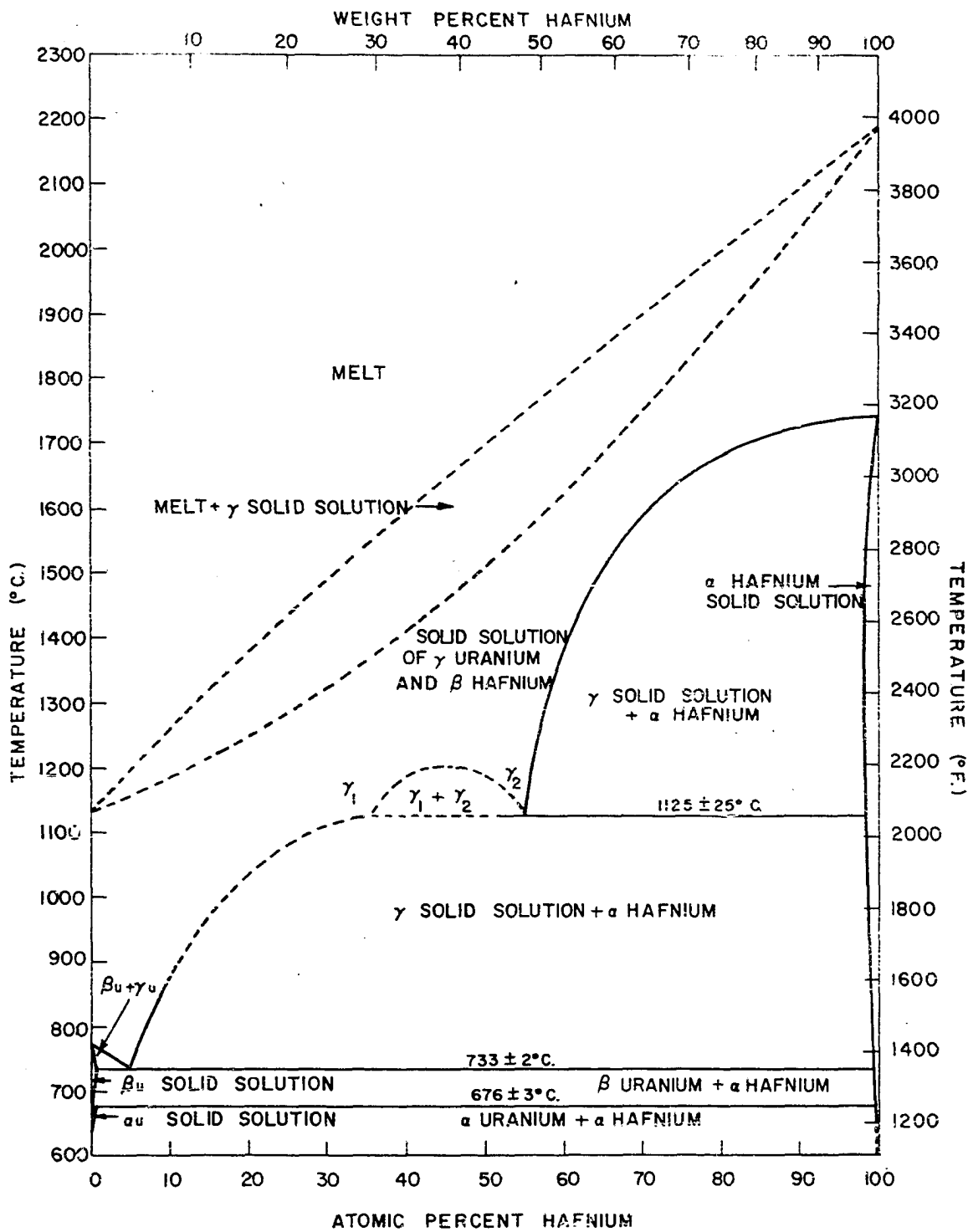


Fig. 5. The uranium-hafnium phase diagram.

Table 3. Thermal data for solid state transitions

Composition (at. % Hf)	Heating arrests (°C.)		Cooling arrests (°C.)	
0.0	668	771	762	648
0.47	674	771	759	652
1.17	678	757	730	657
2.99	680	749	706	647
6.37	678	743	708	657
9.57	678	743	703	650
13.70	676	740	706	645
23.83	678	743	706	646
33.55	672	731	695	635
52.87	675	736	704	636
72.35	686	741	702	652
92.36		718	695	

rate. At the higher heating rates, 10-20°C. per minute, the transformations started a few degrees higher and extended over a slightly longer range. Even at the lowest heating rates, temperature ranges of about 3-8°C. were observed for the transformation. For each alloy three to five different heating rates were used. The values listed are averages of the temperatures at the midpoints of the thermal arrests observed at the lower heating rates. The cooling arrest values were obtained at cooling rates which varied from 1-5°C. per

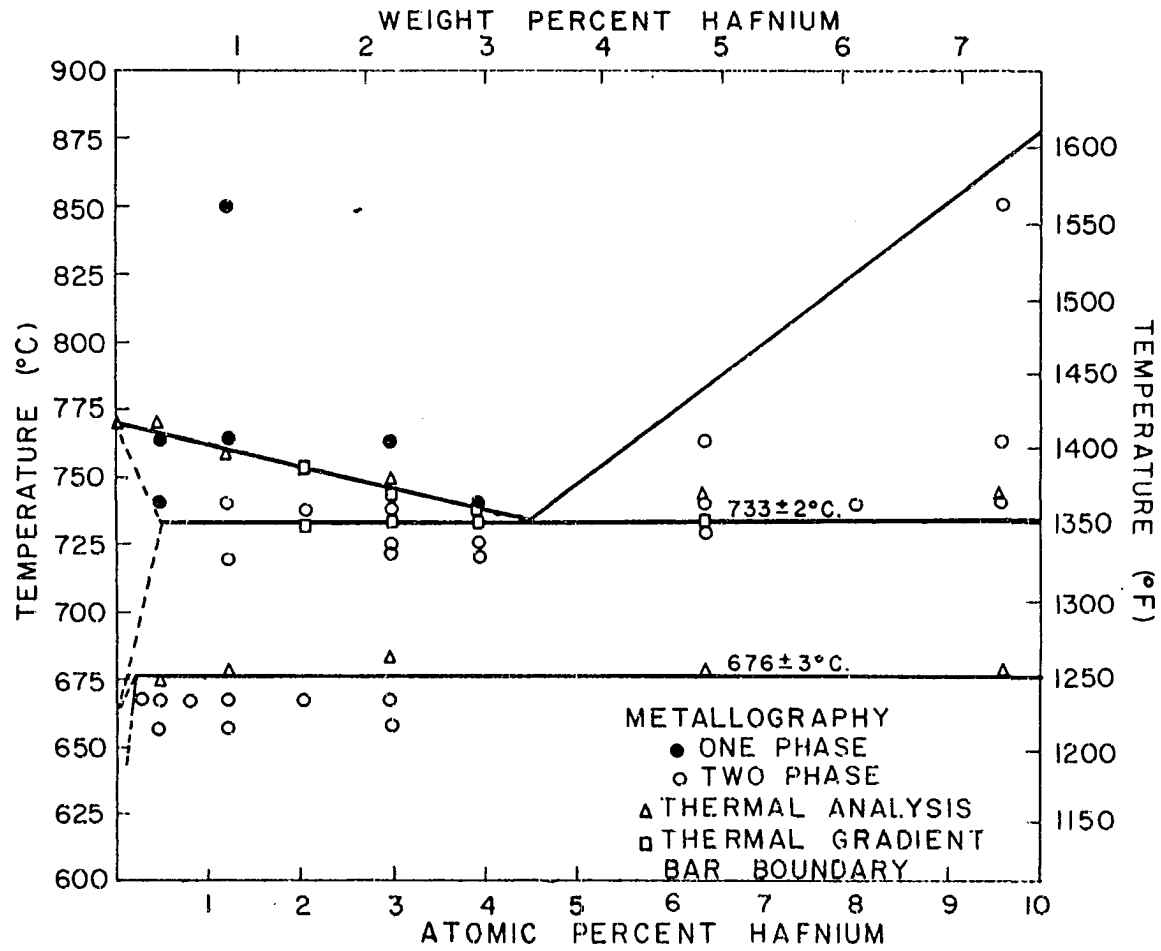


Fig. 6. Metallography and thermal data below 900°C.

minute. The heating and cooling arrests for pure uranium are the average of six measurements.

