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A.E.C. RESEARCH AND DEVELOPMENT REPORT

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**AMES
LABORATORY
IOWA STATE
COLLEGE**

**METALLURGY. QUARTERLY SUMMARY RESEARCH
REPORT
APRIL , MAY, JUNE , 1955**

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QUARTERLY SUMMARY RESEARCH REPORT IN METALLURGY

For April, May, June, 1955

by

Ames Laboratory Staff

February 9, 1955^[6]

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

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QUARTERLY SUMMARY RESEARCH REPORT IN METALLURGY

For the period April, May, and June, 1955

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

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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 Some Extractions with Primene-JMT Solutions (1)*

As reported earlier, increased selectivity could be obtained with the Primene JMT for thorium from a monazite-sulfate solution if the acid solution also contained the chloride ion. Work was continued on this extraction with further studies on variations in chloride additions and on nature of organic solvent.

Several alcohols and ketones were tested as solvents; the organic phase was made up of roughly 25 volume per cent of Primene JMT and 75 volume per cent of the solvent. With other possible variables remaining fixed, it was found that the quantity and quality of the extracted thorium from the monazite-sulfate solution varied with the organic solvent used. Addition of calcium chloride to the monazite sulfate solution to bring its chloride concentration to about 0.5N gave improved results. The calcium sulfate that precipitated on addition of the CaCl_2 was removed by filtration and the resulting aqueous filtrate was then treated with an organic solution of Primene JMT hydrochloride in hexone to remove the thorium. Subsequent treatment of this organic phase with HCl solutions gave fairly pure thorium.

Indications are that the presence of HCl in the system reduces the extractability of other elements by the Primene JMT organic phase much more than it does the thorium. The small amounts of rare earths that are extracted with the thorium may be stripped from the organic phase in preference to thorium by dilute aqueous HCl solutions. The thorium can be subsequently removed with greater HCl concentration. Almost spec-pure thorium has been obtained by such extractions.

1.2 The Separation of Tantalum From Niobium (1)

Work continues with the treatment of niobium and tantalum ore concentrates for the purpose of working out procedures for obtaining high purity niobium and tantalum compounds. The treatment of these ore concentrates with aqueous solutions of hydrofluoric acid is being investigated and results so far are promising.

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

The ore is treated with hydrofluoric acid and the resulting product used directly to prepare a solution from which niobium and tantalum may be separately extracted. In one case, water is added to the product to give a dilute aqueous HF solution which is filtered from any unreacted ore or insoluble material. The objective here is to subsequently extract the tantalum selectively from the niobium by means of an organic solvent.

In the other case, the product obtained by the HF treatment of the ore is contacted directly with an organic solvent in order to extract both the niobium and tantalum into the organic phase. The organic phase is then treated with an aqueous phase for selectively back extracting the niobium from the tantalum. In this latter case, as the niobium and tantalum pass into the organic phase, most of the impurities including titanium are left behind and the problem of their subsequent removal is greatly reduced.

Tests on the HF treatment of the ore concentrates have been made with approximately 70% HF. The acid is placed on the ore in polyethylene equipment and left to stand for a few days. It has been found that the ore should be sufficiently fine to pass through a 20 mesh screen but need not be finer than 70 mesh size for a reasonable rate of reaction. Ratios of 1 to 1.5 ml. of the acid to each gram of ore seems to be in the range to give good reaction and to give appreciable transfer of the niobium and tantalum to the organic phase in subsequent treatment. The small amount of impurities transferred to the organic with the niobium and tantalum is readily removed by scrubbing the organic phase with a small amount of an aqueous phase.

In another approach to the niobium and tantalum problem, the ore is opened by the caustic treatment described earlier. In this approach, the water insoluble acid oxides that are obtained relatively free of other impurities are dissolved in KOH solution. Subsequent treatment of the KOH solution to selectively extract tantalum or niobium have not proven satisfactory.

1.3 Studies on the Separation of Hafnium from Zirconium (1).

Work was continued on the separation of hafnium and zirconium by liquid-liquid extraction using thiocyanate and zirconium sulfate solutions. Experiments were made to determine the distribution of thiocyanic acid between sulfuric acid solutions and various organic solvents. It was believed that there might be some correlation between the capacity of a solvent for thiocyanic acid and its effectiveness for extraction. The experiments seemed to confirm that belief.

As tributyl phosphate looked promising on the basis of thiocyanic acid transfer, it was used for an extraction in the zirconium sulfate, thiocyanate system. Good transfer and

separation was obtained in this test. Less than half as much transfer and poorer separation was obtained, however, upon diluting TBP 50% by volume with hexone. Upon using heptane as the diluent even less transfer and separation was obtained.

Extractions were made using Primene and hexone solutions that were 3 molar in thiocyanic acid as the organic phase. It was found on using 10 volume % Primene 81R in hexone that the transfer was increased to more than four times that given by straight hexone with the same thiocyanic acid concentration. With 25% Primene 81R the transfer was about 8 times that given by hexone. The Primene solutions also gave better separation of Hf and Zr than did hexone alone in these single stage extractions. Since the Primenes were found in earlier work with sulfuric acid solutions to be unsatisfactory for multistage extractions of hafnium from zirconium, it will be necessary to test the thiocyanic acid-Primene system further.

