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METALLURGY AND CERAMICS

UNITED STATES ATOMIC ENERGY COMMISSION

QUARTERLY SUMMARY RESEARCH REPORT IN METALLURGY

For October, November, December, 1953

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QUARTERLY SUMMARY RESEARCH REPORT IN METALLURGY

For the period October, November, December, 1953

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

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METALLURGY

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

1. Purification and Separation Studies

1.1 Niobite-Tantalite Ore Treatment (1)*

Work on treatment of these ores has continued on laboratory test scale in an effort to determine optimum conditions for the basic fusion treatment. However, one relatively large batch of the ore was treated and some difficulties were met that were not evident on the small scale tests.

The large batch was 20 pounds of an ore concentrate containing between 60 and 70 per cent of combined niobium and tantalum oxides. The total charge included also 16 pounds of NaOH and 8 pounds of Na_2O_2. The reaction was carried out in an iron crucible at 650°C for about one-half hour. Following this treatment the product was leached with 1M NaOH solution and the residue treated with dilute HCl. It was found here that filtration to recover the acid oxides from the iron, manganese and other impurities in the HCl solution was exceedingly slow. Further work will have to be done to eliminate or speed up this step for larger scale operations.

Some work was done on the possible use of potassium compounds as substitutes for sodium compounds in the basic fusion. Combination of KOH with and without oxidizing agents showed the KOH with $KClO_3$ gave the best reaction with this particular ore.

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

The separation of niobium and tantalum salts or their acids has been accomplished by liquid-liquid extraction when employing various water-immiscible organic solvents. It was observed that contacting an aqueous HF solution of niobium and tantalum with various ketones, alcohols, esters, aldehydes, ethers, organic phosphates, organic phosphites and amines resulted in a preference for tantalum to transfer to the organic phase. At the present time experiments have shown that a batch extraction consisting of three contacts can produce quite pure tantalum and niobium with greater than 96 per cent recovery of both. Partial or complete neutralization of the excess HF with various amines has also

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

yielded stable systems which could be tested in glass equipment. A ten-stage countercurrent extraction yielded niobium and tantalum products containing less than 300 ppm of each other.

In order to partially reproduce a simulated column experiment five separate batch extraction tests were performed in an effort to prepare pure tantalum and niobium. The initial aqueous phase in all these tests was a 22 per cent Master Feed-1 dilution (see ISC-423). Equal volumes of organic and aqueous phases were employed for each contact. All percentages of niobium and tantalum are given in respect to the combined tantalum and niobium oxides, with minor impurities being disregarded.

In the first batch extraction test the aqueous HF solution of niobium and tantalum was contacted three separate times with virgin diethyl ketone. The equilibrium organic phase from the first contact contained about 40 per cent of the total starting weight and analyzed 0.12 per cent Nb_2O_5. In the second organic contact 8.8 per cent of the total starting weight was transferred and an analysis showed that it contained 0.35 per cent Nb_2O_5. Combination of these two organic portions resulted in about a 96 per cent recovery of the total tantalum having an analysis of 0.15 per cent Nb_2O_5. Since the aqueous phase product after two contacts with diethyl ketone analyzed about 3.7 per cent Ta_2O_5 a third extraction with diethyl ketone was made. This extraction resulted in another 1.8 per cent of the total starting weight being transferred to the third portion of the organic. This portion analyzed about 75 per cent Ta_2O_5. The residual aqueous phase product contained better than 99 per cent of the starting weight of Nb_2O_5 and analyzed approximately 1.0 per cent Ta_2O_5. Further contacts of this aqueous phase with diethyl ketone would probably have yielded pure niobium.

Further experiments have shown that addition of a slight amount of HF to the aqueous phase before the third extraction with diethyl ketone improves this separation. The addition of about 0.7 mole of HF per liter resulted in the recovery of 99 per cent of the total niobium, analyzing less than 300 ppm tantalum, and 96 per cent of the total tantalum, analyzing 0.15 per cent niobium, by three consecutive contacts in a batch extraction. It was also found that the use of isophorone without additional HF for the third contact of the aqueous phase gave results comparable to those obtained by diethyl ketone in the presence of added HF.

The main disadvantages of this HF system is its corrosive nature toward glass and most metals. Consequently, various amines were added to the HF solution of niobium and tantalum to neutralize the acid. A great variety of results were obtained. Addition of dibutyl amine, tributyl amine, tertiary octyl amine, phenylhydrazine, aminohydroquinone dimethyl ether or aminohydroquinone diethyl ether caused immediate precipitation. When aniline, m-toluidine, o-toluidine or o-tolyl propanolamine were added to the aqueous phase, a second phase appeared at a pH of from 4 to 6. These partially neutralized aqueous solutions were not indefinitely stable since precipitates formed slowly on standing. Solutions that were indefinitely stable were obtained by adding monoethanolamine, diethanolamine, triethanolamine, 3-aminopropanol, aminoethyl ethanolamine or diethyl ethanolamine to the HF solution of niobium and tantalum. For the first aliphatic alcohol-amine of this series a pH of 7.5 was reached before precipitation started while for the rest of these compounds no precipitate formed when a pH of from 9 to 10 was reached. Phenyl ethyl ethanolamine, phenyl diethanolamine and m-tolyl diethanol amine formed a second phase at a pH of from 4 to 6 when added to the HF solution of niobium and tantalum. This partially neutralized aqueous solution appears to be indefinitely stable. Corrosion studies on most of these neutralized or partially neutralized aqueous solutions of niobium and tantalum indicated that at a pH of 4 or higher continuous single or multistage extractions could be performed in glass equipment without appreciable attack.

Many single stage extractions employing completely or partially immiscible organic phases were performed on these amine-neutralized solutions of niobium and tantalum. The same relative trends resulted for these systems as were reported for the amine free HF solution of niobium and tantalum. Ketones in general were superior to alcohols, aldehydes, esters, organic phosphates and ethers for the separation of tantalum from niobium. However, both separation factors and mass transfers were lower for the amine-hydrofluoric acid systems than for the corresponding amine free hydrofluoric acid systems.

A ten-stage countercurrent extraction was carried out employing an HF solution of niobium and tantalum which was saturated with phenyl ethyl ethanolamine. Ten milliliters of this feed solution containing the equivalent of 112 g of the combined niobium and tantalum pentoxides per liter was introduced at stage five of the extractor for each cycle. Thirty milliliters of diethyl ketone which constituted the organic scrub were introduced for each cycle at stage one. The aqueous scrub was a 0.53M HF solution saturated with phenyl ethyl ethanolamine. Five milliliters of the aqueous scrub per cycle were added at stage ten.

Approximately 20 cycles were required for the aqueous and organic product phases to reach essentially steady state based on total oxide concentrations and niobium-tantalum analyses. The niobium in the aqueous product contained less than 300 ppm tantalum while the tantalum in the organic product analyzed 100 ppm niobium. The mass transfer to the organic phase was about 52 per cent of the total weight. A qualitative analysis of the product's phases indicated that most of the impurities remained in the aqueous phase.

Some exploratory work on extractions involving a potassium hydroxide solution of niobium and tantalum indicated that niobium might be preferentially extracted by an organic phase containing an amine and a ketone.

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

Results from previous experiments indicated that a separation of titanium from niobium could be obtained by extraction of an aqueous hydrofluoric acid solution with various organic solvents. Analysis indicated that tributyl phosphate gave the best separation of the various organic solvents tried. In order to check the above results and also to determine the effect of the hydrofluoric acid concentration on the extraction employing tributyl phosphate, a series of experiments was performed in which the hydrofluoric acid concentration was varied. The results of these experiments gave separation factors considerably lower than those found in the previous experiment, indicating some possible error in the results of the first experiment. The results of these experiments do, however, indicate a better separation and increased transfer with increasing HF acidity.

The separation of titanium from niobium by liquid-liquid extraction from a basic solution has also been attempted. Before contact with the organic solvent citric acid was added to the aqueous phase to facilitate transfer to the organic phase.

In order to find the amount of citric acid required to give the best transfer, potassium hydroxide solutions of niobium, tantalum and titanium containing various amounts of citric acid were contacted with an immiscible organic solvent. Results showed that a transfer of niobium, tantalum and titanium was not obtained unless enough citric acid was added to give a slightly acidic aqueous solution (pH 6). Results from these experiments also showed that a better transfer was obtained at a pH of 3.0. In order to conserve the amount of citric acid used, experiments were performed to determine if an inorganic acid could be used to acidify the solution, after addition of the citric acid. The results of these experiments showed that hydrochloric acid could be used to acidify the solution, if the solution was first neutralized with citric acid. However, difficulty was encountered in attempts to precipitate compounds of the metals from the potassium hydroxide solution that had been neutralized with citric acid.

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

Work was continued on extraction from an aqueous zirconium sulfate solution which contained about 2.5 per cent hafnium. Ketones such as methyl ethyl, diethyl, and diisopropyl, similar in structure to hexone, were used. They were each contacted with the above zirconium sulfate solution which was 2 molar in titratable sulfuric acid and 6.6 molar in ammonium thiocyanate. The amount of transfer to the ketone phase appeared to be influenced somewhat by the number of carbon atoms on the ketone. It was found that as the number of carbon atoms was increased in the aliphatic ketones the amount of transfer to the organic phase diminished. The best separation was obtained with methyl ethyl ketone. Isophorone also exhibited good separation properties. The percentage by weight of hafnium left in the aqueous phase after contacting once with methyl ethyl ketone was 0.5 per cent when the aqueous phase originally contained 2.5 per cent HF in the zirconium. Similarly, it was 0.4 per cent after contacting with isophorone.