For all of the alloys studied, the lower of the two thermal arrests occurred at essentially the same temperature. The magnitude of the arrest decreased with increasing hafnium content until it was not discernible on the 92.36 atomic percent hafnium alloy. The average value of the heating arrest, ignoring the 72.35 percent alloy which seems somewhat out of line, is 676°C . This temperature for the peritectoid decomposition of the alpha uranium phase may be $5\text{-}10^{\circ}\text{C}$. higher than the equilibrium value. However, the data indicate that the peritectoid temperature is 8°C . above the alpha-beta transformation temperature in uranium. The thermal gradient technique for determining this equilibrium temperature did not give satisfactory results. Since the solubility of hafnium is low in both alpha and beta uranium, one could not detect a difference in the amount of hafnium precipitate in opposite ends of alloy bars heated with a gradient extending across the peritectoid horizontal.

Microscopic examination of quenched alloys was used to determine the solubility of hafnium in alpha uranium. A sample of furnace cooled, arc-melted uranium of the purity used in preparation of the alloys is shown in Fig. 7. This sample was etched electrolytically using the phosphoric acid,



Fig. 7.

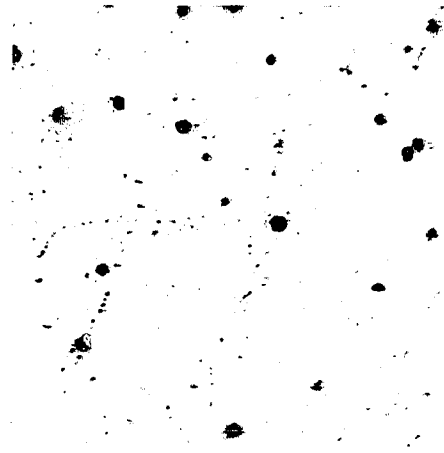


Fig. 8.

Fig. 7. Arc-melted biscuit uranium. Furnace cooled.
 H_3PO_4 elec. etch. X500.

Fig. 8. 0.24 at. % hafnium. Quenched from 660°C . Fine-grained α -Hf plus inclusions in α -U matrix.
 H_3PO_4 elec. etch. X500.

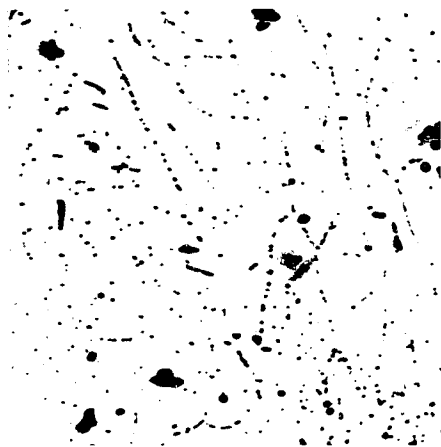


Fig. 9.

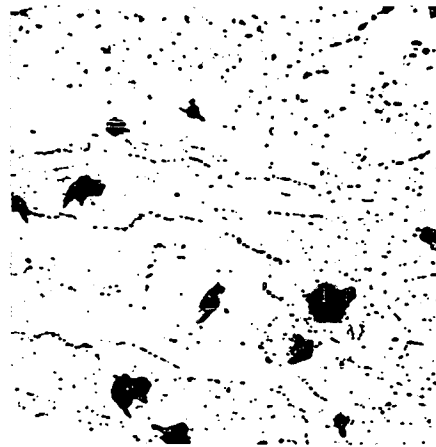


Fig. 10.

Fig. 9. 0.47 at. % hafnium. Quenched from 660°C . Fine-grained α -Hf plus inclusions in α -U matrix.
 H_3PO_4 elec. etch. X500.

Fig. 10. 0.80 at. % hafnium. Quenched from 660°C . Fine-grained α -Hf plus inclusions in α -U matrix.
 H_3PO_4 elec. etch. X500.

ethylene glycol, ethyl alcohol electrolyte. Figs. 8, 9 and 10 show the 0.24, 0.47 and 0.80 atomic percent hafnium alloys quenched from 660°C. The increase in the amount of the fine precipitate with increasing hafnium content should be noted. It seems, therefore, that the solubility of hafnium in alpha uranium at 668°C. is less than 0.24 atomic percent.

There are no intermediate one phase regions in the uranium-hafnium system below 676°C. In all alloys the amount of the hafnium phase present increases as the hafnium content of the alloy increases. Figs. 11, 12, 13 and 14 show this increase in the amount of the hafnium phase for the 33.55, 52.87, 72.35 and 92.36 atomic percent hafnium alloys quenched from 625°C. X-ray diffraction examination of these alloys revealed only alpha uranium and alpha hafnium.

B. Eutectoid Reaction

The temperature of the beta to gamma transformation in uranium is lowered by the addition of hafnium to an eutectoid which, from thermal data, was between three and six atomic percent hafnium and at 742°C. The temperature of the higher thermal arrest was approximately constant in alloys containing more than six percent hafnium. The arrest in the 92.36 percent alloy was somewhat lower but this could be due to impurities concentrating in the uranium phase which at this composition is a minor constituent. The thermal data are given

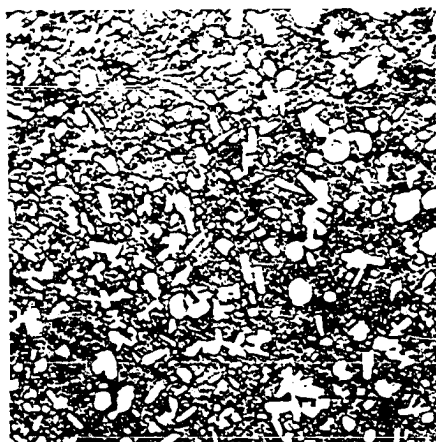


Fig. 11.

Fig. 11. 33.55 at. % hafnium. Quenched from 625°C. α -Hf in unresolved eutectoid matrix. HNO_3 base etch. X250.

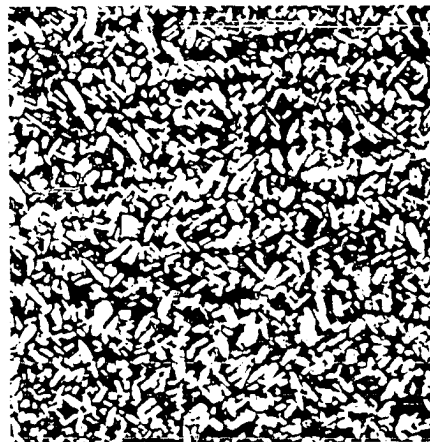


Fig. 12

Fig. 12. 52.87 at. % hafnium. Quenched from 625°C. α -Hf in unresolved eutectoid matrix. HNO_3 base etch. X250.



Fig. 13.

Fig. 13. 72.35 at. % hafnium. Quenched from 625°C. α -Hf in unresolved eutectoid matrix. HNO_3 base etch. X250.