2. Preparation of Pure Compounds

2.1 Preparation of Thorium Tetrachloride (5)

A solution of thorium tetrachloride and hydrochloric acid has been developed as a binder for the mixture of thorium oxide and carbon which is chlorinated to prepare thorium tetrachloride. This binder has the advantages of producing a harder pellet and of not introducing carbon into the charge and thus changing its composition.

Carbon tetrachloride was tested as a chlorinating reagent for the preparation of thorium tetrachloride. Obvious advantages were the ease of intimate contact with the thorium oxide, the exact stoichiometric ratio of carbon and chlorine, and the lower heat of reaction compared to carbon and chlorine. However, carbon tetrachloride reacted very slowly with thorium at temperatures at which carbon and chlorine reacted rapidly with thorium oxide. Raising the temperature increased the rate of the chlorination reaction, but this reaction was still quite slow at temperatures which caused extensive thermal decomposition of the carbon tetrachloride. The conversion of thorium oxide to thorium tetrachloride was only 40 to 65 per cent complete. After obtaining these results, the use of carbon tetrachloride as a chlorinating reagent was abandoned.

The development of the chlorination process into a continuous process seemed to be desirable. A vertical tube reactor in which the charge of thorium oxide and carbon would move down by gravity countercurrent to a stream of chlorine was chosen as the most promising design. A small scale proto-type chlorination apparatus was built and operated. Considerable

difficulty was encountered in moving the charge through the reaction tube. The charge sintered together and also stuck to the tube unless the reaction temperature was kept below 550° and the reaction rate kept very slow. Elimination of sticking in the tube while increasing the rate of the reaction will be sought.

Vacuum sublimation of the thorium tetrachloride was quite effective in removing the thorium oxide and carbon. The use of graphite filter disks to improve this separation was investigated. The filter seemed to improve the purity of the product slightly. However, the filter reduced the rate of sublimation very greatly and the decrease in the amount of thorium oxide and carbon carry-over might have been a result of the decreased rate of sublimation rather than a direct result of the filtering action of the graphite disks.

A semi-continuous vacuum sublimation still was designed and built. The still was constructed of Inconel to reduce the corrosion problem. The crude thorium tetrachloride was changed into an annulus around a perforated cylinder. The vapors passed into this cylinder through a delivery pipe and were condensed on a water cooled pipe. The crystalline product could be removed from the condensor by a scraper. The effectiveness of this apparatus for purifying thorium tetrachloride will be determined.

2.2 Preparation of Yttrium Trifluoride (2,7)

As previously reported, yttrium trifluoride has been prepared by reacting aqueous hydrofluoric acid (70%) with hydrated crystals of yttrium trichloride. This reaction was carried out in a fluorothene reaction vessel with constant stirring of the mixture during the acid addition to insure complete reaction. The hydrated fluoride which is obtained from this reaction can be thermally decomposed in a stream of anhydrous hydrogen fluoride at 575°C . This drying temperature is considerably higher than the 300°C temperature reported previously. A higher drying temperature is desirable in that it results in a fluoride with an increased packing density.

Yttrium trifluoride was also prepared by direct hydrofluorination of yttrium oxide. Screened Y_2O_3 was heated in a platinum tray in a hydrogen fluoride atmosphere for eight hours at 575°C which, according to weight changes, gave nearly complete conversion to the anhydrous trifluoride.

2.3 Preparation of Vanadium Trifluoride (2)

An investigation of the preparation of vanadium metal by the calcium reduction of VF_3 in a bomb is presently underway. A process for preparing anhydrous vanadium trifluoride has been developed. This process consists of reducing V_2O_5 to V_2O_3 by

heating to 550°C in a hydrogen atmosphere. The V_2O_3 is reacted with aqueous (70%) HF which forms bright green crystals of $VF_3 \cdot 3H_2O$. This material may then be dehydrated in a stream of dry HF gas at 130°C to form anhydrous VF_3 . Attempts will be made to reduce this material with calcium or magnesium in a bomb.

3. Metals Preparation Studies

3.1 Preparation of Vanadium Metal (2)

During this period several attempts were made to prepare vanadium metal by the crystal bar process. In the early experiments, a vycor apparatus was used in which iodine vapors were passed over vanadium powder heated to 900°C to form vanadium iodide. The iodide vapors were then thermally decomposed on an electrically heated filament. The unreacted iodine vapors were drawn off by means of a vacuum pump and the iodine was condensed on a cold trap. Some deposits of vanadium were obtained and the resulting metal was quite ductile. However, the amount of vanadium obtained was quite small and the efficiency of the operation was extremely low.

A new apparatus has been designed and constructed of Inconel. This was first tested with zirconium, since the conditions for preparing crystal bar zirconium are well known. A ductile, evenly distributed deposit of zirconium metal was obtained on a tungsten filament and a bar of approximately 3/16 inches diameter by 2 feet in length was produced. One attempt was made to prepare vanadium in this revised apparatus but no crystal bar metal was obtained.

3.2 Preparation of Tantalum and Niobium Metals (2)

An investigation of the preparation of niobium metal by the thermal decomposition of the pentachloride has been continued using a method similar to that described by Van Arkel for niobium and tantalum.

