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METALLURGY AND CERAMICS

UNITED STATES ATOMIC ENERGY COMMISSION

QUARTERLY SUMMARY RESEARCH REPORT IN METALLURGY

For July, August, September, 1953

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For The Atomic Energy Commission

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Chief, Declassification Branch

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For the period July, August, September, 1953

This report is prepared from material
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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 Niobite-Tantalite Ore Treatment (1)*

Several caustic fusions were made with a niobite-tantalite ore concentrate and the products after one leaching were each treated in a different manner. In all cases the fusion charge consisted of 10 grams of the ore concentrate, 8 grams of sodium hydroxide and 4 grams of sodium peroxide. The charge, in a nickel crucible, was placed in a muffle furnace at about 650°C for one-half hour. The product in each case was then cooled and leached with a 1.0M sodium hydroxide solution, a treatment which had previously been found to be effective in removing some of the impurities with insignificant loss of the niobium and tantalum.

The subsequent test leaching treatments were with varying concentrations of NaOH, KOH, HCl and HF. It was found that by leaching the fusion product further with aqueous NaOH solutions having concentrations of less than 0.1M considerable niobium and tantalum product dissolved. Treatment of the residue from the dilute NaOH leach with 4N HCl removed most of the iron and manganese, leaving a residue of the acid oxides and unreacted ore.

This residue, after treating with 2M NaOH, could then be leached with dilute NaOH to dissolve out essentially all of the residual reacted niobium and tantalum leaving a residue of unreacted ore. A good share of the niobium and tantalum was then in dilute NaOH solution and somewhat free from most of the original impurities present in the ore.

One treatment repeatedly employed here is to add dilute hydrochloric acid directly to the fusion product after it has been washed with 1M NaOH. This treatment leaves the white niobic and tantalic acids with the unreacted ore. Dilute HF solution then readily dissolves the niobium and tantalum acid residue leaving the unreacted ore. Some time was spent in an effort to find a combination of mineral acid and HF that would satisfactorily dissolve the niobium and tantalum acid residue and give a stable solution with less HF. It was found that as much as 50 per cent of the HF could be replaced by other mineral acids but the solutions were unstable and precipitated niobium and tantalum acid oxide from the solution on standing.

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

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1.2 Separation of Niobium and Tantalum by Liquid-Liquid Extraction (1)

The separation of niobium and tantalum salts or their acids is a difficult but important problem for the current analytical chemist. Niobium and tantalum metals and salts have found wide application in the steel and ceramic industries. Currently, these metals and their alloys are being considered as container materials in the construction of new atomic reactors. The work carried out in this Laboratory on the separation of these two elements is coupled with treatment of the ores which gives a material for use in separation studies. At the present time experiments have shown that niobium free of tantalum and tantalum free of niobium can be produced by a liquid-liquid extraction process that may have advantages over present commercial methods of separation.

Addition of an excess of aqueous HF to the solid niobic and tantalic acid mixture obtained from the ore treatment described earlier yields a stable solution which when contacted with many organic solvents results in the separation of tantalum from niobium. Treatment of a certain batch of ore resulted in an HF solution of niobium and tantalum having a concentration equivalent to 517 grams of the combined pentoxides per liter. This HF solution containing a mixture of niobium and tantalum is here designated as Master Feed-I, or MF-1. An analysis of this mixture showed it to be equivalent to about 52 per cent Ta_2O_5 and 48 per cent Nb_2O_5 disregarding other minor impurities. The Master Feed-I had a fluoride ion concentration of 15.3 equivalents per liter and a base equivalent of 17.3 per liter. The former was determined by the method of Willard and Winter [Ind. Eng. Chem., 5, 7 (1933)] while a NaOH titration employing phenolphthalein as the indicator yielded the base equivalent. Potentiometric titrations of this solution indicated that at a pH of 9 all the hydrogen ions had been replaced by sodium. Due to the corrosive nature of an acid fluoride solution the Master Feed-I was made up and stored in polyethylene containers. Many of the extractions and tests described with this feed were also carried out in polyethylene vessels.

Single stage and multiple stage batch extractions were carried out on Master Feed-I directly and at various water dilutions. At equilibrium the following determinations were made for each phase: (a) pentoxide weight by calcining the NH_4OH precipitate, (b) Ta/Nb (weight ratio) by x-ray fluorescence, (c) base equivalent, (d) fluoride ion concentration and (e) volume. From these values the distribution factors for niobium and tantalum, the separation factor and the per cent of total oxide transferred to the organic phase were calculated. The classical definitions for distribution and separation factors apply here. In all extractions equal volumes of the starting organic and aqueous phases were employed.

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More than fifty organic solvents have been tested so far in these extraction experiments. These compounds include hydrocarbons, halogenated hydrocarbons, alcohols, ethers, aldehydes, ketones, esters, amines, organic phosphates and organic phosphites. From the data obtained it was apparent that whenever there was transfer to the organic phase a considerable preference for tantalum was evident. As a general class the ketones appeared to be the most effective for obtaining pure tantalum although many of the alcohols, aldehydes, amines, phosphates and phosphites would work in a counter-current extraction employing a number of stages. Diethyl ether appeared to be the only compound in the ether series which transferred an appreciable quantity of tantalum. Very little extraction of either tantalum or niobium could be assigned to an ester group; however, ethyl acetoacetate gave very high transfer and purity of tantalum. The saturated hydrocarbons and their halogen derivatives that were tested gave no detectable transfer.

The lowest molecular weight aliphatic organic compounds in any given class usually gave the greatest transfer, although not necessarily the purest tantalum. Diethyl ketone gave a desirable combination of purity and transfer values for efficient separations. The data also indicated that the presence of a double bond in an aldehyde or ketone considerably increased the amount of transfer to the organic phase with no decrease in separation factor. The aromatic amines were the only class of compounds which consistently transferred more than half the material to the organic phase. However, it was apparent that the separation factors for the amines tested were much lower than for any other class of compounds.

This investigation showed that a great number of common water-immiscible organic compounds separate tantalum from niobium when these elements are together in an HF system. It was observed that tantalum essentially free of niobium (less than 0.2 per cent niobium) can easily be produced in a single stage extraction but that the preparation of tantalum-free niobium would require a series of extractions. Consequently, three separate batch extraction tests were performed in an effort to prepare tantalum-free niobium.

In the first batch extraction test a 22 volume per cent Master Feed-I solution was contacted with successive equal volume portions of virgin di-isopropyl ketone. In each extraction the oxide recovered from the organic phase analyzed greater than 99.8 per cent Ta_2O_5 with respect to the sum of the combined tantalum and niobium oxides. Furthermore, the total extracted oxide from the five contacts represented a 68 per cent recovery of the original Ta_2O_5 present in the mixture. After the fifth extraction the combined oxides from the aqueous phase analyzed 25.9 per cent Ta_2O_5 and 74.1 per cent Nb_2O_5 . As the extractions progressed the amount of tantalum transferred to the organic phase steadily decreased so that the fifth organic contact resulted in a transfer of only

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1.9 per cent of the initial weight of combined oxides. It was determined that rapid decrease in the concentration of fluoride ion paralleled the decrease in the transfer of material. A very large number of such extractions by contact of fresh organic would be required for complete removal of tantalum unless more HF were added to the system. Tantalum spectrographically free of niobium was prepared from a portion of the organic phase from the first contact by scrubbing with three equal volume portions of a 0.77M HF aqueous solution.

A second batch extraction test employed the 100 per cent Master Feed-I as the aqueous phase and di-isopropyl ketone as the organic phase. After four extractions of the aqueous phase with equal volumes of virgin di-isopropyl ketone, greater than 95 per cent of the starting niobium oxide remained in the aqueous phase. This niobium oxide analyzed less than 500 ppm tantalum oxide. If all portions of the organic phase had been combined it was calculated that the resulting tantalum oxide would have had a purity of greater than 90 per cent with respect to the sum of these oxides. Instead the organic phase from the first of the four contacts was scrubbed twice with equal volumes of a 0.77M HF aqueous solution. This resulted in 50 per cent of the original tantalum oxide becoming spectrographically free of niobium oxide.

The third batch extraction test employed a 22 volume per cent Master Feed-I as the initial aqueous phase and virgin tributyl phosphate as the organic phase. This aqueous phase was given two successive contacts with equal volumes of the tributyl phosphate. The residual aqueous phase was then found to contain 88 per cent of the original niobium oxide content and less than 500 ppm tantalum oxide. Two scrubs of the first equilibrium organic phase with 0.72M HF aqueous solution resulted in a 92 per cent recovery of the original tantalum oxide containing less than 0.40 per cent niobium oxide. One more scrub would probably have yielded spectrographically pure tantalum. From these data it appears that a five or six stage column operating countercurrently would be required to yield both pure tantalum and niobium while obtaining 100 per cent recovery of both.

The main disadvantage of this HF system is its corrosive nature toward glass and most metals. Therefore, with this system special HF-resistant countercurrent extraction equipment consisting of a few stages will have to be set up for complete and continuous separation of both tantalum and niobium spectrographically free of each other. Some plastic materials, such as polyethylene, are quite HF resistant and fabrication of a high capacity extractor of such material is entirely feasible.

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

Three approaches to the separation of titanium from niobium have been investigated; first, the precipitation of titanium as $(\text{NH}_4)_2\text{TiCl}_6$ from a solution saturated with HCl at 0°C ; second, a potassium hydroxide fusion followed by a water leach in an attempt to remove the soluble niobium compound from the less soluble titanate; third, a liquid-liquid extraction of an aqueous feed solution by an immiscible organic solvent.

Several separations were attempted using the first approach mentioned above. The procedure followed was that of Josef Wernet for this treatment of a mixture of hydrated oxides of niobium and titanium. The mixed oxides were treated with hydrochloric acid, then cooled to 0°C and the system saturated with HCl gas to complete the solution of the hydrated oxides. Solid NH_4Cl (4 g/100 ml of the solution) was added as HCl gas passed into the solution at 0°C , causing a precipitate of $(\text{NH}_4)_2\text{TiCl}_6$ to form. The solution was filtered in an ice-cooled sintered glass filter and the precipitate ignited to the oxide. The results of these experiments indicated a separation in only one instance. The main difficulty encountered in this method was solution of the hydrated oxides prior to the separation step. It is felt that this procedure could be developed to give a good separation but would probably involve considerable time.