Exploratory work was begun on the use of branched chain amines added to organic solvents to make the organic phase for liquid-liquid extractions of hafnium from zirconium. These solutions were contacted with an acid aqueous zirconium sulfate solution which was 0.5 molar in zirconium sulfate. The extraction behavior varied some with the type of organic solvent used with the amine in the organic phase and the amount of H_2SO_4 added to the aqueous phase. A number of the immiscible ketones such as hexone served quite well as a solvent. Sulphuric acid concentrations of less than 1M were definitely inferior to the 2M and higher concentrations for hafnium separation.

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

A small acale production extraction has been started and it is hoped that approximately 100 pounds of hafnium containing less than 30 ppm of zirconium can be prepared. The starting material contained approximately three per cent zirconium. A 17 stage extractor is being employed on a system involving a tributylphosphate extraction of an aqueous nitric acid solution of hafnium oxychloride. The extraction will require several hundred cycles in turning out between 6 and 7 pounds of the purified hafnium element per day.

2. Preparation of Pure Compounds

2.1 Preparation of Hafnium Tetrafluoride (2)

Hafnium fluoride has been prepared by the addition of aqueous hydrofluoric acid to a hafnium oxychloride-oxynitrate salt mixture. This mixture was obtained by crystallization from the aqueous phase of the liquid-liquid extraction in which the zirconium is removed in the organic phase solution. Complete conversion to the hydrated hafnium fluoride has been obtained using either 48 per cent or 70 per cent hydrofluoric acid. The precipitate of hafnium fluoride monohydrate is white, granular and easily filtered from its mother liquor. The hydrated fluoride was air dried at 70°C and then placed in a magnesium-lined rotary hydrofluorination furnace for 3 hours at 250°C and 5 hours at 400°C and the hydrate thermally decomposed to the anhydrous hafnium tetrafluoride in an anhydrous hydrogen fluoride stream. The fluoride prepared in this manner contains less than 100 ppm of zirconium.

2.2 Preparation of Rare Earth Fluorides (2)

Cerous fluoride was prepared in quantity by the addition of solid cerous chloride hexahydrate to 70 per cent hydrofluoric acid. The reaction was carried out in large scale Kemplas plastic equipment. The reactants were stirred and allowed to cool. The precipitate of cerous fluoride is slightly gelatinous and a prolonged filtering time was required in order to obtain a solid cake. The fluoride was air dried at 70°C to drive off adhering moisture. This fluoride was then heated for eight hours at 300°C in a stream of anhydrous hydrogen fluoride to assure a completely anhydrous product.

Lanthanum fluoride was prepared in quantity by passing anhydrous hydrogen fluoride over lanthanum oxide. Lanthanum oxalate was calcined at 600°C to lanthanum oxide. The oxide was then placed in the stationary hydrofluorination unit and anhydrous hydrogen fluoride passed over it for three hours at 300°C and five hours at 550°C. This treatment yielded lanthanum fluoride with better than 99 per cent conversion.

2.3 Preparation of Thorium Tetrachloride (5)

The preparation of thorium tetrachloride was continued with the object of making the process more rapid and, if possible, continuous. Since thorium dicarbide is much more dense than a mixture of thorium oxide and carbon, it appeared to have the advantage of reducing the bulk of the charge. However, chlorination of thorium carbide left a voluminous residue of carbon. Apparently the carbon in the thorium carbide did not react with the chlorine and all remained as a residue. As a result, the chlorination of thorium carbide was discontinued. The chlorination of thorium oxide and carbon mixtures was improved by reducing the molar ratio of thorium oxide to carbon to one to two. Chlorination of mixtures with this ratio left a residue of less than two per cent of the original charge. A larger furnace will be designed and built for this chlorination process.

2.4 Preparation of Vanadium Chlorides (5)

The preparation of lower chlorides of vanadium by hydrogen reduction of vanadium tetrachloride was investigated. Refluxing vanadium tetrachloride with hydrogen resulted in formation of a solid containing vanadium tetrachloride and a solid vanadium chloride. After the unreduced vanadium tetrachloride was removed, the residue was heated under an inert atmosphere. At about 450°C, additional vanadium tetrachloride was evolved, probably by interaction of vanadium trichloride. Vanadium tetrachloride was reacted with hydrogen at 600°C to give a violet solid which had a chloride-to-vanadium ratio of 2.5. The preparation of lower vanadium chlorides by hydrogen reduction of the tetrachloride does not seem to be promising.

3. Metal Preparation Studies

3.1 Preparation of Rare Earth Metals (2)

Cerium metal was prepared by the reduction of cerous fluoride with calcium. A bomb reduction process was employed in this preparation using an iodine booster and a calcium fluoride liner. Reductions were made on half-pound, 2-pound and 10-pound reduction scales with yields of 90 to 95 per cent metal. By varying the amount of iodine from a 1:2 to a 1:1 ratio with respect to the weight of cerous fluoride used, no significant variation in the yield or quality of cerium metal was apparent.

Lanthanum metal was also prepared in the same manner as was cerium metal. Reductions have been carried out on the half pound scale with only slightly lower yields (85 to 89 per cent). The metal produced analyzed 99.5 per cent lanthanum.

3.2 Preparation of Vanadium from Oxide (1,2)

A study of the reactions of carbon with vanadium oxides was undertaken with a view of determining the manner and temperature at which reduction to lower oxides takes place. The objective was to find a practical method of reduction of vanadium pentoxide to a lower oxide by reaction with carbon and eventually to reduce the cost of preparing vanadium metal.

Vanadium pentoxide and carbon black, intimately mixed, were heated in a zirconium oxide crucible under vacuum. At 650°C an abrupt increase in pressure was noted with considerable amount of the powder mixture being blown out of the crucible. Upon continued heating a similar pressure increase was noted at 860°C. Heating of the charge to 1200°C produced no apparent further reactions. Some V_2O_5 was reduced by hydrogen to V_2O_4 (possibly containing some V_2O_3). This material mixed with carbon was similarly heated and gave no evidence of reaction at 650°C but a pressure increase was noted at 860°C.

One explanation of the above observations is that V_2O_5 is reduced by carbon to V_2O_4 at 650°C and this to V_2O_3 at 860°C. Chemical analyses of samples taken after the various reaction stages were not conclusive in determining the true nature of the products. This may be due to the impure V_2O_4 used, incomplete reactions or instability of some of the lower oxides in air. X-ray diffraction data show that V_2O_5 has been changed into a completely new phase at 650°C. This phase has a pattern identical to that obtained from the V_2O_4 prepared by hydrogen reduction of V_2O_5.

The direct reduction of vanadium pentoxide to metal by carbon showed some promise. Mixtures of the oxide, carbon and another oxide such as calcium oxide or barium oxide gave metal powder when heated in a vacuum to about 1500°C. The powder, when arc melted, usually showed a microstructure indicating the presence of carbide. The metal was very hard and brittle.

A considerable amount of second phase impurities is generally observed in the microstructures of bomb-reduced vanadium and these are believed to greatly affect the ductility of the metal. Chemical analyses showed about 1000 ppm of both nitrogen and carbon in the metal. A method of purifying the metal was attempted by arc-melting the impure vanadium metal with the oxide of vanadium or of a volatile metal in an effort to remove the carbon by reaction to form carbon monoxide. Small additions of V_2O_5, V_2O_3, MgO and CaO were tried with no apparent decrease in the carbon impurity.

3.3 Studies on the Preparation of Niobium (1)

Niobium pentoxide can be reduced with a mixture of calcium and aluminum. If excess aluminum is used, massive metal results which is a niobium-aluminum alloy and very brittle. It is difficult to remove the aluminum from this alloy, so various other metals have been tried, both in co-reductions and as metal additives to the bomb charge, in an attempt to produce massive metal without aluminum. So far no satisfactory additive metal has been found.

To test the possibility of co-reduction of uranium and niobium to produce a niobium-rich alloy, a charge was made up calculated to produce an alloy of 7 per cent uranium-93 per cent niobium. No booster was used, and no evidence of reaction could be found inside the bomb. A similar charge was used in a second run except that a sulfur-calcium mixture was added to boost the amount of heat produced in the bomb reactions. A button of massive metal and several small drops of metal were formed. The one button weighed 50 per cent of the calculated yield. But instead of being 93 per cent niobium as expected the button analyzed 96.55 per cent niobium.

As reported earlier, co-reduction of lead dioxide and niobium pentoxide gave promising enough results to warrant further investigation.

Several reductions were made, each one producing massive metal in the form of drops. The largest yield (48 per cent) was produced by the reaction in which sulfur was used as booster and no lead was present. Another charge was made up by substituting potassium chlorate for the sulfur in a no-lead reduction. This reduction produced a button weighing 36 per cent of the theoretical yield. The lead oxides, it seems, serve essentially as thermal boosters.

3.4 Preparation of Hafnium Metal (2)

Hafnium metal has been prepared by the reduction of hafnium tetrafluoride with calcium. A bomb reduction process was used for this preparation. The charge consisted of hafnium tetrafluoride, the calcium reductant, an iodine booster and metallic zinc. The bomb wall was lined with calcium fluoride.

The zinc content and iodine ratio were varied in a series of reductions to determine optimum conditions. Zinc intermediate alloys containing 16 to 35 per cent zinc all gave a massive metal product but often the yields were poor and the resulting alloy was porous and slag filled. Present indications are that impurities in the tetrafluoride are largely responsible for these difficulties.

When the alloys were heated in a vacuum to 1700°C-1900°C the zinc was removed quantitatively with less than 20 ppm zinc remaining in the metal.

3.5 Preparation of Thorium Metal (5)

The investigation of the reduction of thorium tetrachloride by magnesium was continued. The use of purified magnesium metal and better quality thorium chloride resulted in preparation of thorium metal by this process which was equivalent in purity to that produced by calcium reduction of thorium fluoride. To evaluate the effect of the purity of the thorium tetrachloride on the quality of the thorium metal produced, the preparation of thorium tetrachloride on a larger scale will be necessary.