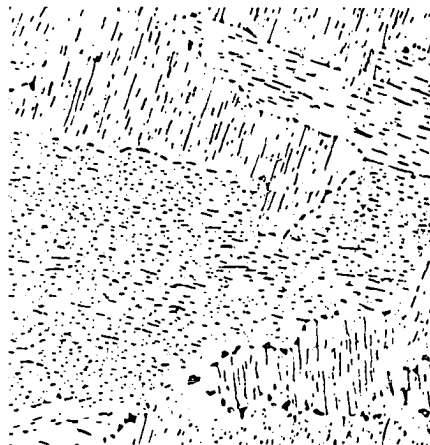


Fig. 14.

Fig. 14. 92.36 at. % hafnium. Quenched from 625°C. α -U in α -Hf matrix. Glycerol, HNO_3 , HF etch. X250.

in Table 3 and the heating thermal arrests are plotted in Fig. 6 against alloy composition.

The thermal arrests in the hypoeutectoid samples appeared as invariant points but the temperature increased with decreasing uranium content. Ideally, these thermal arrests should have occurred over a range because the heat effect is due to the disappearance of the beta phase as the beta plus gamma phase field is traversed. Equilibrium in this two phase field requires mass transfer since the composition of the phases are different. Since diffusion is quite slow in solids at temperatures considerably below their melting temperatures, beta uranium probably transformed directly to gamma after the two phase field was crossed.

Microscopic examination of quenched samples was used to establish the eutectoid temperature and the limits of the beta plus gamma phase field. Sample bars with thermal gradients were especially useful for this purpose. The samples were quenched after five hours of heating in their respective gradients. The temperature at any position along the bar was determined by measuring the distance from one end of the bar and assuming a linear thermal gradient along the bar. A gradient bar with a composition on the uranium side of the eutectoid contained the following regions: a one phase gamma region at the high temperature end, next, a two phase gamma plus beta region in which the gamma-beta ratio decreased with

temperature, and finally a region of beta uranium containing hafnium lamellae formed by eutectoid decomposition. There was a narrow band in the portion of the sample at the eutectoid temperature in which beta and gamma uranium and precipitated hafnium coexisted. The extent of this band corresponded to about a 2°C . temperature difference. Fig. 15 shows this region in the 2.99 atomic percent hafnium alloy. At the position in the bar which was at the eutectoid temperature single hafnium lamellae were observed but at slightly lower temperatures these lamellae showed the parallel arrangement often characteristic of eutectoid precipitation. The spacing of the lamellae decreased rapidly toward the cooler end of the bars. Fig. 16 shows the 2.92 atomic percent hafnium bar quenched from about 2°C . below the eutectoid temperature. Fig. 17 shows the 3.99 atomic percent hafnium bar about 10°C . below the eutectoid temperature.

The highest temperature at which hafnium, precipitated by the eutectoid decomposition, was observed was 733° , 732° , 734° and 732°C . for the 6.37, 3.92, 2.99 and 2.02 atomic percent hafnium bars respectively. The average of these temperatures is 733°C . or 9°C . lower than the average heating arrest in the thermal analysis. The 733°C . value is probably very close to the equilibrium value. A portion of the boundary between the gamma phase and the beta phase in the 6.37 atomic percent hafnium is shown in Fig. 18. The beta phase



Fig. 15.



Fig. 16.

Fig. 15. 2.99 at. % hafnium. Quenched from 733°C. Transformed δ -U (dark) and β -U plus eutectoid structure. H_3PO_4 elec. etch. X500.

Fig. 16. 2.99 at. % hafnium. Quenched from 731°C. Transformed β -U (light areas) plus eutectoid structure. H_3PO_4 elec. etch. X1000.



Fig. 17.



Fig. 18.

Fig. 17. 3.92 at. % hafnium. Quenched from 723°C. Transformed β -U (light areas) plus eutectoid structure. H_3PO_4 elec. etch. X1000.

Fig. 18. 6.37 at. % hafnium. Quenched from 733°C. Eutectoid structure (dark), transformed α -U (light) and α -Hf globules. H_3PO_4 elec. etch. X1000.

contains hafnium lamellae formed by eutectoid decomposition. The globular phase is primary hafnium which precipitated from the gamma solid solution above 733°C . This alloy bar had no beta plus gamma region and a much sharper boundary at the eutectoid temperature than the other three alloy bars.

Measurements from thermal-gradient bars were used to establish the extent of the beta plus gamma phase field. This two phase region was observed to extend from the eutectoid horizontal at 733°C . to 736° , 742° , and 752°C . at 3.92, 2.99 and 2.02 atomic percent hafnium respectively. These measurements indicate that eutectoid composition is about 4.5 atomic percent hafnium.

Uranium-rich alloys quenched from the gamma solid solution region transformed during quenching to alpha uranium. The X-ray diffraction peaks were shifted relative to those of pure alpha uranium. This indicated that the alpha uranium formed on quenching was a supersaturated, nonequilibrium phase. The 1.17 percent sample quenched from 740°C . is shown in Fig. 19. This alloy was quenched from the beta plus gamma field and shows beta transformed to alpha and gamma transformed to alpha. The 2.99 percent alloy shown in Fig. 20 was quenched from 740°C . and contained beta transformed to alpha and gamma transformed to a crosshatched alpha. The gamma transformed to alpha shown in Fig. 18 also has this



Fig. 19.

Fig. 19. 1.17 at. % hafnium. Quenched from 740°C. Transformed α -U (dark) and β -U. H_3PO_4 elec. etch. X250.



Fig. 20.

Fig. 20. 2.99 at. % hafnium. Quenched from 740°C. Transformed α -U (crosshatched) and β -U. H_3PO_4 elec. etch. X250.

acicular appearance which was typical of alloys containing from three to fifteen percent hafnium after quenching from the gamma solid solution region.

Examination of the 1.17 atomic percent hafnium alloy quenched from temperatures below the eutectoid horizontal revealed a considerable amount of hafnium formed by eutectoid decomposition. The solubility of hafnium in beta uranium at the eutectoid temperature is estimated to be less than 0.5 atomic percent.

C. Solidus Determination

The temperature at which melting was first observed was measured for uranium, hafnium and a number of alloys spaced evenly across the system. These temperatures are listed in Table 4 and plotted in Fig. 21. There is no maximum or minimum in the observed melting temperatures. This is good evidence of complete solubility between gamma uranium and beta hafnium below the solidus temperatures. The values obtained for the melting points of uranium and hafnium, 1129°C . and 2190°C . respectively, agree quite well with the best literature values of $1132 \pm 1^{\circ}\text{C}$. (5) and $2222 \pm 30^{\circ}\text{C}$. (17).

An alloy usually melts over a range of temperatures even at equilibrium. Thus an alloy does not have a melting point. The temperature at which liquid is first observed in the black-body hole must be somewhat above the solidus temper-

Table 4. Melting temperature data

Composition (at. % Hf)	Observed melting temperature (°C.)
0.0	1129
13.70	1224
23.83	1310
33.55	1453
52.87	1563
72.35	1880
92.36	2110
100.0	2190

ature. This is because an appreciable amount of liquid must be formed before any liquid can be observed in the cavity. The fraction of liquid necessary to cause observable melting probably varies with composition and would be affected by oxide or nitride surface films in the black-body hole. For this reason the solidus line has been dotted in smoothly below all of the measured points.