Niobium pentachloride was prepared by heating Nb_2O_5 with carbon at 1600°C to form niobium carbide. This was reacted with chlorine at 350 to 400°C to give $NbCl_5$, which vaporized off and was collected in a cooler region of the system.

The thermal decomposition experiments were carried out in an evacuated pyrex bulb containing two electrodes to which was connected a niobium filament. The $NbCl_5$ was placed in the bottom of the bulb and this was slowly vaporized over the hot filament which was maintained at about 2000°C. The diameter of the wire was increased from 0.025 to 0.125 inch in this process but the metal obtained was quite brittle and the process was very inefficient.

An x-ray diffraction powder pattern was taken of the crystalline deposit. This was indexed as body-centered cubic structure, with a lattice constant of 3.300 Å which varies slightly from the literature value of 3.294 Å for niobium metal.

3.3 Preparation of Thorium Metal (5)

An apparatus was designed and constructed for a larger scale reduction of thorium tetrachloride by magnesium. This consists essentially of a 6 inch diameter retort which is 30 inches long. A titanium crucible will be used to contain the reduction charge. This equipment should be capable of producing ten pounds of thorium per reduction.

3.4 Preparation of Yttrium Metal (2,7)

Several pounds of yttrium metal were prepared by the reduction of YF_3 with calcium using ZnF_2 as a booster. The low melting yttrium-zinc alloy was crushed and heated slowly to 1200°C in vacuo in a CaF_2 crucible. Too rapid heating during the zinc removal stage results in partial melting of the alloy and some reaction with the CaF_2 . The resulting sponge contains approximately 0.5% zinc and about the same amount of calcium.

To date no crucible has been found in which yttrium sponge can be melted without excessive crucible interaction and contamination. Therefore, the sponge was melted into cylindrical billets in an arc melting furnace. The melting was done in a water cooled copper pot using a tungsten electrode under a helium atmosphere by continuously feeding pieces of the sponge from a hopper into the melting pot. A double melting procedure was found necessary in order to insure complete removal of the zinc and calcium. Billets 2 inches in height by 2 inches in diameter and weighing approximately one pound were prepared. Efforts to produce a solid casting by the above method were unsuccessful. Upon machining of the surface of the billet small blow-holes or shrinkage pipes were usually exposed.

About 2 kilograms of yttrium metal were prepared, of which a chemical analysis gave the following values for the major impurities: 600 ppm C, 600 ppm N_2 , 500 ppm Fe, 150 ppm Zn, less than 200 ppm Ca, less than 100 ppm Mg, less than 200 ppm Si and less than 1000 ppm of total rare earths.

4. Alloy Systems

4.1 Uranium-Zinc System (6)

Further work has been done to establish the equilibrium phase regions in the uranium-zinc system. The phase regions below 30 w/o uranium have now been established on the basis of thermal analysis, vapor pressure measurements, and solubility data. The final report on the system is being prepared. (ISC-656)

A literature search was made on methods of measuring vapor pressure over metals and alloys. On the basis of the results of this search our dew point apparatus was modified following largely the experience of Hargreaves [*J. Inst. Metals*, 64, 115 (1939)] and Schneider [*Z. Electrochem.*, 48, 627 (1942)], who applied the dew point method quite successfully to the study of several zinc alloy and cadmium alloy systems. The modified setup was calibrated with a sample of pure zinc.

Three uranium-zinc alloys in the composition range from 18 w/o uranium to 28 w/o uranium were run in the dew point apparatus. The boiling points of these alloys were found to be the same, $910 \pm 1^\circ\text{C}$. The maximum solubility of uranium in liquid zinc calculated from this boiling point, assuming Raoult's Law to hold, is 14.6 w/o uranium at 910°C .

A single crystal of the intermetallic compound UZn_9 was obtained from a 5 w/o uranium alloy by dissolution of the zinc matrix with ammonium hydroxide. Weissenberg and precision x-ray diffraction patterns are being studied by Mr. Carl Vold. The decomposition temperature of the compound will be checked by vapor pressure measurements.

4.2 Thorium-Zirconium System (2)

During the quarter the investigation of the Th-Zr phase diagram was continued. As was reported previously, the lattice constants for several alloys in the BCC solid solution region were determined from high temperature x-ray measurements at temperatures above 900°C . The table below shows the composition and the lattice constant for the high temperature phase across the entire solid solution region.

<u>% Composition</u>	<u>a_0 for BCC phase</u>
Th	4.11 Å at 1400°C
Th-15% Zr	3.94 at 1100°C
Th-25% Zr	3.90 at 950°C
Th-40% Zr	3.79 at "
Th-50% Zr	3.74 at "
Th-60% Zr	3.70 at "
Th-75% Zr	3.66 at "
Zr	3.61 at 875°C

The plot of these data gives a smooth curve with a slight negative deviation from linearity.

In addition to the work on the determination of lattice constants of the BCC phase at high temperatures, work was started on the determination of the limit of solid solubility of Th in alpha Zr.

Filings from a Zr-5 w/o Th alloy and crystal bar zirconium were annealed at 625°C for 48 hours and x-ray power patterns were taken on these samples using precision back-reflection power camera. A Cohen's Analytical Method was applied to the hexagonal reflections obtained which gave the following values for the lattice constants:

	<u>a (in Å)</u>	<u>c (in Å)</u>	<u>c/a</u>
Zr Crystal Bar	3.234	5.151	1.593
Zr-5w/o Th	3.239	5.168	1.596

The increase in both a and c indicates that there is some solid solubility of thorium in alpha zirconium. Further work will be done to confirm this and to determine the extent of solid solubility.