4. Alloy Studies

4.1 Uranium-Zinc System (6)

Determination of the liquidus for the U-Zn system by heating zinc in contact with uranium at various temperatures, followed by chemical analysis of the melt, has given inconsistent results. This is believed to be due to cracking and scaling of the diffusion layer formed between the zinc-rich melt and the uranium. Microscopic examination of these alloys shows solid particles which evidently have been carried out into the liquid phase. Therefore samples of the liquid phase would be expected to give uranium analyses which are too high. Attempts are being made to overcome this difficulty.

Thermal analysis and preparation of alloys melting above 900°C present the same difficulties as the preparation of the corresponding Zr-Zn alloys. Previously reported evidence of more than one compound in the U-Zn system has not been substantiated.

Alloys containing up to 15 weight per cent uranium show good corrosion resistance to boiling water. These alloys consist of a uranium-zinc intermetallic phase in an essentially pure zinc matrix.

4.2 Uranium-Silver System (2)

Research on the uranium-silver liquid immiscibility system has been undertaken principally to establish accurately the solubility of silver in the uranium liquid layer. Published literature, NBS-D-121, has reported a eutectic in the silver phase containing 4.3 per cent uranium which lowers the melting point of silver 10°C. A monotectic is reported in the uranium phase at 1132°C at the composition 0.23 weight per cent silver.

The present investigation has consisted of heating silver and uranium toegether under one atmosphere of helium, in MgO, ZrO_2 and Ta crucibles using self-induction heating to assure adequate stirring. The liquid layers were held at 1130°C or higher in a resistance furnace to allow complete separation of the two liquids and then cooled rapidly to room temperature. Chemical analyses were then performed on each layer. The following table lists the analytical results obtained thus far.

Table I
Liquid Solubility of Silver in Uranium

Type of Crucible	Chemical Analysis (Wt. %)				Heat Treatment
	Silver Phase		Uranium Phase		
	U	Ag	U	Ag	
MgO		99.95	99.55	0.03	Mixed by induction heating. Held at 1134°C for 1/2 hr and quenched.
Ta	4.45	95.50	97.7	1.38*	Induction mixed. Heated at 1200°C for 3/4 hr and quenched.
ZrO_2		98.95	100.15	0.05	No induction mixing. Heated in resistance furnace at 1240°C for 2/3 hr and quenched.
ZrO_2	4.00	95.90	99.85	0.04	Induction mixed. Held at 1240°C for 3/4 hr and quenched.

*U phase contained occluded Ag.

These results indicate that the solubility of silver in the uranium phase is close to 0.05 weight per cent Ag at the monotectic temperature although more experimental evidence is needed. The possibility that there has been inadequate mixing of the two liquids will be investigated.

4.3 Vanadium-Aluminum Alloys (2,4)

The physical properties of vanadium-rich alloys of aluminum were investigated during this period. The physical properties investigated were melting points, hardness, malleability, and corrosion behavior.

Specimens containing zero to 24 per cent aluminum were prepared by arc-melting high purity aluminum with bomb-reduced vanadium under an inert helium atmosphere. They were then annealed at 900°C for 144 hours in vacuum.

Aluminum was found to harden vanadium quite appreciably, increasing from Rockwell A-45 for unalloyed vanadium to A-70 for the higher aluminum compositions (see accompanying table). None of the alloys including the pure vanadium could be cold rolled without cracking. The presence of carbide and nitride impurities is believed responsible for the lack of ductility and so the effect of aluminum may not be as deleterious as these tests would indicate.

The melting temperatures were determined for each of the alloys in order to determine more accurately the vanadium-rich solidus in this system. The temperatures at which liquid first appears upon heating were determined and are also reported in Table II.

The alloy series was corrosion tested in super-heated steam at 320°C for periods of 100, 260, 620 and 1000 hours. After each time interval the samples were examined and weighed. No measurable weight changes were observed in any of the alloys.

Work on the determination of the structures of the intermetallic phases of the Al-V system is in progress. Pure β-phase Al-V has been prepared by annealing an arc-melted Al-V alloy containing 6.7 per cent by weight of vanadium for 175 hours at 710°C. After the annealing the aluminum matrix was dissolved with aqueous NaOH. The residue consisted of fine crystals of β-phase Al-V. Chemical analysis of this material showed the weight content of vanadium to be 24.11 ± 0.18 per cent. The theoretical vanadium content of Al_6V is 23.94 per cent. This substantiates the results obtained by Kenney, et al* on the identification of the β-phase as Al_6V.

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*Kenney, D. J., H. A. Wilhelm and O. N. Carlson, U. S. Atomic Energy Commission Report No. ISC-353 (June, 1953).

Table II
Hardness and Melting Temperatures of Vanadium-Aluminum Alloys

Composition % Al	Hardness Rockwell A	Melting Temperature °C
0	44	1843
0.79	45	1890
1.73	47	1873
2.77	55	1865
3.67	55	1875
4.66	56	1853
9.00	67	1855
13.4	67	1825
18.5	69	1815
23.8	too brittle	1758

X-ray diffraction patterns show that the crystal structure of this phase is hexagonal with space group symmetry $C6mc$, $C\bar{6}2c$, or $C\frac{6}{m}mc$. The lattice parameters are $c = 17.12$ Å and $a \cong 7.75$ Å. These values of the parameters and the measured density give a value of eight formula-weights per unit cell.

Intensity data have been taken for hol, hhl, and hko reflections. From these data the following Patterson projections have been made: $P(x,z)$, $P(x+y,z)$, and $P(x,y)$.

4.4 Tantalum-Vanadium System (2)

It has been previously established that the Ta-V system consists of a series of solid solutions at elevated temperatures and that a sigma-type compound exists at lower temperatures. Further work has been done in outlining the phase boundaries for the system. Microscopic examination and x-ray diffraction patterns of alloys which have been annealed at 900°C for 170 hours locate the intermediate phase between 60 and 70 weight per cent tantalum. Powder patterns of the 60 and 70 per cent alloys contained 22 lines which were indexed on the basis of an orthorhombic cell $a_o = 5.05$ kx, $b_o = 4.13$ and $c_o = 3.57$. No lines corresponding to the body-centered cubic phase were detected.

High temperature x-ray studies using a Norelco Diffractometer were made on a 62.5 weight per cent tantalum alloy in an effort to establish the upper boundary of the sigma phase region. At 1035°C the orthorhombic phase only was identified but at 1235°C peaks corresponding to the body-centered cubic solid solution phase appeared, along with reflections from the orthorhombic phase. At 1330°C the only phase present was body-centered cubic solid solution. A similar experiment on a 72.5 per cent Ta alloy indicated the boundary line between the two phase, sigma plus solid solution region and the single phase solid solution region lies in the range 1310° to 1335°C.

4.5 Thorium-Carbon Alloy Studies (6)

The temperature dependence of the electrical resistivity of thorium alloys in the composition range up to 2.0 weight per cent carbon has been investigated. These results have revealed the effect of carbon on the thorium transformation for temperatures up to 1600°C and for carbon concentrations up to 0.25 weight per cent. At higher temperatures and concentrations the results of resistivity measurements have not been amenable to unambiguous interpretation.

X-ray diffraction data have been consistent with the results obtained from electrical resistivity measurements. Attempts to establish the solubility limits of carbon in thorium in the temperature range of 800 to 1600°C from x-ray diffraction data have been complicated by apparent contamination of the samples with carbon. The source of carbon contamination is uncertain but it may be due to back diffusion of oil vapors from the oil diffusion pump used in evacuating the high temperature x-ray camera. The liquid nitrogen trap used in the system is apparently not completely effective in condensing all of the oil vapors from the diffusion pump. Plans are being made to substitute a mercury diffusion pump for the oil diffusion pump in an effort to eliminate this difficulty.

4.6 Uranium-Niobium System (3)

The investigation of the uranium-niobium diagram has been continued. Additional evidence concerning the supposed diagram-wide solid solubility at high temperature was obtained from x-ray powder patterns of alloys quenched from 1000°C. The 40, 50 and 60 per cent niobium alloys all had simple body-centered cubic structures plus a few lines identified as UO_2.

Specimens ranging from 0.25 per cent to 95 per cent niobium have been quenched from three temperatures in the interval from 720 to 800°C and examined under the microscope. The number of phases observed was in general agreement with a partial working diagram set up some time ago. However, these results neither confirmed nor disproved the idea of diagram-wide solid solubility below the solidus line.

Work with the dilatometer has been resumed. A vacuum instrument has been adopted for the measurements because the specimens developed coatings in the supposedly neutral argon atmospheres of the apparatus used previously.

4.7 Zirconium-Niobium System (3)

The zirconium-niobium system appears to be a comparatively simple one. The two elements have complete mutual solid solubility below the solidus line but the solid solution decomposes at lower temperatures. During the quarter, considerable progress was made in establishing the boundary lines in the lower portion of the diagram. X-ray powder patterns have been of great assistance in the determination of these boundaries. Resistance-temperature graphs and dilatometric curves proved to be very useful also.

4.8 Zirconium-Vanadium System (3)

Zirconium and vanadium also form a relatively simple system. The diagram has an intermetallic compound near the center with a eutectic on the zirconium side and a peritectic arrangement on the vanadium side. The transformation in zirconium gives rise to a eutectoidal horizontal.