Although melting temperature observations had indicated that gamma uranium and beta hafnium were soluble in all proportions below the solidus temperatures, alloys up to about 60 atomic percent hafnium quenched from this region showed the gamma solid solution matrix and a globular phase which

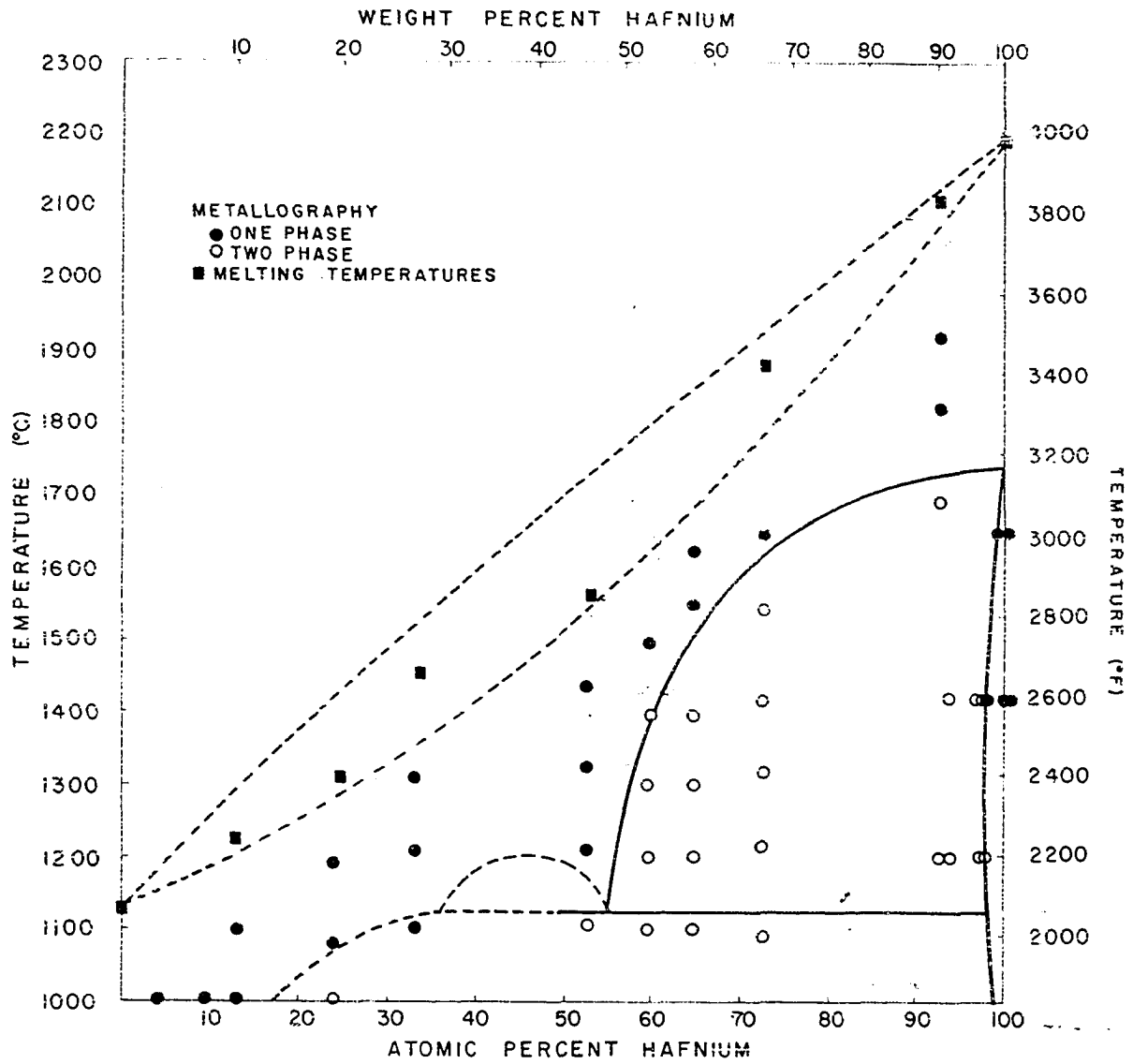


Fig. 21. Melting data and metallography above 1000°C.

appeared to be alpha hafnium. The amount of this second phase showed little temperature dependence for a given composition in the solid solution region. The uranium-rich matrix of a 52.87 atomic percent hafnium sample quenched from 1200°C. was dissolved with warm nitric acid to isolate this globular phase. The residual black powder was identified by X-ray diffraction as alpha hafnium.

The presence of alpha hafnium in these samples has been attributed to the effect of oxygen. Both oxygen and nitrogen are known to markedly stabilize alpha zirconium with respect to transformation to beta (41, 42) and the same effect would be expected with hafnium. Uranium-zirconium alloys containing oxygen, when quenched from the solid solution region, contain alpha zirconium in a globular form (38). Alloys containing about 37 atomic percent hafnium and 0.19 and 0.44 atomic percent added oxygen were prepared by arc-melting to determine whether the amount of the globular phase increased with the oxygen content. Samples of these two alloys and of the 33.55 atomic percent hafnium alloy were heated at 1310°, 1210° and 1100°C. and quenched. A definite increase in the amount of the second phase in proportion to the increase in oxygen content was noted. The amount of globular phase did not change significantly with temperature. Figs. 22, 23 and 24 show the microstructures of the three alloys quenched from 1310°C.

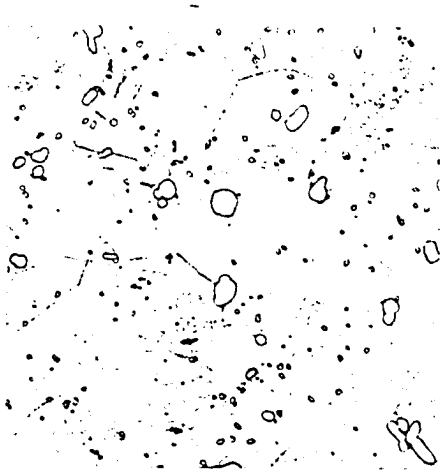


Fig. 22.

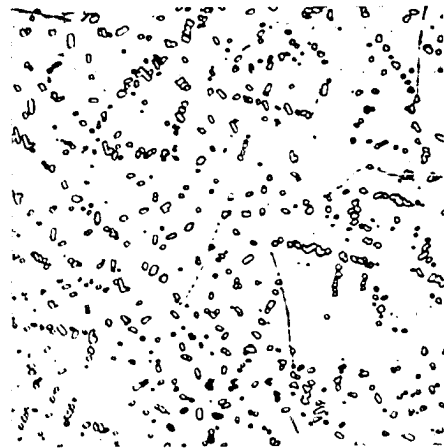


Fig. 23.

Fig. 22. 33.55 at. % hafnium. Quenched from 1310°C. α -Hf globules and transformed γ -solid sol. HNO_3 base etch. X250.

Fig. 23. 37.7 at. % hafnium and 0.19 at. % oxygen. Quenched from 1310°C. α -Hf globules and transformed γ -solid sol. HNO_3 base etch. X250.

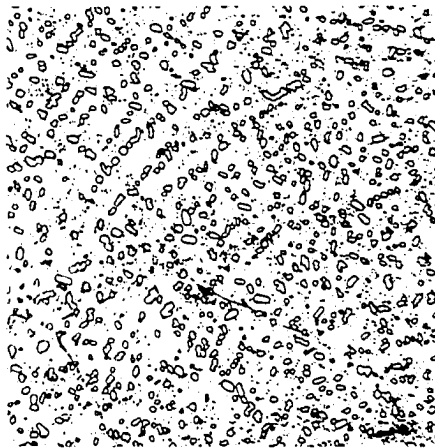


Fig. 24.

Fig. 24. 37.0 at. % hafnium and 0.44 at. % oxygen. Quenched from 1310°C. α -Hf globules and transformed γ -solid sol. HNO_3 base etch. X250.

From the oxygen and nitrogen analyses for uranium and hafnium in Table 1, it can be calculated that a 33 atomic percent hafnium alloy would contain about 79 ppm oxygen and 109 ppm nitrogen. Vacuum fusion analysis of the 33.55 atomic percent hafnium alloy yielded 91 ppm oxygen in good agreement with this calculation. This alloy would thus contain 0.28 atomic percent oxygen plus nitrogen. Adding this to the amount of oxygen added to the oxygen enriched alloys, the samples shown in Figs. 22, 23 and 24 actually contain 0.28, 0.47 and 0.72 atomic percent oxygen plus nitrogen, respectively. Thus the appearance of alpha hafnium in regions which, on a binary basis, should be one phase, can be explained in terms of oxygen and nitrogen impurities.