The second approach employing the potassium hydroxide fusion followed by a water leach, appeared to give a good separation in some instances and practically no separation in others. Further work will be necessary to determine the critical conditions if such exist for a good separation using this method.

In the third approach, liquid-liquid extraction, an aqueous hydrofluoric acid solution containing niobium and titanium was contacted with equal volumes of various organic solvents. The phases were separated, the niobium and titanium precipitated as the hydrated oxides, ignited to the oxides and analyzed for titanium. This method gave very favorable results. Of the fifteen organic solvents tried, nine gave a good separation with considerable transfer of niobium to the organic phase, tributyl phosphate giving the best results.

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

Exploratory work was performed on liquid-liquid extraction of hafnium from an aqueous zirconium sulfate solution. The aqueous solution was one-half molar in zirconium sulfate, $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, and 0.5 molar in sulfuric acid. The extent of hafnium impurity was about 3 per cent. The organic solvents which were used in these extractions included ethers, ketones, esters, and alcohols. For each of these solvents there was found to be no apparent transfer of either hafnium or zirconium from aqueous solution to organic solvent.

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More extensive work was done on the alcohol systems. Higher molecular weight alcohols, immiscible with water, were used as organic solvents. Those used were isobutyl, amyl, heptyl, capryl, and benzyl alcohol. The lower molecular weight alcohols were soluble in both phases and were used as distributors or bridging agents in the transfer of hafnium and/or zirconium to the organic phase. Of these, methyl, ethyl, and isopropyl alcohol were employed for this purpose. Enough of the bridging alcohol was added to a given system such that a loss in aqueous phase occurred after contacting without the precipitation of any material. Transfer occurred in those systems which showed a loss in the volume of aqueous phase after contacting. In one typical experiment the aqueous zirconium sulfate solution was contacted with an equal volume of organic solvent consisting of 60 per cent isobutyl alcohol and 40 per cent ethyl alcohol by volume. Ethyl alcohol was the distributor or bridging agent in this instance. Analyses of the equilibrium concentrations of both phases indicated that there was a drop of 1 per cent in the amount of hafnium impurity which transferred along with the zirconium to the organic phase. Transfer was found to vary directly with the amount of bridging alcohol. The purity of zirconium which transferred to the organic phase varied inversely with the amount of bridging alcohol used. As yet, the optimum conditions have not been determined for these systems.

Further research on extraction from the aqueous zirconium sulfate solution was performed using ammonium thiocyanate as a complexing agent and hexone as the organic solvent. The concentration of ammonium thiocyanate was held constant at 6.6 molar in the aqueous phase feed with no thiocyanate added directly to the hexone. The concentration of sulfuric acid was varied from 0.5 molar to 3.5 molar. When the aqueous phase was 1.0 molar in sulfuric acid it was found that the material which transferred over to the organic phase consisted of 23 per cent hafnium. The loss in the total amount of zirconium was 5 per cent. For a solution 1.5 molar in sulfuric acid there was a 2 per cent loss of zirconium due to transfer to the hexone phase. Forty-four per cent of the material transferred to the organic phase was hafnium. Systems in which the aqueous solutions were 2.5 molar and above in sulfuric acid showed no transfer to the hexone phase. Here the sulfuric acid appeared to hold back all the material in the aqueous phase.

1.5 Separation of Small Amounts of Zirconium from Hafnium (1)

The first of two multistage liquid-liquid extractions made during this period to remove about 4 per cent Zr from Hf employed 15 stages. The conditions for this extraction were almost identical with those reported previously except that all glassware used in preparing the organic solvent was washed with concentrated HNO_3 and the solvent itself was scrubbed with water. This was done to remove any Zr which may have been contaminating the organic solvent causing the previously unaccounted-for increase in Zr at the organic input

end of the extractor. The conditions used in this extraction are given in the following table.

	[HNO ₃]	[HfOCl ₂ ·8H ₂ O]	vol./cycle	Stage Added
Aqueous Feed	5.46 M	730 g/l	20 mls	9
Organic 60% tributyl phosphate 40% dibutyl ether	none	none	20 mls	1
Aqueous Scrub	6.04 M	none	5 mls	15

This extraction gave Hf in the aqueous phase with less than 100 ppm Zr, and transferred a total of about 10 per cent of the solute calculated as oxides to the organic phase. The extractor used in this experimental work will be described in the forthcoming report, ISC-458.

Employing conditions based on the above experimental test, an extraction was made on a larger capacity 15 stage unit. A few pounds of HfO₂ containing only 14 ppm Zr with respect to the Hf were recovered from the aqueous product of this extraction. Qualitative analysis of the HfO₂ showed only trace amounts of Al, Be, Mg, Cd, Sn, and Cu.

2. Preparation of Pure Compounds

2.1 Preparation of Neodymium Fluoride (5,2)

Neodymium oxide was dissolved in 6 N HCl and the purple-colored, hydrated chloride was crystallized from solution. To this hydrated chloride, 70 per cent hydrofluoric acid was added and the product filtered and washed with acetone. The product was purple in color, granular in form, and non-hygroscopic. Neodymium fluoride was also prepared by heating the oxide in gaseous hydrogen fluoride at elevated temperatures. Better than 99 per cent conversion to the fluoride was obtained by heating neodymium oxide in a stream of anhydrous hydrogen fluoride to 300°C and holding for one or two hours, then continuing the heating at 600°C for two hours or more.

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2.2 Preparation of Yttrium Fluoride (5,2)

Yttrium trioxide was dissolved in 6 N HCl and the hydrated chloride crystallized from solution. To this chloride 70 per cent aqueous hydrofluoric acid was added and the resulting precipitate easily filtered and washed with acetone. The product assumed to be the fluoride was white, granular, and non-hygroscopic. Yttrium fluoride when prepared by treatment of the oxide with anhydrous hydrogen fluoride gas at elevated temperatures, in a manner similar to that described for treating neodymium oxide, yielded a product with less than 98 per cent conversion to the fluoride.

2.3 Preparation of Lanthanum Fluoride (5,2)

Treatment of lanthanum oxide with anhydrous hydrogen fluoride under the same conditions as those described for treatment of neodymium oxide above yielded lanthanum fluoride with better than 99 per cent conversion.

2.4 Preparation of Cerous Fluoride (2)

Cerous fluoride was prepared by the addition of 70 per cent hydrofluoric acid to cerous chloride hexahydrate giving a crystalline precipitate of cerous fluoride which was readily filtered. Adhering water was removed by passing anhydrous HF gas over the salt at 300°C. X-ray diffraction patterns gave positive identification of cerous fluoride.

2.5 Preparation of Thorium Tetrachloride (5)

The purity of the thorium chloride produced by chlorination of thorium oxide and carbon was considerably improved. The charge was placed in a closed chamber of Carbolcel 60 carbon which prevented mechanical carry-over of oxide and carbon from the charge. The purity of the product, which was deduced from a chloride analysis, varied from 98 to 99.5 per cent thorium tetrachloride. The quality of thorium chloride produced under these conditions seems to be satisfactory for reduction to thorium metal and can be produced very consistently. The residue remaining in the carbon reaction chamber was principally carbon, showing that the yield of thorium chloride was closed to the theoretical amount. The amount of carbon residue indicated that two carbon atoms per thorium are used in the chlorination reaction.

An order from Dow Chemical Company for ten pounds of anhydrous thorium tetrachloride was filled and shipped. Since the quality of the thorium chloride produced seems to be satisfactory, research will now be concentrated on increasing the rate of production and developing a semicontinuous process for the preparation of thorium tetrachloride.

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2.6 Preparation of Vanadium Chlorides (5)

An investigation of methods of producing vanadium chloride was started in a search for a compound of vanadium which would be desirable as a starting material in a metallothermic reduction to produce vanadium metal. Three chlorides of vanadium are reported in the literature; these are the tetrachloride, the trichloride and the dichloride. Several oxychlorides are also known. Very little information was available on the properties of vanadium trichloride and vanadium dichloride. Also lacking were simple methods of producing these chlorides as pure anhydrous materials.

The reduction of vanadium pentoxide by hydrogen was studied in the hope that a lower oxide might be a good starting material for the preparation of the chlorides. At 600°C and above, hydrogen reduces the pentoxide to vanadium trioxide quite rapidly and completely. The trioxide can be oxidized by air to vanadium tetraoxide at 150°C. These lower oxides do not appear promising as materials for a preparation of pure vanadium chloride because of the formation of stable oxychlorides.

To eliminate oxygen, vanadium carbide was prepared at 1600°C from vanadium pentoxide. This material when treated with chlorine at 600°C produced vanadium tetrachloride. The reaction was quite rapid and easily controlled. The purity of the vanadium chloride produced was not determined. Purification by distillation at atmospheric pressure was not feasible because of extensive decomposition to a product tentatively identified as vanadium trichloride.

3. Metal Preparation Studies

3.1 Preparation of Rare Earth Metals (2)

The preparation of some of the rare earth metals is being undertaken on an enlarged scale to provide adequate amounts of these metals for various research uses and to develop the processing techniques from an economic standpoint. The fluorides are being employed in the reduction step.

Lanthanum metal was prepared from its fluoride by bomb reduction using calcium as the reductant and iodine as the booster. The 2 1/2 inch bomb was ignited by a resistance wire in the charge; the bomb was lined with jolt-packed calcium fluoride. A 93 per cent yield of lanthanum was obtained.

Cerium metal was similarly prepared from its fluoride and a yield of 90 per cent was obtained.

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3.2 Preparation of Vanadium Metal (2,1)

As has been reported previously by other investigators the preparation of vanadium metal can be carried out by a bomb reduction of V_2O_3 or V_2O_5 with calcium using an iodine or sulfur booster. Attempts to reproduce these methods, however, have resulted in metal of variable quality. Not having high purity vanadium available as a standard the following criterion has been set forth to serve as a measure of the quality of the metal obtained.

1. Microscopic appearance and amount of second phase impurities.
2. Chemical analysis of nitrogen and carbon.
3. Hardness of metal--assuming the higher purity, the softer metal.
4. Ductility--assuming pure vanadium will cold-roll.