4.3 Thorium-Hafnium System (2)

Work was continued on the study of the thorium-hafnium alloy system. A series of alloys varying in composition from 0 to 100 per cent hafnium were quenched from three different temperatures 1325°, 1375° and 1425°C. Microscopic examination of the series quenched from 1425°C failed to substantiate a complete series of solid solutions at elevated temperatures, as was previously postulated. Rather, they indicated the existence of a eutectic horizontal at about 1440°C with the eutectic composition lying at about 20 w/o hafnium and with limited solid solubility at either end of the system.

Microscopic examination of the alloys quenched from 1375°C and 1325°C indicate that there is a eutectoid on the thorium rich side of the diagram at 1280°C. Also, they indicate that there is

another eutectoid on the hafnium-rich side of the phase diagram at approximately 1350°C. In no instance has a well defined eutectoid structure been observed so that further confirmation of the two eutectoid reactions is being sought.

4.4 Uranium-Niobium System (3)

Melting points of a number of alloys of intermediate composition have been redetermined. The results still show an undesirably large variation in homogenized specimens. The inhomogeneity originates in the ingots and persists despite high temperature heat treatments.

Investigation of the two phase loop near the center of this diagram has been completed as far as x-ray methods are concerned. The maximum in the loop has been found to lie below 975°C, probably near 960°C.

X-ray patterns of the 70, 80 and 90 per cent niobium alloys quenched from 1000°C have given lattice parameters that lie on the tentative parameter-composition curve presented in the previous quarterly report. (ISC-607)

Dilatometric curves on alloys from 1 to 7 per cent niobium show discontinuities corresponding to the eutectoid horizontal. The curves for alloys on the uranium side of the eutectoid indicate also the crossing of the alloy into the one-phase gamma area but those on the other side of the eutectoid show no evidence of entering this region.

4.5 Zirconium-Tantalum System (3)

In an effort to establish the extent of the eutectic horizontal, additional melting point measurements have been made on a number of zirconium-rich alloys. The data indicate that the horizontal terminates at 2.0 + 0.5 per cent tantalum. Also, a renewed search is under way for the eutectic composition. However, the interval between the beginning and ending of melting is so small over a wide range of composition that the minimum point is not easy to find.

X-ray and metallographic studies intended to determine the boundary of the tantalum-rich solid solution field have been continued. For metallographic work, alloys are quenched in cold helium from temperatures up to 2000°C. The temperatures required to bring the alloys into solid solution are higher than would be anticipated from the position of the eutectic horizontal.

Measurements of electrical resistance at room temperature have not yielded consistent results and have not given any clue as to solid solution boundaries.

4.6 Zirconium-Zinc System (6)

Work on this system was discontinued during this report period but will be continued next quarter.

4.7 Tantalum-Vanadium System (2)

Work has been continued on the tantalum-vanadium alloy system. Several attempts were made to isolate single crystals of the intermetallic compound phase occurring in this system. Since the compound forms by precipitation from a solid solution, it is somewhat difficult to obtain large, easily separable single crystals of this phase. Efforts to isolate single crystals by preferential dissolution in a HNO_3 - HF solution dissolved the entire specimen. Also, reacting a uranium-vanadium alloy with tantalum in a tantalum crucible at 1100°C for 2 hours, produced a small reaction band at the Ta-U interface, but this was not large enough to permit separation of any of the phase. Attempts to isolate a single crystal by fracturing a brittle alloy containing considerable amounts of the intermetallic phase proved somewhat more hopeful. A well formed single crystal was obtained by this method. However, when a rotation pattern was taken of the crystal, it proved to be a single crystal pattern of the BCC solid solution phase with a powder pattern of the intermediate phase superimposed upon it. Additional attempts to index powder patterns of the phase have not been satisfactory. Most of the lines can be indexed on the basis of a tetragonal unit cell but not all of them.

4.8 Niobium-Zinc System (2)

Investigations of the solubility of niobium in zinc has continued. A series of solubility studies were carried out in the temperature range of 600 to 850°C in which zinc was placed in a niobium crucible and these were sealed in an evacuated vycor tube. These were placed in a furnace and held at a given temperature for three to five hours. The samples were then removed from the furnace, allowed to cool in air and broken open. Drillings from the zinc-rich region in the center were analyzed chemically for niobium content. The data secured are plotted in Fig. 1.

5. Metal Coatings and Corrosion

5.1 Corrosion of Refractory Metals by Liquid Metals (5)

During corrosion tests on tantalum carried out at 1200°C , serious embrittlement of the tantalum samples was observed. This embrittlement was observed using either Inconel or type 309 stainless steel as the protective jacket. A series of experiments established that the embrittlement was not associated with the

Fig. 1 Solubility of Niobium in Zinc vs. Temperature

oxide film on the Inconel or stainless steel, and that the cause could not be removed by vacuum heat-treating the protective jackets. Permeability of these alloys to nitrogen from the air seemed to be a possible explanation of this embrittlement. Diffusion data, which were available, indicated that nitrogen might diffuse through this alloy and a vacuum fusion analysis of the brittle tantalum showed a very high nitrogen content. The method of corrosion testing which was used at 1000°C will obviously have to be changed when tests are made at 1200°C.

