**AMES
LABORATORY
IOWA STATE
COLLEGE**

**METALLURGY. SEMI-ANNUAL SUMMARY RESEARCH REPORT
JULY-DECEMBER, 1955**

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.

U N C L A S S I F I E D

ISC-708

U N I T E D S T A T E S A T O M I C E N E R G Y C O M M I S S I O N

L

SEMI-ANNUAL SUMMARY RESEARCH REPORT IN METALLURGY

For July - December, 1955

by

Ames Laboratory Staff

May 29, 1956

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

U N C L A S S I F I E D

U N C L A S S I F I E D

2

ISC-708

This report is distributed according to Metallurgy and Ceramics as listed in TID-4500, January 15, 1956.

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.

Printed in USA. Price 30 cents. Available from the

Office of Technical Services
U. S. Department of Commerce
Washington 25, D. C.

U N C L A S S I F I E D

TABLE OF CONTENTS

METALLURGY

	<u>Page</u>
1. Purification and Separation Studies.	7
1.1 Treatment of Ores and Separation of Niobium and Tantalum	7
1.2 Studies on the Separation of Hafnium from Zirconium.	8
2. Preparation of Pure Compounds.	8
2.1 Preparation of Thorium Tetrachloride	8
2.2 Preparation of Rare Earth Fluorides.	9
2.3 Preparation of Vanadium Trifluoride.	10
3. Metal Preparation Studies.	10
3.1 Preparation of Vanadium Metal.	10
3.2 Preparation of Niobium Metal	11
3.3 Preparation of Thorium Metal	11
3.4 Preparation of Yttrium Metal	12
4. Alloy Systems.	13
4.1 Uranium-Zinc System.	13
4.2 Thorium-Zirconium Alloy.	13
4.3 Thorium-Hafnium Phase Diagram.	15
4.4 Uranium-Niobium System	15
4.5 Zirconium-Tantalum System.	16
4.6 Zirconium-Zinc System.	17
4.7 Tantalum-Vanadium System	18
4.8 Vanadium-Copper Alloy System	19
5. Metal Coatings and Corrosion	20
5.1 Corrosion of Refractory Metals by Liquid Metals.	20
5.2 Corrosion of Tantalum Carbide and Other Crucible Materials.	20
5.3 Corrosion of Uranium by Liquid Lead and the Rate of Growth of Compound Layers in Solid Lead- Uranium Couples.	21
6. Solid State Investigations	23
6.1 Structure of the Compound, V_4Al_{23}	23
6.2 Study of the Alpha, Beta and Gamma Transformations in Uranium	23

TABLE OF CONTENTS (Continued)

	<u>Page</u>
6.2.1 Temperature-Dependence of the Lattice Parameters of Uranium.	24
6.2.2 Refinement of Lattice Parameters	25
6.2.3 Future Work.	25
6.3 Structure of Epsilon Uranium-Zirconium.	29
6.4 Effect of Heat Treatment Upon Physical Properties of Uranium.	29
7. Other Investigations.	29
7.1 Metallography of Thorium.	29
7.2 Vacuum Fusion Analysis of Metals.	29
7.3 Low Melting Alloy Studies	30
7.4 A Study of Calcium Fluoride Bodies.	30
7.5 Growth of Single Crystals of High Melting Metals.	30
8. Rare Earth Metallurgy	30
APPENDIX I: LIST OF REPORTS FROM THE AMES LABORATORY	31
1. Reports for Cooperating Laboratories	31
2. Papers Published in Scientific Journals.	32
APPENDIX II: LIST OF SHIPMENTS	34
APPENDIX III:	37

SEMI-ANNUAL SUMMARY RESEARCH REPORT IN METALLURGY

For the period July - December, 1955

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

Previous 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
ISC-506
ISC-531
ISC-575
ISC-607
ISC-644

April, May, June 1955

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

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 Treatment of Ores and Separation of Niobium and Tantalum (1)*

Work has continued on the treatment of ore concentrates of niobium and tantalum. The treatment of these concentrates with aqueous HF, with fused NaOH and with H_2SO_4 was investigated further. The aqueous HF and fused NaOH treatments are rather efficient in opening most ores of niobium and tantalum. The treatment with concentrated H_2SO_4 requires considerable time at temperatures of about 300°C to open an appreciable fraction of some of these ores. In view of the ease and efficiency of the HF and NaOH treatments most of the attention is now being focused on these two methods.

In the HF treatment the ore is digested with 70% HF solution for a number of hours. Agitation, or stirring, the mixture during this time assists in increasing the reaction yield on the ore. The reaction product is then extracted with an organic which removes the niobium and tantalum with fair purity from the aqueous phase. Some ketones are quite effective in this extraction. A back extraction employing a small amount of an acid aqueous solution removes practically all of the impurities that followed the niobium and tantalum to the organic phase. Titanium, one of the elements usually troublesome in niobium-tantalum purification work, can be removed by this procedure to the extent that it is not detected by ordinary spectrographic tests. Diethyl ketone has been employed as the organic in much of this work to date, although hexone, tributyl phosphate, mesityl oxide and many other organic compounds have possible application in this method of purification.

The separation of niobium from tantalum is accomplished by further extraction of the organic solution phase with aqueous solution. In general the tantalum prefers the organic phase when hydrofluoric acid is present. Niobium that does not show a qualitative spectrographic test for tantalum can be prepared by this separation principle. Tantalum with equal purity with respect to niobium can likewise be prepared during the same extraction.

The NaOH treatment of the ore gives a product that is washed with water to remove most of the silicon, aluminum, tin and some manganese and other impurities. Subsequent treatment of the residue with inorganic acid and then filtration removes most of the iron, manganese, some titanium and other remaining impurities. The niobium and tantalum acid oxides are then dissolved in aqueous HF and extracted into an organic solvent. The subsequent steps here follow closely those outlined above for the organic solution from the HF method of ore treatment.

*Numbers indicate group leaders in charge of work. See Appendix III.

The HF and NaOH treatments will be compared and advantages and disadvantages determined.

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

Tests were made to determine the effectiveness of a liquid-liquid countercurrent extraction separation of hafnium and zirconium in a sulfate solution with Primene 81-R, hexone and thiocyanic acid. The tests indicated that although the single stage data were quite favorable, the continuous countercurrent operation was not practical under the predicted conditions that were employed.

Two amines, dibutyl amine and tributyl amine, were found to give considerable transfer when solutions of 30 volume % amine in hexone were used to extract equal volumes of aqueous zirconium sulfate-sulfuric acid solutions. However, neither of these amines appeared very promising as the separation of hafnium and zirconium was very slight, with zirconium preferring the organic phase.

Some experiments were made on the partial precipitation of zirconyl chloride solutions with citric acid and tartaric acid. Both of these acids gave precipitates from zirconyl chloride solutions which were soluble in an excess of precipitating acid and soluble in ammonium hydroxide. By adding enough of these acids to precipitate only part of the zirconium it was hoped that some enrichment of hafnium or zirconium would be obtained in the precipitate. With citric acid there was no significant difference between the precipitate and the material remaining in the filtrate. With tartaric acid there was a slightly higher percentage of hafnium in the filtrate than in the precipitate, but the separation was not enough to show any promise.

2. Preparation of Pure Compounds

2.1 Preparation of Thorium Tetrachloride (5)

The vertical tube chlorination apparatus continued to be subject to sticking of the charge under all conditions of temperature and reaction rate which were tried. As a result, the operation of a reaction tube of this design on the small scale was discontinued.

A horizontal oscillating reaction tube was designed and constructed using a quartz reaction tube. This reactor functioned very well and no clogging and sticking of the charge occurred. The reaction rate was increased progressively until reaction rates ten-fold faster than those of the vertical tube reactor were used. A decrease in the particle size of the charge permitted a further increase in the reaction rate and produced a higher percentage conversion to thorium tetrachloride. The corrosion of inconel by chlorine at 550°C was tested and found to be quite low. A horizontal chlorination reactor using an inconel tube was designed and construction started.