D. The Monotectoid Reaction

1. Electrical resistance measurements

Preliminary microscopic examination of samples quenched from high temperatures indicated that uranium did not lower the transformation temperature of hafnium in a regular manner to the eutectoid at the uranium side of the system. To obtain more information about the hafnium side of the system above 1000°C., a study was made of the variation in electrical resistance with temperature of the 92.36, 73.35 and 52.87 atomic percent hafnium alloys and crystal bar hafnium.

The sample bars were homogenized by heating to a temperature just below their solidus temperatures. Electrical resistance measurements were then made during both heating and cooling over the temperature range from 900°C . to the solidus temperature. Five or more minutes were allowed after each temperature change to allow equilibrium to be re-established before a resistance measurement was made. Resistance measurements during cooling when plotted against temperature gave curves of the same shape as those obtained on heating but the breaks in the curves were usually shifted to slightly lower temperatures. The data plotted in Fig. 25 are from measurements made during heating runs. The ordinate scale is proportional to the resistance of the samples. The specific resistance of the samples was not calculated because it was difficult to measure accurately the dimensions of the sample bars.

With increasing temperature the electrical resistance versus temperature curves for the alloys begin to deviate from linearity between 1100°C . and 1200°C . The curve for the 52.87 atomic percent hafnium alloy has a change of slope in this range, but then continues in a linear fashion. The slope is positive over the whole range. The high temperature linear portion is indicative of the region of complete solubility. The resistance versus temperature curves for the 72.35 and

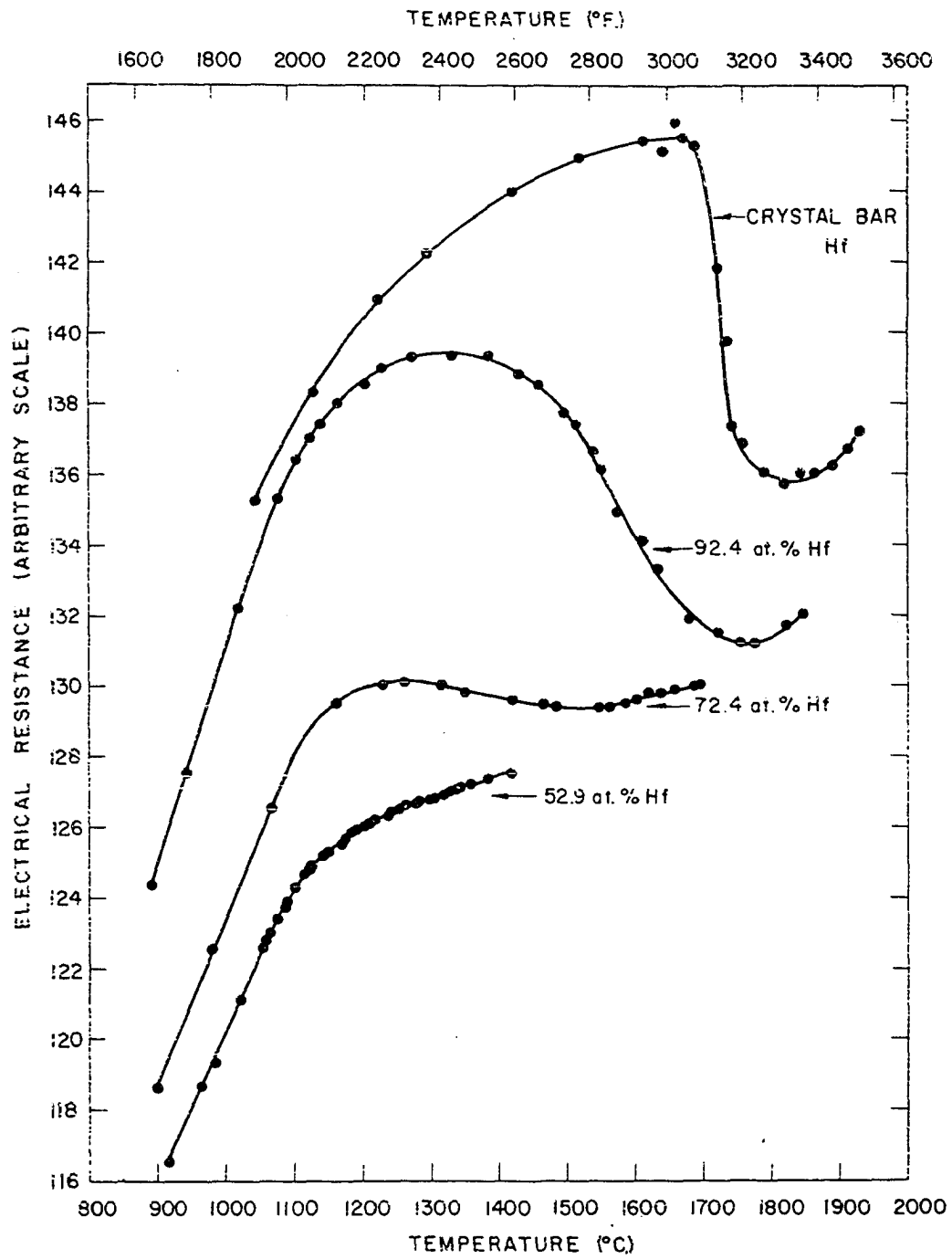


Fig. 25. Electrical resistance data versus temperature.

92.36 percent alloys change in slope until the temperature coefficients of resistance become negative. They remain thus over a considerable temperature range. As the region of complete solubility is reached, the electrical resistance of these alloys also increases in a linear fashion. Since it is difficult from electrical resistance data alone to specifically identify a phase reaction, further discussion of this point will be postponed until the metallography data are presented.

The decrease in electrical resistance of the arc-melted crystal bar hafnium specimen between 1690°C . and 1820°C . is due to transformation from the hexagonal close-packed structure to the body centered cubic structure. This phase change should be invariant in temperature but there are a number of reasons why the resistance change might occur over a range. Impurities would cause the transformation to occur over a temperature range. Variations in temperature either between the resistance probes or from the surface to the center of the sample are also possible explanations. The midpoint of the resistance decrease between the maximum and the minimum was at 1730°C . This agrees well with the 1735°C . transformation temperature reported by Gibson et al. (2). It is higher than the $1310 \pm 10^{\circ}\text{C}$. reported by Duwez (16) and lower than the value of $1950 \pm 100^{\circ}\text{C}$. given by Fast (14).

2. Metallography

The presence of impurity-stabilized alpha hafnium made it very difficult to establish the boundaries of the gamma solid solution region. This was particularly true of alloys up to about 55 atomic percent hafnium. At higher hafnium concentrations, a second difficulty arose. The rate of cooling in quenching was not sufficiently rapid to retain all of the hafnium in solid solution. The alloys containing 59.59, 64.53 and 72.35 atomic percent hafnium quenched from within the region of complete solubility contained alpha hafnium which had precipitated during quenching in a sharply pointed, needlelike form. Fig. 26 shows this type of precipitation in the 72.35 atomic percent hafnium alloy quenched from 1645°C. The metallography data from samples heat treated above 1000°C. are plotted in Fig. 21.

To determine the nature of the reaction which caused the electrical resistance anomalies, samples of the 23.83, 33.55, 52.87, 59.59, 64.53 and 72.35 atomic percent hafnium alloys were quenched at approximately 100°C. intervals from 1100°C. up into the region of complete solid solubility. The most significant difference observed was in the four alloys of highest hafnium content quenched from about 1100°C. and about 1200°C. In all of these there was a significantly greater increase in the amount of the alpha hafnium phase



Fig. 26.