A procedure for coating tantalum with tantalum carbide, which will improve the resistance of tantalum to corrosion by liquid metals, is being developed. No coating at all is obtained below 1650°C. Heating at this temperature for one hour produces a carbide layer which is 0.3 mils thick. The corrosion resistance of this coating has not been determined.

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

Carbide-coated tantalum crucibles still appear to be the most satisfactory containers for molten uranium-chromium alloys. A carbide coated crucible contained the eutectic alloy for 1080 hours at 1100°C with very little evidence of attack. A layer of high-melting material formed on the walls of the cup. Probably this layer acted as a barrier against the attack. At the conclusion of the test, the tantalum was still ductile and the eutectic still had its characteristic appearance.

The test described above was made with the specimen in a vacuum. A similar test conducted under an atmosphere of helium showed a less satisfactory result. Impurities present in the helium reacted with the eutectic and also embrittled the tantalum.

Tests on silicide-coated crucibles have not yielded promising results but the silicide coating was less uniform than the carbide layer. Methods of improving the silicide deposit are under study.

5.3 Casting Uranium Into Zirconium Cans (2)

(See Report ISC-641)

5.4 Dip Coating of Uranium (6)

(See Report ISC-641)

6. Solid State Investigations

6.1 Electrical Measurements on Calcium (4)

The electrical properties of 99.6% calcium and 99.9% calcium have been investigated further. Anderson and Legvold measured the Hall coefficient of 99.9% calcium from 80-300°K and found it to be essentially constant with a value of $-2.28 \times 10^{-4} \text{ cm}^3/\text{coulomb}$. [G. Anderson and S. Legvold, Ames Laboratory, unpublished work.] Also the Hall coefficient of 99.6% calcium was measured at room temperature showing a value of $-1.8 \times 10^{-4} \text{ cm}^3/\text{coulomb}$. Since the Hall coefficient is the reciprocal of the net number of charge carriers times the unit charge, these data show that in both cases electrical conduction is predominantly by electrons rather than holes. The data further show a decreasing density of charge carriers with increasing purity. The carrier density of 99.6% calcium was calculated to be $3.47 \times 10^{22} \text{ electrons/cm}^3$ or 1.53 electrons/atom. The corresponding value for 99.9% calcium was $2.74 \times 10^{22} \text{ electrons}$ or 1.19 electrons/atom. The values were calculated with the assumption that no charge was carried by holes.

Combining resistivity data with the measured Hall coefficients made possible the calculation of electron mobilities. At room temperature the electron mobility in 99.9% calcium was found to be about 25% greater than in 99.6% calcium. At room temperature the resistivities of both purities was found to be approximately equal with a value of 4 micro-ohm cm. Above room temperature the resistivity of 99.6% calcium is greater than in 99.9% calcium while below room temperature the inverse is true. Thus the results show that the greater carrier density in 99.6% calcium is outweighed above room temperature by lower mobility.

The results clearly indicate that impurities in calcium contribute conduction electrons. However, the carrier densities are so high that the impurity contribution does not seem adequate to account for all of the conduction electrons. Pure calcium, therefore, is expected to show a negative Hall coefficient.

6.2 Uranium Transformation Studies (6)

A program has been initiated to study the solid state transformations of uranium. Electrical resistivity data and x-ray data at various temperatures as a function of time will be taken in an attempt to establish the kinetics of these transformations. High temperature x-ray data will also be utilized to determine the temperature dependence of the lattice parameters of the α , β , and γ phases and to determine the volume changes which occur

on transformation. These data and published data will be combined and an effort made to establish the mechanisms of these transformations.

6.2.1. Temperature Dependence of the Lattice Parameters of Uranium

High temperature x-ray data have been obtained using the high temperature x-ray diffractometer designed by Chiotti. /P. Chiotti, "Adaptation of a Geiger-Counter X-ray Diffractometer for High-Temperature Investigations", Rev. Sci. Instr. 25, 683-688 (1953)_. Massive samples of Hanford Slug uranium and of biscuit uranium were used. Contamination of the metal surface with carbon and the coarsening of the grain size of the samples after heating for several hours at temperatures above 600°C proved troublesome. Large grain size and orientation of the grains reduces the number of peaks picked up by the Geiger counter. However, two samples of biscuit uranium each gave two well defined peaks showing α_1 and α_2 resolution for the gamma phase at 800, 900 and 1005°C. A larger number of gamma peaks were obtained by employing uranium-zirconium alloy samples. Measurements were made on alloys containing 0.5, 2.5, 5.0, 10.0 and 20.0 w/o zirconium. Four to five gamma peaks were observed with each of these alloys at 800, 900 and 1005°C. The values for the refined lattice constants at each temperature were extrapolated to zero per cent zirconium. The extrapolated values were in good agreement with those obtained with biscuit uranium.