A larger scale batch chlorination apparatus was operated to produce the thorium tetrachloride needed for research on sublimation-purification and on thorium metal preparation. This apparatus produced 15 pounds of thorium tetrachloride per batch, of an average purity of 75 per cent. A total of 120 pounds of thorium tetrachloride was made.

The semi-continuous vacuum sublimation still for purifying thorium tetrachloride was placed in operation and its performance evaluated. A number of minor modifications were made to remedy mechanical difficulties. The performance of the still was excellent and the rate of sublimation was about one pound per hour, which was the designed capacity. The sublimed thorium tetrachloride was a dense, white, crystalline mass which was easily removed from the condenser. The product purity was adequate, the main impurities being thorium oxide and carbon carried over from the charge, and small amounts of iron, nickel and chromium. The amount of thorium oxide and carbon in the product can be decreased by reducing the rate of sublimation. The iron, nickel and chromium content can be reduced by very careful temperature control which effects a fractional sublimation separation. However, these methods of improving the purity of the product result in a slower rate of sublimation and other methods of obtaining the desired purity will be sought.

2.2 Preparation of Rare Earth Fluorides (2,7)

The trifluorides of lanthanum, yttrium, gadolinium, neodymium, erbium and dysprosium have been prepared by the reaction of anhydrous HF with the trivalent oxides. This reaction was carried out in platinum trays at a furnace temperature of 575°C for an 8 hour period. Although chemical analyses of the fluorides have not been obtained the weight changes observed after hydrofluorination indicate that conversions of greater than 97% are obtained. CeO_2 and Pr_6O_{11} have been similarly hydrofluorinated and, although the exact formula of the resulting fluoride is not known, a fluoride is obtained which is suitable for use in reduction to the respective metals.

Neodymium, praseodymium, cerium and yttrium fluorides may also be prepared by an aqueous precipitation method. Hydrated crystals of the rare earth trichloride are formed by crystallization from an HCl solution of the oxide. These are reacted with aqueous 70% hydrofluoric acid, which yields the rare earth fluorides as granular precipitates. These fluorides are hydrated, or at least contain adhering moisture, so that a drying treatment in an HF atmosphere at elevated temperatures is considered necessary.

It was found that as much as 0.1 to 0.2% iron is introduced into the various fluorides when commercial aqueous 70% hydrofluoric acid is used in their preparation. The source of this contamination is believed to be the steel drums in which the acid is shipped and stored. Aqueous 70% hydrofluoric acid, free of iron, was prepared

by condensing anhydrous hydrogen fluoride gas in a copper coil, which was packed in dry ice, and dripping this liquid into water, contained in a graduated fluorothene vessel. The mixture was stirred by a teflon-covered, magnetically-rotated iron rod. The entire operation was carried out in a ventilated hood, the vents of which were connected to a scrubbing tower. Several liters of acid have been prepared in this manner, and a scale up of the operation appears to be feasible.

2.3 Preparation of Vanadium Trifluoride (2)

The present method of preparing VF_3 consists of passing moist O_2 over V_2O_5 at 600°C , which reduces the carbon and nitrogen impurities in the oxide. The pentoxide is reduced to vanadium trioxide with hydrogen at $600\text{--}800^\circ\text{C}$, and the V_2O_3 is reacted with pure 70% HF to form a hydrated vanadium trifluoride. Chemical analysis has shown the hydrate to be approximately $\text{VF}_3 \cdot 2\text{H}_2\text{O}$.

It was found that, in order to avoid pyrohydrolysis during dehydration of the $\text{VF}_3 \cdot 2\text{H}_2\text{O}$, a two step drying process is most satisfactory. This process consists of heating in an HF atmosphere at 150°C for 2 hours, which removes about 85% of the water of hydration. This is followed by a 4 hour treatment at 400°C which removes most of the remaining water. Chemical analysis of the latter material indicates that there is 1 to 2% water still present, although the accuracy of this determination is somewhat questionable.

3. Metal Preparation Studies

3.1 Preparation of Vanadium Metal (2)

Several experiments have been performed on the preparation of vanadium metal by the iodide process. Machine turnings from bomb prepared vanadium metal were placed in an evacuated inconel reaction chamber. After the apparatus temperature had reached 900°C , iodine was added in measured quantities from a hopper into the reaction vessel. During the run the approximate temperature of the electrically heated tungsten wire filament was maintained at about 1400°C . The major difficulty encountered during these experiments was the extremely slow deposition rate of vanadium on the filament. By adding small quantities of iodine intermittently throughout the run it was possible to keep the reaction going, as indicated by the continued decrease in resistance of the filament. Over a period of several hours the diameter of the filament was increased from the original diameter of 0.020 inches to about 0.125 inches. The metal deposit was crystalline in appearance but was very ductile and was readily rolled into thin sheet. Because of the difficulty encountered in removing the tungsten, a filament of vanadium wire has recently been fabricated. This will be used in future crystal bar experiments.

A study is being made to determine the feasibility of preparing vanadium metal by a bomb reduction of VF_3 . Several pounds of VF_3 were prepared using the method described in a previous section of this report. Calcium was employed as the reductant in these tests and vanadium metal was obtained in yields of 90 per cent. The metal was obtained in massive form with good slag-metal separation. Microscopic examination of this metal revealed considerable impurities, and hardness tests indicated that the metal was quite brittle.

3.2 Preparation of Niobium Metal (1)

Possibilities of obtaining ductile niobium by reductions of Nb_2O_5 with calcium and aluminum are being reinvestigated. The calcium and aluminum react with the oxide to form a low melting slag ($5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$). Small amounts of manganese in the form of MnO_2 are also added to increase the heat of the reaction and to lower the melting point of the niobium alloy. A number of bomb reductions of Nb_2O_5 were carried out by this method, all giving very good metal-slag separations with average yields of 85% relative to Nb.

After obtaining the Nb-Al-Mn alloy, the prime difficulty is removal of aluminum. Manganese removal presents no problem since this constituent readily volatilizes off during subsequent heating. This was verified by taking samples after arc-melting in an atmosphere of helium and quantitatively analyzing for manganese. Results showed no manganese present. However, these same samples show from 0.4 to 1% aluminum remaining in the arc-melted sample. Possibly arc-melting at reduced pressure, or essentially under a vacuum, will reduce the aluminum to insignificant amounts.

The reduction of Nb_2O_5 with carbon was studied further. The purpose of this effort is to explore the possibility of obtaining a satisfactory product without the use of vacuum-sintering by high temperature resistance heating. At present the oxide is mixed with a slight excess of carbon and sintered in a vacuum by induction heating at a temperature just sufficient to essentially complete the reaction. The reaction seems to proceed in stages from about 1150°C to 1800°C. The product obtained is a slightly sintered metallic sponge. Subsequent arc-melting in a helium atmosphere gives a metal that has considerable malleability. It is conceivable that arc-melting this sponge by consumable electrode in a vacuum will readily give metal of satisfactory quality.

3.3 Preparation of Thorium Metal (3,5)

The reduction of thorium tetrachloride by magnesium was carried out on a larger scale using a larger apparatus. The size of the reduction charge was limited to about four pounds by the limited availability of purified thorium tetrachloride. The operation of the larger reduction apparatus was entirely successful. At 900°C, the reduction yields of thorium ranged up to 94 per cent and the quality of the metal was satisfactory. The magnesium and magnesium

chloride were removed by heating under vacuum at 925°C. This resulted in a sponge thorium which could be arc-melted with only slight vaporization of residual volatile materials. The reduction and magnesium removal steps seem to be developed satisfactorily and need only to be increased in scale of operation.