Fig. 26. 72.35 at. % hafnium. Quenched from 1645°C. α -Hf precipitated during quenching and transformed γ -solid sol. HNO_3 base etch. X250.

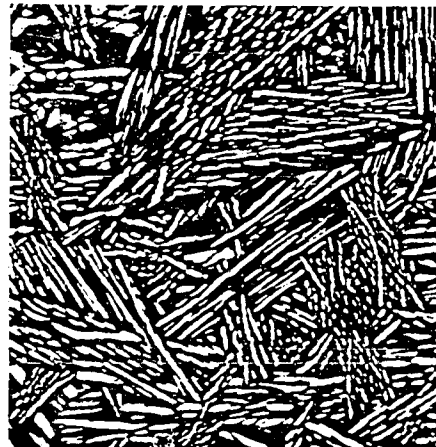


Fig. 27.

Fig. 27. 72.35 at. % hafnium. Quenched from 1220°C. α -Hf (light) and transformed δ -solid sol. HNO_3 base etch. X250.

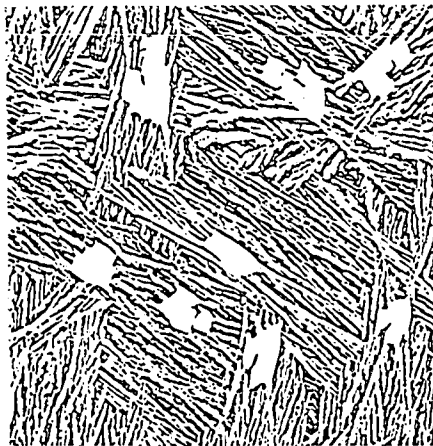


Fig. 28.

Fig. 28. 72.35 at. % hafnium. Quenched from 1090°C. α -Hf (light) and transformed γ -solid sol. HNO_3 base etch. X250.

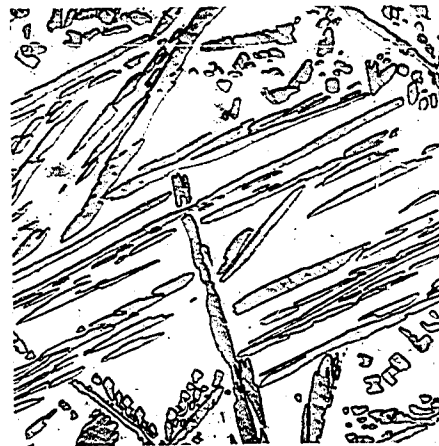


Fig. 29.

Fig. 29. 64.53 at. % hafnium. Quenched from 1210°C. α -Hf (gray) and transformed γ -solid sol. HNO_3 base etch. X250.

going from 1200°C. to 1100°C. than there was in going from 1300°C. to 1200°C. Figs. 27 and 28 show the 72.35 atomic percent hafnium samples quenched from 1220°C. and 1090°C. respectively. The 64.53 atomic percent hafnium samples quenched from 1210°C. and 1090°C. are shown in Figs. 29 and 30. The effect in the 59.59 atomic percent hafnium samples was similar. The 1430°C., 1330°C. and 1215°C. samples containing 52.87 atomic percent hafnium revealed a considerable amount of the globular alpha hafnium phase which did not vary significantly with temperature. The 1330°C. and 1215°C. samples are shown in Figs. 31 and 32. The amount of alpha hafnium in the 1100°C. sample containing 52.87 atomic percent hafnium was significantly greater than that in the 1215°C. sample. The 1100°C. sample is shown in Fig. 33. The 33.55 atomic percent hafnium samples quenched from 1100°C., 1210°C. and 1305°C. contained about the same amount of alpha hafnium and were assumed to be one phase at these temperatures. This was also true of the 23.83 atomic percent hafnium samples quenched from 1085°C. and 1190°C. The 13.70 atomic percent hafnium samples quenched from 1100°C. and 1000°C. were one phase alloys but the same composition quenched from 850°C. contained two phases. The 13.0 atomic percent hafnium samples quenched from 1100°C. and 850°C. are shown in Figs. 34 and 35. The 23.83 and 33.55 atomic percent alloys quenched from 1000°C. and 850°C. were definitely two phase.

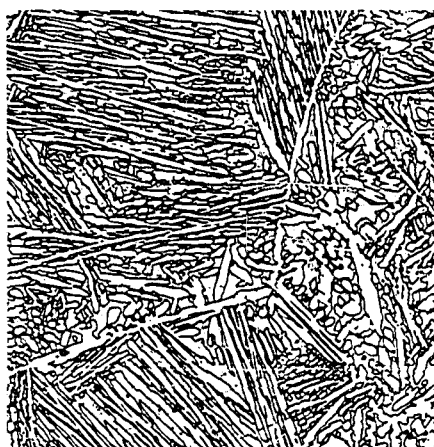


Fig. 30.

Fig. 30. 64.53 at. % hafnium. Quenched from 1090°C. α -Hf (light) and transformed γ -solid sol. HNO_3 base etch. X250.



Fig. 31.

Fig. 31. 52.87 at. % hafnium. Quenched from 1330°C. α -Hf globules and transformed γ -solid sol. HNO_3 base etch. X250.



Fig. 32.

Fig. 32. 52.87 at. % hafnium. Quenched from 1215°C. α -Hf globules and transformed γ -solid sol. HNO_3 base etch. X250.



Fig. 33.

Fig. 33. 52.87 at. % hafnium. Quenched from 1100°C. α -Hf grains and transformed γ -solid sol. HNO_3 base etch. X250.

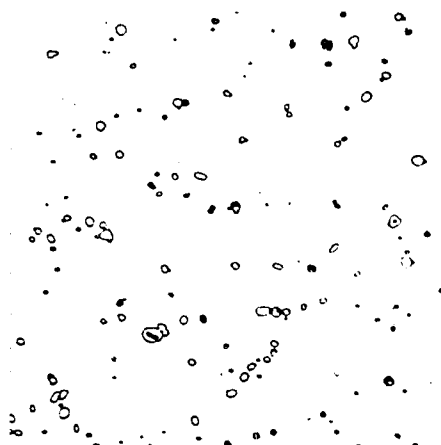


Fig. 34.

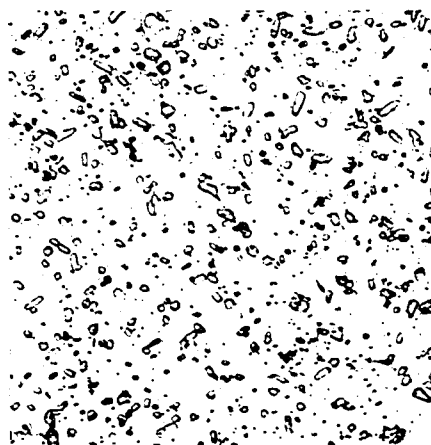


Fig. 35.

Fig. 34. 13.70 at. % hafnium. Quenched from 1100°C. α -Hf globules and transformed γ -solid sol. HNO_3 base etch. X250.

Fig. 35. 13.70 at. % hafnium. Quenched from 850°C. α -Hf globules and transformed γ -solid sol. H_3PO_4 elec. etch. X250.



Fig. 36.



Fig. 37.

Fig. 36. 59.59 at. % hafnium. Quenched from 1300°C. α -Hf needles and transformed γ -solid sol. HNO_3 base etch. X250.

Fig. 37. 59.59 at. % hafnium. Quenched from 1100°C. α -Hf needles and transformed γ -solid sol. HNO_3 base etch. X250.