Attempts to refine the lattice constants of alpha and beta uranium were not very satisfactory. A method described by Thewlis /J. Thewlis, "A Graphical Method for the Determination of Unit-Cell Dimensions of Non-Cubic Materials from X-ray Powder Photographs", Acta Cryst. 15, 849-850 (1952)_. was tried; however, there was an insufficient number of suitable reflections for good accuracy. Some degree of refinement was obtained by solving simultaneous equations for the three parameters employing the measured angles of three adjacent peaks and then using a mean value of the angles used to extrapolate the lattice constants by Nelson and Riley's method. /J. B. Nelson and D. P. Riley, Proc. Phys. Soc. (London) 57, 160 (1945)_.

The preliminary results obtained for the lattice constants of alpha uranium, with the exception of b_0 , are in fairly good agreement with values reported by other investigators. /"Metallurgy of Uranium and Its Alloys", N.N.E.S., Division IV, Volume 12a, 1953, p. 75. The results obtained indicate that the volume expansion of alpha uranium is a linear function of the temperature.

Modifications are being made in the apparatus in the hope of increasing the precision of the measurements and the above measurements will be repeated.

For further details and data see ISC-641.

6.3 Structure of ZrGe₂ and HfGe₂:

The structure parameters of ZrGe₂ were further refined by difference Fourier methods. [Ames Laboratory Staff, Quarterly Summary Research Report in Metallurgy, Oct., Nov., Dec., 1954, ISC-575.] The best parameters are:

$$y(\text{Zr}) = 0.106$$

$$y(\text{GeI}) = 0.750$$

$$y(\text{GeII}) = 0.441$$

After application of absorption and temperature factors, the reliability factor, $R = \frac{\sum |F_o - F_c|}{\sum |F_o|}$, was 12.7% with these parameters.

Precision lattice constants were obtained by applying Cohen's least squares method to data obtained from the focusing back-reflection powder camera. [M. U. Cohen, Rev. Sci. Instr. 6, 68 (1935).] The lattice constants are:

$$a_o = 3.7893 \text{ \AA}$$

$$b_o = 14.9745 \text{ \AA}$$

$$c_o = 3.7606 \text{ \AA}$$

The structure of HfGe₂ was found to be isomorphous with ZrGe₂. The structure determination was made with {OKL} intensity data. The intensity data were obtained on a Weissenberg camera equipped with a Geiger-Müller tube and scaler. Copper K α radiation was employed. Using the same

parameters as in ZrGe_2 , a reliability factor of 8.1% was obtained. Precision lattice constants for HfGe_2 were also obtained by Cohen's method:

$$a_0 = 3.8154 \text{ \AA}$$

$$b_0 = 15.004_1 \text{ \AA}$$

$$c_0 = 3.7798 \text{ \AA}$$

7. Other Investigations

7.1 Reclamation of Zirconium Chips (2)

As was previously reported, the ductility of zirconium turnings may be greatly improved by a H_2SO_4 leaching treatment. Corrosion tests made on arc-melted specimens of the treated scrap indicated that the material had poor corrosion resistance after 56 days in 300°C water. However, since the original stock material which was tested simultaneously also exhibited high corrosion rates, additional corrosion tests were conducted to determine whether the H_2SO_4 treatment had a detrimental effect upon the corrosion resistance of the zirconium. Corrosion tests were run on the following specimens: (1) High purity crystal bar zirconium; (2) Arc-melted pieces of crystal bar zirconium; (3) Lathe turnings of crystal bar zirconium which were treated with H_2SO_4 and arc melted; and (4) Westinghouse scrap zirconium millings chips and lathe turnings which were treated with H_2SO_4 and subsequently melted.

Triplicate specimens of each of the above samples were prepared by sectioning them into small discs or plates. These were polished through #600 grit inserted length-wise through strips of teflon and were then immersed in distilled water in stainless steel bombs. The teflon strips were to keep the samples separated from the walls of the bomb and to prevent the possibility of galvanic action. The bombs were sealed, placed in a furnace and heated at 300°C for a period of 49 days. The teflon appeared to have disintegrated during the test and most of the specimens were badly corroded. The above experiment is now being repeated eliminating the teflon sample holder in the corrosion bomb.

7.2 Vacuum Fusion Analysis of Metals (5)

The nickel bath for vacuum fusion analyses of lanthanum appears very promising. All of the nitrogen and part of the oxygen are evolved at 1600°C . Complete evolution of the oxygen required temperatures of about 1850°C . The bath was allowed to cool to 1300° before the sample was dropped to reduce the rapid evolution

of gas when the sample was introduced. The temperature was then raised to 1900°C in about four minutes. The evolution of gas was complete within ten minutes after the crucible reached 1900°C. Samples of lanthanum containing known amounts of oxygen were analysed by this procedure and recoveries of between 90 and 100 per cent of the oxygen content were achieved.

7.3 Low Melting Alloy Studies (1)

A study of the aluminum-rich corner of the aluminum-thorium-uranium system has been started. This work is being undertaken to determine whether or not the low melting alloys existing in this part of the system can contain sufficient amounts of uranium and thorium in the liquid phase to suggest their use as a liquid fuel medium.

The metals being used to make the ternary alloys are Ames thorium, slug uranium, and Alcoa ingot aluminum of the following purity: Al-99.59%, Fe-0.33%, Si-0.08%.

