UNCLASSIFIED

ISC-506(Del.)

UNITED STATES ATOMIC ENERGY COMMISSION

QUARTERLY SUMMARY RESEARCH REPORT IN METALLURGY

For April, May, June, 1954

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission to the extent that such employee or contractor prepares, handles or distributes, or provides access to, any information pursuant to his employment or contract with the Commission.

by

Ames Laboratory Staff

December 8, 1954

Photostat Price \$ 4.80

Microfilm Price \$ 2.70

Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

Ames Laboratory
at
Iowa State College
F. H. Spedding, Director
Contract W-7405 eng-82

UNCLASSIFIED

465-1

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

QUARTERLY SUMMARY RESEARCH REPORT IN METALLURGY

For the period April, May, June, 1954

This report is prepared from material
submitted by the group leaders of
the Laboratory

Previous quarterly research reports in this series are:

ISC-35
ISC-41
ISC-56
ISC-69
ISC-74
ISC-76
ISC-79
ISC-113
ISC-130
ISC-133
ISC-137
ISC-171
ISC-193
ISC-220
ISC-248
ISC-290
ISC-300
ISC-323
ISC-339
ISC-396
ISC-423
ISC-453
ISC-485

TABLE OF CONTENTS

METALLURGY

	<u>Page</u>
1. Purification and Separation Studies.	7
1.1 Niobite-Tantalite Ore Treatment.	7
1.2 Separation of Niobium and Tantalum by Liquid-Liquid Extraction.	8
a. Extraction of HF solutions of niobium and tantalum	8
b. Extraction of potassium hydroxide solution of niobium and tantalum	9
1.3 Studies on the Separation of Titanium from Niobium	9
1.4 Studies on the Separation of Hafnium from Zirconium	10
2. Preparation of Pure Compounds.	11
2.1 Preparation of Thorium Tetrachloride	11
3. Metal Preparation Studies.	11
3.1 Preparation of Vanadium Metal.	11
3.2 Studies on the Preparation of Niobium.	12
3.3 Preparation of Thorium Metal	12
4. Alloy Studies.	13
4.1 Uranium-Zinc System.	13
4.2 Uranium-Chromium/Silver System	14
4.3 Thorium-Hafnium System	15
4.4 Thorium-Carbon Alloy Studies	15
4.5 Uranium-Niobium System	15
4.6 Zirconium-Niobium System	15
4.7 Zirconium-Vanadium System.	16
4.8 Zirconium-Zinc System.	16
4.9 Tantalum-Zirconium System.	16
4.10 Zirconium-Germanium System	17
5. Rare Earth Metallurgy.	17
6. Metal Corrosion.	17
6.1 Corrosion of Metal Containers by Liquid Alloys . .	17
6.2 Corrosion of Tantalum Alloys	18

TABLE OF CONTENTS (Continued)

	<u>Page</u>
7. U/Coating Program.	18
8. Solid State Investigations.	20
8.1 Physical Constants of Metals from Ultrasonic Measurements.	20
8.2 Structure of Al-V Intermetallic Phases.	21
8.3 Growth of Metal Single Crystals	22
9. Other Investigations.	22
9.1 Investigation of the Pyrophoric Film Formed on Uranium Alloys by Pickling in Nitric Acid	22
9.2 Reclamation of Zirconium Chips.	22
9.3 Immiscibility of Uranium and Yttrium.	23
9.4 Vacuum Fusion Analysis.	23
9.5 Experiments on High Aluminum Eutectic with Thorium	24
9.6 The Preparation and Testing of Some Mold Dressings	24
APPENDIX I: LIST OF REPORTS FROM THE AMES LABORATORY.	25
1. Reports for Cooperating Laboratories.	25
2. Papers Published in Scientific Journals	26

METALLURGY

Under the direction of F. H. Spedding, H. A. Wilhelm,
B. A. Rogers, O. N. Carlson, P. Chiotti,
D. Peterson, and J. F. Smith

1. Purification and Separation Studies

1.1 Niobite-Tantalite Ore Treatment (1)*

A number of caustic fusions of a niobite-tantalite ore were made with variations in the charge, the fineness of grind of the ore, the temperature of fusion and the subsequent leaching procedures. In these fusions an excess of ore was employed in place of an inert filler or carbon and the results obtained were more satisfactory than any previous results.

The fusions involved sodium hydroxide, sodium peroxide and in some cases potassium hydroxide and potassium nitrate with the ore. The charges were placed in a cast iron crucible, covered and heated in a muffle furnace at temperatures varying from 400°C to 700°C for 30 minutes or one hour. It was found that a very satisfactory fusion was obtained when a charge of 20 g. of ore, 8 g. of sodium hydroxide and 4 g. of sodium peroxide was heated for one-half hour at 700°C. Heating the charge for more than 1/2 hour at 700°C was found to be unnecessary.

A tentative method for the small scale treatment of columbite-tantalite ore was set up on the basis of the preceding experiments. The procedure is as follows. Fuse 20 parts ore, 8 parts sodium hydroxide and 4 parts sodium peroxide for one-half hour at 700°C. Leach the fused product with 300 parts of boiling 2 molar sodium hydroxide. Wash the residue with cold 1 molar sodium hydroxide. The residue is then stirred with 50 parts of concentrated nitric acid and 5 parts of 30% H₂O₂. The mixture is then heated to boiling and the reaction is completed. The hot slurry is then diluted with 150 parts of water and another 5 parts of hydrogen peroxide is added. This mixture is boiled until the liquid becomes colorless; it is then filtered and the residue washed with water. The earth acid residue is then treated with a minimum amount of hydrofluoric acid to give an acid fluoride solution which is filtered leaving the unreacted ore as a residue. Ammonium hydroxide may be employed to precipitate the hydrated oxides of niobium and tantalum from the acid fluoride solution.

*Numbers indicate group leaders in charge of work.