A few melting point determinations that were made early in the quarter yielded additional points on the solidus line. Measurements on the change of electrical resistance with temperature have been useful in establishing lines related to the transformation in zirconium. Besides having a pronounced change in resistance at the temperature of the eutectoidal horizontal, the resistance-temperature graphs showed points of inflection that were interpreted as the crossing of the boundary between the two phase region above the horizontal and the solid solution region lying at still higher temperatures. Because of their brittleness, alloys containing more than 10 per cent vanadium could not be reduced to the wire form desirable for resistance measurements.

4.9 Thorium-Magnesium Alloy System (5)

The intermetallic compounds in this system were studied by x-ray methods, and chemical analysis. The thorium-rich compound was found to crystallize in the cubic system with a lattice constant of 8.57 Å. This crystal belongs to the space group Fd3m. The composition of the compound is $ThMg_2$ and the compound has the Cu_2Mg

structure. The magnesium-rich compound is hexagonal with a = 6.1 Å and c = 19.8 Å. The space group has not been definitely established. Analyses and density measurements indicate the composition is $ThMg_3$. However, this composition does not fit x-ray diffraction intensity data very well. Further work is planned to establish the composition of this compound.

4.10 Zirconium-Zinc System (6)

Six alloys ranging in composition from 19.0 to 35.6 weight per cent zirconium were prepared by the bomb technique described in ISC-423. X-ray diffraction analysis, thermal analysis and metallographic examination of these alloys indicate that another compound exists at near 32 per cent zirconium. Work on identification of the phases present in this system is continuing.

4.11 Tantalum Alloys (3)

Attempts to roll out the tantalum-rich alloys mentioned in the previous report have met with varying degrees of success. The low-niobium, the low-molybdenum and the low-titanium alloys could be rolled cold without difficulty. All of the chromium alloys were brittle and the tantalum-rich zirconium alloys were nearly as bad. An alloy containing 2 per cent zirconium could be rolled only to 25 per cent reduction in thickness. Molybdenum-rich alloys of tantalum also showed little ductility. Alloys that could not be rolled cold behaved very little better at 800° or 850°C.

A vacuum furnace for operation at 1200°C was made for annealing the rolled-out sheets. Pressures below 3×10^{-6} mm Hg and usually considerably less, could be maintained in it. An apparatus for measuring tensile strength at temperatures up to 1200°C is being built for tests of the behavior of tantalum alloys. Also, the tungsten-arc furnace is being rebuilt in preparation for additional melting operations.

5. Metal Corrosion and Canning

5.1 Corrosion of Metal Containers by Liquid Uranium (2,5)

The investigation of high melting alloys was initiated during this period. The purpose of this investigation was to ascertain the physical properties, fabricability and resistance to corrosion by liquid U-Cr eutectic of high melting alloys. Since resistance to corrosion by U-Cr eutectic was of primary interest, it was decided to approach the problem from this standpoint first, subsequently investigating the fabrication properties of those alloys which showed promising corrosion resistance.

A "screening" test for the initial corrosion test consisted of placing small cube-shaped test samples plus U-Cr eutectic mixture in a sealed tantalum "sack". The sack and its contents were sealed under argon within an iron crucible and heated to 900°C. After cooling, the sack was cross-sectioned so as to expose the interface between the U-Cr eutectic and the tested alloy. Photomicrographs were taken and the decrease in thickness and width of the reaction band was measured by use of a filar eyepiece on a microscope.

Several of the alloys were severely attacked by the U-Cr alloy after 3 days at 900°C. Some of these alloys partially dissolved in the eutectic alloy with some diffusion of the eutectic into the grain boundaries of the tested alloy. Alloys which corroded in this manner were Nb-20 weight per cent V, Nb-80 per cent V, Nb-30 per cent Mo, Nb-75 per cent Mo, Nb-5 per cent Ta-5 per cent Zr, Zr-5 per cent Ta-5 per cent Nb, Nb-25 per cent Ta-7 per cent Zr. These alloys have been eliminated from further consideration.

Other alloys tested appeared to have formed a compound layer at the interface which in most cases broke away from the interface after it had reached a certain maximum thickness. However, in one or two alloys the layer appeared continuous and may have formed a protective band which could reduce the total corrosion. These alloys are being investigated further. As can be seen from the results presented in Table III the tantalum-rich-niobium-zirconium ternary alloys show the greatest amount of promise and are worthy of extended investigation.

An investigation of the corrosion of tantalum and other metals by liquid uranium-chromium eutectic alloy was continued. Small crucibles were made from thin sheets of the metal to be tested, filled with the eutectic, sealed in stainless steel outer crucibles and heated at the testing temperature for definite periods of time in a muffle furnace. They were then opened, sectioned, examined by metallographic means, and the remaining wall thickness measured with the calibrated eyepiece on a Tukon hardness tester. Results obtained from tests conducted on tantalum, zirconium and thorium are given in the accompanying Tables IV, V, VI, and VII. Crucibles made from molybdenum failed completely within 2 days. The results of these tests indicate that, of the metals tested, tantalum is the most resistant to the liquid uranium-chromium alloy.

The intermetallic compound formed on tantalum in contact with uranium-chromium is being investigated. An x-ray diffraction pattern of this compound has been obtained. This pattern was not the same as that of the chromium-tantalum compound prepared by arc-melting. Crystals of an intermetallic compound formed by heating a mixture of uranium, chromium and tantalum to 1600°C did give an x-ray pattern identical to that of the compound layer observed in the corrosion experiments. Identification of this compound by x-ray diffraction and chemical analysis is under way.

Table III
Corrosion of High Melting Alloys in Molten U-Cr Eutectic

Nominal Comp. Wt %	Time at 900°C	Thickness or Reaction Band (mil)	Type of Layer Formed
90 Ta-10 V	3 days	2	Broke off and floated into U-Cr alloy
90 Ta-5 Nb-5 V	3 days	1	Broke off and floated into U-Cr alloy
90 Ta-5 Nb-5 Mo	3 days	0.6-2	Broke off and floated into U-Cr alloy
50 Ta-45 Nb-5 Zr	12 days	2	Broke off and floated into U-Cr alloy
90 Ta-5 V-5 Zr	12 days	2	Continuous protective layer
75 Ta-23 Nb-2 Zr	12 days	0.5	Continuous protective layer
90 Ta-5 Nb-5 Zr	3 days	0.5-0.8	Continuous protective layer
90 Ta-5 Nb-5 Zr	12 days	1	Continuous protective layer
90 Ta-5 Nb-5 Zr	18 days	1	Continuous protective layer

An investigation was begun to determine whether or not there is an element which will inhibit or stop the corrosion of tantalum by uranium-chromium eutectic. Calcium, magnesium, sulfur, oxygen, and nitrogen did not change the rate of corrosion of tantalum. Other elements are being investigated.

Investigation of the corrosion of tantalum and other metals by liquid thorium-magnesium eutectic was concluded. The results are given in the accompanying Tables VIII, IX, X and XI.

Table IX

Corrosion of Niobium by Thorium Magnesium Eutectic at 1000°C

Time	Loss in Thickness
20 days	0.5×10^{-3} in. ± 0.1×10^{-3} in.
40 days	0.2×10^{-3} in. ± 0.1×10^{-3} in.
60 days	0.4×10^{-3} in. ± 0.1×10^{-3} in.
150 days	0.9×10^{-3} in. ± 0.1×10^{-3} in.

Table X

Corrosion of Molybdenum by Thorium-Magnesium Eutectic at 1000°C

Time	Loss in Thickness
40 days	0.3×10^{-3} in. ± 0.1×10^{-3} in.
90 days	0.0×10^{-3} in. ± 0.1×10^{-3} in.

Table XI

Corrosion of Vanadium by Thorium-Magnesium Eutectic at 1000°C

Time	Loss in Thickness
30 days	1.9×10^{-3} in. ± 0.1×10^{-3} in.

Tantalum, niobium, molybdenum and vanadium all show excellent resistance to thorium-magnesium eutectic alloys at 1000°C in static tests. Some type of dynamic test will be made on these metals to determine whether this corrosion resistance will continue under dynamic conditions.

5.2 Casting U into Zr Cans (2)

Thin-wall zirconium tubes were fabricated from 2 mil zirconium sheet and uranium metal was cast into them in an unheated mold. Even bonding was obtained with some diminution in the wall thickness but with no penetration through the thin sheet. When a similar tube was flash-coated with copper prior to pouring, complete penetration of the wall was observed in several places.

5.3 Casting U into Uranium Alloy Cans (2)

A U-5 weight per cent Zr alloy was used in the initial investigations. The alloy was prepared by bomb co-reduction of UF_4 and ZrF_4 and then melted in vacuum and poured into graphite molds to produce cylinders of 1/16 inch wall thickness, 3/4 inch outside diameter, and 2 inches in length. To obtain a complete metallurgical bond between the uranium and the alloy can, it was found necessary to flash-coat the inner wall with copper. It was also found necessary to preheat the cans to 800°C before pouring the uranium at 1250°C and to follow this by a postheat of the filled can to 1100°C to complete the bonding.

The strength of the bond between the U and the uranium-5 per cent Zr alloy was determined to be 45,500 psi.

5.4 Zinc Base and Composite Coatings on Uranium (6)

Smooth adherent zinc coats approximately one mil thick can be produced on uranium by dipping the metal in a molten zinc bath at 475°C for one minute and then centrifuging to remove the excess zinc. A copper electroplate can readily be deposited on this zinc base which gives a composite coat with reasonably good corrosion resistance to boiling water. However, as previously reported in ISC-423, attempts to reduce the porosity of the copper plate by annealing resulted in the development of blisters, and heating for several hours at 300°C resulted in the formation of a brittle and friable phase between the outer copper coat and the uranium.