The alloys are made by vacuum induction co-melting of the metals contained in a refractory crucible of magnesium oxide and calcium fluoride. The crucible is contained in a graphite heater equipped with a lid and chimney for temperature measurements with an optical pyrometer. A three kilowatt Ajax high-frequency source is used to heat the metals to about 1100°C. The temperature of the melt is maintained between 950°C and 1100°C for about 15 or 20 minutes. The alloy is then cooled in vacuo, after which it is sectioned and prepared for thermal, microscopic and chemical analysis. Alloys are made to weigh 50 grams and successive alloys differ in composition by five per cent. Thermal analysis is performed using a chromel-alumel thermocouple protected from the melt by a thin-walled tube of magnesium oxide. The thermal analysis is expected to aid in locating the liquidus surfaces, the course of the eutectic lines and the areas of compound formation.

7.4 High Temperature Furnace for Growing Single Crystals (2)

During this period a series of metal single crystals were grown using the high temperature crystal growing furnace. Several apparently successful attempts were made to grow single crystals of nickel, some as large as one and one-half inches in length by one inch in diameter. Two attempts to produce thorium crystals failed, as did three attempts with cobalt metal. Large grains resulted in the cobalt runs, but extensive twinning occurred within the grains.

A liquation experiment was tried with uranium metal, the experiment consisting of holding the metal several hundred degrees above its melting point for several hours and cooling slowly from the bottom upward. The object of this treatment was to float out the major insoluble impurity of UO_2 in the metal. While marked segregation of the larger UO_2 particles took place, much of the UO_2 remained in its original finely divided, well dispersed condition.

8. Rare Earth Metallurgy

See ISC-643.

APPENDIX I: LIST OF REPORTS FROM THE AMES LABORATORY

1. Reports for Cooperating Laboratories

- ISC-531 Ames Laboratory Staff. Metallurgy, Quarterly Summary Research Report. July, August, September, 1954.
- ISC-574 Ames Laboratory Staff. Chemistry. Quarterly Summary Research Report. October, November, December, 1954.
- ISC-576 Compiled by P. Chiotti and O. N. Carlson. Hanford Slug Program. Quarterly Summary Research Report. October, November, December, 1954.
- ISC-577 Ames Laboratory Staff. Physics, Quarterly Summary Research Report. October, November, December, 1954.
- ISC-598 W. A. Rhinehart and D. J. Zaffarano. A Voltage Calibration System for Accurate Pulse Height Measurement.
- ISC-599 R. A. Lowry, J. E. Osher and G. H. Miller, A Pressure Regulator for a Low Pressure Continuous Flow Ionization Chamber.
- ISC-601 R. W. Fisher. Comprehensive Report on Production of Thorium. IA. Thorium Fluoride Preparation.
- ISC-602 R. N. Kniseley and V. A. Fassel. A Rotating Step Sector for Use with AC or Other Intermittent Spectrographic Light Sources.

2. Papers Published in Scientific Journals

- Banks, C. V. and R. J. Davis
Analytical Applications of the Reaction of Thorium with Benzenephosphoric Acid. Anal. Chim. Acta 12, 418-31, (May, 1955).
- Banks, C. V. and R. E. Edwards. Separation and Determination of Thorium and Aluminum. Anal. Chem. 27, 947-49 (June, 1955).
- Dooley, M. E. and D. F. Atkins
A New Electronic Vacuum Dilatometer. Rev. Sci. Instr., 26, 568-71 (June, 1955).
- Duke, F. R. and R. W. Laity
The Measurement of Transport Numbers in Pure Fused Salts. J. Phys. Chem., 59, 549-52 (June, 1955)
- Duke, F. R. and F. R. Parchen
Kinetics of the Reduction of Ferric Ion by Hydroquinone in the Presence of 1,10-Phenanthroline. J. Am. Chem. Soc. 77, 3198-99 (June, 1955).

- Fassel, V. A., B. Quinney, L. C. Krotz and C. F. Lentz
Quantitative Spectrographic Analysis of the Rare Earth Elements. *Anal. Chem.*, 27, 1010-14 (June, 1955).
- Fassel, V. A. and H. J. Hettel
Isotopic Assay of Lithium by Means of Hydride Band Emission Spectra. *Spectrochim. Acta*, 7, #3, 175-78 (May-June, 1955)
- Grantham, L. F., T. S. Elleman and D. S. Martin, Jr.
Exchange of Chlorine in Aqueous Systems Containing Chloride and Tetrachloroplatinate. II. *J. Am. Chem. Soc.*, 77, 2965-71 (June, 1955).
- Hammer, C. L. and A. J. Bureau
A Method for the Prompt Destruction of the Electron Beam in a Conventional Synchrotron. *Rev. Sci. Instr.*, 26, 594-98 (June, 1955).
- Hammer, C. L. and A. J. Bureau
A Method for the Prompt Destruction of the Electron Beam in a Conventional Synchrotron. II. *Rev. Sci. Instr.*, 26, 598-600 (June, 1955).
- Hansen, R. S. and R. D. Hansen
The Adsorption of Hydrocarbons for Methanol and Ethanol Solutions by Non-Porous Carbons. *J. Phys. Chem.*, 59, 496-498 (June, 1955).
- Hansen, R. S., F. A. Miller and S. D. Christian
Activity Coefficients of Components in the System Water-Acetic Acid, Water-Propionic Acid, and Water-n-Butyric Acid at 25°C. *J. Phys. Chem.*, 59, 391-95 (May, 1955).
- Hughes, F. J. and D. S. Martin, Jr.
Kinetics of the Oxidation of Selenious Acid by Hydrogen Peroxide. *J. Phys. Chem.*, 59, 410-15 (May, 1955).
- Klingman, D. W., D. T. Hooker and C. V. Banks
Photometric Titration Assembly for Beckman Model DU Spectrophotometer. *Anal. Chem.*, 27, 572 (April, 1955).
- Nadler, M. R. and E. S. Fitzsimmons
Preparation and Properties of Calcium Zirconate. *J. Am. Ceram. Soc.*, 38, 214-17 (June, 1955).
- Nichols, R. T., A. V. Pohm, J. H. Talbot, Jr. and E. N. Jensen
A Beta-Ray Spectrometer for Coincidence Measurements. *Rev. Sci. Instr.*, 26, 580-83 (June, 1955).