Because of a need for a superior grade of thorium for use in the study of alloy systems, work has been started on production of the metal by decomposition of the iodide on a hot wire. A number of runs have been made and some deposits of apparently satisfactory nature have been obtained, but the rate of deposition is slower than desirable.

3.4 Preparation of Yttrium Metal (2,7)

Yttrium metal can be prepared by a bomb reduction process in which YF_3 and ZnF_2 are simultaneously reduced by calcium to yield a massive Y-Zn alloy. It was found, however, that it is very difficult to remove the zinc from this alloy without melting and spattering of yttrium and without interaction with the crucible.

Attempts were made to prepare a Y-Mg alloy by reacting yttrium fluoride with calcium in the presence of magnesium and iodine in a bomb lined with sintered calcium fluoride. This was heated to 1000°C. A massive vein of Y-Mg alloy, surrounded completely by slag, was obtained. Preliminary experiments demonstrated that the magnesium could be readily distilled away from the yttrium and a piece of this yttrium metal which was arc-melted was relatively free of microscopic impurities. Density calculations made on the resulting Y-Mg alloy and the CaF_2 - CaI_2 slag revealed that the alloy and the slag had approximately the same density. This partially accounts for poor metal-slag separation.

Further studies showed that fused anhydrous calcium chloride added to the charge in place of the iodine would give a lower density, low-melting $CaCl_2$ - CaF_2 slag. This resulted in very good separation of alloy and slag. Although the alloy was obtained in a massive form, the slag penetrated and dissolved the CaF_2 liner, making removal of the slag and alloy from the bomb quite difficult. In order to avoid this difficulty, the CaF_2 liner was replaced by MgO . Very little penetration of slag into the MgO liner was noted, although some interaction between the Y-Mg alloy and the MgO liner was observed.

Magnesium can readily be removed from the alloy by crushing the brittle alloy and heating the pieces slowly in an MgO crucible under vacuum to 1300°C. This yields a bright yttrium sponge free of calcium and magnesium. Attempts were made to "demag" the biscuit as a solid piece; however, this resulted in partial melting and interaction with the crucible. No melting is encountered during "demaging" of the smaller pieces and no interaction with the crucible is encountered.

The hardness of the arc-melted yttrium sponge is R_A 20-30. This metal contains less inclusions and impurities than that prepared by the zinc-alloy process.

4. Alloy Systems

4.1 Uranium-Zinc System (6)

Work on the uranium-zinc system has been completed and the results summarized in Report No. ISC-656. A manuscript has been prepared from the report and submitted for publication in The Transactions of the American Institute of Mining and Metallurgical Engineers. An abstract of the paper follows.

The phase fields existing in the uranium-zinc system at one atmosphere pressure and at five atmospheres pressure have been determined from x-ray, metallographic, thermal, and vapor pressure data.

Only one compound, UZn_9 , is formed in this system. At 910°C and one atmosphere pressure this compound exists in equilibrium with zinc-rich liquid containing approximately 14.6 w/o uranium and zinc vapor. The solubility of uranium in zinc decreases to 0.45 w/o at 600°C and to 0.025 w/o at 419°C . The compound forms a eutectic with uranium which contains 42.0 ± 0.5 w/o uranium and melts at $944 \pm 5^\circ\text{C}$. The solid solubility of zinc in uranium is very low and was beyond detection by the experimental methods employed. The compound UZn_9 shows little or no solid solubility for either zinc or uranium. At one atmosphere pressure alloys in the composition range between the compound and pure uranium dissociate into zinc vapor and gamma uranium at temperatures of 947°C or above.

At five atmospheres pressure additional features of the phase diagram become evident. A monotectic horizontal is formed at $1050 \pm 20^\circ\text{C}$. The monotectic composition lies between 91 and 95 w/o uranium. The immiscibility gap at 1050° extends from 47 to about 93 w/o uranium. The compound UZn_9 is thought to melt congruently at $1050 \pm 20^\circ\text{C}$ at 5 atmospheres.

4.2 Thorium-Zirconium Alloy (2)

During this period the investigation of the high temperature phases of the Th-Zr phase diagram was continued. The lattice constants of the high temperature B.C.C. phase as a function of composition were determined at 1000°C and are now believed to be more accurate than those values reported previously. Rectangular specimens were cut from seven alloys for this investigation. The temperature was measured by means of an optical pyrometer sighted into a small hole drilled into the edge of the x-ray specimen. In this manner the temperature measurement could be compared with

simultaneous thermocouple readings. A refinement in the lattice constant calculations was made by a graphical method using the Nelson-Riley function [J. B. Nelson and D. P. Riley, Proc. Phys. Soc. (London), 57, 160 (1945)]. These extrapolated values and corresponding compositions are given in Table I.

Table I

Lattice Constant Vs. Composition for B.C.C. Th-Zr Alloys

Per Cent Composition	Lattice Constant at 1000°C
Th-20% Zr	3.91 Å
Th-25% Zr	3.88 Å
Th-30% Zr	3.84 Å
Th-40% Zr	3.79 Å
Th-50% Zr	3.74 Å
Th-60% Zr	3.71 Å
Th-75% Zr	3.66 Å

The lattice constants in higher zirconium alloys have not yet been determined. Attempts were made to determine the lattice constants in the thorium-rich region, but no B.C.C. reflections were obtained at 1000°C in alloys containing 10 w/o Zr or less.

Attempts were made to determine the upper boundary of the thorium-rich alpha + beta region, using high temperature x-ray techniques. All of the points on the boundary were determined by raising the temperature of the alloy to a point where all the F.C.C. reflections were absent, and then slowly lowering the temperature until a F.C.C. peak was recorded. In this manner the phase boundary was determined for six alloys. The alloy composition and the phase transition temperatures are listed in Table II. These transition temperatures are about 50 degrees higher than the values obtained for thermal analyses, but the general curve parallels the boundary as determined by the other methods.

Table II

Upper Boundary of $\alpha + \beta$ Field in Th-Zr Alloys

Alloy Composition	Transition Temperature - °C
Th- 8% Zr	1105-1120°
Th- 11.5% Zr	980-990°
Th- 25% Zr	930-950°
Th- 40% Zr	925-948°
Th- 50% Zr	893-902°
Th- 60% Zr	822-832°

4.3 Thorium-Hafnium Phase Diagram (2)

Work was continued on the study of the thorium-hafnium phase diagram. Microscopic examination of quenched and slow-cooled alloys confirmed the presence of a eutectoid on the thorium-rich side of the diagram at approximately 9 weight per cent hafnium and at 1280°C. However, no microscopic evidence for a eutectoid at the hafnium-rich end of the diagram was found.

Microscopic examination of additional arc-melted alloys confirmed the presence of a eutectic at 1450°C and at 24.75 weight per cent hafnium.

Microscopic examination of quenched alloys indicated that the extent of primary solid solubility of hafnium in F.C.C. thorium is less than 5 weight per cent hafnium at 1280°C. It was also shown that the limit of primary solid solubility of thorium in alpha hafnium is less than 5 weight per cent thorium at 1280°C.

High temperature x-ray investigations of 69.6, 91.4 and 94.7% Hf alloys indicated that the alpha hafnium exists to at least 1450°C and that the thorium-rich phase changes from F.C.C. to B.C.C. at 1280°C upon heating.

4.4 Uranium-Niobium System (3)

The inhomogeneous character of the uranium-niobium alloys of intermediate composition, about which complaint was made in the previous report (ISC-644), appears to have both chemical and

physical components. Chemical inhomogeneity exists on a microscopic scale. Because of excessive coring, the alloys appear dendritic. Prolonged heating of the alloys in the 1200°C to 1400°C range of temperature has little effect on the coring. Improvement can be obtained by working and subsequent heating, but the method can scarcely be called successful because the alloys crack considerably under either hot or cold deformation. The soft centers in the billet appear to be caused by porosity. This region is the last to solidify, and, apparently, the shrinkage upon freezing is considerable; hence, the space is incompletely filled.