In an effort to obtain a uniformly ductile product, various liner materials were tested, different methods of igniting the bomb charge were tried, and the effect of different boosters was studied.

No conclusive evidence was obtained concerning a bomb liner preference. The refractories studied included sintered CaO , sintered dolomitic oxide, jolt-packed CaO , jolt-packed dolomite, and sintered $MgO-CaF_2$ liner. The indications are that the use of a sintered MgO liner containing 15 per cent CaF_2 gives best reproducibility in quality.

Comparison of firing methods was likewise inconclusive. Early studies seemed to indicate that firing the bomb by electrical resistance heating of a coil of wire embedded in the charge was highly advantageous while later experiments indicated that gas firing gives a more ductile metal. Results showed that the use of a sulfur booster gave a somewhat more ductile metal in the reduction of technical grade V_2O_5 (containing approximately 90 per cent V_2O_5) whereas an iodine booster gave better results in the reduction of C. P. grade V_2O_5 (99.5 per cent V_2O_5).

As a result of these tests a set of conditions has been derived which gives a reproducible metal product. A typical 4 inch bomb charge of 320 g C. P. V_2O_5 , 700 grams Ca (50 per cent excess) and 160 g iodine is placed in the bomb lined with sintered MgO -15 per cent CaF_2 and gas fired. The metal thus obtained has a Rockwell A hardness of approximately 30 and cold-rolls readily. Upon arc melting in a helium atmosphere, metal of Rockwell A 50 hardness is obtained which can be cold-rolled successfully into thin sheets.

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Annealing the arc-melted button reduces the hardness to A 40-45 but also causes increased cracking upon cold rolling. This is believed to be due to the migration of impurities to the grain boundaries during annealing, resulting in softer metal but weaker grain boundaries.

Microscopic examination of the metal confirms this observation since there is a large amount of impurity finely distributed along the grain boundaries and within the grains. The identification of the impurity is not complete although it is considered to be nitride, carbide or oxide. Chemical analyses of the metal thus produced indicate the presence of 500 to 1500 ppm nitrogen although neither the calcium nor the V_2O_5 used contains more than 25 ppm N_2 . Analyses tentatively indicate considerable amounts of carbon as well.

The reduction of vanadium compounds by electrolytic means was attempted. It was found that the conductivity of molten vanadium pentoxide could be increased by the addition of sodium hydroxide to the melt. The electrolysis of such a mixture only resulted in the deposition of a lower oxide of vanadium on the cathode. The electrolysis of a mixture of vanadium pentoxide and zinc oxide was also unsuccessful.

An article was found describing the production of VO by the electrolysis of an equal molar mixture of vanadium pentoxide and potassium pyrophosphate. A quantity of shiny black crystals was obtained in an effort to duplicate the experiment. However, analysis showed the composition of the crystals to be closer to V_2O_3 than VO.

Reduction of vanadium pentoxide with sodium metal was tried, but no metallic vanadium was obtained in this way.

3.3 Preparation of Uranium Metal from Oxide (1)

Work on the reduction of uranium oxides was continued. An approach similar to that used in England was investigated. A mixture of 100 g of uranium dioxide was reduced with 39 g of calcium in a calcium oxide lined steel crucible. The product was leached first with water and acetic acid. Following this was a leach with 5 per cent nitric acid for two and one-half hours at a temperature below 25°C . The material was then washed with water and vacuum dried. This procedure seemed to leave considerable calcium oxide in the product.

Experiments were made to find methods of removing oxide from the surface of the powdered uranium. Both a solution of 5 per cent sodium carbonate in 1 per cent hydrogen peroxide and a solution of 5 per cent ammonium oxalate in 1 per cent hydrogen peroxide showed promise.

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Experiments were made using equal amounts by weight of aluminum and calcium for the reduction of uranium oxide, as this should have resulted in a low melting slag. A small amount of hard, shiny, brittle metal was obtained in this manner. The metal was apparently an aluminum-uranium alloy although a stoichiometric deficiency of aluminum and calcium was used.

3.4 Studies on the Preparation of Niobium Metal from the Oxide (1)

The reduction of Nb_2O_5 with carbon under reduced pressure (below 1 mm) is being studied. The observations so far made have been given the following tentative interpretation:

- (a) No reduction below 950°C.
- (b) Between 950°C and 1000°C the pentoxide is reduced to the blue oxide, Nb_2O_3 .
- (c) A second reduction begins between 1150° and 1200°C giving the black monoxide.
- (d) A third reduction begins between 1250° and 1300°C giving the carbide if an excess of carbon is used. If only enough carbon to form metal is used, a mixture of carbide, monoxide and possibly metal is formed.
- (e) The carbide and oxide react only when a temperature of approximately 1700°C is reached and should give pure metal if stoichiometric amounts of oxide and carbide are present. But, this being a solid-solid reaction, even when the mixture is pressed into pills at 30 tons/in² pressure, the reaction has been incomplete when tried. Further attempts will be made, however.

The reduction of niobium oxide with mixtures containing calcium metal is also being studied. A niobium-aluminum alloy has been obtained by reducing niobium pentoxide with a mixture of calcium and aluminum. Excess aluminum is used to form the alloy. Attempts were made to remove the aluminum from the alloy by distillation, but so far without notable success.

The aluminum-calcium mixture produces massive metal, not only because of the high heat of the reaction and the low melting point of the aluminum-niobium alloy produced, but because the slag, a mixture of calcium oxide and aluminum oxide, is also low melting. So, one of the problems in using a metal other than aluminum for the low melting alloy lies in producing a low melting slag at the same time.

Some metals which appeared worth testing for alloying with niobium in bomb reduction because of their low boiling points and other considerations included zinc, bismuth, antimony and lead. Antimony had been tried earlier with negative results so a series of runs was made to try zinc as an alloying agent and to test a thirty per cent excess of calcium which has been reported to give a somewhat fusible slag. Zinc added as metallic zinc appeared to inhibit the bomb reduction. To get more heat, zinc oxide was used. A reaction took place but the products did not melt. To add still more heat, the zinc was added as zinc fluoride. The products of this reaction were never molten. In an attempt to form a low melting triple alloy of niobium, zinc and antimony, zinc oxide and antimonous oxide were added to a bomb charge. Nothing melted.

Because lead has low melting and boiling points and loosely bound oxygen in its oxides, lead oxides were mixed with niobium pentoxide and the oxides co-reduced with calcium. Lead monoxide was mixed with niobium pentoxide in such proportions that the contained lead was in a one-to-one atomic ratio with the contained niobium. This produced drops of metal. The same oxide in a one-lead-to-two-niobium ratio produced no massive metal and resulted in no melting. Lead dioxide in a one-lead-to-two-niobium atomic ratio did produce drops of metal. This is considered due to the extra heat available from reduction of the lead dioxide. This evidence indicates that lead co-reduction warrants further investigation.

When the bomb products from the zinc-niobium co-reductions were treated with water and HCl, a gray powder was produced. Some of this powder was dried and pressed into pellets. These pellets were then heated in a BeO crucible under vacuum. Heated to 1400°C and held at that temperature for six hours, the pellets appear to have sintered on the surface. Heated to 1600°C and held for two hours, the pellets increased in density and hardness and had a metallic sheen inside and out. They are brittle and porous but the results indicate further work should be done along this line.

4. Alloy Studies

4.1 Zinc-Uranium (2)

Preliminary investigation of the zinc-uranium alloy system was started. Liquidus studies of the zinc-rich end of the diagram were conducted using the following procedure. The center portion of a uranium cylinder was drilled out and zinc metal placed inside the cylinder. This was then sealed in a graphite-lined steel bomb and agitated during heating at the desired temperature. Following furnace cooling to room temperature the zinc-rich center portion was drilled out and these drillings were analyzed for dissolved uranium. The accompanying table relates temperature, time interval

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of heating, and weight per cent of uranium dissolved in zinc. Data from the table indicate that equilibrium between zinc and uranium has not been established. Further studies are being conducted.

Temperature	Heating Time	Wt. Per Cent U in Zn
520°C	1 hour	0.04
520	2 hours	0.14
640	1 hour	2.21
640	2 hours	3.34

Alloys in the zinc-rich end of the diagram have also been prepared by heating zinc and uranium metal in a double-wall, steel bomb with the inner bomb lined with a 20 per cent CaF-MgO crucible. Microstructure data indicate that a peritectic compound is formed which appears to decompose between 745°C and 820°C.

Attempts have been made to prepare uranium-rich alloys by bomb reduction of UF_4 using calcium as the reductant in the presence of zinc metal, but no encouraging results have been obtained. It is very probable that these alloys can not be prepared in this manner without segregation occurring or contamination with calcium. This conclusion is based on two reductions; one, an attempt to prepare a ten weight per cent zinc alloy and the other, an attempt to prepare a fifteen weight per cent zinc alloy. According to chemical analysis the former biscuit contained no zinc while in the latter case two metal layers formed, the bottom layer being uranium and the top layer, a zinc-calcium alloy.

A uranium-rich alloy has been prepared by melting zinc and uranium together at 1200°C in a double-wall, steel bomb with welded end caps. Some difficulty has arisen in this method as the zinc vapors have been reacting with the welds at elevated temperatures.

4.2 Zirconium-Tin System (2)

As has been reported previously, the addition of small amounts of carbon (500 ppm or greater) inhibits the formation of the peritectoid compound Zr_4Sn . Subsequently, experiments have been conducted on the effects of small additions of nickel, chromium, and iron on the stability of the Zr_4Sn phase in the tin-zirconium

alloy system. Introducing approximately 0.1 weight per cent of nickel, chromium, and iron respectively to three, 24 weight per cent tin-zirconium alloys produced no inhibiting effects on the peritectoid formation in any one of the three alloys. A 24 per cent tin-zirconium alloy containing 0.1 per cent chromium, 0.1 per cent nickel, and 0.15 per cent iron showed similar results. The arc-melted alloys were annealed for 100 hours at 1000°C and in all of the above cases a peritectoid compound was observed in the microstructure, leading to the conclusion that these elements have no observable affect upon the stability of Zr_4Sn .

Chemical analysis showed the percentage of the impurities to be lower than calculated in each alloy. This may be explained by a tendency to blow out loose powder upon striking the arc in the arc-melting chamber.