APPENDIX II: LIST OF SHIPMENTS

<u>Destination</u>	<u>Item</u>
Mallinckrodt Chemical Works 3600 North 2nd Street St. Louis, Missouri	50 mg thulium oxide 50 mg lutetium oxide
Dr. Daniel Laszlo, Chief Div. of Neoplastic Diseases Montefiore Hospital New York 67, N. Y.	25 gm yttrium oxide 99.9%
Dr. S. Jaffe Air Reduction Co., Inc. Research Laboratory Murray Hill, New Jersey	2 gm pure thulium oxide
U. S. Bureau of Mines Rare and Precious Metals Experiment Station Reno, Nevada	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 1 gm erbium oxide 1 gm ytterbium oxide 100 mg holmium oxide 100 mg thulium oxide 100 mg lutetium oxide 100 mg terbium oxide
Dr. Charles E. Holley, Jr. Los Alamos Scientific Laboratory Los Alamos, New Mexico	20 gm yttrium metal 20 gm dysprosium metal 20 gm erbium metal 20 gm ytterbium metal
Brookhaven National Laboratory Upton, Long Island, New York	50 gm cerium metal
Supply Officer Naval Research Laboratory Washington, D. C.	100 gm thorium metal
University of California Los Alamos Scientific Laboratory Los Alamos, New Mexico	100 gm ytterbium oxide 100 gm erbium oxide 100 gm dysprosium oxide
Litton Industries Beverly Hills, California	2 thulium buttons

<u>Destination</u>	<u>Item</u>
Dr. LeRoy Eyring Department of Chemistry State University of Iowa Iowa City, Iowa	20 gm lanthanum oxide 20 gm cerium oxide 20 gm neodymium oxide 20 gm praseodymium oxide 20 gm samarium oxide 20 gm ytterbium oxide 10 gm gadolinium oxide 5 gm terbium oxide 5 gm thulium oxide
Dr. Howard E. Kremers Lindsay Chemical Co. West Chicago, Illinois	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 dysprosium oxide 100 mg holmium oxide 100 mg erbium oxide 100 mg ytterbium oxide 100 mg thulium oxide 100 mg lutetium oxide
Supply Officer Naval Research Laboratory Washington 25, D. C.	0.5 gm erbium metal 0.5 gm dysprosium metal
Research Laboratories of Colorado, Inc. Newton, Ohio	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

<u>Destination</u>	<u>Item</u>
Battelle Memorial Institute Columbus, Ohio	2 gm neodymium oxide 2 gm gadolinium oxide
State University of Iowa Purchasing Department Iowa City, Iowa	5 gm lanthanum metal 5 gm praseodymium metal 5 gm samarium metal 5 gm ytterbium metal
Trans World Airlines, Inc. Kansas City 15, Kansas	2 thulium buttons
M.I.T. Lincoln Laboratory Lexington, Massachusetts	1 gm gadolinium metal 1 gm dysprosium metal 1 gm erbium metal
Argonne National Laboratory Lemont, Illinois	30 mg thulium oxide 30 mg holmium oxide
Dr. Paul V. Harper Chicago, Illinois	20 gm yttrium oxide 99.8%
Dr. Nathan Sugarman Chicago, Illinois	2 gm praseodymium metal 2 gm holmium metal
National Bureau of Standards Washington, D. C.	1 lb lanthanum metal 1 lb cerium metal
Mallinckrodt Chemical Works 65 Destrehan Street St. Louis, Missouri	50 mg terbium oxide 50 mg dysprosium oxide 50 mg erbium oxide 50 mg lutetium oxide 50 mg thulium oxide
Argonne National Laboratory Lemont, Illinois	1 sample samarium metal 1 sample neodymium metal
Commanding Officer U. S. Naval Hospital St. Albans, New York	5 gm Y_2O_3 99.9%
Florida State University Tallahassee, Florida	2 gm ytterbium oxide
Carbide and Carbon Chemicals Co. X-10 Plant Oak Ridge, Tennessee	200 gm erbium oxide 500 gm neodymium oxide 200 gm holmium oxide 400 gm yttrium oxide 400 gm neodymium oxide
American Metallurgical Prod. Co. New Castle, Pennsylvania	1 lb lanthanum metal (99% pure)

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