Extensive electrical-resistance temperature measurements have been made on uranium-rich alloys up to 15 per cent niobium. These measurements have proven the most satisfactory of all methods for the determination of phase boundaries in this area. In general, the resistance measurements and dilatometric results agree closely but the former reveal more details. Resistance measurements do not give an indication of the position of the solvus line but this can be determined within reasonable limits by metallography.

According to metallographic examinations, the uranium-rich alloys show solid solution out to about 0.3 per cent niobium at 550°C. In general, metallographic results agree with the boundaries determined by resistance and dilatometric measurements.

4.5 Zirconium-Tantalum System (3)

In the investigation of the zirconium-tantalum system additional measurements of melting points have been made. New measurements on zirconium-rich alloys confirm that the solidus line is horizontal to a tantalum content as low as 2 per cent. Tantalum-rich alloys, also, have yielded melting points in agreement with previous determinations. Attempts to find a eutectic composition have not been successful. The interval between first evidence of melting and complete melting scarcely exceeds 15°C for any composition from 3 to 45 per cent tantalum.

Metallographic work has been concentrated on the solubility of tantalum in zirconium. Samples sealed in evacuated silica capsules have been quenched from temperatures from 300° to 1200°C. The samples show that the alpha-zirconium solid solution extends to 2 per cent tantalum at 800°C and that the solubility may be nearly this much at considerably lower temperatures. The beta-zirconium solid solution field evidently is more extensive than anticipated as alloys containing considerable tantalum are single phase. For example, the 15 per cent tantalum alloy was single phase above 1050° and the 20 per cent was single phase above 1065°C.

In general, the x-ray data confirm the metallographic results. Thin wires quenched in helium from 1330°C give strong evidence of two-body-centered cubic solid solutions. Alloys containing from 30 to 80 per cent tantalum all have shown lines corresponding to a solid solution of approximately 10 per cent zirconium in tantalum. The pattern of the tantalum-rich alloys cannot be detected in the 30 per cent tantalum alloy but the zirconium-rich solid solution may not extend to such a high tantalum content at 1330°C.

Electrical resistance-temperature measurements have been resumed but without graphic recording. Direct readings with a potentiometer have given increased accuracy and have brought out features not clearly indicated by the graphs. In particular, these measurements have given evidence of a possible complication in what has been considered a simple eutectoid horizontal near 800°C.

Dilatometric measurements are being continued and are in general agreement with the results of resistance-temperature measurements. A 60 cps circuit is being substituted in place of the 2000 cps circuit previously used. The 60 cps circuit is considerably simpler and should require less maintenance, but no decision has been reached as to the desirability of the change.

4.6 Zirconium-Zinc System (6)

Thermal, x-ray and diffusion band analyses from previous work indicated that the Zr-Zn system contained four compounds. Approximate zinc to zirconium ratios of ZrZn_{15} , ZrZn_6 , ZrZn_2 , and ZrZn have been assigned to the four compounds. It was believed that the two highest zinc compounds decompose peritectically at 550° and 750°C, respectively, and a decomposition temperature somewhat above 1050°C has been proposed for the ZrZn phase. Recent work indicates these temperatures are substantially correct. However, a proposed peritectic decomposition for the ZrZn_2 phase at 850°C does not appear substantiated. Vapor pressure measurements, which will be discussed subsequently, and older thermal analysis results indicate the compound may decompose at 900°C or higher.

It was decided to employ the rather volatile properties of zinc to advantage by taking vapor pressure measurements to help establish the phase boundaries. A dew point method for determining vapor pressures was used. This method consists of observing the alloy temperature and the temperature at which zinc begins condensing on a cooled area directly above the alloy. The vapor pressure of zinc over the alloy is then equal to the known vapor pressure of pure zinc at the temperature of the cooled area.

Plots of log vapor pressure vs. $1/T$ were then made for various alloy compositions. The temperatures at which the alloys had a zinc pressure of one atmosphere could then be determined. Phase changes or peritectic decompositions were made evident by discontinuities in the slopes of the plots. Table III gives a summary of boiling points and slope change temperatures. Especially noteworthy was the large drop in vapor pressure for alloys containing over 41% Zr. This would indicate (at least under the closed conditions in which the measurements were made) that the ZrZn_2 phase does not decompose peritectically until considerably above 900°C and might possibly melt congruently at one atmosphere pressure.

Table III
Vapor Pressure of Zirconium-Zinc Alloys

Alloy Composition (%Zr)	Temp. at which Zinc Pressure Equals One Atm. (°C)	Temp. of Observed Change in Slope of Log P vs. T Curves (°C)
1.08	910°C	none
4.0	914	none
8.74	915	750
9.0	915	?
12.0	916	760?
15.0	921	780 760
23.73	921	890
24.7	921	749 736
41.0	921	898
44.0	1004	none
46.0	1000	none

4.7 Tantalum-Vanadium System (2)

The melting points of several Ta-V alloys have been determined by observing the temperature at which liquid first appears on heating. This temperature is observed with an optical pyrometer sighted on a small hole drilled in the specimen. The melting points are shown in Table IV and should correspond closely to the solidus temperature. There appears to be a minimum in the solidus at about 70% vanadium.

It will be noticed that all of the runs which were made under vacuum, except the first, have large sight glass corrections due to film formations on the sight glass, whereas those which were run under an atmosphere of helium do not. Apparently vanadium has an appreciable vapor pressure at these temperatures.

Table IV
Melting Points of Ta-V Alloys

Nominal Comp. (w/o V)	Apparent Temp. (°C)	Sight Glass Correction	Corrected M.P. (°C)
100 V	1854 1850	18 50	1872 1900
79	1855 1800	55 75	1910 1875
70	1790	35	1825*
60	1864 1860	99 30	1963 1890*
40	1850	35	1885*
30	1950 1975	62 35	2012 2010*
20	2045	35	2080*
100 (Pure Ta)			Approx. 3000

* Determined under a partial pressure of He. All others run under vacuum.

Difficulty has been encountered in revealing the microstructure of the intermediate phase in this system. A chemical etch of 2 parts HNO₃, 1H₂O, 1H₂SO₄ and 1HF etches the alloy but does not provide sufficient contrast to distinguish readily one phase from another. An electrolytic etch of 60 g H₂O, 180 cc HAc, and 50 g CrO₃ has been used successfully because it stains the intermediate phase while having little effect on solid solution phase. The procedure used has been to etch the specimen chemically and to follow this with the electrolytic etch for about 10 seconds at a current density of approximately 100 milliamps per square centimeter.

4.8 Vanadium-Copper Alloy System (2)

An investigation of the vanadium-copper alloy system has been initiated. An attempt was made to prepare copper-rich alloys by melting the pure metals together in a BeO crucible using induction heating. However, non-homogeneous alloys were obtained. By successively arc-melting and inverting the alloy, it was possible

to attain homogeneity in the copper-rich alloys. The difficulty encountered in mixing the two metals, as well as microscopic evidence, indicates that liquid immiscibility occurs in this system. Liquid immiscibility has been reported for Cu-V alloys by Hansen et al. [M. Hansen, D. J. McPherson and W. Rostoker, NP-3903, Armour Research Foundation Report, Feb. 1952]. X-ray patterns of a 46.5% Cu-V alloy which had been annealed at 950°C for 68 hours identified vanadium and copper as the phases present in this alloy.