4.3 Thorium-Zirconium System (2)

The existence of a two phase region above the 900°C temperature horizontal in the thorium-zirconium system has been postulated, although no evidence has been found for it. A group of arc-melted alloys, 16, 23, 25, and 35 weight per cent zirconium in thorium, lying in the composition range of the horizontal were quenched from slightly above the 900°C transformation. Using a differential thermocouple to indicate the thermal arrest, it was possible to quench alloys from a few degrees above the transformation. All alloys appeared as one phase microscopically and apparently, if a two phase region does exist, it extends over only a very short temperature range or is very difficult to bring out by chemical etching.

4.4 Vanadium-Aluminum Alloys (2)

The preparation of ductile vanadium by the reduction of vanadium pentoxide with calcium and aluminum has been attempted and a more massive-appearing product and considerably higher yields have been obtained than by reduction with calcium alone. The results obtained were similar to those of McKechnie and Seybolt who reported good yields by this method but obtained brittle metal.

Yields of from 88-95 per cent have been obtained with the hardness varying from Rockwell A 59 to A 81. Chemical analysis indicated about 10 per cent aluminum in the vanadium, which undoubtedly accounts for some of the hardening observed.

Previously reported work on the Al-V system has shown that more than 10 per cent aluminum is soluble in solid vanadium. A study is now under way to determine the physical and chemical properties of these solid solution alloys since they may be prepared so easily. A series of alloys containing additions of 1 to 25 per cent vanadium is being prepared for this study. Corrosion tests, hardness, cold rollability and melting points are some of the properties to be investigated.

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In the study of the phase diagram some doubt has existed as to the actual composition of the ϵ phase, tentatively identified as Al_6V . A series of alloys in the region of Al_6V (23.9 weight per cent V theoretical) were prepared and examined microscopically. A 22.0 per cent V alloy contained small amounts of a second phase as did a 25.3 per cent alloy. A 24.3 per cent alloy appeared to be most nearly one phase in structure thus supporting Al_6V as the probable composition.

Attempts have been made to determine the actual structure from x-ray precision pictures taken on a ϵ single crystal. Patterson projections have been made of hhl and hol data but the large number of atoms per unit cell make interpretation difficult.

4.5 Th-Ni Alloy Preparation (2)

Experiments were performed to determine the possibility of preparing a 10 weight per cent Ni in Th alloy by direct bomb reduction. A charge consisting of:

500 g	ThF ₄
42 g	Ni (powder)
198 g	I ₂
175 g	Ca (10% x 5)

was packed into a sintered 12 per cent CaF_2 in MgO liner in a bomb and the charge was gas fired. A massive biscuit of approximately 85 per cent yield was obtained. The alloy was extremely brittle and shattered when attempts were made to knock the slag from the biscuit. Metallographic examination indicated the composition to be on the nickel-rich side of the nickel-thorium eutectic. Chemical analysis showed the nickel content to be 11.0 weight per cent.

A second charge was prepared designed to yield a 9 weight per cent Ni-Th alloy. Results were similar to the first reduction. Analysis of this alloy showed the nickel content to be 8.96 per cent. A large scale 1 kilogram reduction was attempted yielding a well formed biscuit analyzing 10.5 per cent nickel.

4.6 Ta-V Alloy System (2)

The investigation of the Ta-V alloy system has continued. A tentative phase diagram has been proposed by workers at the Armour Research Foundation. Their diagram consists of complete solid solubility at elevated temperatures with formation at lower temperatures of a sigma phase type compound similar to that found in the Ni-V system. The two phase region was proposed to extend from approximately 25 weight per cent Ta to 85 weight per cent Ta at room temperature. No temperature limits were proposed for either the solidus-liquidus curves or the solid immiscibility boundaries.

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An investigation was initiated here for the purpose of establishing the sigma phase boundary. A series of alloys was prepared by arc melting in a helium atmosphere. The materials used in preparing the alloys consisted of Ames-reduced vanadium and remelted tantalum scrap sheet which was obtained originally from the Fansteel Metallurgical Corporation. The as-arc-melted Ta scrap had a R_A hardness number of 61 which could be cold-rolled easily to a 95 per cent reduction in thickness. During the arc melting, each sample was inverted and remelted four times to insure thorough mixing of the components.

After arc melting, the alloys were quartered and one portion of each alloy was sealed in an evacuated Vycor tube. The sealed tubes were placed in a resistance furnace, held at 900°C for 170 hours, and quenched to room temperature. Hardness data and photomicrographs were then taken for each sample. Data concerning these alloys were as follows:

Nominal Comp. Wt. % Ta	Hardness, R_A		Microstructure No. of Phases
	As-Arc-Melted	After 900°C Anneal	
22.5	65	66	1
25	64.5	--	1
27.5	65.5	65.5	1
30	66	67.5	2
35	67	70	2
40	69.5	70.5	2
50	74	--	2
60	73.5	84	2
70	70	85	2
75	68.5	84	2
77.5	71	80.5	X
80	--	80	X
82.5	70.5	75.5	X
87.5	65.5	73.5	X
90	61.5	--	1

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Examination of the microstructures of the alloys disclosed only a very small amount of precipitated second phase in the 30 weight per cent Ta alloy, indicating that this sample was very close to the sigma phase boundary. The relative amount of lamellar-type second phase increased up to 70 weight per cent Ta. It was noted also that the reactivity to the $H_2SO_4:HF:HOH:2HNO_3$ etch was greater for the precipitated phase than for its matrix. The samples marked X in the above table appeared to have a "cored" structure. This will necessitate a homogenization treatment of these alloys at a high temperature in order to obtain an equilibrium structure.

Hardness data and microstructures indicate that the solid immiscibility region and the "sigma phase" will extend to a much higher temperature than $900^\circ C$. Also failure to obtain an alloy with a high ratio of "sigma phase" to solid solution structure indicates that the pure "sigma phase" region may be rather narrow.

4.7 Thorium-Carbon Alloy Studies (5,6)

The electrical resistivity of thorium-carbon alloys is being measured in order to determine the effect of carbon on the transformation of thorium and to determine the limits of solubility of carbon in thorium as well as other aspects of the thorium-rich end of the thorium-carbon phase diagram. Samples are being prepared by arc melting. The results obtained on these samples will be compared with those obtained earlier on samples prepared by powder metallurgy methods.

Some difficulty has been encountered in preparing samples for resistance measurements by arc melting. These samples must be approximately 10 cm long with a cross-sectional area of 0.5 to 0.25 cm^2 . Since arc-melted samples containing more than 0.25 weight per cent carbon are brittle, some difficulty has been encountered in removing these samples from the copper mold without breaking them. However, samples containing up to 1.5 weight per cent carbon have been prepared by this method. It is hoped that samples containing up to 4.0 weight per cent carbon can be prepared by this method.

Resistivity data obtained thus far show that the transformation temperature of thorium is rapidly raised as the carbon content is increased. Further data will have to be obtained before any definite statements can be made relative to the other phase regions for this system.

High temperature x-ray diffraction studies are being made on the Th-C alloys prepared by arc melting in order to confirm results obtained by electrical resistivity measurements. Diffraction patterns have been taken with samples containing up to 1.5 weight per cent carbon. It has been found that after heating the samples for several hours at 600 to $800^\circ C$, the diffraction lines corresponding to thorium gradually disappear and only lines corresponding

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to the monocarbide phase remain. This is believed to be due to surface contamination of the specimen by carbon from the furnace atmosphere. This occurs even though the pressure within the furnace is of the order of 1 to 10×10^{-6} mm of mercury pressure. At temperatures above 1000°C the effect of surface contamination by carbon is not noticed, probably because the rate of diffusion of carbon in thorium is much greater than the rate of incident carbon-carrying gases on the specimen surface. Attempts are being made to determine the source of carbon and to eliminate this difficulty.

The solubility of carbon in solid thorium has been investigated with samples that were prepared by arc melting Ames thorium with pure graphite. The samples were heated at various temperatures and quenched. The final solid solubility limits that were established by x-ray diffraction and confirmed by microscopic examination of the quenched sample do not differ appreciably from the tentative values reported in ISC-396.

4.8 Uranium-Niobium System (3)

Fabrication of these alloys subsequent to arc melting is possible although the ductility of some compositions still leaves something to be desired. Most of the ingots can be rolled in steel jackets at 750°C and most of them can be rolled cold to some degree. More melting points have been determined. They show that the solidus line extends out from each side of the diagram as if complete mutual solid solubility existed at elevated temperatures. However, the situation near the center of the diagram is less certain and additional measurements will be needed.

Hardness measurements show maximum values very near the uranium side of the diagram.

Metallography is still a problem in the study of this alloy system. Most of the recommended reagents proved unsatisfactory for one reason or another. A solution of Cr_2O_3 in water etched the one per cent niobium alloy but gave poor results on other compositions. Ionic bombardment appears to be the most satisfactory general etching procedure.

Patterns obtained by x-ray methods on powders cooled slowly from 600°C have given no evidence of an intermediate compound. Niobium-rich solid solution appears to be present in all alloys containing more than 5 per cent niobium.

4.9 Zirconium-Niobium System (3)

Production of new softer ingots in the niobium-rich region plus experience in heat treatment have made possible the fabrication of all compositions of ingots. Presumably, alloys of all

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proportions of the component metals can be fabricated if proper procedures are followed.

The determination of melting points has been continued and the complete solidus line has been established. The line has a shape that is characteristic of alloy systems in which diagram-wide solid solubility exists. It has a minimum in the vicinity of 20 per cent niobium and 1740°C.

A vacuum dilatometer designed here has functioned quite satisfactorily and curves have been obtained for a number of specimens. The data show that the horizontal line, assumed to be of eutectoid type, extends beyond 70 per cent niobium. The curves also suggest that the eutectoid composition lies between 15 and 20 per cent niobium but as this result has not been confirmed by measurements of other properties, a conclusion cannot be formed at present.

X-ray patterns of several zirconium-niobium alloys indicate that the solubility of zirconium in niobium at 500°C is less than 20 per cent. Specimens of powdered alloys cooled rapidly from the single phase region at higher temperatures show values of the lattice parameter that are just slightly lower than appear probable if the literature value of 3.61 Angstrom units for the lattice parameter of beta zirconium is correct.