On the supposition that blistering might be due to evolution of hydrogen initially dissolved in the uranium, samples were prepared from uranium which had previously been outgassed at 850°C under vacuum. The samples were dry polished and without further treatment were immediately dipped in the zinc bath, then centrifuged and electroplated with copper in the usual way. These samples behaved in the same manner as samples prepared from metal which had not been previously outgassed, showing that the cause of the blistering was most probably due to the evolution of gases occluded or adsorbed during plating.

Samples all having a zinc coat of 1.0 to 1.3 mils thick were plated with from 0.1 to 2.3 mils of copper. It was found that copper plates 0.6 mil or less in thickness which had been outgassed under vacuum at room temperature for 15 hours did not blister when heated in silicone oil to 220°C, while samples with 1.0, 1.2 and 1.3 mil copper plates did develop blisters under the same conditions. Copper plates up to 2.3 mils thick were successfully outgassed by evacuation at room temperature for 15 hours followed by heating for 14 hours at 100°C under a slow stream of helium. Two samples with copper coats 2.2 and 2.3 mils thick were further heated, after this outgassing treatment, to 425°C over a period of four hours, held at this temperature for half an hour and then furnace cooled to room temperature. These samples showed no evidence of blistering. Severe buffing with a wire wheel, however, did loosen and wrinkle the copper coat. The coats could then be cut and peeled from the uranium. The under side of the peeled coat was metallic gray with spots that were a yellow brass color. Between this peeled coat and the sample was a fine black powder, evidently a brittle intermetallic phase which had been shattered by the action of the buffing wheel. Enough of this black powder was collected to permit Debye-Scherrer x-ray diffraction patterns to be taken. The pattern obtained could be indexed as simple cubic with $a_o = 6.247$ Å. This excluded the possibility that the brittle phase responsible for bond failure might be due to the formation of UH_3, UN, UO_2, or one of the Cu-Zn binary intermetallic phases. The amount of powder collected was not sufficient for chemical analysis so the composition is not known; however, it is believed to be a ternary phase containing uranium, zinc, and copper, since the material directly beneath this powder was identified as a U-Zn compound and since this type of bond failure is not observed so long as any free zinc remains in the composite coat. Furthermore, copper-plated zinc given the same treatment did not show this type of bond failure and zinc-coated uranium heated at 300°C for 60 hours in an inert atmosphere did not develop a band or surface that could be readily powdered or cracked by severe buffing. Microscopic and x-ray examination of zinc-coated samples heated at 300°C for 60 hours showed that the free zinc had been completely converted to a single Zn-U phase of unknown structure and that zinc had penetrated along the uranium grain boundaries. In view of these results no further work was done with the composite zinc-copper coats.

Chromium plating over the zinc dip coat has also been further investigated. The problem is essentially that of chromium-plating zinc. A search of the literature reveals that chromium plates on zinc are unsatisfactory, supposedly due to the formation of a dark-colored chromium-zinc phase which results in subsequent peeling of the chromium.[1] Chromium plates deposited directly on the zinc coat in the present investigation showed a tendency to brittleness and scaling on heating at 300°C for several hours. A specimen with a composite coat of approximately 1.0 mil of zinc and 1.0 mil of chromium was heated in silicone oil slowly (2 1/2 hours) to 250°C, then held at this temperature for 3 1/2 hours, followed by 2 hours at 300°C and then cooled to room temperature. This sample was tested in boiling water and found to have lost 4.83 mg/cm^2 after 138 hours, whereas a zinc-coated sample simultaneously tested showed a weight loss of 3.84 mg/cm^2. The unannealed chromium-zinc coats also show approximately the same corrosion rate. The chromium plates thus far produced have not improved the corrosion resistance of the zinc-coated uranium.

Composite coats of zinc-copper-chromium have been developed for the corrosion protection of beryllium.[2] Using procedures similar to those described by Beach and Faust, an attempt was made to produce a corrosion resistant copper-chromium plate over zinc-coated uranium. Ten uranium samples were cleaned, hot-dipped in zinc, centrifuged and prepared for copper plating as previously described, ISC-423. The thickness of the zinc coat on these samples was 1.2 ± 0.2 mils. Eight of the samples were then copper plated using the copper plating bath for zinc described by Beach and Faust. The thickness of the plate on four samples was 0.1 mil; on the other four samples it was 0.5 mil thick. The copper surface was cleaned in a NaCN bath followed by a dilute H_2SO_4 dip and then electroplated with chromium. A commercial chromium plating bath was used and a double cathode clamp was employed in order to avoid current interruption during changes in contact positions on the sample.

Two of the Zn-Cu-Cr coated samples along with a zinc-coated sample were tested for corrosion in boiling distilled water. The results are given in Table XII. Failure in each case was due to pitting. These results show that the electroplates are too porous to offer effective corrosion protection.

The remaining samples were heated in silicone oil at 310°C for periods of 2 1/2 to 5 hours. In each case the coat could be either peeled or chipped off with a knife, exposing a black surface next to the uranium. This dark material is believed to be the same intermetallic U-Zn-Cu phase which is apparently responsible for the separation of the Cu-Zn coats. Some penetration of silicone oil through the electroplates was also observed.

No further work on the Cu-Zn or the Zn-Cu-Cr composite coats is contemplated.

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[1] W. A. Kohler, Principles and Applications of Electrochemistry, Vol. II, John Wiley and Sons, New York, Second Edition, 1944, p. 127.

[2] J. G. Beach and C. L. Faust, Electroplating on Beryllium, U. S. Atomic Energy Commission Report No. BMI-732, April 1, 1952.

Table XII

Corrosion of Zn-Cu-Cr Coated Uranium

Time Hours	Weight Loss in Mg/Cm^2		
	1.2* Zn-0.5 Cu-0.3 Cr Coat	1.2 Zn-0.1 Cu-0.3 Cr Coat	1.2 Zn Coat
168	1.6	4.2	5.5
237	6.1	42.5	9.8
309	12.4	---	19.0

*Number preceding the chemical symbol gives the coat thickness of that metal in mils.

5.5 Diffusion Coating of Uranium (6)

Diffusion coats can be formed on the surface of uranium metal by soaking it in a molten magnesium bath containing the desired metal or metals in solution. Magnesium is insoluble in uranium and under favorable conditions the solute element diffuses into the uranium and forms either a solid solution or one or more intermetallic phases, depending on the relative activity of the solute in the magnesium bath and the various phases concerned.

The molten bath is contained in a magnesia-plus 10 per cent CaF_2 crucible fitted inside a graphite crucible, and this combination is contained inside a stainless steel tube equipped with a water-cooled head and port so that samples may be introduced and removed from the bath. The bath is kept covered with a KCl-LiCl eutectic flux. During prolonged soaking periods an inert atmosphere is maintained in the stainless steel tube.

The uranium specimens are prepared for dipping in the magnesium bath by the usual polishing, cleaning and etching procedure.

It has been found advantageous to precoat the cleaned samples by dipping them into a fused $KCl-LiCl-ZnCl_2$ bath for a few seconds just prior to dipping them into the magnesium bath, or alternatively by dipping them into molten zinc at 475°C for one minute and then centrifuging to remove the excess zinc.

This treatment serves to protect the uranium surface, as it is introduced into the magnesium bath, from oxidation or direct contact with impurities on the surface of the bath. Most of the preceding steps may be eliminated by dipping the uranium in a 400°C fused bath of KCl-LiCl eutectic to which 20 weight per cent of $ZnCl_2$ has been added. When the sample is first dipped into this bath a solid coat momentarily freezes on its surface. Once the metal attains the fusion temperature of the salt mixture, oxide is rapidly removed from the uranium surface. However, the surface obtained is relatively rough if the initial uranium surface is badly oxidized or if the metal remains in the bath for more than five to ten seconds after it has attained the temperature of the bath. The optimum time will depend on the amount of oxide to be removed and the size of the sample. The metal is then dipped in a molten magnesium bath of the desired composition and temperature for a specific period of time, removed, quenched in oil, and then cleaned with dilute nitric acid. The samples thus prepared are used for further testing.

No further work has been done with a magnesium bath saturated with zirconium. The solubility of zirconium in magnesium is small at temperatures below 950°C, and the rate of diffusion of the zirconium into the uranium surface is slow. Experimental difficulties make operation of this bath at still higher temperatures impractical. Other metals which were considered are Nb, Mo, Cr, W, and Fe. The solubilities of Nb, Mo, and Fe in magnesium at temperatures up to 850°C are negligible or very low and it is doubtful that the production of alloy coats of these metals on uranium by this method is practical. Chromium and tungsten do not form intermetallic phases with uranium and only very dilute solid solutions and consequently any alloy formed by diffusion is limited to these very dilute solid solutions. Furthermore, these two metals also show little or no solubility in magnesium at temperatures of 850°C or below.

Work during the quarter has been concerned principally with magnesium baths saturated with either nickel or silicon, and some preliminary work has been done with magnesium-copper-nickel and magnesium-copper baths.