5. Metal Coatings and Corrosion

5.1 Corrosion of Refractory Metals by Liquid Metals (5)

The corrosion of tantalum by several aluminum-uranium-thorium ternary alloys was measured at 900°C under static conditions. The alloys to be tested were placed in tantalum capsules which were closed by welding under an inert atmosphere. These capsules were placed in stainless steel enclosures to protect them from oxidation. The sample assembly was then placed in a muffle furnace for a length of time at the desired temperature. The results of these tests are shown in Table V.

Table V

Corrosion of Tantalum by Aluminum-Uranium-Thorium Alloys
at 900°C

Composition	Time to Penetrate 5 Mils of Ta
90% Al, 5% U, 5% Th	< 24 hr.
55% Al, 20% U, 25% Th	< 24 hr.
80% Al, 10% U, 10% Th	< 120 hr.
65% Al, 20% U, 15% Th	< 120 hr.

The corrosion resistance of tantalum to these alloys was quite poor and further work on this combination is not contemplated.

5.2 Corrosion of Tantalum Carbide and Other Crucible Materials (3)

A 2000 hour test at 1100°C, of a carbide-coated tantalum crucible as a container for molten uranium-chromium alloy was completed. Microscopic examination of wall sections did not reveal definite evidence of an attack on the coating. A 4000 hour test under similar conditions was undertaken, but the vacuum pumping system used to evacuate the space around the crucible failed at 1680 hours.

Because of the promising results obtained on the small crucibles, several attempts have been made to form a uniform coating on a tantalum crucible 3 inches high by 1 inch in diameter, but the results have not been satisfactory; new apparatus of a radically altered type has been made but has not been tried as yet.

Several tantalum-niobium alloys have been rolled to sheet for forming small crucibles for trials of carbiding.

The investigation of silicide coatings has been shelved. The coatings have not been uniform in thickness, appear to be brittle and have been found to be composed of loosely knit crystals.

5.3 Corrosion of Uranium by Liquid Lead and the Rate of Growth of Compound Layers in Solid Lead-Uranium Couples (6)

The purpose of the investigation was to determine the rate at which uranium is corroded by molten lead under static conditions and to determine the rate of interpenetration of these two components in the solid state. Since lead has been considered as a possible component in composite protective coatings for uranium, it is desirable to know the behavior of lead in contact with uranium.

Two compounds are formed in the lead-uranium system, [J. T. Maskrey and R. R. T. Frost, The System U-Pb, Atomic Energy Research Establishment Report, No. A.E.R.E. M/R 1027, (1952)], UPb_3 and UPb , the latter being pyrophoric. Neither of the two compounds shows much resistance to corrosion in boiling water.

To obtain adequate wetting of the uranium by the lead, the uranium samples were degreased, and etched in HNO_3 , then dipped in a molten $KCl-LiCl$ eutectic + $ZnCl_2$ salt flux for a short period of time. The samples were then suspended in the molten lead at different temperatures for various periods of time. This procedure did not produce diffusion bands that could be measured. The lead-uranium compounds formed by reaction with the lead scaled off into the bath and no diffusion bands were observed. The thickness of the uranium samples ($2" \times 1\frac{1}{4}" \times 1\frac{1}{8}"$), with the two large sides milled parallel to ± 0.0002 inches was accurately measured, both prior to and after dipping in the lead, by means of a microscope equipped with a micrometer stage and a filar eye piece. The rates of decrease in thickness at three temperatures were investigated. The lead bath was not agitated during the time the samples were suspended in the lead. Table VI lists the results obtained at each temperature. The data show a decrease in corrosion rate with an increase in time. The reason for this behavior is uncertain. One might suspect the formation of a concentration gradient of uranium in the lead at the uranium-lead interface. However, the solubility of uranium in lead at the temperatures investigated is believed to be slight.

Samples for determining the growth of reaction bands in the solid state were prepared as described above. Each sample was dipped in molten lead for 1 minute at $450-475^\circ C$ to insure complete

Table VI
Corrosion of Uranium by Liquid Lead

Temperature °C	Time in Bath (min)	Loss of Uranium on One Side (cm)	Av. Corrosion Rate (cm/sec) x 10 ⁷
350	60	1.38 x 10 ⁻³	3.84
350	150	1.82 x 10 ⁻³	2.04
350	260	2.76 x 10 ⁻³	1.77
350	300	4.97 x 10 ⁻³	2.76
350	390	3.96 x 10 ⁻³	1.70
350	660	6.67 x 10 ⁻³	1.68
350	660	7.36 x 10 ⁻³	1.86
350	1140	13.80 x 10 ⁻³	2.04
450	30	1.61 x 10 ⁻³	8.95
450	60	2.53 x 10 ⁻³	7.03
450	90	3.30 x 10 ⁻³	6.12
450	270	5.80 x 10 ⁻³	3.38
450	270	6.78 x 10 ⁻³	4.18
450	1230	13.34 x 10 ⁻³	1.81
600	37	1.27 x 10 ⁻²	57.2
600	100	2.05 x 10 ⁻²	34.2
600	120	2.43 x 10 ⁻²	33.8
600	120	2.47 x 10 ⁻²	34.3
600	150	3.17 x 10 ⁻²	35.2
600	240	5.87 x 10 ⁻²	40.8
600	360	6.34 x 10 ⁻²	29.4
600	420	10.39 x 10 ⁻²	39.6

wetting by the lead. They were then submerged in molten lead contained in a small graphite crucible and immediately quenched in water. The graphite crucible was removed, leaving the uranium sample encased in solid lead. A section was then cut off and the remaining piece was sealed under an atmosphere of helium in a pyrex capsule. Twenty samples were prepared in this way and heated at 200, 250, and 300°C. Samples were removed after 350 hours, 600 hours, and 1100 hours. They were sectioned, polished, etched and examined under a microscope at magnifications up to 500X. In all of the samples that were examined, no well defined diffusion band was observed. The lead was still well bonded to the uranium. It may be concluded from these observations that the rate of growth of compound layers at the uranium-lead interface is very slow at temperatures up to 300°C.

Some preliminary observations with this couple had indicated the formation of a reactive friable material at the uranium-lead interface as previously reported in ISC-641. No evidence of this was observed in the above experiments. The primary difference in procedure was that greater precautions were taken in the more recent work to exclude air from the samples during the heat treatment. No further work is contemplated on this problem.

6. Solid State Investigations

6.1 Structure of the Compound, V_4Al_{23} (4)

The determination of the structure of the β -phase compound in the aluminum-vanadium system has been completed. The empirical formula is V_4Al_{23} , and there are two formula weights per unit cell. The crystals are hexagonal and belong to the space group $P6_3/mmc$. Back-reflection Weissenberg patterns were used to determine the lattice parameters: $a = 7.6928 \text{ \AA}$ and $c = 17.040 \text{ \AA}$. The complete structure is determined by nine structure parameters as follows:

6V (I) in 6(h) $x, 2x, 1/4$ with $x = 0.781$
 2V (II) in 2(a) $0, 0, 0$

12Al (I) in 12(k) $x, 2x, z$ with $x = 0.213, z = 0.029$
 12Al (II) in 12(k) $x, 2x, z$ with $x = 0.124, z = 0.618$
 12Al (III) in 12(k) $x, 2x, z$ with $x = 0.455, z = 0.166$
 6Al (IV) in 6(h) $x, 2x, 1/4$ with $x = 0.126$
 4Al (V) in 4(f) $1/3, 2/3, z$ with $z = 0.617$.

Comparison between observed and calculated structure factors was made through use of the formula,
$$R = \frac{\sum |F_o - F_c|}{\sum |F_o|}$$

An R value of 12% was found for (h0l) reflections which contain all of the adjustable parameters. Each atom in the structure has a coordination number of twelve with neighbors at varying distances. The average Al-Al bond in the structure is $2.86 \text{ \AA}$; the average V-V bond is $2.64 \text{ \AA}$; and the average Al-V bond is $2.72 \text{ \AA}$. The values are in excellent agreement with the values of the atomic sizes based on the elemental structures. However, the individual bond lengths vary greatly. The Al-V bond in the structure varies from $2.54 \pm 0.03 \text{ \AA}$ to $2.88 \pm 0.02 \text{ \AA}$. This indicates a significant variation of bond strengths within the structure.