4.10 Zirconium-Vanadium System (3)

Spectrographic analyses of the ingots made in the tungsten arc furnace have shown no tungsten, no iron and only a trace of copper. This result indicates that the melting operation can scarcely be held responsible for any contamination that may be found in the alloys.

The solidus line in this system appears to be established with little room for doubt. It consists of lines descending rapidly from each side of the diagram to connect with two horizontals that terminate near the middle of the diagram in what appears to be an intermediate phase, probably a compound. The temperatures of these horizontal portions are approximately 1230°C and 1290°C.

Electrical resistance measurements and dilatometric curves show anomalies that correspond to a eutectoid horizontal at about 780°C.

4.11 Thorium-Magnesium Alloy System (5)

Crystals of the two intermetallic compounds in this system have been isolated by micromanipulation. These crystals are being analyzed by microchemical methods and studied by single crystal x-ray diffraction methods. The solubility of magnesium

in thorium metal at 800°C was investigated by heating a sample of thorium and magnesium to this temperature and quenching to room temperature. The lattice constant of the thorium was then determined and found to be very close to that of pure thorium. This indicates a very low solubility of magnesium in thorium at this temperature.

4.12 Zinc-Zirconium System (2)

Progress in the study of the zinc-rich end of the Zn-Zr system has been limited by the difficulty in preparing alloys. Alloys in the composition range from 8 to 40 weight per cent zirconium cannot be heated to their melting points without rapid loss of zinc at one atmosphere pressure. A double bomb technique has proved partially satisfactory. The charge of massive zinc and zirconium is placed in a sintered ($\text{MgO} + 10$ weight per cent MgF_2) crucible. The crucible is then placed in a steel bomb which is welded shut under a helium atmosphere. This bomb is then enclosed inside a stainless steel bomb which is also welded shut. The final assembly is then heated at 1000°C in a muffle furnace for several hours. Alloys containing 10 to 32 weight per cent zirconium have been prepared in this manner. The alloys obtained are still quite porous. So far these alloys show no evidence of a low melting eutectic. It had been previously suspected that possibly a low melting eutectic existed within this composition region.

An alloy with a nominal composition of 35 weight per cent zirconium was prepared by bomb reduction. A single crystal was obtained from this alloy and Weissenberg patterns taken. A zero layer line and a first layer line pattern both showed six fold symmetry. This places the crystal in the hexagonal class. The c_0 parameter was calculated from a rotation pattern to be 7.31 Å. The a_0 parameter calculated from the zero layer Weissenberg pattern was 8.02 Å which gives a c/a ratio of 0.91.

4.13 U-Zr-Nb Ternary Alloys (2)

The corrosion testing and physical testing of uranium-rich alloys of zirconium and niobium have been continued. The alloys of the following compositions were weighed out to the nearest 0.01 g and arc-melted: % Zr - 20, 10, 5 and 2, % Nb - 10, 5, and 3 and the ternaries 5% Zr-5% Nb, 2% Zr-4% Nb, 3% Zr-3% Nb, 5% Zr-2% Nb. The buttons resulting from arc-melting these compositions were sectioned into pieces of suitable size for corrosion testing. Two sets of the above series were prepared. One set was alpha annealed (750°C, 2 hours-600°C, 2 hours-500°C, 20 hours) and furnace cooled. The other set was gamma quenched (850°C, 2 hours, water quenched). Samples from the annealed series are being corrosion tested in boiling H_2O and the quenched series are being tested in 178° H_2O . The maximum temperatures at which the quenched alloy can be maintained without transforming to the less corrosion resistant annealed state are being determined for the two binary series as well as for the ternaries.

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4.14 Tantalum Alloys (3)

A number of tantalum-rich alloys have been prepared in the tungsten arc furnace. They are intended for experiments in fabrication and eventually are to be tested for resistance to attack by hot liquid metals.

Alloys with chromium, molybdenum, niobium, titanium, and zirconium have been prepared. Usually the alloying elements were added in amounts of 2, 5 and 10 weight per cent.

5. Other Metallurgical Studies

5.1 Corrosion of Metal Containers by Liquid Uranium Alloys (5)

Small crucibles were made from thin sheets of the container metal to be tested, filled with the alloy, placed in stainless steel outer crucibles, and held at the testing temperature for definite periods of time. The crucibles were then opened and examined by metallographic methods and the thickness of the remaining crucible wall measured by a calibrated eyepiece.

At 900°C, niobium reacted with or dissolved in the uranium-chromium alloy in less than 24 hours. Tantalum reacted slowly with the alloy, a diffusion layer or band being formed at the interface between the tantalum and the liquid alloy. Results obtained from tests using the uranium-chromium alloy prepared by two different methods are given in the accompanying tables. The width of the diffusion or reaction band is given in each case.

Corrosion of Tantalum by Uranium-Chromium Eutectic Alloy* at 900°C

Time	Loss in Thickness of Crucible Wall	Diffusion Band Width
1 day	$1.0 \times 10^{-3} \text{ in.} \pm .1 \times 10^{-3} \text{ in.}$	$0.4 \times 10^{-3} \text{ in.} \pm .1 \times 10^{-3} \text{ in.}$
4 days	$0.9 \times 10^{-3} \text{ in.} \pm .1 \times 10^{-3} \text{ in.}$	$0.5 \times 10^{-3} \text{ in.} \pm .1 \times 10^{-3} \text{ in.}$
7 days	$1.1 \times 10^{-3} \text{ in.} \pm .1 \times 10^{-3} \text{ in.}$	$0.4 \times 10^{-3} \text{ in.} \pm .1 \times 10^{-3} \text{ in.}$
14 days	$1.2 \times 10^{-3} \text{ in.} \pm .1 \times 10^{-3} \text{ in.}$	$0.3 \times 10^{-3} \text{ in.} \pm .1 \times 10^{-3} \text{ in.}$

* Alloy prepared by melting under vacuum in an MgO crucible and remelting under vacuum in a tantalum crucible.

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Corrosion of Tantalum by Uranium-Chromium Eutectic Alloy* at 900°C

Time	Loss in Thickness of Crucible Wall	Diffusion Band Width
1 day	$1.1 \times 10^{-3} \text{ in.} \pm .1 \times 10^{-3} \text{ in.}$	$0.4 \times 10^{-3} \text{ in.} \pm .1 \times 10^{-3} \text{ in.}$
4 days	$1.8 \times 10^{-3} \text{ in.} \pm .1 \times 10^{-3} \text{ in.}$	$0.6 \times 10^{-3} \text{ in.} \pm .1 \times 10^{-3} \text{ in.}$
7 days	$0.8 \times 10^{-3} \text{ in.} \pm .1 \times 10^{-3} \text{ in.}$	$0.3 \times 10^{-3} \text{ in.} \pm .1 \times 10^{-3} \text{ in.}$
14 days	$1.5 \times 10^{-3} \text{ in.} \pm .1 \times 10^{-3} \text{ in.}$	$0.4 \times 10^{-3} \text{ in.} \pm .1 \times 10^{-3} \text{ in.}$

*Alloy prepared by melting under vacuum in an MgO crucible and remelting under vacuum in a tantalum crucible.

At 1000°C, tantalum crucibles with 5 mil walls had completely failed in less than 15 days, but the minimum time for failure was not known. Vanadium crucibles with 5 mil walls had failed in 24 hours.

5.2 Casting U into Zr Cans (2)

Vacuum casts were made to determine the lower limit for bonding uranium to a zirconium can. The zirconium can, one inch in diameter, was preheated before the molten uranium was poured into it. The lowest preheat temperature which produced a microscopically satisfactory bond was 940°C. Several tests were made at lower temperatures, but the bonds obtained were irregular and discontinuous.

Using larger zirconium cans, one and one-half inches in diameter, good bonds were obtained with no preheating. Two such castings were made and on both occasions the bonding was very satisfactory. It thus appears that as the mass of uranium is increased, the bond is formed more readily.

Thermal cycling tests were made on the one inch cans. A complete cycle consisted of heating a section by induction to 700°C in a vacuum, and then water quenching. Sections from the 940°C preheat run and from a partially bonded 465°C preheat run were cycled. All of the sections from the 940°C run withstood 6 or more such cycles, while sections from the 465°C run separated completely in the bond area after only two cycles.

The effect of a flash coat of copper on the zirconium upon the bonding conditions has been investigated. Sections of both the one inch and one and a half inch diameter cans were electroplated

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with a layer of copper about one-half mil in thickness. Using these plated sections, good bonding was obtained upon pouring into cold cans, eliminating the necessity of preheating. These also withstood thermal cycling without evidence of bond failure.

The copper plate was electrodeposited from a copper cyanide bath at a current density of 50 ma/sq. in. for 5 minutes producing a thin, even coat. This was followed by a deposit from a CuSO_4 bath for 15 minutes at a current density of 200 ma/sq. in. This two stage process gave a fairly adherent plate with a minimum of porosity. The zirconium surface prior to electroplating was pickled in a solution of HF , HNO_3 and $\text{Pb}(\text{NO}_3)_2$ dissolved in water.

The cans were prepared for corrosion testing by inert atmosphere welding of zirconium caps onto both ends of the bonded slugs. These were then immersed in water in stainless steel bombs and heated to 178°C for a minimum of 50 hours. The rate of failures in corrosion testing has been nearly fifty per cent with the point of failure usually just below the weld area. No definite explanation for this failure has been made as yet.

5.3 Casting Uranium into Uranium-Niobium Alloy Cans (2)

Uranium can be bonded to an alloy of uranium-7 1/2 per cent niobium by pouring uranium into cans of alloy composition. It has been found necessary to electrodeposit a film of copper on the can surface to facilitate bonding. Temperature conditions required to obtain a bond have been examined and the minimum conditions have been worked out. Satisfactory bonding to a 3/4 inch diameter can having a wall thickness of 1/8 inch can be accomplished by preheating the can to 800°C in vacuum and pouring uranium at 1250°C into it. Pouring into unheated alloy cans did not produce bonding.

Tensile strength tests of two specimens prepared under the above preheating conditions gave a rupture strength in excess of 40,000 psi for the uranium to uranium-niobium bond. Thermal cycling tests, consisting of heating the bonded specimen to 750°C and quenching into water, have been carried out on several specimens. No bond failures after six such cycles have been observed.