The growth of the diffusion band formed on uranium in a mganesium bath saturated with nickel has been measured. The results obtained at 715 ± 15°C are given in Table XIII. These data show that the diffusion band reaches a maximum thickness of about 0.43 mil after one to two hours. The reason for this is uncertain but is possibly due to scaling of the coat once its thickness has reached some critical value. Microscopic examination shows an increased tendency toward crack formation in the thicker diffusion coats. This effect is also reflected in the corrosion rates given in Table XIV. These samples were cleaned in dilute nitric acid prior to corrosion testing in order to remove the adherent magnesium-nickel bath and expose the nickel-uranium diffusion coat. The higher corrosion rates for the samples dipped for 240 minutes is believed to be due to the presence

Table XIII

Diffusion Band Thickness on Uranium after Various Periods of Time in a Mg-Ni Bath

Bath Temperatures °C	Time in Bath Min.	No. of Samples Measured	Average Thickness of Diffusion Band in Mils
715±15	8	2	0.17±0.01
715±15	15	2	0.23±0.02
715±15	30	6	0.25±0.02
715±15	60	6	0.30±0.02
715±15	90	5	0.39±0.02
715±15	120	5	0.43±0.02
715±15	180	2	0.43±0.02
715±15	240	2	0.41±0.02

Table XIV

Corrosion Rates of Uranium Samples Dipped in a Molten Magnesium Bath Saturated with Nickel

Sample No.	Temp. °C	Time in Mg-Ni Bath Min.	Time in Boiling Water Hours	Weight Loss mg/cm^2/hr.
PWI-38A	733	30	139	0.024
PWI-38B	733	30	139	0.031
PWI-52A	733	90	116	0.088
PWI-33A	733	240	139	0.200
PWI-33B	733	240	139	0.242

of cracks in the nickel diffusion coat. The nickel alloy coat in any case is not free of defects or weak spots since corrosion tests on uranium-nickel alloys of approximately the same composition show excellent corrosion resistance to boiling water.

Corrosion tests have also been made on two U-Ni alloys of near eutectic composition which were prepared by arc melting. These samples formed a shiny black adherent coat and showed a gain in weight after 1000 hours in boiling distilled water. The results on these two alloys along with the results obtained on two uranium-zinc alloys are given in Table XV. The latter samples are two-phase alloys consisting of a uranium compound in a matrix of essentially pure zinc.

The nickel diffusion coats are readily wet by molten zinc. A sample which had been dipped in a Mg-Ni bath for 240 minutes was cleaned with dilute nitric acid and then dipped in a zinc bath at 500°C for two minutes, centrifuged and quenched. This sample when corrosion tested in boiling water showed a weight gain after 200 hours, pits became evident after 275 hours, and at the end of 300 hours showed an average weight loss of 0.011 $mg/cm^2/hr$. The sample was then sectioned and examined under the microscope. Much of the composite coat was still intact after the corrosion test.

Table XV

Corrosion Resistance of Some Uranium Alloys to Boiling Water

Alloy Composition Weight Per Cent	Time in Boiling Water Hours	Corrosion Rate $mg/cm^2/hr$.
11.3 Ni, 88.7 U	1326	$+4.6 \times 10^{-5}$
11.5 Ni, 88.5 U	1006	$+1.9 \times 10^{-4}$
84.8 Zn, 15.2 U	1006	-2.2×10^{-4}
87.9 Zn, 12.1 U	855	$+1.05 \times 10^{-3}$

Samples dipped in a magnesium-silicon bath also appear to have an upper limit to the thickness of the diffusion coat which can be formed by this method. As in the case of nickel, this is believed to be due to cracking and scaling of the coat as it grows beyond some limiting thickness. The diffusion layer formed in this case also appears to be made up of two bands, presumably epsilon and

U_5Si_3 phases. If other phases exist in the diffusion band they are not readily evident microscopically. The thickness of the diffusion band formed after various periods of time in a molten magnesium bath saturated with silicon are given in Table XVI. All the samples listed in this table with the exception of the first were zinc coated prior to dipping into the Mg-Si bath. The corrosion resistance of these samples is comparable to that of samples dipped in a Mg-Ni bath.

With both the Mg-Si and Mg-Ni baths, the initial growth of the diffusion band apparently follows the parabolic law,

$$X^2 = k\,t,$$

where X is the thickness of the diffusion layer at time t, and k is the penetration constant, but deviates from this relation for periods greater than about 60 minutes. This is believed to be due to cracking and scaling of the coat formed. From measurements of the diffusion band thickness formed in sixty minutes or less, the k value for the U/Mg-Ni couple was found to be 2.8×10^{-10} cm^2/sec at 715±15°C and the k value for the U/Mg-Si couple, to be 2.0×10^{-9} cm^2/sec at 715±15°C.

The band thickness formed after a given period of time and temperature was found to vary as much as 27 per cent in the case of the U/Mg-Si couple, and approximately 15 per cent in the case of the U/Mg-Ni couple. Various factors such as surface preparation and the concentration of the solute and uranium in the magnesium bath might be expected to influence the rate of growth of the diffusion layer. An excess of solute was added in order to keep the bath saturated in each case; however, dissolution by the flux and oxidation at the flux-air interface might result in variation of bath composition. However, the values obtained for the penetration constants are believed to be of the correct order of magnitude.

Table XVI
Diffusion Band Thickness on Uranium after Various Periods of Time in a Mg-Si Bath

Bath Temperature °C	Time in Bath Min.	Number of Samples Measured	Ave. Thickness of Diffusion Band Mils
715±15	15	2	0.27
715±15	15	4	0.59±0.02
715±15	30	4	0.71±0.08
715±15	45	4	0.92±0.19
715±15	75	2	0.76±0.20
715±15	90	1	0.83

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

It has been observed that uranium in contact with Al-Si eutectic at 640°C is rapidly attacked with the formation of alternate layers of eutectic and some intermetallic phase or phases. The formation of this structure at the (Al-Si)/U interface is believed to be due to the rapid growth and subsequent cracking or scaling of the diffusion band on the uranium surface and penetration of the cracks by the Al-Si eutectic. The reaction is still quite rapid at 600°C and both the time and temperature of dipping must be carefully controlled in order to obtain uniform wetting and bonding without the formation of large amounts of reaction products.

A number of cleaned uranium samples were dipped in Al-Si eutectic at 600±5°C for periods of time ranging from five minutes to six seconds. A dipping time of one minute or more resulted in the formation of a heavy, badly cracked, diffusion layer or reaction band. A dipping time of six to 10 seconds gave a narrow reaction band of 1.0 mil or less in thickness. Measurement of the thickness of the diffusion band formed on several samples shows that for periods of up to one minute the penetration constant for Al-Si eutectic diffusing into uranium at 600°C is of the order of 6.0×10^{-7} cm^2/sec. An accurate determination of this constant is difficult since the diffusion band formed tends to scale or crack once it has reached a thickness of one or two mils.

The possibility that small additions of nickel or chromium to the Al-Si bath might reduce the rate of reaction between the bath and uranium was investigated. A bath having a nominal composition of five weight per cent nickel was prepared by adding nickel shot to the bath. After approximately five hours at 600°C a sample of the bath was quenched and analyzed for nickel. The bath was found to contain only 2.5 weight per cent nickel. This Al-Si-Ni bath, however, shows no pronounced improvement in its reactivity toward uranium over an Al-Si bath with no nickel. Attempts to dissolve chromium in the bath were still less successful. The amount dissolved at 600°C was found to be less than one weight per cent.

Uranium with a nickel alloy surface, prepared by dipping it in a Mg-Ni bath, is readily wet by the Al-Si; alloy coats 0.2 to 0.3 mil thick will withstand the action of the bath at 600°C up to two minutes without complete dissolution. The U-Ni diffusion coat is brittle, however, and may be undesirable from this standpoint.

Uranium, diffusion coated with silicon by dipping in a Mg bath saturated with silicon, is not readily wet by the Al-Si bath. This is probably due to oxide formed on the surface of the alloy coat in the process of removing the outer layer of Mg-Si with dilute nitric acid. However, once wetted, these coats show little or no resistance to penetration by the Al-Si bath.

5.7 Corrosion of U-Zr-Nb Alloys (2)

Corrosion studies made on the eleven alloys listed in the table below furnished corrosion rate data for these alloys in the alpha-annealed state. The alloys have been tested in boiling distilled water, and the rates given for various time intervals up to and including seven hundred hours. These alloys were prepared by arc-melting derby uranium with high purity zirconium and niobium metal; sections were taken from the resulting button for corrosion testing. The samples were first gamma-quenched by heating under vacuum at 850°C for two hours and water quenching. They were then annealed as follows: 750°C for 2 hr, 600°C for 2 hr, 500°C for 20 hr, and furnace cooled.

Table XVII

Corrosion of U-Zr-Nb Alloys in 100°C Distilled Water

Alloy Composition Wt. %	Corrosion Rate (mg/cm^2/hr) at end of each time interval				
	48 hrs.	168 hrs.	336 hrs.	400 hrs.	700 hrs.
20 Zr-U	0.02	0.04	0.23	0.009	0.03
10 Zr-U	0.56	0.61	0.54	0.46	0.45
5 Zr-U	1.56	1.64	1.43	1.30	1.14
2 Zr-U	1.72	2.29	1.99	1.50	1.32
10 Nb-U	0.03	0.25	3.66	disintegrated	
5 Nb-U	0.05	0.37	0.47	0.46	0.39
3 Nb-U	1.13	1.21	1.12	0.92	0.93
5 Zr-5 Nb-U	0.01	0.05	0.10	0.05	0.02
5 Zr-2 Nb-U	0.33	0.70	0.68	0.56	0.02
3 Zr-3 Nb-U	0.52	0.93	0.82	0.55	0.48
2 Zr-4 Nb-U	0.09	0.46	0.34	0.27	0.16

The production of a quantity of 5 and 10 per cent Zr-U alloys for special in-pile radiation tests at Hanford was completed during this period. The alloys were melted in a graphite crucible and poured into a graphite mold forming 3/4-inch diameter rods 4 to 8 inches in length. These were sliced into 1/4-inch long sections which were then heat treated. The heat treatment consisted of quenching all of the alloys from the gamma region by heating them at 850°C for 2 hours and water quenching. Half the quantity of each alloy was transformed from the quenched state by alpha annealing (750°C for 2 hrs., 600°C for 2 hrs., 500°C for 20 hrs. and furnace cooled.)