1.2 Separation of Niobium and Tantalum by Liquid-Liquid Extraction (I)

a. Extraction of HF solutions of niobium and tantalum

It has previously been reported that many water-immiscible organic liquids preferentially extract tantalum from a hydrofluoric acid solution containing both tantalum and niobium. The effect of excess hydrofluoric acid on this separation will be discussed here. Generally it will be shown that the presence of excess acid inhibits a good separation of tantalum from niobium by liquid-liquid extraction.

A series of extractions was carried out on a 12.8 M aqueous solution of hydrofluoric acid containing various amounts of niobium and tantalum. In all cases an equal volume of diethyl ketone was used as the organic phase. These extractions showed that the percent material extracted by the organic phase decreased as the concentration of niobium and tantalum increased. However, the material extracted also increased in tantalum purity. Both the tantalum and niobium distribution coefficients decreased considerably with increasing niobium and tantalum content in the initial aqueous phase while the tantalum-niobium separation factor increased. It appears therefore that the lower the concentration of free hydrofluoric acid in the system, the lower the mass transfer and the higher the tantalum purity in the organic phase becomes.

A second series of extractions was carried out in which the equivalent of 172 g. per liter of combined tantalum and niobium pentoxides was dissolved in various concentrations of hydrofluoric acid. These aqueous fluoride solutions were extracted with an equal volume of diethyl ketone. The data obtained from these extractions indicated that the addition of hydrofluoric acid to the system increased mass transfer to the organic phase, decreased the tantalum purity in the organic phase and decreased the tantalum-niobium separation factors. The distribution coefficients for niobium gradually increased with hydrofluoric acid concentration while the values of tantalum reached a peak at about 9.0 M acid. Very little separation of tantalum from niobium was effected above 20 M hydrofluoric acid since the tantalum-niobium separation factors for these hydrofluoric acid concentrations were below 2.0. From these extraction studies it appears that the preferential extraction of tantalum requires that the ratio of hydrofluoric acid concentration to niobium plus tantalum concentration be relatively low.

A possible explanation for the lack of preferential extraction of tantalum at high hydrofluoric acid concentrations results from consideration of the probable niobium and tantalum species in this acid aqueous medium. It has been reported that fluotantalates,

TaF_7^- , and pentafluoniobates, NbOF_5^- crystallize from a super-saturated fluoride solution. Consequently for nearly saturated solutions of niobium and tantalum it appears reasonable to assume that these species are present in the aqueous phase. The formation of these species by the reaction of hydrofluoric acid with the earth acids probably results when little or no excess hydrofluoric acid is present. However, in the presence of excess hydrofluoric acid it is possible that the pentafluoniobate would tend to form NbF_7^- . It is apparent that on the basis of this reasoning the compounds containing the niobium and tantalum are very similar in solutions with high excess HF , while in low excess HF the compounds are quite different. It would be expected that the relative extractability of the fluotantalates and the fluoniobates might be similar while for the fluotantalates and the pentafluoniobates it might be different. If this assumption is correct an insufficient amount of hydrofluoric acid would yield appreciable amounts of the pentafluoniobate and should result in a considerable relative difference in niobium and tantalum extractability. Although this approach is very qualitative, it does offer an explanation of the high tantalum-niobium separation factors at low hydrofluoric acid concentrations and low separation factors at high acid concentrations.

b. Extraction of potassium hydroxide solution of niobium and tantalum

A basic solution of niobium and tantalum was prepared by dissolving the earth acids in about 2.0 M potassium hydroxide. This solution was indefinitely stable although a concentration equivalent to only about 65 g. per liter of combined tantalum and niobium oxide could be obtained.

Many single stage extractions were carried out directly on this basic solution of niobium and tantalum. In no case was any material extracted by the organic liquid. However, when citric acid was added to the basic solution to neutralize it to a pH as low as 4 a small amount of material was extracted by the organic liquid. In all of these experiments niobium was preferentially extracted. However, the effectiveness of separation and mass transfer did not compare favorably with extraction of the hydrofluoric acid solutions of niobium and tantalum.

1.3 Studies on the Separation of Titanium from Niobium (1)

Results from previous experiments indicated that a separation of titanium from niobium could be obtained by extraction of niobium from an aqueous hydrofluoric acid feed solution, by tributylphosphate or isophorone, and a subsequent scrub of the organic phase with 1.5 M hydrofluoric acid. Isophorone was found to give satisfactory results, and is being employed in the separation studies. Small amounts (0.5 g.) of niobium spectrographically

free of titanium have been obtained using isophorone, but when an attempt was made to obtain it in larger amounts (5.0 g.), the niobium was found to contain titanium. Since 20 to 30 g. of niobium spectrographically free of titanium are required in order to set up a spectrographic method of analysis for small amounts of titanium in the presence of niobium, this difficulty will have to be overcome before a quantitative method of analysis can be developed.

1.4 Studies on the Separation of Hafnium from Zirconium (1)

Work was continued on the use of Primene JM-T for the separation of hafnium and zirconium by liquid-liquid extraction. The best results had been obtained upon extracting a 0.5 M zirconium sulfate solution 2.0 M in sulfuric acid with an equal volume of organic phase containing 25 volume per cent Primene JM-T. Of the various solvents tried for diluting Primene, paraldehyde gave the best results; hexone gave fair results; and heptane, poor results. However, it was found that paraldehyde could be diluted with heptane to 10% of the volume of the organic phase and still give good results.

The effects of increasing the Primene concentration in the organic phase were investigated. More Primene resulted in a proportional increase in transfer but gave little increase in the purity of the zirconium remaining in the aqueous phase. Moreover, increasing the Primene concentration increased the time required for the two phases to separate after shaking.

Experiments were made on the extraction of zirconyl chloride solutions with Primene JM-T. No transfer was obtained with zirconyl chloride or with zirconyl chloride and hydrochloric acid. While some transfer was obtained with the addition of oxalic acid and salicylic acid, satisfactory separation was obtained only with the addition of sulfuric acid.