Electrical resistance and metallographic data indicate the existence of a reaction isotherm between 1100°C. and 1200°C. To best fit the metallographic data from the 13.70, 23.83 and 33.55 atomic percent hafnium alloys the temperature of transformation has been placed at 1125°C. and the composition range from the alpha hafnium solid solution boundary to between 30 and 40 atomic percent hafnium. The invariant point has been placed at about 55 atomic percent hafnium because the gamma solid solution boundary begins to rise sharply between 52.87 and 59.59 atomic percent hafnium. Also the character of the alpha hafnium phase changes considerably in this range. This can be seen by comparing Fig. 36, which shows the 59.59 atomic percent hafnium alloy quenched from 1300°C., with Fig. 31 showing the 52.87 percent alloy quenched from 1315°C. The γ_1 - γ_2 immiscibility loop has been dotted since no direct experimental evidence of its existence was found. The phase rule, however, requires that three two-phase regions originate upon every three-phase isotherm. An immiscibility loop is the most reasonable two-phase region which can be drawn in accord with the other data. This makes the invariant point a monotectoid.

A number of attempts were made to obtain microstructures with a lamellar precipitation characteristic of the monotectoid reaction. Since the lamellar precipitate might sphero-

idize rapidly at high temperature, samples of the 52.87 and 59.59 atomic percent hafnium alloys were heated at about 1400°C., cooled rapidly and held for varying lengths of time at about 1100°C. and quenched. It was hoped a lamellar hafnium precipitate would develop as the solid solution rejected hafnium and be retained by immediately quenching the samples but no lamellar structures were observed. Diffusion in these alloys at 1100°C. is probably rapid and the precipitate is formed as rather coarse crystals. Even after only 45 seconds at 1100°C. coarse hafnium needles had developed in the 59.59 atomic percent hafnium which is shown in Fig. 37. In as little as 2.5 minutes the precipitation of hafnium was complete. Fig. 38 shows the 59.59 atomic percent hafnium alloy quenched after 2.5 minutes at 1120°C.

3. X-ray diffraction examination

Alloys quenched from 1100°C. or above, in which the gamma phase contained 20-65 atomic percent hafnium, contained a phase which gave the same X-ray diffraction pattern as the delta phase in the uranium-zirconium system. The diffraction pattern from the 52.87 atomic percent hafnium alloy, quenched from 1330°C., contained 21 lines which could not be attributed to alpha hafnium. All of these could be indexed on the basis of a body-centered cubic lattice with $a = 10.54 \text{ \AA}$. Although the true unit cell is primitive hexagonal, the cubic symmetry

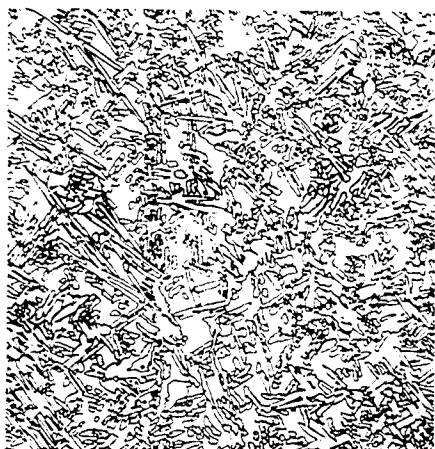


Fig. 38.

Fig. 38. 59.59 at. % hafnium. Quenched from 1120°C. α -Hf needles and transformed γ -solid sol. HNO_3 base etch. X250.

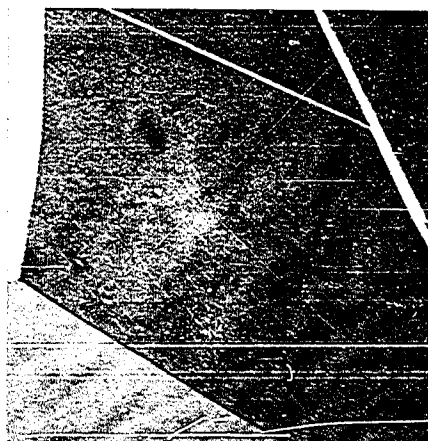


Fig. 39.

Fig. 39. Arc-melted crystal bar hafnium. Quenched from 1425°C. Glycerol, HNO_3 , HF etch. X250.

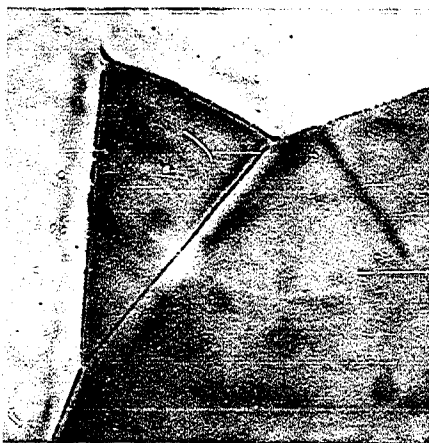


Fig. 40.

Fig. 40. 98.02 at. % hafnium. Quenched from 1425°C. Glycerol, HNO_3 , HF etch. X250.



Fig. 41.

Fig. 41. 97.70 at. % hafnium. Quenched from 1425°C. Transformed γ -solid sol. in α -Hf matrix. Glycerol, HNO_3 , HF etch. X250.

of the diffraction pattern results because equal amounts of the hexagonal phase are formed with the 001 axis in the 111 directions of the cubic gamma phase and the $11\bar{2}0$ directions of the hexagonal phase along the 110 cubic directions. The lattice constants of the primitive hexagonal cell are $a = 4.97$ A. and $c = 3.04$ A. The hexagonal lattice constants of the uranium-zirconium delta phase are $a = 5.03$ A. and $c = 3.08$ A. (34, 35). The delta phase in uranium-hafnium alloys is not believed to be stable at room temperature since it is not observed in samples quenched from below 800°C . or in furnace cooled samples. It is believed to be a metastable transition state in the decomposition of the gamma solid solution to alpha hafnium and alpha uranium.

Quenching of alloys in which the gamma phase contains more than 65 atomic percent hafnium resulted in decomposition directly to alpha uranium and alpha hafnium. The 64.53 atomic percent hafnium sample quenched from 1625°C . gave a delta phase diffraction pattern of medium intensity, a strong alpha hafnium pattern and a medium intensity alpha uranium pattern. The 72.35 atomic percent hafnium alloy quenched from 1645°C . revealed only alpha uranium and alpha hafnium lines. However, the same composition quenched from 1220°C . gave a strong delta phase pattern and a strong alpha hafnium pattern with only a very weak alpha uranium pattern. This

is because the gamma phase of the sample quenched from 1220°C. contained only 55-60 atomic percent hafnium and was in the composition range which formed the delta phase on quenching.

When the gamma solid solution contained only 13.70 atomic percent hafnium, it transformed to the alpha uranium structure keeping the hafnium in solution although some of the gamma solid solution structure may be retained. The 36.2 atomic percent hafnium sample quenched from 1310°C. and the 36.2 and 23.83 percent samples quenched from 1200°C. showed strong delta phase diffraction pattern and weak hafnium patterns. The 13.70 atomic percent hafnium sample quenched from 1100°C. revealed a strong alpha uranium diffraction pattern, no delta phase or alpha hafnium but a medium intensity pattern of retained body-centered cubic gamma solid solution structure.

The 6.37 and 9.57 atomic percent hafnium alloys quenched from 740°C. and 850°C., respectively, gave strong alpha uranium diffraction patterns but no delta phase or gamma phase lines and only weak alpha hafnium lines. The alpha uranium lines were observed at slightly lower angles than for pure uranium. This indicates an expansion of the alpha uranium structure and probably means that the hafnium was retained in solution in the alpha uranium lattice. Re-examination after a three hour heat treatment at 650°C. revealed diffraction lines at essentially the same angles as those ob-

served for pure uranium. The 13.70, 23.83 and 52.87 atomic percent hafnium alloys quenched from 756°C. gave only alpha uranium and alpha hafnium patterns. The intensity of each was approximately proportional to its concentration in the sample.