A study of age hardening with respect to corrosion and electrode potential measurements was begun during this period. Twelve U-Zr, U-Nb and U-Zr-Nb alloys are being used in the study. These alloys include the eleven alloys mentioned in the included corrosion table plus the U-1 per cent Nb alloy. Four series of the alloys have, to date, been prepared from arc-melted buttons, gamma quenched from 900°C and given the following ageing treatments:

Series 1 - annealed at 100°C for 477 hrs.
Series 2 - annealed at 200°C for 499 hrs.
Series 3 - annealed at 300°C for 449 hrs.
Series 4 - annealed at 400°C for 335 hrs.

In Series 1, 2 and 3 a microscopic examination did not reveal that a second phase precipitation had taken place. In Series 4, however, a distinct change in the etching character of the alloys was noted. The structure revealed in this series, even though a heavy film was formed by the etching, seemed to indicate the presence of a lamellar-type precipitation.

Age-hardening study and corrosion testing of these alloys will be continued with the emphasis on detection of corrosion resistance change by the electrode potential method.

Since these alloys in the gamma-quenched condition exhibit better corrosion resistance than in the annealed state, electrode potential investigations were undertaken. It was hoped these studies might be helpful in understanding this phenomenon. Correlation of electrode potentials and corrosion rates in high temperature water might also prove useful as a means of evaluating the corrosion resistance of an alloy.

Initial potential measurements were made in 2N NaCl stagnant solution using a saturated calomel electrode as the reference electrode. In order to prevent polarization from occurring during measurements, a high impedance dc amplifying circuit was used, thus allowing continuous recording of time vs potential.

Experiments were conducted on uranium in order to establish conditions for obtaining reproducible potentials. The following variables seemed to have an appreciable effect on the measured potential:

1. the surface preparation of the specimen
2. concentration of the electrolyte
3. pre-immersion exposure time
4. temperature of the electrolyte
5. whether electrolyte is stirred or remains in a stagnant condition.

The measurements were made for a period of 2-4 hours during which time the potential usually has reached a steady value.

Electrochemical potential measurements were made on the following alloy series: 1, 3, 5 and 10 weight per cent Nb alloys in both the gamma-quenched and the alpha-annealed conditions, and 2 Zr-4 Nb-U, 5 Zr-2 Nb-U, 3 Zr-3 Nb-U, and 5 Zr-5 Nb-U ternary alloys in quenched and annealed conditions.

Since the annealed binary and ternary alloys are microscopically two phase, with the major constituent being α-uranium, it is not too surprising that all the annealed alloys were found to have potential values close to that of pure uranium. The measured potential of pure uranium is 0.855 ±0.005 volt.

The gamma-quenched alloys showed a pronounced difference in electrochemical potential as the composition was varied. The niobium binary alloys became more noble approaching lower potentials as the niobium content was increased. The 3 per cent Nb-U alloy had a potential of 0.755 ±0.005 volt and the 10 per cent Nb-U alloy had a potential of 0.401± 0.015 volt. Similar decreases in the potential were observed in the quenched ternary series also. The influencing factor in shifting the electrochemical potential to a more noble value seemed to be principally the niobium although the zirconium does contribute somewhat to a lower potential in the ternary alloy.

6. Other Investigations

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

Attempts to identify the pyrophoric film on uranium-zirconium alloys have so far not been completely successful. Exhaustive leaching of the pyrophoric material with nitric acid produced a residue which was still pyrophoric and sedimented into three layers. One of these layers contained alpha zirconium as one constituent. The other layers have not been identified.

Uranium-rich alloys of uranium with vanadium, molybdenum, and titanium were prepared and annealed at a temperature just below the lowest transformation temperature. These alloys were pickled in nitric acid and tested to determine whether a pyrophoric film was formed. In no case was a pyrophoric film observed in these alloys.

6.2 Sodium Tungsten Bronze (4)

Additional anomalous behavior of sodium tungsten bronze, Na_xWO_3, near the concentration $x = 0.75$ has been found. Measurements of the linear coefficient of expansion when plotted against sodium concentration exhibit a maximum near $x = 0.75$. The linear coefficients of expansion were obtained from measurements of the lattice parameter using x-ray diffraction in the temperature range, 25°-500°C.

The possibility of an ordered arrangement of sodium ions at $x = 0.75$ which was first proposed by W. Gardner and G. C. Danielson, Phys Rev. 93, p. 46 (1954), is being investigated. Detection of a superlattice by x-ray diffraction techniques has been attempted without success. The reflection occurring at $2\theta = 28.6°$ which was reported in the last report as a possible superlattice peak has been identified as a weak reflection from the regular lattice due to Cu $K\beta$ radiation. The relatively high scattering power of tungsten for x-rays masks the sodium contribution, and thus the negative results of the attempt to detect a superlattice by x-ray diffraction is not conclusive. For the same reason electron diffraction would not be expected to be able to detect the existence of a superlattice. Inquiries have been made as to the possibility of detection of a superlattice by means of neutron diffraction, and successful detection by present techniques is doubtful.

Calculations of the electrostatic energy for various ordered configurations have been made for sodium tungsten bronze near $x = 0.75$. These calculations indicate that there is a significant energy difference between random sodium distribution and an ordered sodium distribution which retains cubic symmetry and doubles the lattice parameter. These calculations have not as yet been made for other concentration ranges.

An experiment is in progress which may clarify the question of ordering in the sodium distribution. An electrochemical cell has been assembled in which sodium tungsten bronze serves as an electrode. The E.M.F. of the cell is measured as a function of temperature to determine an entropy value for the cell. This is being done for several sodium tungsten bronze samples of different sodium concentration. When the experiment is complete, entropy will be plotted against sodium concentration. An ordered sodium distribution should have a pronounced effect on such a plot.

6.3 Growth of Metal Single Crystals (4)

Apparatus for the growth of metal single crystals has been constructed. The apparatus consists of a resistance furnace with controls which move a steep temperature gradient (~100°C/inch) along a stationary sample. The temperature gradient can be moved in either direction so that crystals can be grown upon solidification from a melt in the manner of Bridgman or crystals can be grown by the strain-anneal technique. As yet only the Bridgman technique has been used. Several single crystals of lead and of zinc have been grown. The maximum size so far attained is one inch in diameter by three inches long.

Single crystallinity is easily checked by the flash pattern of reflected light after an appropriate etch. Exact crystal orientation by x-ray diffraction is possible by using the back-reflection Laue technique. A suitable orientation camera has been designed and built. Initial tests of the camera have been satisfactory.

Considerable difficulty has been experienced in converting the single crystals (particularly Zn) into suitable shapes for projected experiments. Several different cutting and grinding techniques are being tried.

6.4 Physical Constants of Metals from Ultrasonic Measurements (4)

The initial phase of a program to measure physical constants of metals by an ultrasonic technique has begun. Apparatus has been assembled for the measurement of longitudinal and transverse elastic wave velocities in metals using a frequency range of 0.5 Mc to 10 Mc.

The first tests on the apparatus were run to determine a practical size for test specimens. Cylindrical specimens of magnesium about 4 cm long were used in the tests; frequency and specimen diameter were the adjusted parameters. It was found that diameters as small as 1 cm could be used satisfactorily at a frequency of 10 Mc. For lower frequencies the smallest useful diameter increased; at 2.25 Mc this diameter was found to be about 2 cm. The diameter limit results from a modification of the bulk velocity toward the thin rod velocity with decreasing diameter and increasing wave length.

Measurements at 25°C of transverse and longitudinal elastic wave velocities have been made on polycrystalline Mg, Zr, Al, and Cu. From these measurements Young's modulus, Poisson's ratio, shear modulus, compressibility, characteristic frequency, and the Debye temperature have been calculated. Satisfactory agreement between calculated values and literature values has been found. Measurements at 25°C were also made on dysprosium which gave the following results:

Longitudinal velocity $V_L = (2.958 \pm 0.006) \times 10^5$ cm/sec

Transverse velocity $V_S = (1.724 \pm 0.009) \times 10^5$ cm/sec.

Using these velocities and a density of 8.562 g/cm^3, the following values were calculated for dysprosium:

Young's modulus	$Y = 6.32 \times 10^{11}$ dyne/cm^2
Shear modulus	$= 2.54 \times 10^{11}$ dyne/cm^2
Poisson's ratio	$= 0.243$
Characteristic frequency	$= 3.75 \times 10^{12}$ sec^{-1}
Debye temperature	$\Theta = 182°$A
Compressibility	$= 2.44 \times 10^{-12}$ cm^2/dyne.

Since dysprosium is ferromagnetic at very low temperatures, the calculated characteristic frequency and Debye temperature will probably have no meaning below the Curie point. Measurement at -71°C showed within the limits of experimental error that the longitudinal sound velocity in dysprosium was the same as at room temperature.

6.5 The CaO-CaF_2 System (1)

Study of CaF_2-CaO system is continuing in hopes of more closely locating the eutectic and of determining the extents of solid solubilities if any of CaO and CaF_2 in one another. Microscopic and x-ray methods were used for this work, and cooling curves were made whenever it was necessary to obtain a new sample. The rate of cooling was decreased and size of samples increased so that more satisfactory thermal breaks were obtained. Samples for microscopic examination were polished using absolute alcohol with the grinding powder on the polishing cloth. A smooth surface was obtained and samples were not attacked by the alcohol as they had been by water. Pictures were taken on the metallograph at 100 and 200 magnifications of many of the polished samples. However, microscopic evidence is as yet indefinite. Powder pattern x-ray pictures were made of samples at 10 per cent intervals from 0 to 50 per cent CaO. No lines appeared that indicated presence of any phase except CaO and CaF_2. Back reflection pictures were made using a 60 cm R camera, on samples containing 0 per cent, 4 per cent and 10 per cent CaO. No evidence of solubility was obtained.