The effects of varying the zirconium sulfate concentration in the aqueous phase were investigated. It was found that for a given amount of Primene the amount of material transferred remained nearly constant, independent of the zirconium sulfate concentration in the aqueous phase. This was true for zirconium sulfate concentrations from 2.0 M down to 0.063 M where practically all the zirconium and hafnium were transferred to the organic phase. The Primene then exhibits a fixed capacity for the metal in the presence of sulfate. Indications are then that this is not the type of distribution required for an ordinary liquid-liquid extraction separation. The fact that the organic phase product for a single stage is enriched in hafnium is interesting but the utilization of this differential is not apparent for a continuous process for producing pure zirconium.

2. Preparation of Pure Compounds

2.1 Preparation of Thorium Tetrachloride (5)

The continuous chlorination furnace for the preparation of thorium tetrachloride was completed. A test run indicated that the furnace would reach operating temperature with the power supply which was available. A test chlorination run had to be discontinued due to failure of the exhaust system to remove the chlorine gas. A complete renovation of the ventilating system will be necessary to remove this difficulty.

3. Metal Preparation Studies

3.1 Preparation of Vanadium Metal (5,2)

Vanadium metal powder was prepared by reacting vanadium tetrachloride with magnesium at 800°C under an inert atmosphere. The product consisted of a suspension of powdered vanadium in magnesium chloride. The vanadium metal was separated from the mixture by distilling the magnesium chloride under vacuum or by dissolving the magnesium chloride in water. The product was then arc-melted into a button. Separation by leaching gave a purer product than vacuum distillation of the magnesium chloride. The carbon content of the vanadium metal was reduced by a fractional vacuum distillation of the vanadium tetrachloride. Further improvement of the purity of the vanadium metal is necessary since the hardness was greater than Rockwell A-60 and the metal was brittle.

A small quantity of crystal bar vanadium was prepared during this period employing the method described by Nash et al.¹ High purity vanadium is desired for alloy studies and for a study of the effects of impurities upon the physical properties of vanadium. The apparatus used consisted of a Vycor bulb in which pieces of crude vanadium were placed. The crude vanadium was prepared by bomb reduction of V_2O_5 with calcium. Iodine was placed in an adjacent bulb which was connected by means of a ground glass joint to the Vycor tube. The entire system was evacuated and flushed with argon. The bulb containing the crude vanadium was heated to 900°C and iodine vapors were distilled into it. This operation was performed to prepare vanadium iodide. The system was then evacuated and the vanadium iodide volatilized at 800°C. These vapors decomposed on a tungsten filament heated electrically to 1400°C to deposit vanadium crystals on the wire.

Only a few grams of metal have been prepared by this method, an insufficient amount with which to determine its physical properties. The failure to obtain a larger amount of vanadium was

¹J. W. Nash, H. R. Ogden, R. E. Durtsehi and J. E. Campbell, J. Electrochem. Soc., 100, 272-5 (1953).

attributed to the fact that not enough iodide was formed because of the massive form of the crude metal. In succeeding attempts to prepare vanadium by this process, metal powder or droplets will be used as the crude starting material.

3.2 Studies on the Preparation of Niobium (1)

The reduction of Nb_2O_5 with mixtures of calcium and aluminum metal gives quite reproducible results on the small scale tests. The niobium metal, as niobium-rich alloys with aluminum, formed in this manner is acid resistant but more study is needed to improve its physical properties.

The co-reduction of Nb_2O_5 and ZrO_2 , using calcium and aluminum in a one-to-one atomic ratio as reducer, was tried. The niobium and zirconium were to be in a one-to-one atomic ratio in the alloy. Three bomb reductions were made. The first run used only enough calcium and aluminum to reduce the oxides. There was no massive metal and thus no separation of metal and slag in this run. For the second run, enough calcium and aluminum were used to reduce the oxides and enough excess aluminum to put one atom of aluminum with each ten atoms of niobium and ten atoms of zirconium in the alloy was used. Massive metal was formed but it was veined with slag. The third run used three times as much excess aluminum as the second run and a solid biscuit of massive metal, well separated from the slag, was formed. This metal, however, was very brittle. The problems of removing the aluminum or making malleable metal will be the same for both this alloy and for niobium without the zirconium.

3.3 Preparation of Thorium Metal (5,1)

The development of the reduction of thorium tetrachloride by magnesium was inactive during this period due to the work being done on the equipment for producing a larger supply of thorium tetrachloride.

Earlier work by other investigators at the Ames Laboratory showed that magnesium and thorium form a low melting alloy at 25 w/o magnesium. Also a low melting eutectic is indicated in the calcium fluoride-magnesium fluoride system at 46 mole per cent CaF_2 . So ThF_4 was mixed with enough calcium and magnesium calculated to give this low melting alloy as the metal product and the low melting eutectic as the slag. A charge containing one-tenth mole of thorium was packed in a bomb (filling it about one-third full) and heated to 1000°C . The charge reacted but no massive metal was formed. A three-tenths mole charge was packed in the bomb (nearly filling it). This charge was heated to 1000°C , then held, with furnace fluctuations, at an average of 980°C for one hour. Still no massive metal was formed.

4. Alloy Studies

4.1 Uranium-Zinc System (6)

Further work has been done on the determination of the liquidus for the zinc-rich end of the U-Zn system. Zinc was heated in contact with excess uranium under a helium atmosphere. The melt was slowly heated to the desired temperature with continuous stirring then held at constant temperature for several hours without stirring. At the end of this period a sample from the top of the melt was removed, quenched in water and analyzed for uranium. Microscopic examination was used to determine whether the specimen removed was homogeneous or whether suspended compound had been removed with the melt. This process was repeated over two heating and cooling cycles. A summary of the results obtained are shown in Table I.