The alloy cans were fabricated by melting the alloy in a graphite crucible containing a graphite plug around which the can is formed. The alloys used in the investigation were prepared by co-reduction of UF_4 and Nb_2O_5 in a bomb, giving alloys of desired uniformity and composition. An attempt was made to fabricate cans by hot rolling the alloys into thin sheets, forming and seam welding these into tubing. The metal was so brittle after rolling that forming the sheet into tubes proved extremely difficult if not impossible.

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5.4 Zinc Base and Composite Coatings on Uranium (6)

Zinc base coats approximately one mil thick have been obtained on uranium by dipping uranium in zinc at 475°C for one minute and centrifuging to remove the excess zinc. Copper and chrome plates electrodeposited on the zinc gave composite coats showing good corrosion resistance. Heat treatment results in separation of the copper plate. The chrome plate does not appear to be as susceptible to separation on heat treatment, but it is more difficult to apply.

The zinc bath is covered with a KCl-LiCl eutectic flux. The addition of a small amount of $ZnCl_2$ to the flux helps to promote uniform wetting of the uranium. Uranium specimens prior to dipping are polished free of oxide on 240 grit silicon carbide paper, degreased in trichloroethylene, then anodically treated for several seconds in a solution of five parts H_2SO_4 , three parts H_2O , and one part glycerine, rinsed first with water, then with acetone and air dried. The specimens are then dipped in the zinc bath for about one minute, removed and centrifuged and then quenched in mineral oil. The zinc coats obtained are usually smooth, bright and uniform in thickness except at sharp edges on the specimen where the coat is quite thin. The variation of the coat thickness at sharp edges may be reduced by rounding off the edges prior to dipping. The surface is sometimes stained with impurities which collect in the fused salt flux. The oil from the quench bath is removed with trichloroethylene or benzene, and the stains removed by light buffing or with dilute acid.

Three samples coated in this manner were corrosion tested in boiling distilled water. The data obtained are shown in the accompanying table. The samples were removed at the times indicated and the average weight losses recorded.

Corrosion of Zinc Coated Uranium in
Boiling Distilled Water

Time Hours	Average Weight Loss mg/cm ²	Corrosion Rate mg/cm ² /hr.
49	0.05	0.00102
96	0.08	0.00083
191	1.28	0.0067
239	2.87	0.012
313	9.94	0.031

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The weight loss indicated in the table is due principally to the development of pits in the specimen surface. The change in weight in this case is the result of two processes, (1) the gain in weight of the zinc coat due to the formation of adherent corrosion products and (2) the loss in weight due to pitting, the latter being predominant after 48 hours. Tests on high purity zinc in boiling distilled water showed a weight gain of approximately $0.03 \text{ mg/cm}^2/\text{hr}$ after 528 hours and an average weight gain of $0.02 \text{ mg/cm}^2/\text{hr}$ after 1320 hours. Since the pitted area on the zinc-coated uranium samples is a small fraction of the total surface, it may be assumed that the actual rate of weight loss due to pitting is of the order of $0.064 \text{ mg/cm}^2/\text{hr}$ at the end of 313 hours. This is still a rather low corrosion rate, particularly since pits were evident after 48 hours. It may be concluded that the coat is not rapidly undercut and that the zinc apparently offers effective anodic protection to the uranium. Microscopic examination also shows little or no undercutting of the zinc coat. After 49 hours two or three small pits were visible on each of the samples. After 313 hours the three samples showed 3-2-3 large pits, 15-60-10 small pits, and 6-10-3 just visible pits, respectively. These samples were rectangular in shape with an average surface of 10.5 cm^2 . The zinc thickness over the flat surfaces was 1.0 to 1.3 mils and somewhat less than this at the rounded corners and edges.

Copper plates have been electrodeposited over the zinc using standard cyanide and sulfate baths. The cyanide bath was used to deposit an initial copper coat at a current density of about 20 ma/cm^2 for 12 minutes. This layer was then built up in a sulfate bath, at about the same current density, to a thickness of between one and two mils. Composite coats, 1.0 to 1.3 mils of zinc and 1 to 1.3 mils of copper, produced by the above procedure, have shown a weight loss of $0.02 \text{ mg/cm}^2/\text{hr}$ after 312 hours and $0.029 \text{ mg/cm}^2/\text{hr}$ after 377 hours. Failure of these samples was also due to pitting.

Attempts to reduce the porosity of the copper plate by submersion annealing in a fused salt or lead bath resulted in blistering and loosening of the entire copper plate as previously reported. This is believed to be due to rapid hydrogen evolution by the copper plate on sudden heating. The formation of blisters and evolution of gas from pores in the plate may be observed by heating the samples in silicone oil (Dow-Corning #703). Aging the samples for several days greatly reduces the tendency to gas evolution and blistering when the samples are heated. Various procedures for outgassing the copper plates are being tried. Results thus far obtained indicate that the initial outgassing will have to be done between room temperature and 100°C . Treatment in boiling water for a prolonged period of time reduces the amount of adsorbed or occluded gases but, since the coats are porous, pits develop, making this method unsatisfactory as a pretreatment for annealing at higher temperatures.

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Another difficulty which has been encountered with copper-zinc coats is the formation of a brittle and friable layer between the outer copper coat and the uranium on heating at 300°C for several hours. This brittle phase is most predominant after the free zinc is converted to some intermetallic phase. Whether this brittle phase is a zinc-copper or a zinc-copper-uranium intermetallic phase has not been determined.

Chrome plates have also been deposited on zinc-coated uranium. The tendency for plate separation on rapid heating is much less pronounced with these plates than with the copper plates. The chromic acid plating solution reacts with the zinc and a high striking current density is necessary to prevent rapid dissolution of the zinc coat. The application of a flash copper coat prior to chrome plating appears to be more satisfactory. The composite Zn-Cr coats show about the same corrosion resistance to boiling water as do the Zn-Cu coats. Heat treating of the Zn-Cr coat at about 300°C has not shown any pronounced improvement in the corrosion protection of this coat. The application of a copper flash coat between the zinc and chrome plate gives a composite coat which tends to separate on heat treatment. This might be due to outgassing by the copper and chrome plates.

5.5 Diffusion Coating of Uranium (6)

Diffusion coats have been produced by dipping uranium in a magnesium bath containing nickel, silicon, or zirconium. A diffusion band containing nickel or silicon, approximately 0.4 mil thick, can be produced in one to two hours at about 700°C. These diffusion coats show fairly good corrosion resistance to boiling distilled water. The weight loss after 72 hours in boiling water is approximately 0.002 mg/cm²/hr, and after a period of 116 to 165 hours show a weight loss ranging from 0.3 to less than 0.1 mg/cm²/hr. However, these coats are rapidly dissolved in contact with Al-Si at temperatures of 600°C or above. Thin zirconium-uranium alloy coats can be formed on uranium by heating the uranium in a magnesium bath, saturated with zirconium, at about 850°C for several hours. These zirconium coats are rapidly undercut in boiling water.

Uranium-nickel alloy coats have been produced by dipping uranium in a molten magnesium-nickel eutectic (23.5 weight per cent Ni) bath at temperatures up to 738°C. A bath saturated with nickel at 738°C has also been used. The bath is contained in a sintered magnesia plus 10 weight per cent magnesium fluoride crucible. The crucible is enclosed in a stainless steel tube. The bath is protected from the atmosphere with a layer of potassium chloride-lithium chloride eutectic flux, and by maintaining a small positive helium pressure inside the stainless steel tube during the soaking period. Samples are placed in and removed from the bath through an opening (fitted with a rubber stopper) in a water-cooled cover on the stainless

steel tube. During this operation some air has access to the molten bath; however, oxidation of this bath has not been a serious problem. The uranium samples can be held suspended in the bath in a small basket made from tantalum, tungsten, or molybdenum wire. None of these metals react to any appreciable extent with the Mg-Ni bath, but some attack at the surface of the fused salt has been observed. Samples have also been supported on the end of a wire by simply wrapping several turns of wire around the sample.

Several procedures have been tried in preparing the uranium surface prior to dipping. Oxide is removed by rough grinding followed by polishing on 240 grit silicon carbide paper. Then the usual procedures of degreasing in trichloroethylene, followed by alternate treatment with hydrochloric and nitric acids, or anodic treatment in either trichloroacetic acid solution or sulfuric acid-glycerine-water solution have been tried. The uranium surface prepared by these procedures is not uniformly wet when dipped in the magnesium-nickel bath. The failure of the uranium to wet completely is believed to be due principally to oxidation or contamination of the surface by impurities in the fused salt flux on submersion of the specimen into the bath. Precoating the specimen with zinc as described in the above section gives samples that, when dipped into the magnesium-nickel bath, are almost invariably wet by the bath. The zinc coat apparently protects the uranium surface until it is submerged. The zinc is believed to be completely removed by the bath. The microstructure of the diffusion coat formed after dipping for a period of 30 minutes or longer appears the same as diffusion coats on samples which have not been precoated with zinc. Another procedure which has proved very satisfactory is to pre-dip the uranium in a fused salt bath consisting of KCl-LiCl eutectic to which about 20 weight per cent of $ZnCl_2$ has been added. Samples dipped in this mixture at about $400^\circ C$ for a few seconds to form a thin solid coat of flux on the surface, and then immediately submerged into the Mg-Ni bath, are uniformly wet. Equally good results have been obtained with uranium which is quite badly oxidized. In this case the uranium is left in the fused salt mixture for a few seconds after vigorous reaction between the uranium and the salt is evident. Vigorous reaction begins as soon as the metal surface reaches the fusion temperature of the salt mixture. The oxide dissolves in the bath and some of the zinc which is displaced by the uranium adheres to the uranium surface. The thin layer of salt adhering to the uranium when it is removed from the bath has a brown color.

No noticeable difference has been observed in the diffusion coats formed by dipping samples prepared by either of the latter two procedures. A coat approximately 0.45 mil thick is formed at $738^\circ C$ when uranium is dipped in Mg-Ni eutectic bath for about two hours. The exact nature of the diffusion layer is uncertain but it is believed to be essentially free of magnesium. Microstructures indicate

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that the diffusion layer is a single phase, although four compounds are known to exist in the U-Ni system.