6.2 Study of the Alpha, Beta and Gamma Transformations in Uranium (6)

This investigation includes a study of the kinetics and mechanism of the alpha, beta and gamma transformations in uranium. The temperature dependence of the lattice parameters of the three crystalline forms of uranium is being measured. The volume changes which take place on transformation, combined with the values of the lattice parameters at the transformation temperatures might make

possible an analytical treatment of these transformations similar to the mathematical treatment developed by D. S. Lieberman, M. S. Wechsler and T. A. Read [Journal of Applied Physics, 26, 473 (1955), and Journal of Metals 5, 1503 (1953)]. An attempt will also be made to determine the kinetics of these transformations and to determine the relative orientations of the phases during the transformation.

6.2.1 Temperature-Dependence of the Lattice Parameters of Uranium

The change in lattice parameters as a function of temperature for alpha, beta, and gamma uranium as determined with a Norelco x-ray diffractometer, has been complicated by carbon contamination. The results previously reported (ISC-641) for gamma uranium (cubic) which were obtained by extrapolation from uranium-zirconium alloys and checked with pure uranium samples, are thought to be reliable, but further checks on pure uranium samples are desirable. The partial or complete masking of the uranium reflections above approximately 700°C by uranium monocarbide reflections has prevented these high temperature checks.

The results previously reported for the alpha and beta phases were in question. The determination of the beta parameters at temperature is complicated not only by surface contamination, but also by the narrow temperature range over which the beta phase is stable, and the difficulty of refining the parameters. The determination of the alpha uranium parameters, although not complicated by sample contamination, is not straightforward because of the difficulty of parameter refinement. The available analytical methods for refinement of parameters for low symmetry phases demand back-reflection peaks, i.e., reflections for which the Bragg angle, theta, is greater than 60 degrees. Normally only two or three uranium back-reflection peaks are observed using the high temperature diffractometer.

The above-described problems demanded special adaptations of the high temperature diffractometer and its vacuum system, as well as an investigation of means for obtaining refined lattice parameters from diffractometer data for low symmetry phases. Partial or complete masking of uranium reflections above approximately 700°C, due to carbon contamination of the sample surface, has been a serious barrier to the studies underway. Several possible sources of contamination have been considered and steps have been taken to eliminate them.

An "Evaporion" high vacuum pump, developed by Consolidated Vacuum Corporation, has a pumping action that is due to electronic ion entrapment and the gettering action of evaporated titanium. This pump has no oil pumping fluid and metal gasket seals are employed. A pump of this type has been ordered for the high temperature x-ray system and is expected to eliminate sources of carbon from the pumping system and to produce a much lower pressure in the camera.

6.2.2 Refinement of Lattice Parameters

The Nelson-Riley graphical extrapolation of diffractometer data for the lattice constants of cubic phases such as alpha and beta thorium and gamma uranium has been shown to be fairly satisfactory. However, the analytical treatment of the diffractometer data to obtain refined lattice parameters for the tetragonal beta uranium phase and the orthorhombic alpha uranium phase has caused considerable difficulty.

Cohen's analytical treatment of x-ray diffraction errors is applicable to tetragonal and orthorhombic lattices, but as originally developed, the method applies only to reflections for which the Bragg angle, theta, is greater than 60 degrees. Consideration of the diffractometer camera geometry and the fact that massive samples are used indicates that the largest error in the data is the eccentricity error. This error arises from the displacement of the sample from the goniometer axis. Mathematical analysis gives the form

$$\Delta d = K \left(\frac{1}{\sin^2 \theta} - 1 \right)$$

for the eccentricity correction term for the diffractometer.

Empirically a plot of Δd versus $\left(\frac{1}{\sin^2 \theta} - 1 \right)$ (using both front and back reflection data) for cubic samples purposely displaced from the center of the diffractometer, gives a linear extrapolation to zero error. It follows from the correction given above that the appropriate form of the error term in the Cohen method applied to the diffractometer data should be

$$\delta = \cos^2 \theta \sin \theta.$$

Refinements using this error term give values for the room temperature lattice parameters of alpha uranium in good agreement with values determined by other methods, and the scatter in the values obtained at high temperatures has been reduced.

The most recent data on the alpha uranium lattice parameters as a function of temperature are shown graphically in Figures 1, 2, and 3. These data were taken on a sample of massive biscuit uranium in the high temperature diffractometer, and the experimental and analytical refinements described above were employed. More samples will be run to substantiate these results.

6.2.3 Future Work

A new "Evaporion" pump will be installed on the high temperature diffractometer system. The study of the change of lattice parameters as a function of temperature for the alpha, beta, and gamma uranium phases will be completed. The kinetics of the uranium transformations will be studied employing x-ray diffraction and resistivity measurements.

26

Fig. 1 - Temperature-Dependence of a_0 for Alpha Uranium

27

Fig. 2 - Temperature-Dependence of b_0 for Alpha Uranium

Fig. 3 - Temperature-Dependence of C_0 for Alpha Uranium

6.3 Structure of Epsilon Uranium-Zirconium (5)

Samples of uranium-zirconium alloys were prepared by arc-melting, homogenizing at 1000°C for several days, and heat-treating at 550°C. Etching these samples revealed a rather large-grained structure. Small slivers were cut from within individual grains of the 40, 50 and 60 weight per cent samples. These slivers were reduced in size by pickling in a nitric acid-hydrofluoric acid solution until they were approximately 0.1 mm in diameter. Rotating single crystal and Weissenberg x-ray diffraction patterns were taken of these samples, and the data showed evidence of single crystals. The x-ray diffraction pattern could be indexed on the basis of a large body centered cubic unit cell with a lattice constant equal to 10.67 angstroms. This unit cell contains 54 atoms and the determination of five parameters would be necessary to complete the structure determination. The intensities of the diffraction peaks from a 40 weight per cent zirconium sample were relatively the same as those from sixty weight per cent alloy. This would indicate that the diffraction pattern is not very sensitive to the type of atom which gives rise to the scattering. The determination of the parameters, starting with the cubic unit cell, has been attempted but so far has not been achieved.

6.4 Effect of Heat Treatment Upon Physical Properties of Uranium (2)

The investigation of this problem was initiated during this report period, and has been reported in detail in ISC-709.

7. Other Investigations

7.1 Metallography of Thorium (5)

A new electro-etching and polishing procedure was developed for and used on thorium metal. The results of this investigation were presented at the October 24, 1955, AEC Metallographic Group Meeting and will appear in the transactions of that meeting.

7.2 Vacuum Fusion Analysis of Metals (5)

The study of the vacuum fusion analysis of rare earth metals was continued. A series of ten lanthanum samples containing known additions of oxygen was prepared and analyzed. The recovery of oxygen in the analysis was 90.7 per cent of that added. The results of this investigation on lanthanum are being prepared for publication.

Lanthanum samples containing known additions of oxygen were analyzed by vacuum fusion using a platinum bath. The precision of the analyses was excellent and the recovery of the added oxygen was between 97 and 100 per cent. The use of a platinum bath may be desirable when very accurate vacuum fusion analyses are needed. Several samples of neodymium metal were analyzed employing a nickel

bath and, although the results are not conclusive, it appears that the procedure as developed for lanthanum will be suitable for neodymium.