Table I
Uranium-Zinc Liquidus Composition

Temperature °C	Composition w/o Uranium
420	0.025
450	0.24
500	0.28
550	0.31
600	0.45
650	1.28
700	3.12

The value, 3.12%, obtained at 700°C is doubtful since the microstructure of the quenched alloy showed a considerable amount of large particles of compound which apparently were suspended in the melt when the sample was taken.

Only one compound, UZn_9 , has been found in this system. The compound and uranium form a eutectic which melts at $1050 \pm 25^\circ\text{C}$. The composition of the eutectic is uncertain, but is believed to be near 50 w/o zinc.

465

41

4.2 Uranium-Chromium/Silver System (2)

The extent of liquid immiscibility between the U-20 a/o Cr eutectic and silver is of interest, so this investigation was undertaken. Thermoanalysis of both layers of this system has been completed. The melting point of the eutectic in the Ag layer was observed to be 946°C, slightly lower than the temperature of the uranium-silver eutectic at 950°C. There were no detectable differences observed in the eutectic (860°C) or transformation temperatures in the U-Cr layer.

Table II gives the chemical analysis of each of the liquid layers and conditions for a series of equilibrium studies on this system. The metals were mixed by heating in an induction furnace to 1200°C and then allowed to separate into layers by heating in a resistance furnace under a purified helium atmosphere at the temperature and time shown in the table.

Table II
Chemical Analysis of U-Cr and Ag Immiscible Layers

Temp. °C	Time hrs.	Crucible	U Phase w/o				Ag Phase w/o		
			U	Cr	Ag*	Ag**	U	Cr	Ag
----	----	BeO	93.78	5.375	0.035	-----	3.27	0.40	94.58
960	11	BeO	94.67	5.62	0.02	0.028	2.66	0.033	95.89
975	20	BeO	94.74	5.61	0.01	0.017	2.84	0.03	96.44
950	1.5	Ta	94.52	5.28	0.01	0.022	2.92	0.03	96.33
950	18	Ta	94.27	5.42	0.01	0.016	2.72	0.02	95.79

*Chemical analysis.

**Spectrographic analysis.

Portions of the U-Cr layer were heated in vacuo, one at 1000°C for one hour and one at 1100°C for two hours. This was done to determine whether or not the silver could be distilled from the uranium-rich layers at these temperatures. Spectrographic analysis indicated that none of the silver was removed at 1000°C and only partially removed at 1100°C. It has previously been shown that the silver is quantitatively removed by heating in vacuo at 1200°C and above.

4.3 Thorium-Hafnium System (2)

A study of the thorium-hafnium alloy system has been initiated. A thorium-10 w/o hafnium alloy was prepared by the bomb co-reduction of ThF_4 and HfF_4 with calcium in the presence of zinc and iodine. Good yields were obtained on the reduction.

4.4 Thorium-Carbon Alloy Studies (6)

Melting point determinations of Th-C alloys in the composition range of 0.02 to 0.10 w/o carbon indicate that the solidus is lowered from 1750°C to 1700°C. There is very little change in the solidus temperature as the carbon concentration is increased from 0.1 to 0.5 w/o. As the carbon concentration is increased beyond 0.5 w/o the temperature at which melting is first observed rises rapidly.

4.5 Uranium-Niobium System (3)

In the previous report, a comment was made that the single phase, stable at high temperature, in alloys of intermediate composition was sluggish about decomposing into the two phases presumed to exist at room temperature. Recent metallographic examination of four alloys held at 1300°C for 72 hours and cooled slowly showed that 40, 50 and 60% niobium alloys did not decompose but that a 25% niobium alloy did have heavy precipitation along the grain boundaries. A reconsideration of the boundary between the two phase field at intermediate compositions and the one phase field of the niobium-rich alloys may be necessary.

Measurements of resistance against temperature have been made on 4.5% and 10% niobium alloys. Both showed evidence of transformation slightly above 640°C with rising temperature and at 620°C on cooling. The change on cooling is sensitive to rate of change of temperature as the alloys behave sluggishly.

A 1% niobium alloy could be swaged cold without difficulty after it had been cooled rapidly from 800°C.

4.6 Zirconium-Niobium System (3)

Experimental work on this system was completed during the quarter and a report (ISC-500) of the investigation prepared. Most of the late work consisted of checking previous data on the electrical resistance-temperature behavior of several compositions and in redetermining some x-ray results. Experiments were conducted also on age hardening effects in zirconium-rich alloys quenched from 600°C. Some age hardening was observed in specimens reheated to 300°C to 350°C but the results were not sufficiently definite to be of assistance in locating the solvus line.

465

63

The general form of the constitutional diagram of this alloy system is easy to describe. The solidus line is continuous with a wide flat minimum region of which the low point is at 22% niobium and 1740°C. The solid solution existing at high temperature breaks up as the alloys cool because of the transformation in zirconium-rich alloys and also because of a decomposition of alloys of intermediate composition into two phases. The result is a eutectoid at 17.5% niobium and 610°C. The eutectoid horizontal extends from 6.5% to 87% niobium. Solvus lines extending downward from the ends of this horizontal have not been determined accurately.

4.7 Zirconium-Vanadium System (3)

The investigation of this system was nearing completion at the beginning of the quarter but a final effort was made to determine the structure of the intermediate compound. However, the results were unsatisfactory as no individual crystal large enough for study could be prepared and patterns from the powdered alloy had lines that did not fit into a simple structure. The investigation has been written up in ISC-491.

The constitutional diagram is a simple one. It shows a compound near 53% vanadium. On the zirconium side, a eutectic horizontal at 1230°C extends from 10 to 53% vanadium. On the vanadium side, a peritectic horizontal at 1300°C extends from about 40% to about 87% vanadium. The eutectic composition is 30% vanadium. At lower temperature, there is a eutectoid at 5% vanadium and 777°C. The solubility of vanadium in zirconium is very small below the eutectoid temperature. Vanadium appears able to take up about 5% zirconium at 600°C.