APPENDIX I: LIST OF REPORTS FROM THE AMES LABORATORY

1. Reports for Cooperating Laboratories

ISC-244	Preparation of Vanadium Metal, by J. R. Long and H. A. Wilhelm. UNCLASSIFIED.
ISC-339	Metallurgy. Quarterly Summary Research Report. January-March, 1953, by the Ames Laboratory Staff. SECRET.
ISC-354	Conductances and Transference Numbers of Some Rare Earth Perchlorates, Nitrates and Sulfates in Aqueous Solution, by S. Jaffe and F. H. Spedding. UNCLASSIFIED.
ISC-377	Magnesium-Uranium Alloy System, by G. Tracy and H. A. Wilhelm. SECRET.
ISC-389	Hanford Slug Program. Quarterly Summary Research Report. April-June, 1953, by P. Chiotti and O. N. Carlson. SECRET.
ISC-393	Engineering. Quarterly Summary Research Report. April-June, 1953, by the Ames Laboratory Staff. SECRET.
ISC-394	Chemistry. Quarterly Summary Research Report. April-June, 1953, by the Ames Laboratory Staff. SECRET.
ISC-395	Physics. Quarterly Summary Research Report. April-June, 1953, by the Ames Laboratory Staff. UNCLASSIFIED.
ISC-396	Metallurgy. Quarterly Summary Research Report. April-June, 1953, by the Ames Laboratory Staff. SECRET.
ISC-401	The Niobium-Vanadium Alloy System, by J. M. Dickinson, O. N. Carlson and H. A. Wilhelm. UNCLASSIFIED.
ISC-407	A Process for Separating Thorium Compounds from Monazite Sands, by K. G. Shaw, M. Smutz and G. L. Bridger. SECRET.
ISC-408	Thorium-Titanium Alloy System, by H. A. Wilhelm, O. N. Carlson and H. E. Lunt. DECLASSIFIED.
ISC-409	A Simple Line-Operated Constant Current Supply, by D. E. Winkel and H. J. Svec. UNCLASSIFIED.
ISC-411	Direct Titrimetric Determination of Sulfate, by J. S. Fritz and M. Q. Freeland. UNCLASSIFIED.
ISC-412	Adaptation of a Geiger-Counter X-Ray Diffractometer for High Temperature Investigations, by P. Chiotti. UNCLASSIFIED.

ISC-415	Purification of Thorium by Solvent Extraction, by M. E. Whatley, M. Smutz and G. L. Bridger. SECRET.
ISC-416	Separation of Hafnium from Zirconium by Liquid-Liquid Extraction, by H. C. Peterson and G. H. Beyer. CONFIDENTIAL.
ISC-418	A Theoretical Study of the Electrical Structure of Water, by F. O. Ellison and H. Shull. UNCLASSIFIED.
ISC-419	Particle Distributions from a Thin Source in Contact with a Collimator, by G. H. Miller. UNCLASSIFIED.
ISC-420	Engineering. Quarterly Summary Research Report. July-September, 1953, by the Ames Laboratory Staff. SECRET.
ISC-425	Separation of Ra^{228} in Thorium Metal Production, by D. T. Peterson, R. W. Moore and M. Allison. SECRET.
ISC-426	Hanford Slug Program. Quarterly Summary Research Report. July-September, 1953, by P. Chiotti and O. N. Carlson. SECRET.
ISC-427	Analysis of Uranium-Zinc Alloys, by J. S. Fritz, M. O. Fulda, S. L. Margerum and E. I. Lane. UNCLASSIFIED.

2. Papers Published in Scientific Journals

Brehm, R. K. and V. A. Fassel
A New Approach to Direct Reading Spectrochemical Analysis. J. Opt. Soc. 43, 886-889 (1953).

Carlson, J. F. and T. J. Hendrickson
Variational Methods for Problems in Resistance. J. App. Phys. 24, 1462-1465 (1953).

Daane, A. H. and F. H. Spedding
Preparation of Yttrium and Some Heavy Rare Earth Metals. J. Electrochem. Soc. 100, 442-444 (1953).

Duke, F. R. and C. E. Borchers
The Kinetics of the Cerium(IV)-Chloride Reaction. The Cerium(IV) Thallous Reaction in the Presence of Chloride. J. Am. Chem. Soc. 75, 5186-5188 (1953).

Fritz, J. S. and J. J. Ford
Titrimetric Determination of Thorium. Anal. Chem. 25, 1640-1642 (1953).

Fritz, J. S. and M. O. Fulda
Titration of Weak Bases in Acetic Anhydride Solvent Mixtures. Anal. Chem. 25, 1837-1839 (1953).

Griffel, M.
The Thermodynamic Functions of Potassium Vapor. J. Chem. Phys. 21, 1908 (1953).

Griffel, M. and R. E. Skochdopole
The Heat Capacity and Entropy of Thorium from 18° to 300°K. J. Am. Chem. Soc. 75, 5250-5251 (1953).

Hansen, R. S. and W. V. Fackler, Jr.
A Generalization of the Polanyi Theory of Adsorption from Solution. J. Phys. Chem. 57, 634-637 (1953).

Hoffman, M. M. and A. G. W. Cameron
Angular and Energy Distribution of Photoprotons from Aluminum and Tantalum. Phys. Rev. 92, 1184-1191 (1953).

Stirpe, D.
Electrodeposition of Metals on Sodium Tungsten Bronze Crystals. Rev. Sci. Inst. 24, 1071 (1953).

Svec, H. J. and D. S. Gibbs
The Reaction between Calcium Metal and Water Vapor. I. J. Am. Chem. Soc. 75, 6052-6053 (1953).

APPENDIX II: LIST OF SHIPMENTS

Destination	Item
Argonne Cancer Research Hospital Chicago, Illinois	10 g 99% yttrium oxide
Argonne National Laboratory Lemont, Illinois	2 lbs thorium chloride
American Electro Metal Corporation Yonkers, New York	50 g samarium oxide 50 g gadolinium oxide 50 g ytterbium oxide (on loan)
Army Medical Research Laboratory Fort Knox, Kentucky	3 1/2 g thulium metal - 7 cyl. slugs
Bartol Research Foundation Franklin Institute Swarthmore, Pennsylvania	250 g 98% praseodymium oxide (on loan) 1 g best quality praseodymium oxide

Destination	Item
Brookhaven National Laboratory Upton, Long Island, New York	2 g thulium oxide (99.9%) 2 g holmium oxide (99.9%) 2 g lutetium oxide (99.9%) (on loan)
California Institute of Technology Pasadena, California	0.1 g thulium 1 g lanthanum oxide 1 g cerium oxide 1 g praseodymium oxide 1 g neodymium oxide 1 g samarium oxide 1 g yttrium oxide 1 g ytterbium oxide 1 g erbium oxide 0.1 g dysprosium oxide 0.1 g holmium oxide 0.1 g lutetium oxide
Carbide and Carbon Chemical Company Oak Ridge, Tennessee	2 1/2 lbs thorium from Billet A-521
Carbide and Carbon Chemical Company Oak Ridge, Tennessee	10 g thulium oxide
Carnegie Institute of Washington Department of Terrestrial Magnetism Washington, D. C.	0.5 g dysprosium oxide 0.5 g holmium oxide 0.5 g erbium oxide 0.5 g thulium oxide (on loan)
Dow Chemical Company Midland, Michigan	20 g pure neodymium oxide 20 g pure lanthanum oxide 20 g pure praseodymium oxide 10 lbs anhydrous thorium chloride
Duke University Durham, North Carolina	1 sample yttrium metal (on loan)
Frick Chemical Laboratory Princeton University Princeton, New Jersey	10 g neodymium oxide (on loan)
Harvard University Cambridge, Massachusetts	3 g yttrium metal (on loan)
C. A. Hutchison Chicago, Illinois	5 g praseodymium oxide 5 g neodymium oxide

Destination	Item
Institute for Nuclear Studies University of Chicago Chicago, Illinois	1 g lutetium metal (on loan)
Iowa State College Ames, Iowa (Engineering Experiment Station)	250 g lanthanum metal (99%) 250 g cerium metal (99%) 250 g neodymium metal (99%)
Ledoux and Company Teaneck, New Jersey	100 mg lanthanum oxide 100 mg cerium oxide 100 mg praseodymium oxide 100 mg neodymium oxide 100 mg samarium oxide 100 mg gadolinium oxide 100 mg yttrium oxide 100 mg erbium oxide 100 mg holmium oxide 100 mg dysprosium oxide 100 mg ytterbium oxide 100 mg lutetium oxide 100 mg thulium oxide
Los Alamos Scientific Laboratory Los Alamos, New Mexico	10 lbs zirconium tetrafluoride, C. P. anhydrous
A. D. Mackay, Inc. New York, New York	1 g pure yttrium oxide
Mallinckrodt Chemical Works St. Louis, Missouri	200 mg ytterbium oxide 40 mg holmium oxide 2 g yttrium oxide 150 mg erbium oxide 200 mg dysprosium oxide
Massachusetts Institute of Technology Cambridge, Massachusetts	10 g erbium oxide (99%) (on loan)
State University of Iowa Iowa City, Iowa	1 g ytterbium oxide
University of California Radiation Laboratory Berkeley, California	10 g dysprosium oxide (95-98%)(on loan)
University of California Radiation Laboratory Livermore, California	3 g gadolinium metal (98%) (on loan)

Destination	Item
Vreeland Laboratory Mill Valley, California	100 mg erbium oxide
	100 mg dysprosium oxide
	100 mg holmium oxide
	100 mg thulium oxide
	100 mg ytterbium oxide
	100 mg lutetium oxide

APPENDIX III

(1) H. A. Wilhelm

(2) O. N. Carlson

(3) B. A. Rogers

(4) J. F. Smith

(5) D. Peterson

(6) P. Chiotti