E. The Solubility of Uranium in Alpha Hafnium

Microscopic examination of quenched alloys was used to determine the solubility of uranium in alpha hafnium. The solubility limit is between 2.0 and 2.3 atomic percent uranium at 1425°C. Figs. 39, 40 and 41 show crystal bar hafnium and the 98.02 and 97.70 atomic percent hafnium alloys quenched from 1425°C. Below 1000°C. it was difficult to determine the solubility because of the amount of precipitate in the unalloyed hafnium. Figs. 42 and 43, showing crystal bar hafnium quenched from 985°C. and arc-melted hafnium, illustrate this precipitate. It was possible to determine that the solubility of uranium in hafnium was less 0.6 atomic percent at 650°C. by examination of microstructure, shown in Fig. 44, of the 99.37 atomic percent hafnium alloy.

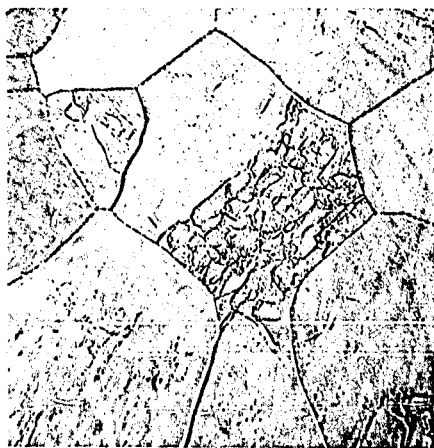


Fig. 42.



Fig. 43.

Fig. 42. Arc-melted crystal bar hafnium. Quenched from 985°C. Note inclusions. Glycerol, HNO₃, HF etch. X75.

Fig. 43. Crystal bar hafnium. As arc-melted. Note inclusions. Glycerol, HNO₃, HF etch. X250.



Fig. 44.

Fig. 44. 99.37 at. % hafnium. Quenched from 650°C. Fine-grained α -U plus inclusions in α -Hf. Glycerol, HNO₃, HF etch. X250.

IV. DISCUSSION OF GENERAL FEATURES

The uranium-hafnium system has been found to conform in general to the alloying behavior of the other Group IV A metals with uranium. The differences can be explained in terms of the properties of hafnium.

Hafnium was only very slightly soluble in alpha uranium. This is not surprising since in the alpha uranium structure hafnium is forced to occupy a position which is 14 percent smaller in its smallest dimension than the metallic diameter of hafnium. It is not able to overcome this restriction on solubility by participating to any significant extent in the covalent bonding as plutonium presumably does. In spite of this, hafnium is slightly more soluble in alpha uranium than in beta uranium as indicated by the slight raising of the alpha-beta transformation. In this respect hafnium resembles titanium and zirconium and gives some support to the assumption that alpha uranium has a valence of four since only Group IV A metals raise this transformation and all other metals either lower the transformation or leave it essentially unchanged.

Hafnium shows a very decided preference for the body-centered cubic gamma uranium structure over that of beta uranium. This is shown by the fact that hafnium lowers the

beta-gamma transformation and beta hafnium and gamma uranium are soluble in all proportions at elevated temperatures while the solubility of hafnium in beta uranium is very limited. The complete solubility of uranium and hafnium at high temperature is not surprising when one considers that in their body-centered cubic structures the atomic radii differ by only about two percent. Since these two metals have very similar electronegativities there is little tendency for the formation of highly stable compounds which might restrict extensive solubility. The immiscibility gap, reported in the system to comply with the phase rule, would be an expression of a tendency toward limited solubility of the terminal phases rather than compound formation.

The uranium-hafnium system has no intermediate phases stable at low temperatures. In this respect it differs from the uranium-zirconium system. However, uranium-hafnium alloys containing 20-65 atomic percent hafnium and quenched from above 1100°C. do contain a phase which gives the same X-ray diffraction pattern as the uranium-zirconium delta phase. Uranium-hafnium alloys which were furnace cooled or quenched from below 800°C. revealed only alpha uranium and alpha hafnium when examined by X-ray diffraction. This delta phase of the uranium-hafnium system is believed to be a metastable transition state in the decomposition of the solid solution to alpha uranium and alpha hafnium.

Zirconium and hafnium are very similar in their chemical properties and behavior. In metallic reactions and equilibria they show one very striking difference. The temperature at which hafnium transforms from the hexagonal close-packed structure to the body-centered cubic structure is about 900°C. higher than the same transformation point in zirconium. This large difference in transformation temperature is the principal reason that hafnium and zirconium phase systems are not more similar. It is probably the reason why the uranium-hafnium system has no stable, low temperature delta phase.

The delta phase of the uranium-zirconium system is stable because its free energy is lower than the combined free energy of an equivalent amount of alpha uranium and alpha zirconium. Any change which decreases the activity of either alpha uranium or alpha zirconium will cause the extent of the delta phase to contract. Since most elements are quite insoluble in alpha uranium the activity of the alpha uranium phase in any system is near unity. The addition of oxygen or nitrogen markedly decreases the activity of alpha zirconium and raises the alpha-beta transformation temperature to above 1900°C. The delta phase field can not only be constricted but completely eliminated from the equilibrium phase diagram by the addition of oxygen (38, 41, 42).

The greater thermal stability of alpha hafnium relative to alpha zirconium can be taken to indicate a greater stabil-

ity toward other phase changes. At a given temperature, alpha hafnium would be expected to be less soluble than alpha zirconium and this is confirmed by the solubility limits on gamma uranium. The greater stability of alpha hafnium would restrict the extent of the delta phase and possibly make this phase unstable. The impurities in the alloys which were studied may have been responsible for the decomposition of the delta phase. However, the marginal stability of this phase in the uranium-zirconium system and the greater stability of alpha hafnium make the metastability of this phase quite reasonable.

V. SUMMARY

The uranium-hafnium system has been investigated using metallography, thermal analysis, X-ray diffraction identification, melting point observations and electrical resistance measurements. Thermal analyses indicate that hafnium increases the temperature of the alpha-beta transformation on heating from 668°C. to about 676°C. Above this temperature the alpha uranium phase decomposes to beta uranium and alpha hafnium. The maximum solubility of hafnium in alpha uranium appears to be less than 0.25 atomic percent. The addition of hafnium to uranium lowers the beta to gamma transformation to an eutectoid at 733°C. and 4.5 atomic percent hafnium. Further cooling causes the gamma phase to decompose to beta uranium and alpha hafnium. The solubility of hafnium in beta uranium at the eutectoid temperature is less than 0.5 atomic percent.

Melting point data indicate that at elevated temperatures, the body-centered cubic modifications of uranium and hafnium are soluble in all proportions and exhibit neither a maximum nor a minimum in the solidus temperatures. Alloys containing 20-65 atomic percent hafnium quenched from 1100°C. and above contain a phase whose X-ray powder pattern is almost identical to that of the delta phase of the uranium-zirconium system. The lattice constants for the hexagonal delta phase in the 52 atomic percent hafnium alloy quenched from 1300°C. are

$a = 4.97$ A. and $c = 3.04$ A. This phase is believed to be a metastable phase in the uranium-hafnium system which at equilibrium decomposes to alpha hafnium and uranium.

Metallographic and electrical resistance data indicate that uranium lowers the alpha-beta transformation in hafnium from about 1730°C . to a monotectoid at about 1150°C . and 55 atomic percent hafnium. Oxygen was found to have a very significant effect on the equilibria in uranium-hafnium alloys. Even very small amounts caused alpha hafnium to occur in alloys which, on a binary basis, should have been one phase body-centered cubic alloys.

At 1425°C . the solubility of uranium in hafnium is between 1.9 and 2.3 atomic percent. At temperatures below 1000°C . it was difficult to determine the solubility because of a considerable number of inclusions in the unalloyed hafnium metal. However, the solubility of uranium in hafnium at 650°C . was estimated to be less than 0.6 atomic percent.

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