4.8 Zirconium-Zinc System (6)

Apparatus is being assembled for the determination of the vapor pressure of zinc-rich Zr-Zn alloys. The data obtained will be used to determine the phase boundaries of this system.

Attempts to prepare massive alloys in the composition range of 5 to 60 w/o Zr by melting the components together have consistently given alloys of non-uniform compositions. Therefore, powder metallurgy techniques have been used in preparing these alloys. The pressed compacts have been sealed in Vycor tubes to prevent loss of zinc by volatilization and sintered at various temperatures. The nature of these alloys is being investigated by x-ray diffraction techniques.

4.9 Tantalum-Zirconium System (3)

Melting point determinations have been started. Points obtained up to the present time suggest a horizontal, probably of eutectic character, near 1775°C and extending roughly from 20% to 50% tantalum. The course of the solidus curve on either end of the horizontal is less definitely known.

465

14

Dilatometric tests and resistance-temperature measurements have been made on several alloys. The dilatometric measurements, made on specimens turned from slabs of ingot, show that a eutectic horizontal lies at 800°C and extends from 5% tantalum or less to a point beyond 40% tantalum. Apparatus has now been constructed for automatic plotting of resistance-temperature measurements and is proving to be satisfactory.

Fabrication of the alloy wires for resistance-temperature measurements has shown that if the tantalum content is 5% or less, the alloys can be swaged cold but from 5% to 60% tantalum, they must be swaged hot in the initial stages. Preliminary tests indicate that tantalum-rich alloys are difficult to work.

4.10 Zirconium-Germanium System (2)

An attempt was made to prepare high purity germanium metal and to establish the melting point of this material. This information was deemed necessary to correlate the solidus temperatures of germanium-rich alloys in the zirconium-germanium alloy system.

The metal was prepared from C.P. GeO_2 by hydrogen reduction at 650°C followed by vacuum fusion at 1100°C. Yields of metal approaching the theoretical amount were obtained by this method.

The melting point was determined from cooling curve measurements using a calibrated chromel-alumel thermocouple. The average of melting points of several samples was 925°C with a precision of $\pm 2^\circ\text{C}$.

Bell Laboratories report the melting point of pure germanium as 936°C, using material having greater than 20 ohm-centimeters electrical resistivity. The resistivity of the samples giving the 925°C melting point varied from 0.6 to 3.2 ohm-centimeters.

5. Rare Earth Metallurgy

This work is reported in ISC-505.

6. Metal Corrosion

6.1 Corrosion of Metal Containers by Liquid Alloys (5)

Investigation of the corrosion of tantalum by uranium-chromium eutectic containing additions of various elements was continued. This was done in an effort to find an element or elements which when added to the eutectic alloy would inhibit or stop the corrosion of tantalum by this alloy. Samples of uranium-chromium eutectic which contained additions of fifteen different elements were tested at 1000°C. None of these elements had a detectable effect on the corrosion rate.

465
LS

The corrosion of some of the more common metals and alloys by thorium-magnesium eutectic at 1000°C and 650°C was studied. The only alloy, of those tested, which was not excessively attacked after a testing period of seven days was type 430 stainless steel.

The corrosion of niobium, molybdenum, zirconium, and thorium by the eutectics of uranium with iron, manganese, and nickel was studied. All four metals were excessively attacked by the three eutectics at 1000°C.

The dynamic corrosion of tantalum by thorium-magnesium eutectic was investigated. The apparatus used caused the liquid eutectic alloy to flow inside tantalum tubing through a thermal gradient of 140°C. There was no measurable amount of corrosion after a period of 28 days. The gradient used was between 700°C and 840°C.

6.2 Corrosion of Tantalum Alloys (3)

Tantalum-rich binary alloys with aluminum, chromium, molybdenum, titanium and zirconium that were subjected to tests of their resistance to attack by uranium-chromium eutectic have all performed poorly. None of them has demonstrated as good resistance to attack as unalloyed tantalum has. A single test of a tantalum carbide disk indicated that this material has good resistance to attack.

As a result of the test on the tantalum carbide disk, an investigation is being started into the possibility of using carburized tantalum for containing uranium-chromium eutectic. A tantalum crucible with a light coating of carbide showed almost no corrosion by the eutectic after 3 days at 950°C.

7. U Coating Program (6,2)

A number of materials and procedures for coating uranium have been investigated. The most promising coats thus far obtained are zinc, copper-magnesium eutectic (9.7 w/o Mg), and magnesium coats, applied by the hot-dip method, and a nickel-uranium diffusion coat produced by soaking uranium in a molten magnesium bath. Further work has been done in evaluating these coats. These coats have certain desirable as well as undesirable properties. The ideal coat is presumably one which is highly corrosion resistant to water, serves as an effective diffusion barrier between uranium and aluminum, is ductile, does not form brittle intermetallic phases with either uranium or aluminum and has a low capture cross section for neutrons. The copper-magnesium eutectic has excellent corrosion resistance to both 100°C and 178°C water and from results thus far obtained is a satisfactory diffusion barrier between uranium and aluminum, but is somewhat brittle. Zinc is not as effective as a

465
14

diffusion barrier, is more ductile, but has rather poor corrosion resistance to 178°C water. Magnesium forms no intermetallic phases with uranium, but forms an extremely brittle bond with aluminum and is rapidly corroded in 178°C water.

The possibility of hot-press bonding aluminum to these coats is being investigated. Good bonds between aluminum and Cu-9.7 w/o Mg have been obtained at 475°C in 20 minutes at 15,000 psi. At higher temperatures good bonding can be obtained at lower pressure and in a shorter period of time, however, fusion at the interface sets in at 515°C. The occurrence of fusion at the interface is to some extent dependent on time and the applied pressure. Bonded specimens tested in 178°C water for 168 hours showed no evidence of galvanic corrosion or under-cutting at the exposed bond area. Thermal cycling of bonded Al/Cu-Mg/U specimens by dipping them in a fused salt at 450°C for twenty seconds and then quenching in water showed that two to three cycles was sufficient to produce small cracks extending normal to the uranium interface, across the bond to the aluminum interface. However, the components were still firmly bonded after twelve cycles.

Aluminum can be hot-press bonded to magnesium but the bond obtained is very brittle and friable and in general is very unsatisfactory.

Attempts were also made to hot-press bond aluminum to nickel-uranium diffusion coats. At 15,000 psi and 575°C the bond obtained was very irregular. Lower temperatures will be tried.

A thin lead coat over zinc-coated uranium would be expected to serve as an effective diffusion barrier between the zinc and the aluminum. Therefore, attempts have been made to coat aluminum with lead. The coats thus far obtained appear to be well bonded but rapidly blister and separate from the aluminum after a short period in boiling distilled water.

Apparatus for coating and hot-press canning standard four-inch uranium slugs is being constructed.

The corrosion resistance of pure magnesium to 178°C distilled water is poor; five gram samples are completely disintegrated in fifty hours. A number of magnesium-rich alloys containing tin, aluminum, and manganese have been prepared and tested. The results have not been particularly encouraging.

Experimental casting of uranium has been carried out successfully in two-mil zirconium sleeves of one and one-half inch diameter. Capping of these zirconium-clad slugs by various welding techniques is under investigation.

Studies on the corrosion resistance, electrode potentials and aging effects of gamma-quenched U-Zr-Nb alloys have been continued. Several quenched alloys were found to have good corrosion resistance in 300°C water. Good correlation was shown between corrosion rates and electrode potentials. The relative effectiveness of zirconium and niobium in ternary combinations was established. Age hardening data have been determined for three quenched alloys at a 350°C annealing temperature. Annealing at 400°C for 408 hours is shown to have no adverse effect upon the corrosion resistance of the quenched alloys.

Study of the U-Nb, U-Zr, and Zr-Zn systems has continued. The solubility of uranium in zinc is 1.28 w/o at 650°C, and decreases to 0.025% at 420°C. At temperatures above 650°C the values obtained were very erratic.

8. Solid State Investigations

8.1 Physical Constants of Metals from Ultrasonic Measurements (4)

Measurements on the elasticity of single crystals of Zn have been made. Table III shows values reported by previous investigators and compares these data with the experimental values obtained by the measurement of ultrasonic wave velocities at this Laboratory.

Table III
Elastic Constants of Zn
(in units of 10¹¹ dyne/cm²)

C_{11}	C_{33}	C_{44}	C_{12}	C_{13}	Reference ¹
15.8	6.16	4.00	3.15	4.75	Bridgman Gruneisen & Goens
16.2	5.47	4.00	3.55	4.45	
17.2	6.55	3.79	2.62	5.31	Goens
17.9	7.46	3.98	2.42	6.09	Hanson
16.5	5.67	4.10	2.73	4.45	Hanson
16.35	6.29	3.79	2.66	5.17	Jones
<hr/>					
16.66	6.27	3.94	2.86	5.04	Average This Laboratory
16.36	6.30	3.90	3.14	5.98	

¹P. Bridgman, Proc. Nat. Acad. Sci. Wash., 10, 411 (1924);
E. Gruneisen and E. Goens, Z. Physik, 26, 235 (1924);
E. Goens, Ann. Physik, 16, 793 (1933);
A. Hanson, Phys. Rev., 45, 324 (1934);
H. Jones, Physica, 15, 13 (1949).

Several factors contribute to the variation in reported values. First, a static method of measurement will produce a slightly different set of values for the elastic constants than a dynamic method of measurement. This results because a static evaluation is an isothermal evaluation while a dynamic measurement is an adiabatic measurement. Second, Hanson has suggested that zinc is particularly susceptible to variation in elasticity due to impurity content; however, Bridgman questions this. Third, evaluation of C_{12} and C_{13} cannot be made from independent measurements. The obtained value of C_{12} depends upon C_{11} , while C_{13} depends upon C_{11} , C_{33} , and C_{44} . Thus the shear constants C_{12} and C_{13} have a greater spread in reported value than C_{11} , C_{33} , and C_{44} . Finally it should be noted that the values of C_{11} , C_{33} , C_{44} , and C_{12} determined at this Laboratory were obtained from one crystal of zinc while the value of C_{13} was obtained from a second crystal. This is not believed to be serious since the crystals were grown by the same method from the same purity zinc.

Velocities of propagation of ultrasonic waves through polycrystalline yttrium have been measured:

$$v_l = (4.28 \pm 0.02) \times 10^5 \text{ cm/sec.}$$

$$v_t = (2.42 \pm 0.02) \times 10^5 \text{ cm/sec.}$$

The characteristic temperature calculated from these measured values is 268°K.

8.2 Structure of Al-V Intermetallic Phases (4)

Work has continued on the structure of the β -phase of the Al-V system. The following Harker projections have been run on the basis of three dimensional intensity data: $P(0,0,z)$, $P(1/3,2/3,z)$, $P(x,y,0)$, $P(x,y,1/2)$ and $P(x,0,z)$. Statistical evaluation of the intensity distribution data in the manner¹ of Wilson indicates that the centric space group, $C_{6h}^{2/3}$, is the more probable. A

trial structure has now been postulated. On the basis of this trial structure, structure factors have been calculated and the Fourier projection $\rho(x,y)$ has been run with the seven most intense reflections. A plot of this projection is consistent with the postulated structure. The trial structure must be further checked.

¹H. Lipson and W. Cochran, The Determination of Crystal Structures, (London, G. Bell & Sons, Ltd., 1953), p. 35.

Isolation of single crystals of the α -phase, $Al_{11}V$, has been accomplished. The measured value of the lattice parameter is in good agreement with the value reported by D. J. Kenny.¹ However, on the basis of extinctions and symmetry the structure has been assigned to the space group $Fd3m$, while Kenny had assigned $Fd3$. Further work is being done to verify which of these space groups is correct.

Microanalysis of the unidentified crystals mentioned in the previous report gave a probable value of 79.2 w/o Al and a value of 20.93 ± 0.07 w/o V. Spectrographic analysis showed Al and V to be the major constituents with lines of Cu, Mn, Fe, Si and Ti appearing. The evidence indicates that these crystals are really an Al-V phase. It remains to be determined whether this is a metastable phase or whether it has a place in the equilibrium diagram.

8.3 Growth of Metal Single Crystals (4)

The program for growing metal single crystals is progressing satisfactorily. Crystals of lead or zinc can now be grown with a high percentage of single crystals produced per attempt. Single crystals of indium have also been grown. A furnace and controls have been constructed which will be used in an attempt to grow single crystals of α -uranium.

9. Other Investigations

9.1 Investigation of the Pyrophoric Film Formed on Uranium Alloys by Pickling in Nitric Acid (5)

A series of uranium-zirconium alloys containing from 30% to 60% zirconium by weight was prepared by arc-melting. These alloys were heated at 575°C and furnace-cooled to room temperature. The x-ray diffraction patterns of these samples were obtained, from massive samples, with a diffractometer. Diffraction lines were found which were not part of the uranium or zirconium patterns and must be due to the epsilon intermediate phase.

The strong lines of the epsilon diffraction pattern correspond to the x-ray diffraction pattern of the pyrophoric film formed on uranium-zirconium alloys. The zirconium which was isolated from the pyrophoric film previously must have been due to non-homogeneity as the arc-melted alloys. The pyrophoric film seems to be definitely identified as the epsilon phase in the uranium-zirconium system.

9.2 Reclamation of Zirconium Chips (2)

A shipment of zirconium lathe turnings and mill chips were received from Westinghouse Atomic Power Laboratory. The average thickness of individual pieces of scrap was determined to be approximately 5 mils for the turnings and 2 mils for the chips.

¹D. J. Kenny, Ph.D. Thesis, Iowa State College (1953).

The scrap was coated with a film of oil which was removed by three washings with acetone and then dried in air. It also contained a considerable amount of iron impurities which were removed by passing the chips over an electromagnet.

During the machining of the stock zirconium a slight oxide or nitride film apparently is formed on the surface of the machined chips. This oxide layer prevents a simple recasting of the scrap to a workable billet. Zirconium chips which had been acetone-washed and demagnetized were melted in graphite in vacuo. The hardness of the melted material was Rockwell 58 A.

The problem then is the removal of the oxide film without an appreciable loss of metal in order to obtain ductile zirconium. In order to do this various chemical treatments have been tried. The first of these was a hydrofluorination of the scrap material with anhydrous HF at temperatures of 100, 130, 200, 225 and 250°C. This was done, hoping to convert the oxide on the surface to ZrF_4 which could then be removed by sublimation during the vacuum melting. These treatments resulted in 10 to 20 per cent loss in material without an appreciable reduction in hardness.

Since zirconium oxide may be converted to a more soluble compound by a caustic fusion treatment, immersion of the scrap in fused NaOH at temperatures of 450 and 600°C was tried. The scrap was then washed with dilute acid and dried. This treatment did not result in a lower hardness of the cast metal; in fact, a slight increase in hardness was observed.

Recently it has been shown that a leaching treatment with dilute sulfuric acid at elevated temperatures reduces the hardness of the material quite markedly. The scrap was thoroughly washed with water after this acid treatment to remove any sulfate and then rinsed with acetone and air dried. The material which has been treated in this manner, when melted in graphite, had a hardness of Rockwell 44 A with less than 1% loss in weight. To date this appears to be the best chemical treatment for cleaning zirconium chips. Work is continuing on this problem.

9.3 Immiscibility of Uranium and Yttrium (3)

Microscopic examination of uranium-yttrium alloys containing 70, 80 and 90% yttrium melted in a tantalum crucible by induction showed that all alloys had a two phase structure. Evidence for the existence of two liquid layers in the molten state was inconclusive. The yttrium-rich alloys did not attack the tantalum noticeably, but some experiments with uranium-rich alloys produced severe attack on the crucible.

9.4 Vacuum Fusion Analysis (5)

The vacuum fusion apparatus was completed. A number of analyses were made on samples of Armco iron. The results of these analyses were very reproducible and showed high precision. A series of National Bureau of Standards steel samples will be analyzed to demonstrate the accuracy of the apparatus.

9.5 Experiments on High Aluminum Eutectic with Thorium (3)

An investigation was started into the possibility of using a molten thorium-aluminum alloy as a carrier of uranium. According to the published data, the thorium-aluminum system has a eutectic at 650°C and 25% thorium, but a piece of the eutectic alloy did not melt at a furnace temperature of 750°C. A charge of the same alloy to which had been added a small but undetermined percentage of uranium melted at 800°C. This charge was kept molten for 80 hours without apparent attack on the tantalum crucible, but the alloy structure no longer had the typical eutectic appearance.

9.6 The Preparation and Testing of Some Mold Dressings (1)

In connection with the casting of uranium metal in steel molds the walls of the molds may be coated with a material which prevents direct contact between the liquid uranium and the solid steel. Coatings of carbon, certain oxides and other materials have been used. In the present work, the molds are for casting uranium rods and are tubes about 30 inches in length with a one and one-half inch bore. The oxide mold dressings may be applied as a water suspension. It is important for metal quality that the coating material release practically all of its water at a low drying temperature.