At temperatures above 738°C, the uranium reacts with the nickel bath to form uranium-nickel eutectic which separates to form a liquid layer at the bottom of the bath. The microstructure and chemical analysis of the solidified bottom layer of a Mg-Ni bath into which several uranium specimens had been dissolved at 850°C show that the alloy formed here is essentially free of magnesium. This alloy containing 83.5 per cent uranium and 17.2 per cent nickel has good corrosion resistance to boiling water. The corrosion rate after 115 hours was found to be approximately 0.005 mg/cm²/hr.

In order to test the corrosion resistance of the uranium-nickel diffusion layer the outer coat of Mg-Ni eutectic was removed with dilute nitric acid (one part concentrated nitric acid to three parts water). The eutectic outer coat can also be removed by soaking the samples in water for about five hours.

The magnesium may be removed by heating in vacuo at about 700°C for a few minutes. Samples prepared for corrosion testing by this method show the same corrosion rate as samples prepared by either of the above methods. The corrosion rates were calculated from the total weight loss after exposure to boiling water for periods up to 165 hours. Samples dipped in the eutectic for periods of sixty minutes or longer show little or no weight change in boiling water after forty-eight hours, and a weight loss of about 0.002 mg/cm²/hr after seventy-two hours. On exposure to boiling water a smooth, dark-to-black adherent layer forms on the surface. At the end of the test period much of the nickel-uranium diffusion layer is still intact and most of the corrosion has taken place at a number of isolated patches on the surface. The affected areas spread quite rapidly and some evidence of undercutting of the diffusion layer has been observed. It has been noted that the diffusion band penetrates surface imperfections and works around impurity particles on the metal surface. However, some weak spots in the coat still remain, since failure of the coat occurs at isolated spots and then spreads over the rest of the surface.

Since the epsilon phase in the uranium-silicon system is known to have good corrosion properties, a study is being made of the diffusion coat formed on uranium when it is dipped in magnesium saturated with silicon. The rate at which a diffusion layer forms on uranium is somewhat more rapid in this bath than in the Mg-Ni bath. The corrosion rate of these samples compares closely to those for samples dipped in a Mg-Ni bath for the same time and temperature.

Samples similarly dipped in a magnesium bath saturated with zirconium at temperatures ranging from 725 to 950°C for a period of

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30 to 120 minutes have shown relatively poor corrosion resistance to boiling water. A zirconium-uranium alloy coat which is corrosion resistant can be produced on the surface of the uranium, but the coat is very thin and is rapidly undercut by boiling water. The undercut coat falls off as thin flakes. Chemical analyses of flakes from two different samples gave 29.1 and 21.0 weight per cent zirconium. These values are in agreement with results previously reported. Heating for a longer period of time to form a heavier coat might eliminate this difficulty.

An attempt was also made to produce a titanium-uranium alloy coat by this method. The results obtained were all negative, and no corrosion resistant coat could be detected.

5.6 Behavior of Uranium and Coated Uranium in Molten Al-Si Eutectic (6)

Uranium coats which are to serve as a secondary line of defense against corrosion failure of Al-Si canned slugs must have good corrosion resistance, withstand thermal shock, reduce the rate of diffusion between the uranium and Al-Si, and be able to withstand the Al-Si canning process. An investigation is, therefore, underway to determine the behavior of diffusion coats of nickel, zirconium etc., in molten Al-Si eutectic. The composite electroplates are also being investigated in this respect.

Preliminary tests show that a nickel diffusion coat produced by dipping uranium in a magnesium-nickel bath is completely dissolved in a few minutes in Al-Si eutectic at about 640°C. This rapid dissolution suggests the possible formation of a multicomponent eutectic.

Uncoated uranium has been observed to dissolve rapidly in Al-Si at 640°C. At about 600°C the reaction is still quite rapid. The Al-Si coat formed on uranium after one minute at 620°C shows poor corrosion resistance when compared to pure Al-Si. Two samples dipped in Al-Si at 620°C for one minute were tested in boiling water. After three days the coat on one sample began scaling off and the other sample showed a weight gain of 0.10 mg/cm²/hr. After five days the latter sample showed a weight gain of only 0.0064 mg/cm²/hr, but scaling of the coat was evident. Pure Al-Si, tested simultaneously with the two samples, showed no tendency to scale and showed only a slight gain in weight after five days.

Zinc coats offer little or no protection against the Al-Si. A zinc-dipped and chrome-plated sample dipped in Al-Si at 610 ± 5°C for two minutes showed that the chrome plate had been raised from the zinc by the Al-Si over most of the surface, but the Al-Si had not yet penetrated the uranium-zinc diffusion layer.

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6. Other Investigations

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

The pyrophoric film formed on uranium-zirconium alloys was investigated by removing the film and exhaustively leaching the alloy with nitric acid. The residue was then analyzed and studied by x-ray diffraction, and was observed to form two layers on sedimentation. Only the bottom layer was pyrophoric. X-ray diffraction patterns indicated that alpha zirconium was one of the phases present in this layer. The presence of an additional phase was also indicated. The non-pyrophoric layer of residue contained this unidentified phase but no alpha zirconium. Further work will be done to identify the components of the pyrophoric film.

Certain uranium-niobium alloys were found to form a pyrophoric surface layer when pickled in nitric acid. The alloy composition was seven weight per cent niobium. Annealing at 625°C was necessary before the film could be formed. This film was very similar in behavior to that formed on uranium-zirconium alloys. X-ray diffraction patterns of this film revealed a body-centered cubic phase with a lattice constant of 3.37 angstroms as the major constituent. This is probably a solid solution of uranium in niobium which was left on the surface as a very fine powder after treatment with acid which removed some uranium.

6.2 Sodium Tungsten Bronzes (4)

Work was continued on the metallic sodium tungsten bronzes, Na_xWO_3 , in which x varies from 0 to 1. Hardness values on a series of these bronzes of varying sodium concentration exhibit a minimum near the concentration, $x = 0.75$. This concentration value corresponds to the region of minimum electrical resistivity reported by other investigators. The hardness values were obtained from small single crystals using a Tukon tester with a Knoop indenter.

An explanation of the anomalous behavior near $x = 0.75$ is being sought. The first approach has been to investigate the possibility of a superlattice at $x = 0.75$. Prolonged exposures (~6 days) taken with a Weissenberg camera using both Cu and Mo x-radiation have not indicated the presence of such a superlattice in a small single crystal of $\text{Na}_{0.75}\text{WO}_3$. The superlattice reflections might be obscured in these long period exposures by the streaking in the diffraction patterns which results from the white background radiation which penetrates the filters. This is particularly bad in the Mo radiation.

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Calculations based upon an ordered structure which doubles the original lattice parameter show that superlattice reflections, if they occur, would be extremely weak compared with the normal lattice reflections. These calculations give orders of magnitude for the intensity ratios of 1:1000. The initial experimental results with the diffractometer have shown an extremely weak reflection near an angle of $2\theta = 28.6^\circ$ which could correspond to a (211) superlattice peak. This peak is reproducible although it must be resolved by taking fixed time counts with the Geiger tube set at small angular increments near the peak position. This is necessary since a normally scanned pattern shows the reflection only as a slight wiggle in the background intensity.

A second phase of the investigation of the sodium tungsten bronzes is the calculation of the electrostatic energy of these materials. The calculations are being made using a modification of the Ewald method. The work was started in an attempt to account for the high activation energy which was measured for the diffusion of sodium through $\text{Na}_0.78\text{WO}_3$. The results of the calculations show that electrostatic interaction alone could account for an energy barrier two to three times as high as the value measured. In addition, the calculation of activation energy for diffusion as a function of sodium concentration showed that the activation energy became positive at low sodium concentration indicating a spontaneous diffusion and thus a region of instability for the cubic form of sodium tungsten bronze. In view of this result calculation of the total electrostatic energy for the sodium tungsten bronzes was undertaken. Calculations were made for a cubic phase with a unit cell with sodium at the origin, (000), oxygen at the face centered positions, $(\frac{1}{2}\frac{1}{2}0; 0\frac{1}{2}\frac{1}{2}; \frac{1}{2}0\frac{1}{2})$, and tungsten at the body centered position, $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$, and for a tetragonal phase with the tungsten and oxygens unchanged but with the sodium shifted by a translation of one-half unit to the edge-centered positions, $(\frac{1}{2}00; 0\frac{1}{2}0)$. The tungsten was assumed to have a charge of +6 which is consistent with the reported magnetic susceptibilities. Sodium was assumed to have a random distribution with the number of sodium sites occupied being proportional to the sodium concentration. The results of the calculations show:

- 1) Tetragonal: $E_e = (-143.2776 - 3.0220x - 1.7102x^2)\epsilon^2/a$
- 2) Cubic: $E_e = (-143.2776 - 2.6244x - 2.8373x^2)\epsilon^2/a.$

The symbols in the equations are: E_e , the electrostatic energy; x , the sodium concentration in the formula Na_xWO_3 ; ϵ , unit electrostatic charge; and a , the lattice parameter. Solving of the two simultaneous equations shows that the phases should be in equilibrium at $x = 0.352$. At concentrations above that value the cubic phase is the lower in energy; at concentrations below that value the tetragonal phase is the lower in energy. Literature values for the concentration below which the cubic phase is

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unstable are about $x = 0.3$. The agreement between the calculated value and experimental value is remarkably good. Since the calculations were based upon a uniform distribution of the sodium electrons, the results provide additional evidence for the treatment of the metallic properties of these materials on the basis of free electron theory.

6.3 The CaO-CaF₂ System (1)

Cooling curve data indicate that the melting point of CaF₂ is lowered from 1404°C to 1361°C by the addition of 12 per cent CaO. The eutectic probably lies between 12 and 18 per cent CaO. The liquidus for compositions of 50 per cent or more CaO goes beyond the limits of the platinum vs platinum-rhodium thermocouple.