7.3 Low Melting Alloy Studies (1)

Work is continuing on the aluminum-rich corner of the Al-U-Th ternary phase diagram. Data that can be interpreted as evidence of a binary eutectic valley have been obtained. Evidence of a ternary eutectic in this region of the diagram is very meager at this time. A low temperature break in the cooling curves at just below 620°C for a number of alloys may or may not be associated with a ternary eutectic.

7.4 A Study of Calcium Fluoride Bodies (1)

Different batches of calcium fluoride slip showed a difference in working properties, particularly in thixotropy and castability. Calcination temperature, grinding time, specific gravity of slip and pH of slip were varied. Particle size distribution of various batches of slip was determined by the Casagrande hydrometer method. Although it is not certain that optimum conditions are yet realized, a calcium fluoride slip that gives satisfactory fired products for melting metals and alloys can be prepared.

A program on the investigation of the disintegration of calcium fluoride crucibles was also initiated. British scientists have published a report wherein it is postulated that silica, present as an impurity, reacts to form calcium trisilicate during a pre-calcination treatment at 1300°C. The tricalcium silicate is said to be unstable, breaking down to leave dicalcium silicate and free lime. It is the free lime which directly causes disintegration. In their research, they did not use silica-free calcium fluoride as a control and it appeared indefinite whether or not their point had been proven. The program undertaken here proposes to compare silica free fluoride with silica contaminated fluoride in an attempt to pin-point the cause of disintegration.

7.5 Growth of Single Crystals of High Melting Metals (2)

Several attempts were made to produce single crystals of thorium and uranium by the Bridgman technique of cooling from the melt. None of the experiments produced single crystals, probably because of the impurity content of the metal, or the introduced impurities from the reaction with the crucible materials. BeO and ZrO₂ were tried as crucible materials for thorium, and UO₂ for uranium.

Preliminary experiments with zirconium indicated that extremely large beta grains can be produced by prolonged heating in a temperature gradient in vacuo. Upon slow cooling, each grain transforms into highly oriented alpha grains. Further experiments are being conducted on these and other metals.

8. Rare Earth Metallurgy - See ISC-706.

APPENDIX I: LIST OF REPORTS FROM THE AMES LABORATORY

1. Reports for Cooperating Laboratories

- ISC-575 Ames Laboratory Staff. Metallurgy. Quarterly Summary Research Report. October, November, December, 1954.
- ISC-604 F. H. Spedding, J. E. Powell and E. J. Wheelwright. The Stability of the Rare Earth Complexes with N-Hydroxyethylethylenediaminetriacetic Acid.
- ISC-605 Ames Laboratory Staff. Engineering. Quarterly Summary Research Report. January, February, March, 1955.
- ISC-606 Ames Laboratory Staff. Chemistry. Quarterly Summary Research Report. January, February, March, 1955.
- ISC-607 Ames Laboratory Staff. Metallurgy. Quarterly Summary Research Report. January, February, March, 1955.
- ISC-608 Ames Laboratory Staff. Physics. Quarterly Summary Research Report. January, February, March, 1955.
- ISC-609 Compiled by P. Chiotti and O. N. Carlson. Hanford Slug Program. Quarterly Summary Research Report. January, February, March, 1955.
- ISC-611 F. H. Spedding and J. E. Powell. A Laboratory Method for Separating Nitrogen Isotopes by Ion-Exchange.
- ISC-612 A. W. Andresen and G. L. Bridger. Recovery of Uranium from Superphosphates.
- ISC-617 J. E. Powell and F. H. Spedding. Basic Principles Involved in the Macroseparation of Adjacent Rare Earths from Each Other by Means of Ion-Exchange.
- ISC-620 R. D. Kross and V. A. Fassel. The Infrared Spectra of Aromatic Compounds. III. The 1045-1185 cm^{-1} Vibration in Monosubstituted Benzenes.
- ISC-621 R. D. Kross and V. A. Fassel. An Infrared Study of Picric Acid Molecular Complexes.
- ISC-623 L. S. Gray and V. A. Fassel. Emission Spectrometric Determination of Low Percentages of Zirconium in Hafnium.
- ISC-625 R. D. Kross, V. A. Fassel and M. Margoshes. The Infrared Spectra of Aromatic Compounds. II. Evidence Concerning the Interaction of π -Electrons and σ -Bond Orbitals in C-H Out-of-Plane Bending Vibrations.

- ISC-629 R. T. Nichols and E. N. Jensen. The Decay Scheme of Sc^{147} .
- ISC-630 P. Hall and S. Legvold. Remanent Magnetism in Toroids.
- ISC-632 J. T. Jones, Jr., and J. K. Knipp. Notes on Hyperfragments.
- ISC-633 E. M. Layton, Jr., R. D. Kross and V. A. Fassel. A Correlation of Bond Length with Stretching Frequency for C-O and C-N Systems.
- ISC-634 G. H. Beyer, E. L. Koerner and E. H. Olson. Conversion of Zirconium Sulfates to Anhydrous Zirconium Tetrafluoride.
- ISC-637 E. Wheelwright and F. H. Spedding. The Use of Chelating Agents in the Separating of the Rare Earth Elements by Ion-Exchange Method.
- ISC-640 P. Chiotti, P. F. Woerner, H. H. Klepfer, K. J. Gill and R. E. Cutrell. Application of Metal Coatings on Uranium-Summary Report.
- ISC-641 Compiled by P. Chiotti and O. N. Carlson. Hanford Slug Program. Quarterly Summary Research Report. April, May, June, 1955.
- ISC-642 Ames Laboratory Staff. Engineering. Quarterly Summary Research Report. April, May, June, 1955.
- ISC-643 Ames Laboratory Staff. Chemistry. Quarterly Summary Research Report. April, May, June, 1955.
- ISC-645 Ames Laboratory Staff. Physics. Quarterly Summary Research Report. April, May, June, 1955.
- ISC-656 P. Chiotti, H. H. Klepfer and K. J. Gill. Uranium-Zinc System.
- ISC-661 J. S. Fritz and S. A. Sutton. Titration of Mercury with Bis(2-Hydroxyethyl)Dithiocarbamate.
- ISC-665 M. C. Day and A. F. Voigt. The Molecular Chemistry of Antimony and Tellurium.

2. Papers Published in Scientific Journals

Corbett, J. D. and R. K. McMullan
The Lower Oxidation States of Gallium. I. The GaI_3 -GaI System. J. Am. Chem. Soc. 77, 4217-19 (August, 1955).

- Corbett, J. D. and S. vonWindbush
The Solubility of Some Metals in Their Molten Halides.
J. Am. Chem. Soc. 77, 3964-66 (August, 1955).
- Day, M. C., G. W. Eakins and A. F. Voigt
The Disintegration Schemes of the Te^{127} and Te^{129}
Ground States. Phys. Rev. 100, 796-8 (November, 1955).
- Freeland, M. Q. and J. S. Fritz
High Precision Micro Spectrophotometric Analysis with
Application to V-Al alloys. Anal. Chem. 27, 1737-41
(November, 1955).
- Fritz, J. S. and M. Johnson
Volumetric Determination of Zirconium. Anal. Chem. 27,
1653-5 (October, 1955).
- Fritz, J. S. and S. S. Yamamura
Rapid Microtitration of Sulfate. Anal. Chem. 27, 1461-64
(September, 1955).
- Hansen, R. S.
The Theory of Vibration Jets in Liquids of Variable Surface
Tensions. ISC J. of Sci. 30, 301-11 (November, 1955).
- Happe, J. A. and D. S. Martin, Jr.
Isotope Exchange of Manganese during the Reaction between
Manganese(II) and Permanganate. J. Am. Chem. Soc. 77,
4212-17 (August, 1955)
- Herwig, L. O., G. H. Miller and N. G. Utterback
Some Characteristics of a Gridded Parallel-Plate Ionization
Chamber. Rev. Sci. Instr. 26, 929-36 (October, 1955).
- Hettel, H. J. and V. A. Fassel
Determination of Fractional Part Per Million Amounts of
Certain Rare Earths in Zirconium Metal: Ion Exchange
Separation-Spectrographic Determination. Anal. Chem. 27,
1311 (August, 1955).
- Jones, J. T., Jr. and J. K. Knipp
Notes on Hyperfragments, Nuovo Cimento 2, 857-9 (October, 1955).
- Kniseley, R. N. and V. A. Fassel
A Rotating Step Sector for Use with AC or Other Intermittent
Spectrographic Light Sources. J. Opt. Soc. 45, 1032-4
(December, 1955).
- Kross, R. D. and V. A. Fassel
The Infrared Spectra of Aromatic Compounds. III.
The 1045-1185 cm^{-1} Vibration in Monosubstituted Benzenes.
J. Am. Chem. Soc. 77, 5858-9 (November, 1955).