Zirconium oxide and aluminum oxide appear promising from the standpoint of loss of weight on drying. Water suspension of these finely ground oxides will dry at a low temperature practically completely after application if the oxides are prefired at temperatures well above 1000°C.

APPENDIX I: LIST OF REPORTS FROM THE AMES LABORATORY

1. Reports for Cooperating Laboratories

- ISC-423 Metallurgy. Quarterly Summary Research Report. July, August, September, 1953. Ames Laboratory Staff. SECRET.
- ISC-429 The Effect of Electronic Quadrupole-Quadrupole Interactions on the Specific Heat of Cerium Metal. E. Koenigsberg and J. M. Keller. UNCLASSIFIED.
- ISC-450 Chemistry. Quarterly Summary Research Report. October, November, December, 1953. Ames Laboratory Staff. SECRET.
- ISC-451 Physics. Quarterly Summary Research Report. October, November, December, 1953. Ames Laboratory Staff. UNCLASSIFIED.
- ISC-453 Metallurgy. Quarterly Summary Research Report. October, November, December, 1953. Ames Laboratory Staff. SECRET.
- ISC-460 Electrostatic Energy Calculations for Sodium Tungsten Bronze (Na_xWO_3). J. F. Smith. UNCLASSIFIED.
- ISC-462 The Decay of UX_1 , UX_2 and UZ . Sven A. E. Johannson. UNCLASSIFIED.
- ISC-463 Solubility of Carbon in Thorium. R. Mickelson and D. Peterson. SECRET.
- ISC-470 Titration of Bismuth with Ethylenediaminetetraacetic Acid. J. S. Fritz. UNCLASSIFIED.
- ISC-471 Time Dependent Variational Principle. S. Altshuler and J. F. Carlson. UNCLASSIFIED.
- ISC-473 The Beta-Spectra of Pr^{142} , Tm^{170} and Rb^{86} . A. V. Pohm, W. E. Lewis, J. H. Talboy, Jr. and E. N. Jensen. UNCLASSIFIED.
- ISC-475 The Separation of Isotopes by Ion Exchange. F. H. Spedding, J. E. Powell, H. J. Svec, R. E. Harrington, J. S. Fritz, M. O. Fulda, and J. L. Evans. SECRET.
- ISC-480 Etching Metals by Ionic Bombardment. A. J. Carlson, J. T. Williams, B. A. Rogers and E. J. Manthos. UNCLASSIFIED.

ISC-483 Engineering. Quarterly Summary Research Report. January, February, March, 1954. Ames Laboratory Staff. SECRET.

2. Papers Published in Scientific Journals

Allison, M., R. W. Moore, A. E. Richardson, D. T. Peterson and A. F. Voigt

The Determination of Mesothorium in Thorium Nitrate. Nucleonics 12, 32-34 (1954).

Banister, J. R., S. Legvold and F. H. Spedding

The Structure of Cd, Dy and Er at Low Temperatures. Phys. Rev. 94, 1140-1142 (1954).

Elliott, J. F., S. Legvold and F. H. Spedding

Some Magnetic Properties of Dysprosium Metal. Phys. Rev. 94, 1143-1145 (1954).

Elliott, J. F., S. Legvold and F. H. Spedding

The Magnetic Susceptibility of Neodymium Metal. Phys. Rev. 94, 50-51 (1954).

Fritz, J. S., M. O. Fulda, S. L. Margerum and E. I. Lane

Analysis of Uranium-Zinc Alloys. Analytical Chimica Acta 10, 513-516 (1954).

Goodman, L. and H. Shull

Modification of the Naive MO Method. J. Chem. Phys. 22, 1138 (1954).

Goodman, L. and H. Shull

A Semiempirical Treatment of $n-\pi$ Transitions. J. Chem. Phys. 22, 1138-1139 (1954).

Herwig, L. O. and G. H. Miller

Alpha Particle Ionization Yields in a Gridded Chamber. Phys. Rev. 94, 1183 (1954).

Kniseley, R. N. and V. A. Fassel

The Effect of Stray Light in Prism and Grating Spectrographs on Emulsion Calibration Curves and Its Significance in Spectrographic Analysis. J. Opt. Soc. 44, 390-393 (1954).

Lane, R. O. and D. J. Zaffarano

Transmission of 0-40 Kev Electrons by Thin Films with Application to Beta-Ray Spectroscopy. Phys. Rev. 94, 960-964 (1954).

Nichols, R. T. and E. N. Jensen

Radioisotope P33. Phys. Rev. 94, 369-371 (1954).

265

24

- Schupp, F. D. and D. S. Martin, Jr.
The $\text{Mg}^{24}(\gamma, 3p, 3n)\text{Fl}^{18}$ Reaction Induced by 70 Mev
Bremsstrahlung. Phys. Rev. 94, 80 (1954).
- Spedding, F. H., A. H. Daane and J. E. Powell
Portable Thulium X-Ray Unit. II. Methods for Preparing
Thulium Oxide or Metal. Nucleonics 12, 37 (1954).
- Spedding, F. H. and J. E. Powell
The Separation of Rare Earths by Ion-Exchange. VIII.
Quantitative Theory of the Mechanism Involved in Elution
by Dilute Citrate Solution. J. Am. Chem. Soc. 76, 2550-
2557 (1954).
- Spedding, F. H. and J. E. Powell
The Separation of Rare Earths by Ion-Exchange. VII.
Quantitative Data for the Elution of Neodymium. J.
Am. Chem. Soc. 76, 2545-2550 (1954).
- Spedding, F. H., J. E. Powell and E. J. Wheelwright
The Use of Copper as the Retaining Ion in the Elution
of Rare Earths with Ammonium Ethylenediaminetetraacetate
Solutions. J. Am. Chem. Soc. 76, 2557-2560 (1954).
- Spencer, W. R. and F. R. Duke
The Cerium(IV) Sulfate Oxidation of Phenols. Anal.
Chem. 26, 919-920 (1954).

465

25