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APPENDIX I: LIST OF REPORTS FROM THE AMES LABORATORY

1. Reports for Cooperating Laboratories

- ISC-228 The Titanium-Vanadium System, by R. Powers and H. A. Wilhelm. UNCLASSIFIED.
- ISC-229 The Resistivity of Lanthanum, Cerium, Praseodymium and Neodymium at Low Temperatures, by N. R. James, S. Legvold and F. H. Spedding. UNCLASSIFIED.
- ISC-230 Inner-Complex Compounds of Alicyclic Vic-Dioximes, by R. C. Voter and C. V. Banks. UNCLASSIFIED.
- ISC-235 Activity Coefficients of Aqueous Methanol Solutions, by W. S. Brown and D. S. Martin. UNCLASSIFIED.
- ISC-250 Magnetic Studies of Nickel Complexes with Some Vic-Dioximes, by R. Van der Haar and C. V. Banks. UNCLASSIFIED.
- ISC-257 Nucleation of Tetraphenylarsonium Perchlorate Crystals, by F. R. Duke and L. M. Brown. UNCLASSIFIED.
- ISC-273 Compounds of Thorium with Transition Metals of the First Period, by J. V. Florio and R. E. Rundle. UNCLASSIFIED.
- ISC-278 Conductances, Transference Numbers and Activity Coefficients of Some Rare Earth Halides, by F. H. Spedding and I. S. Yaffe. UNCLASSIFIED.
- ISC-291 Angular Distribution of Photoprotons from Aluminum and Tantalum, by D. J. Zaffarano and M. Hoffman. UNCLASSIFIED.
- ISC-304 Titrimetric Determination of Thorium, by J. S. Fritz and J. J. Ford. UNCLASSIFIED.
- ISC-305 Temperature Dependence of Electrical Resistivity of Metals, by L. Weiner and P. Chiotti. UNCLASSIFIED.
- ISC-307 Orbital Electron Ejection in Large Angle Scattering, by J. K. Knipp and M. Ebel. UNCLASSIFIED.
- ISC-309 The Adsorption of Aliphatic Alcohols and Acids from Binary Aqueous Solution by Non-Porous Carbons, by R. P. Craig and R. S. Hansen. UNCLASSIFIED.
- ISC-321 Quarterly Summary Research Report-Chemistry (October, November, and December, 1952), by the Ames Laboratory Staff. SECRET.

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- ISC-336 Quarterly Summary Research Report-Engineering. January, February, and March, 1953, by the Ames Laboratory Staff. SECRET.
- ISC-337 Quarterly Summary Research Report-Chemistry. January, February, and March, 1953, by the Ames Laboratory Staff. SECRET.
- ISC-338 Quarterly Summary Research Report-Physics. January, February, and March, 1953, by the Ames Laboratory Staff. UNCLASSIFIED.
- ISC-340 The Thorium-Vanadium System, by H. L. Levingston and B. A. Rogers. SECRET.
- ISC-341 Some Studies on the Diffusion of Sodium in the Sodium Tungsten Bronzes, by J. F. Smith, G. C. Danielson and H. A. Wilhelm. UNCLASSIFIED.
- ISC-342 Structure of Rare Earth Metal at Low Temperatures, by J. R. Banister, S. Legvold and F. H. Spedding. UNCLASSIFIED.
- ISC-345 A Beta-Ray Spectrometer for Coincidence Measurements, by R. T. Nichols, A. V. Pohm, J. H. Talboy and E. N. Jensen. UNCLASSIFIED.
- ISC-346 Hanford Slug Program Quarterly Report (January, February, and March, 1953), by P. Chiotti and O. N. Carlson. SECRET.
- ISC-347 A Proportional Counter Spectrometer Study of the Beta-Decay of Radioactive S^{35} , Pm^{147} , Ni^{63} and Cl^{34} , by J. P. Mize and D. J. Zaffarano. UNCLASSIFIED.
- ISC-348 Separation of Individual Rare Earths by Liquid-Liquid Extraction from Multicomponent Monazite Rare Earth Nitrates. I, by J. Bochinski, M. Smutz and F. H. Spedding. UNCLASSIFIED.
- ISC-349 A Practical Separation of Yttrium Group Rare Earths from Gadolinite by Ion-Exchange, by F. H. Spedding and J. E. Powell. UNCLASSIFIED.
- ISC-350 Electrical Resistivity and Hall Effect in Sodium Tungsten Bronze, by W. R. Gardner and G. C. Danielson. UNCLASSIFIED.
- ISC-351 A Fast Sweep Generator, by C. Harper and E. Sanford. UNCLASSIFIED.
- ISC-352 Radioisotope P^{33} , by R. T. Nichols and E. N. Jensen. UNCLASSIFIED.

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- ISC-353 The Aluminum-Vanadium System, by D. J. Kenney, H. A. Wilhelm and O. N. Carlson. UNCLASSIFIED.
- ISC-356 Correlation of Vickers Hardness Number, Modulus of Elasticity and the Yield Strength for Ductile Metals, by E. Arbtin, Jr. and G. Murphy. UNCLASSIFIED.
- ISC-359 A Multichannel Pulse Height Analysis System Utilizing a 35 mm. Film Record, by W. A. Hunt, W. Rhinehart, J. Weber and D. J. Zaffarano. UNCLASSIFIED.
- ISC-363 The Magnetic Susceptibility of Neodymium Metal, by J. F. Elliott, S. Legvold and F. H. Spedding. UNCLASSIFIED.
- ISC-364 Spectral and Total Emissivity, A Guide to Literature (1910-1951), compiled by M. P. Bauleke. UNCLASSIFIED.
- ISC-366 Spectrophotometric Determination of Iron in Vanadium, Chromium, Manganese, Nickel and Zinc, by D. W. Margerum and C. V. Banks. UNCLASSIFIED.
- ISC-367 The Heat Capacity of Gadolinium from 15°K to 355°K, by M. Griffel, R. E. Skochdopole and F. H. Spedding. UNCLASSIFIED.
- ISC-378 Magnetic Properties of the Rare Earth Metals, by J. F. Elliott, S. Legvold and F. H. Spedding. UNCLASSIFIED.
- ISC-382 Titrimetric Determination of Zirconium, by J. S. Fritz and M. O. Fulda. UNCLASSIFIED.
- ISC-383 The Separation of Rare Earths by Ion-Exchange. VII. Quantitative Data for the Elution of Neodymium, by F. H. Spedding and J. E. Powell. UNCLASSIFIED.
- ISC-385 The Separation of Rare Earths by Ion-Exchange. VIII. Quantitative Theory of the Mechanism Involved in Elution by Dilute Citrate Solution, by F. H. Spedding and J. E. Powell. UNCLASSIFIED.
- ISC-386 Nucleation of Nickel Nioxime Crystals, by F. R. Duke and L. M. Brown. UNCLASSIFIED.
- ISC-387 Design and Analysis of a 100 Cycle Hall Effect System, by A. A. Read, C. J. Kevane and E. B. Harris. UNCLASSIFIED.
- ISC-388 Non-Localizable Interactions in Quantum Field Theory, by M. Ebel. UNCLASSIFIED.
- ISC-390 Kinetics of the Reaction between Lithium and Water Vapor, by B. E. Deal and H. J. Svec. UNCLASSIFIED.

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- ISC-391 The Niobium-Thorium Alloy System, by J. M. Dickinson, O. N. Carlson and H. A. Wilhelm. SECRET.
- ISC-403 Stability of Zirconium Oxide in Graphite Surroundings, by D. R. Wilder and E. S. Fitzsimmons. UNCLASSIFIED.
- ISC-404 The Crystal Structure of Samarium, by A. H. Daane, R. E. Rundle, H. G. Smith and F. H. Spedding. UNCLASSIFIED.

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Some Magnetic Properties of Gadolinium Metal. Phys. Rev. 91, 28-30 (1953).
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- Rundle, R. E.
The Structure and Residual Entropy of Ice. J. Chem. Phys. 21, 1311 (1953).
- Smith, H. G.
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Manganese(II), -(III), -(IV) Equilibrium in Iodic Acid.
J. Am. Chem. Soc. 75, 4162-4167 (1953).

Wheelwright, E. J., F. H. Spedding and G. Schwarzenbach
The Stability of the Rare Earth Complexes with Ethylene-
diaminetetraacetic Acid. J. Am. Chem. Soc. 75, 4196-4201
(1953).

APPENDIX II: LIST OF SHIPMENTS

<u>Destination</u>	<u>Item</u>
Argonne National Laboratory Lemont, Illinois	.9444 kgs. uranium-chromium rods 30 kgs. thorium oxide
Brookhaven National Laboratory Upton, Long Island, New York	10 g. cerium metal 2 g. lanthanum metal 2 g. neodymium metal 2 g. praseodymium metal
California Research and Development Co. Livermore, California	50 g. lanthanum metal 25 g. neodymium metal 15 g. praseodymium metal 25 g. yttrium metal
Carbide and Carbon Chemical Co. Oak Ridge, Tennessee	1137 lbs. zirconium tetra- chloride
Columbia University New York, New York	1 cylinder lanthanum metal (on loan)
General Electric Company Hanford, Washington	1486.90 lbs. uranium rods
George Washington University Washington, D. C.	5 g. 99.9% thulium oxide 5 g. 98.0% thulium oxide (on loan)
Harvard University Cambridge, Massachusetts	1 g. metallic samarium 1 g. metallic ytterbium 1 g. metallic thulium 1 g. metallic lutetium (on loan)
Jet Propulsion Laboratory Pasadena, California	100 g. pure cerium metal

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<u>Destination</u>	<u>Item</u>
Lamp Development Laboratory Cleveland, Ohio	thorium sheet 0.005 inches thick
W. F. Libby Institute for Nuclear Studies University of Chicago	100 g. 90% yttrium oxide
Oak Ridge National Laboratory Oak Ridge, Tennessee	50 g. uranium deuteride
United Lead Company Middlesex, New Jersey	18,588.36 lbs. thorium nitrate tetrahydrate
University of California Radiation Laboratory Berkeley, California	250 mgs. lutetium metal 250 mgs. thulium metal 250 mgs. holmium metal 250 mgs. samarium metal (on loan)
University of Southern California Los Angeles, California	500 mgs. samarium metal 500 mgs. ytterbium metal (on loan)
Vitro Manufacturing Company Canonsburg, Pennsylvania	305 lbs. uranium fluoride waste
Yale University New Haven, Connecticut	10 g. gadolinium oxide (on loan)

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APPENDIX III

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

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