- Laslett, L. J. and D. J. Zaffarano
Nuclear Research with High Energy X-Rays at Iowa State College. The Science Counselor (September, 1955).
- Nichols, R. T. and E. N. Jensen
Decay Scheme of Sc^{47} . Phys. Rev. 100, 5, 1407-1409 (December, 1955).
- Ring, L. S., Jr.
The Photodeuteron/Photoproton Yield from Sulfur. Phys. Rev. 99, 137-8 (July, 1955).
- Rundle, R. E.
The Structure of Ice. J. Phys. Chem. 59, 680-81 (August, 1955).
- Simmons, C. R. and R. S. Hansen
Solvolysis of Hafnium and Zirconium Tetrachlorides in Methyl and Ethyl Alcohols. J. Phys. Chem. 59, 1072-3 (October, 1955).
- Skochdopole, R. E., M. Griffel and F. H. Spedding
The Heat Capacity of Erbium from 15-320°K. J. Chem. Phys. 23, 12, 2258-63 (December, 1955).
- Spedding, F. H. and J. L. Dye
The Vapor Pressure of Mercury at 250-360°C. J. Phys. Chem. 59, 581-3 (July, 1955).
- Spedding, F. H. and J. E. Powell
A Laboratory Method for Separating Nitrogen Isotopes by Ion-Exchange, J. Am. Chem. Soc. 77, 6125-32 (December, 1955).
- Stone, J. F., D. Kirkham and A. A. Read
Soil Moisture Determination by a Portable Neutron-Scattering Moisture Meter. Soil Sci. Soc. of Am. Proc. 19, 419-23 (October, 1955).
- Wilhelm, H. A. and B. A. Rogers
The Physical Metallurgy of Thorium. IMD. Spec. Report Series #1 (American Institute of Mining, Metallurgical and Petroleum Engineering) (October, 1955).

APPENDIX II: LIST OF SHIPMENTS

<u>Destination</u>	<u>Item</u>
National Bureau of Standards Washington, D. C.	1 lb. lanthanum metal 1 lb. cerium metal 1 lb. neodymium metal 1 lb. praseodymium metal 10 gm cerium metal

<u>Destination</u>	<u>Item</u>
Argonne National Laboratory Lemont, Illinois	1 sample each of: neodymium metal samarium metal
Dr. J. R. Gump Michigan Chemical Corporation St. Louis, Michigan	1 gm lanthanum oxide 1 gm cerium oxide 1 gm praseodymium oxide 1 gm neodymium oxide 1 gm samarium oxide 1 gm gadolinium oxide 1 gm yttrium oxide 100 mg terbium oxide 100 mg dysprosium oxide 100 mg holmium oxide 100 mg erbium oxide 100 mg ytterbium oxide 100 mg thulium oxide 100 mg lutetium oxide
Battelle Memorial Institute Columbus, Ohio	1 gm thulium metal, tantalum-free
New Brunswick Laboratory New Brunswick, New Jersey	2 gm dysprosium oxide 2 gm erbium oxide 2 gm samarium oxide 20 gm yttrium oxide 100 mg lutetium oxide 1 gm ytterbium oxide
Research Laboratories of Colorado, Inc. Newtown, Ohio	3 thulium pellets
State University of Iowa Department of Physics Iowa City, Iowa	5 gm N ¹⁴ isotope
University of California Los Alamos Scientific Laboratory Los Alamos, New Mexico	2 gm pure terbium oxide 10 gm neodymium metal 20 gm erbium metal 20 gm yttrium metal 66 gm neodymium metal 69 gm samarium metal 72 gm gadolinium metal 77 gm erbium metal
Transportation Officer Fort Totten, New York	6 thulium buttons
University of Minnesota Minneapolis, Minnesota	1 gm lanthanum metal 1 gm cerium metal 1 gm praseodymium metal 1 gm neodymium metal 1 gm samarium metal 1 gm gadolinium metal 1 gm erbium metal 1 gm yttrium metal

<u>Destination</u>	<u>Item</u>
University of Minnesota (Continued)	1 gm dysprosium metal 1 gm ytterbium metal
Professor C. D. Jefferies University of California Berkeley, California	200 mg high purity lanthanum oxide 2 gm lanthanum oxide 10 mg terbium oxide
Knolls Atomic Power Laboratory Schenectady, New York	100 mg neodymium oxide 100 mg lanthanum oxide 200 mg erbium oxide 100 mg samarium oxide 100 mg praseodymium oxide 200 mg holmium oxide 200 mg lutetium oxide 200 mg ytterbium oxide 200 mg thulium oxide 200 mg dysprosium oxide 200 mg terbium oxide 100 mg gadolinium oxide 100 mg cerium oxide 100 mg yttrium oxide 1 gm lanthanum oxide 1 gm cerium oxide 1 gm praseodymium oxide 1 gm neodymium oxide 1 gm samarium oxide 1 gm gadolinium oxide 1 gm yttrium oxide
American Metallurgical Products Co. New Castle, Pennsylvania	$\frac{1}{4}$ lb. praseodymium metal $\frac{1}{4}$ lb. neodymium metal
Brookhaven National Laboratory Upton, Long Island, New York	5 gm pure thulium oxide 10 gm yttrium oxide 25 gm lanthanum metal 25 gm praseodymium metal 25 gm samarium metal 100 gm cerium metal
Dr. R. B. Price Battelle Memorial Institute Columbus, Ohio	2 gm thulium metal
Army Medical Research Laboratory Fort Knox, Kentucky	8 thulium buttons
C. A. Hutchison Chicago, Illinois	2 gm praseodymium oxide 1 gm neodymium oxide 1 gm gadolinium oxide $\frac{1}{2}$ gm terbium oxide

<u>Destination</u>	<u>Item</u>
Mr. H. A. Boorse Pupin Physics Bldg. New York, New York	1 cylinder lanthanum metal
Dr. Richard L. Caldwell Magnolia Petroleum Co. Dallas, Texas	1 thulium pellet
Dr. J. M. Daniels Department of Physics University of British Columbia Vancouver, B. C., Canada	5 gm ytterbium oxide
Dr. Wm. F. Wagner Chemistry Department University of Kentucky Lexington, Kentucky	1 gm lanthanum oxide 1 gm cerium oxide 1 gm praseodymium oxide 1 gm neodymium oxide 1 gm samarium oxide 1 gm gadolinium oxide 1 gm yttrium oxide 100 mg terbium oxide 100 mg dysprosium oxide 100 mg holmium oxide 100 mg erbium oxide 100 mg ytterbium oxide 100 mg thulium oxide 100 mg lutetium oxide
Johns Hopkins University Baltimore, Maryland	10 gm terbium oxide

APPENDIX III

- (1) H. A. Wilhelm
- (2) O. N. Carlson
- (3) B. A. Rogers
- (4) J. F. Smith
- (5) D. Peterson
- (6) P. Chiotti
- (7) F. H. Spedding

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK