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ISC-396(Del.)

UNITED STATES ATOMIC ENERGY COMMISSION

QUARTERLY SUMMARY RESEARCH REPORT IN METALLURGY

For April, May, and June, 1953

Photostat Price \$ 6.30

Microfilm Price \$ 3.00

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

By

Ames Laboratory Staff

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November 16, 1953

Ames Laboratory
at
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QUARTERLY SUMMARY RESEARCH REPORT IN METALLURGY

For the period April, May, June, 1953

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

Previous quarterly research reports in this series are:

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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 R. W. Fisher

1. Zirconium1.1 Hafnium-Zirconium Separation Studiesa. Separation of Low Hafnium from Zirconium (1)*

The effects of several complexing agents on transfer and separation of hafnium and zirconium in the tributyl phosphate-nitric acid and in the hexone-thiocyanate systems were studied. The presence of an alkyl aryl sulfonate in the aqueous phase resulted in increased transfer of hafnium to the organic phase in the hexone-thiocyanate system with an increased purity of zirconium in the aqueous phase. Similar work with the tributyl phosphate-nitric acid system indicated that a purer zirconium was being transferred to the organic phase, however, to a lesser extent than in the absence of the sulfonate.

Sulfide ion was found to affect transfer in the hexone-thiocyanate system. In a series of experiments the concentration of thiocyanate ion in both phases was varied. The aqueous phases were saturated with hydrogen sulfide gas and then contacted with the hexone phases. The presence of sulfide ion, as compared with its absence, served to increase the transfer of both hafnium and zirconium to the organic phase without any significant change in separation.

Organothiophosphate solvents such as trihexylthiophosphate and tributylthiophosphate were prepared by adding sulfur to the corresponding trialkyl phosphites. Extractions were performed using the thiophosphates as organic solvents in the nitric acid system. Transfer took place with the tributyl thiophosphate, but analytical results are not completed to determine if separation was effected.

b. Separation of Low Zirconium from Hafnium (1)

The conditions for the separation of a few per cent of zirconium from hafnium by solvent extraction has been fairly well established. Preliminary tests on a small-scale twenty-stage extractor have been made in order to select operating conditions to be used on the higher capacity fifteen stage extractor.

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

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Four multiple stage extractions were run in this period. The organic solvent used in all of these runs was 60% tributyl phosphate-40% dibutyl ether by volume. The flow rate ratios used in all extractions were the same and as follows:

<u>Flow Rate Ratios</u>	
Feed	20
Organic	20
Scrub	5

On the first extraction all 20 stages were used with the feed entering at stage eleven. The scrub and feed were 5.9 and 5.6 M in HNO_3 , respectively, and the organic solvent was not pre-equilibrated with HNO_3 solution. Stagewise analysis after the run showed hafnium containing only 50 ppm zirconium in stage 3, but in stage 1 it contained over 150 ppm zirconium in the hafnium. This increase in zirconium where it should decrease seemed to indicate that the organic solvent may have been contaminated with some zirconium, so in future extractions the organic phase was washed several times with water before the extraction.

The next run was made using only 15 of the 20 stages and pre-equilibrating the organic phase with 2.7 M HNO_3 . The scrub and feed were both 3.15 M in HNO_3 . This extraction gave only about 2.6% transfer of total oxide to the organic phase. The oxide in the organic phase contained more than 99.5% ZrO_2 , while the oxide in the aqueous phase was only about 99% HfO_2 . In this extraction there was evidently not enough transfer, so in the third run the HNO_3 concentration in the feed and scrub was raised to 5 M and in the organic solvent to 2.9 M. This extraction gave hafnium in the aqueous phase containing about 240 ppm zirconium.

The last multiple stage extraction during this period was a duplication of the first, except that only 15 stages were used. This run gave hafnium in the aqueous phase with about 350 ppm zirconium. It is still suspected that there may be some zirconium contamination of the organic solvent before it enters the extractor. Since the room in which the extractions were made had been used for zirconium research work for a number of years, it is possible this area is a source of the zirconium contamination. Tests on the ash of cigarettes smoked in this area showed the presence of zirconium. More extractions are to be made with added precautions against contamination in an attempt to get hafnium with less than 100 ppm in zirconium.

1.2 Preparation of Zirconium Tetrafluoride (2)

a. Zirconium Tetrafluoride from Zirconium Oxyhydroxide

One hundred pounds of wet zirconium-oxyhydroxide cake were obtained from Bureau of Mines, Albany, Oregon. The approximate

percentage composition is as follows for the wet cake received:

55% moisture

15% phthalate (as phthalic acid or phthalate)

30% zirconium oxyhydroxide

The phthalate can be removed for our purpose at low temperatures by passing anhydrous hydrogen fluoride over the dried cake at 250°C. The phthalate is removed as the phthalic anhydride. Prior to this removal, the wet oxyhydroxide cake was dried of surface moisture at 60°C and a molecular amount of aqueous (70%) hydrofluoric acid was added to form zirconium tetrafluoride monohydrate. A ten pound batch of the tetrafluoride monohydrate was prepared in this manner.

The drying conditions in an anhydrous hydrogen fluoride atmosphere for converting the tetrafluoride monohydrate to the anhydrous tetrafluoride were studied in some detail. It was found that the temperatures at which the monohydrate was dried to the anhydrous product did not seem to be too critical. However, the quality of the metal produced, when cast in graphite, was of somewhat poorer quality than that obtained by the hydrofluorination of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$. Rockwell hardnesses of A-48 to A-53 were obtained consistently.

b. Zirconium Tetrafluoride from Zirconium Tetrachloride

Five hundred fifty-three pounds of zirconium tetrachloride were received from Bureau of Mines, Albany, Oregon. The zirconium oxychloride was prepared from this by the usual hydrolysis reaction. Zirconium fluoride monohydrate was then prepared by the reaction of 70% hydrofluoric acid on the prepared oxychloride. The zirconium tetrafluoride monohydrate was then dried in the rotary hydrofluorination furnace. Fifty pounds of the anhydrous zirconium fluoride were sent to National Lead Company, Cincinnati, Ohio. Two hundred fifty pounds were sent to Argonne National Laboratory, Chicago, Illinois.

1.3 Zirconium and Hafnium Metals by Bomb Reduction (2)

a. Bomb Reduction of Zirconium Fluoride

Spectrographic analyses of some bomb reduced zirconium has shown that the aluminum and silicon contents are relatively high. Investigations were made in an attempt to locate the source or sources of aluminum and silicon contamination. The aluminum content of the zirconium has ranged from 100 to 800 ppm and silicon from 150 to 750 ppm. The data obtained seemed to indicate the CaF_2 liner

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was the source of contamination although it is difficult to comprehend the manner in which such a large contamination could be derived from the liner material. The evidence was fairly conclusive, however, that HF leaching of the CaF_2 lowered the amount of contamination but not sufficiently.

b. Reduction of Hafnium Fluoride

Hafnium fluoride containing approximately 3% zirconium fluoride has been reduced to a hafnium-zinc alloy by the bomb reduction process with calcium as the reductant and iodine as the booster. The conditions required to prepare zirconium metal in the bomb were duplicated with variations only in the iodine and zinc ratios. Best yields (90% of theoretical) have been obtained by preparing a 16% zinc-hafnium alloy which was then dezincd by heating in vacuum to temperatures of 1700 to 1800°C. The resulting sponge hafnium has been arc-melted but the metal obtained was hard and somewhat brittle.

1.4 Zirconium Alloy Studies

a. Zirconium-Niobium Alloys (3)

A few more zirconium alloys containing from 13 to 23 weight per cent niobium have been made. They are being used in a study of changes that occur as the result of the transformation in zirconium at 862°C.

Determinations of the resistance of alloys at room temperature have shown that the resistance of rapidly cooled alloys increases sharply as the niobium content reaches 8 to 10 per cent. All alloys in the range from 5 to 40 per cent niobium undergo large changes in resistance with heat treatment.

Measurements of the temperature at which melting begins have been completed for 13 alloys. The curve of melting points indicates that complete solid solubility exists for an interval below the solidus line.

b. Zirconium-Vanadium Alloys (3)

Thermal analyses of zirconium-vanadium alloys containing 1, 2, 3, 5, 10, 20 and 40 per cent vanadium by weight have shown arrest points in the vicinity of 795°C. No thermal effects were observed in alloys with 50 and 60 weight per cent vanadium. These data point to a eutectoidal horizontal extending from less than 1 to more than 40 per cent vanadium at 795°C. Resistance-temperature curves of the alloys with 1 and 5 per cent show anomalies at about 792°C that confirm the existence of the eutectoidal horizontal.

X-ray diffraction patterns from powdered 30 per cent and 70 per cent vanadium alloys have lines that do not belong to either

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of the terminal solid solutions. Hence by inference, the patterns tell that, at least, one intermediate phase exists in the system. As the microstructure of the 50 per cent alloy quenched from 1100°C is almost all one constituent, the intermediate phase probably is near the 50 per cent proportion.

A few determinations of the temperature at which zirconium-rich alloys begin to melt have shown that the addition of vanadium lowers the melting point of the alloys sharply. The melting behavior of 20 and 50 weight per cent vanadium alloys suggests that a eutectic horizontal lies near 1225°C.

c. Zinc-Zirconium Alloys System (2)

An intermetallic compound (ZnZr) at 41 weight per cent zinc with a density of approximately 7.0 gm/cm³ and a lattice parameter of $a_0 = 3.238$ Kx has been tentatively interpreted as having the cesium chloride type structure with one molecule per unit cell. The space group is Pm3m.

Alloys containing large amounts of zinc were found to contain excessive amounts of calcium when prepared by coreduction. The high zinc alloys were best prepared by comelting the pure constituents under pressure in a sealed iron chamber. On the zinc-rich side of the diagram there is evidence that a eutectic having a temperature of 416°C may occur at only about 0.1% zirconium. A peritectic with a decomposition temperature of 550°C is associated with an alloy phase of about 8% zirconium. The liquidus line rises very sharply from the eutectic to about 850°C for 1.25% zirconium.

2. Thorium

2.1 Thorium Metal Production (1)

Since the thorium plant was scheduled to be completely closed down, cleaned up and most of the workmen laid off by the end of June, the main production line was shut down before the end of April. During the short production period, which amounted to three weeks at full production, over 10,400 pounds of finished billets were produced, utilizing the new casting cars recently completed. All of the material produced during this period was made from sulfate-free thorium nitrate and was hydrofluorinated through the rotary hydrofluorination furnace.

During the remainder of the period, all of the outlying scrap material and thorium compounds were reclaimed by purification or casting to reduce the over-all inventory. All usable metal was cast into the form of billets of various shapes, the remainder being shipped to Fernald for storage and future processing.

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It was decided by the various groups in the Laboratory that there was a chance that thorium metal and compounds of comparable purity might not be readily available or obtainable for some time and that it would be wise to stockpile quantities of the various thorium compounds as well as some of the crude biscuits and finished billets. Consequently, the following stockpile was carefully prepared, weighed, and sealed for future use:

Thorium Nitrate Tetrahydrate	3998.06 lbs.
Thorium Oxalate	1000.00 lbs.
Thorium Oxide	3010.14 lbs.
Thorium Fluoride	2037.10 lbs.
Thorium Biscuits	640.00 lbs.
Thorium Billets	2317.53 lbs.
Thorium Scrap	114.20 lbs.

This material will be used from time to time by the various research programs preparing various alloys and to improve upon the wet hydrofluorination methods.

Some material was produced during the month of May, but the greater portion of this month was spent cleaning and decontaminating the various thorium areas in the Metallurgy Building. This cleaning program involved scrubbing the rooms from ceiling to the floor, decontaminating and removing equipment, and monitoring the entire area to see that a satisfactory job had been accomplished. In many instances a number of scrubblings and dilute acid washes were required before acceptable limits could be reached. After the decontamination was complete, most of the areas were placed in stand-by condition with the equipment in readiness for any future pilot plant work. It was decided not to dismantle much of the equipment at this time since future developments might possibly utilize this equipment with only minor changes for other development programs. The need for laboratory space will also be a factor in determining the future disposal of some of the more special pieces of equipment.

The first large scale uranium metal plant for producing the metal for the Manhattan District during the war years was set up in a temporary building, known as Annex #1. Later it served as a pilot plant area for thorium production and then as storage space. The dismantling team in cooperation with Health Physics and Safety Groups worked carefully to remove all of the inside equipment and wall and ceiling lining of Annex #1 to decontaminate same wherever feasible, and to destroy either by burning or burying the remaining contaminated equipment. A set of tolerances for the activity level was set up by the Radiochemistry Section and was followed with regard to the disposal of the various materials. It was discovered after removing the inside lining that most of the dimensional lumber and sheathing was not contaminated and could be salvaged. Consequently, care was taken in its removal so as to give the most possible salvage value. The electric switches and plumbing fittings were cleaned

and stored for further use throughout the project. The windows were saved for their glass. Other materials too numerous to mention were added to the maintenance stock for further use. The resulting material, including the bag-house dust-filtering equipment, amounted to some ten or twelve truck loads which were hauled to the synchrotron site and buried under six to eight feet of dirt by the use of a bulldozer and a dragline. After the entire superstructure of the building had been removed, the area was hosed down and turned over to the Physical Plant Department of the College for the destruction and removal of concrete work.

2.2 Preparation of Thorium Chloride (5)

Development of a method of preparing pure anhydrous thorium chloride was continued. The chlorination of a mixture of thorium oxide and carbon was carried out on a slightly larger scale. A temperature of about 1000°C was necessary to achieve distillation of the product at a reasonable rate. Mechanical carry-over of thorium oxide and carbon resulted in contamination of the product. Attempts were made to reduce this contamination by the use of porous diaphragms or by baffles. These changes improved the quality of the product but some contamination still occurred. The principal problem at the present time is improvement of the purity of the thorium chloride so that it will be suitable for reduction to thorium metal.

Chlorination of thorium oxide with carbon tetrachloride was investigated. Conversion of thorium oxide to chloride without distillation by maintaining the temperature below the distillation temperature of thorium chloride was incomplete and resulted in a product containing considerable amounts of thorium oxide even after five hours. Carbon tetrachloride was unsatisfactory as a chlorinating agent at temperatures above 800°C because of decomposition of the carbon tetrachloride. This resulted in contamination of the product by carbon.

2.3 Reduction of Thorium Oxide (1)

Work was continued on the reduction of thorium oxide. Some thorium oxide was produced by drying thorium hydroxide at 350°C . This oxide reduced with calcium to give a nearly 100% yield of powdered metal. A slug pressed from this material was sintered in a calcium atmosphere at 1100°C for eight hours. The sintered slug had a density of 68% of cast metal and a hardness of Rockwell B65.

An attempt was made to reduce thorium oxide with a mixture of calcium and sodium; 12 g. of calcium and 9.2 g. of sodium were mixed with 52.8 g. of thorium oxide. The reaction apparently did not go to completion as there was much thorium oxide in the product.

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2.4 Melting and Casting of Thorium (1)

An experiment set up with the idea of improving the quality of the castings made in regular thorium production was attempted. The desired improvements were better surface on the ingot and less pipe. Since the production mold was made of two sections of graphite it was decided to change the design and/or material of the upper section in order to give a slower cooling rate on that part of the ingot. The effect was to be that of increasing the hot-top and should tend to give the two improvements desired.

Since carbon has a much lower thermal conductivity than graphite the upper section of a mold was made of carbon with the same form as the graphite which it replaced. The carbon is much more difficult to machine than graphite; however, the section was shaped and fit in place. A melt was poured into this combination mold. The carbon broke, however, and let most of the metal in that section loose. There was sufficient residual metal surface left in contact with the mold to show that a very good surface was obtained on the casting in the upper section. This indicated a very good hot-top effect which should have given a better quality ingot had the mold not broken. Further work should be done employing a low thermal conductivity upper section of the mold. This variation in mold design should also be quite effective in eliminating many of the defects now obtained in uranium ingots by present production methods. Since we have turned thorium production over to industry, it has been necessary to suspend work on this development at this time.

2.5 Properties of Thorium Metal (6)

It was previously reported that the lattice constant of thorium was a linear function of the temperature; however, additional work has been done at higher temperatures. This work reveals that the lattice constant of thorium is a straight line function of the temperature up to approximately 1200°C. Above 1200°C there is a slight increase in the slope of the lattice constant vs. temperature curve. The lattice constant for production grade thorium at room temperature was found to be 5.089 angstrom units, at 1200°C the lattice constant was 5.161, and at 1450°C the lattice constant had increased to 5.181 angstrom units. The accuracy of these lattice constants are believed to be $\pm .005$ angstrom units.

The lattice constant of thorium oxide in contact with thorium metal was also calculated. The lattice constant for thorium oxide was plotted against the temperature and was found to gradually increase with temperature, but was not a linear function.

The transformation temperature is increased by the impurities in production grade thorium. The limit of this increase has not yet been determined. The thorium transformation temperature

extrapolated to zero carbon impurity is $1380 \pm 25^{\circ}\text{C}$. The room temperature resistivity extrapolated to zero carbon impurity is about 15×10^{-6} ohm-cm.

2.6 Thorium Alloys

a. Thorium-Magnesium Alloy System (5)

Evidence of a peritectic reaction in this system at 770°C was found. It is believed that at this temperature the thorium-rich compound reacts with the liquid to form the magnesium-rich compounds. Work is being continued on the isolation and identification of the intermetallic compound in this system.

b. Thorium-Titanium System (2)

The thorium-titanium alloy system has been investigated and a phase diagram proposed. A final report of the work is now being written. The system is of the eutectic type with no detectable terminal solid solubility. The eutectic temperature is 1190°C , and the eutectic composition 12 weight per cent titanium. The titanium allotropic transformation temperature is not altered by the presence of thorium. The effect of titanium on the thorium allotropic transformation was not studied directly, but no evidence was found to indicate appreciable solid solubility of titanium in beta thorium. The thorium liquidus and the titanium liquidus were determined experimentally and found to be smooth curves with no points of inflection.

The addition of titanium to thorium was found to increase the hardness rapidly as the eutectic composition was approached after which it was found to rise gradually to the titanium hardness value. A marked decrease was observed in the ability of the alloys to withstand cold-rolling as compared to pure thorium. However, all the alloys withstood 80 per cent or more reduction before cracking excessively.

Corrosion tests were conducted on alloys containing 0, 2.5, 5, 10, 15 and 25 per cent titanium all of which had been melted in graphite. After four weeks in boiling distilled water at atmospheric pressure none of the specimens had disintegrated. The weight changes increased with increasing amounts of titanium so that it would appear that titanium has a slight deleterious effect on the corrosion resistance of thorium melted in graphite. However, the melting of the thorium-rich alloys in graphite introduced considerable carbon that imparted marked hardness to the metal.

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c. Niobium-Thorium Alloy System (2)

The investigation of the niobium-thorium system has been completed and a phase diagram proposed. A final report of the work is now being written.

Niobium forms a eutectic with beta thorium at about 1435°C at 8 per cent niobium. The extent of solid solubility is very limited at both ends of the system at all temperatures. The maximum solubility is considered to be less than 1% niobium in thorium at the eutectic temperature. The addition of niobium to thorium lowers the reported alpha-beta transformation slightly. No intermediate phases were found in this investigation.

d. Thorium-Carbon Alloys (5)

The investigation of the solubility of carbon in solid thorium was continued. The samples prepared previously were heated at several temperatures and quenched. The solubility limits were determined by x-ray diffraction and confirmed by microscopic examination. The solubility limit at room temperature is 0.37 weight per cent, at 1018°C is 0.53 weight per cent, and at 1215°C is 0.87 weight per cent.

3. Other Process Metallurgy Studies

3.1 Treatment of Ores Containing Niobium and Tantalum (1)

A basic fusion of ores containing niobium and tantalum values is being employed quite successfully for a great variation in ore composition. High grade niobite-tantalite ores as well as ores containing smaller amounts of niobium and tantalum associated with rare earths are opened quite readily by the basic fusion.

In general small scale charges contain 10 grams of the powdered ore, 8 grams of NaOH and 4 grams of Na₂O₂. The charge is heated for about one half hour in a furnace held at 650°C. The product is treated with 1 M-NaOH solution giving a residue that is treated with dilute HCl. The residue from the HCl treatment is usually white and contains essentially all of the niobium and tantalum as acids. These acids are soluble in aqueous KOH and in aqueous HF; thus, they give solutions for making further separations and purifications. The residue from these solution treatments contain essentially the unreacted ore which can be recycled.

The most troublesome impurity associated with the niobium and tantalum seems to be titanium. It appears that removing the titanium to trace amounts is more difficult than the separation of niobium and tantalum. So far, experiments on removal of the titanium have indicated, essentially on a qualitative basis, that

a liquid-liquid extraction might be successfully employed. The results cannot be fully evaluated until an analytical procedure now being developed to give quantitative data is completed.

3.2 Niobium and Tantalum Separation Studies (1)

Work was continued on separations of Nb and Ta by means of liquid-liquid extraction. These two elements can be separated quite readily by liquid-liquid extraction employing a strong HF solution. Good separations and good material transfers are obtainable with a variety of organic compounds. Several methods have been tried to reduce or dispense with the HF. These attempts have not yet been too successful.

NH₄F was found to increase the pH of the feed material and in extractions increased the purity of the Ta transferred to the organic phase. However, the amount of material transferred was reduced considerably. This seemed to be generally true of any of a number of materials that have been used so far to increase the pH of the feed solution.

3.3 Separation of Rare Earths by Liquid-Liquid Extraction (1)

The separation of rare earth mixtures by liquid-liquid extraction has been investigated with tributyl phosphate primarily being employed as the organic phase. However, in this treatment a series of organic phosphites have been reported and their results compared with similar organic phosphates.

Single stage extractions were carried out employing the various pure organic solvents. The aqueous phase was 0.5 M in AlCl₃, 0.12 M in HNO₃ and contained rare earth nitrates equivalent to 280 grams of rare earth oxides per liter. The rare earth mixture was prepared from a product obtained by a sodium hydroxide-sodium peroxide fusion of gadolinite ore. Equal volumes of the organic and aqueous phases were employed in each extraction. The following table contains the results of this investigation in terms of the separation of yttrium and gadolinium. The distribution values, K, (concentration in organic phase divided by concentration in aqueous phase) are given together with Gd-Y separation factors.

Several generalities were evident from the data obtained when employing these organic phosphites. As their molecular weight increased less material was extracted into the organic phase. However, as the distribution values decreased the separation factors increased. A plot of the distribution value against the separation factor indicated a fairly linear inverse relationship. The values for di-2-ethylhexyl hydrogen phosphite did not follow the above trends because of low stability in this acid system. Partial hydrolysis of this organic phosphite resulted in the formation of rare earth phosphite and subsequently inaccurate

oxide weights. Diethyl hydrogen phosphite because of its rapid hydrolysis gave a completely miscible system. On a basis of percentage in the recovered rare earth oxide, gadolinium was enriched in the aqueous phase in each case, while for the low molecular weight stable phosphites, yttrium tended to concentrate in the organic phase. This trend for yttrium was reversed for the high molecular weight organic phosphites.

Separation of Yttrium from Gadolinium Employing Organic Solvents

Organic Solvent	Number of Carbon Atoms	K_{Gd}	K_Y	Separation Factor
1. Dibutyl hydrogen phosphites	8	1.15	1.79	1.56
2. Tri-2-propyl phosphite	9	0.88	1.43	1.63
3. Tributyl phosphite	12	0.61	1.07	1.76
4. Di-2-ethylhexyl hydrogen phosphite	16	0.33	0.58	1.74
5. Trihexyl phosphite	18	0.35	0.64	1.83
6. Tri-2-ethylhexyl phosphite	24	0.21	0.41	1.98
7. Tri-isooctyl phosphite	24	0.21	0.42	2.00
8. Tributyl phosphate	12	0.61	0.83	1.36
9. Tri-2-ethylhexyl phosphate	24	0.28	0.38	1.41
10. Tricresyl phosphate	21	0.080	0.095	1.19
11. Tributoxyethyl phosphate	18	0.38	0.65	1.71

Upon comparison of similar organic phosphites and phosphates as solvents, it appears that higher separation factors and distribution values were obtained in the phosphite systems. More material was extracted into the organic phosphite than the corresponding phosphate. On a percentage basis there was little difference in the Y_2O_3 content in the organic phase, but the amount of Gd_2O_3 was observed to be greater for the organic phosphite phase than for the corresponding phosphate. The assumption that the organic phosphites do not oxidize to phosphates in this dilute HNO_3 medium has been

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made. These data indicate that less stages would be required for separation of yttrium from gadolinium when employing the phosphites rather than the phosphates. The low stability of the organic phosphites, however, would probably decrease their utility for a continuous operation.

All the above comparisons were made with the organic radicals containing aliphatic chains. When an aromatic substituted phosphate, such as tricresyl phosphate, was employed a low transfer and separation factor were observed. This indicates that not only the number of carbon atoms is important in this extraction but perhaps their spacial arrangements are also significant. The cresyl groups appear to be less effective for gadolinium-yttrium separation than the normal paraffin constituents. These extractions indicated that the doubly bonded oxygen of the phosphate radical is not an important factor in this extraction.

3.4 Niobium Metal Preparation Studies

a. Reduction of Nb₂O₅ with Carbon (1)

On the reduction of niobium pentoxide to pure metal by carbon some progress has been made in determining the nature of the reduction. Apparently two of the five oxygen atoms are removed below 1000°C in vacuo; the black Nb₂O₄ first being formed, then the blue Nb₂O₃. At higher temperatures, the black Nb₂O₂ is formed; then after the evolution of much gas the sample is distinctly gray in color. After this, more gas is evolved before a metallic appearing sponge is formed at a temperature of about 1650°C as read by optical pyrometer. An attempt will be made to find out if this gray powder is in reality an unreported lower oxide, the metal, a carbide or a mixture.

b. The Reduction of Nb₂O₅ with Calcium (1)

A mixture of calcium and aluminum with excess aluminum yields biscuits of a niobium-aluminum alloy. Feeling that the aluminum might be difficult to remove, a lower boiling alloying metal was sought. Two metals to replace aluminum were tried. Magnesium oxide forms a lowered melting mixture with calcium oxide; magnesium can be distilled at a relatively low temperature and it is reactive enough to reduce Nb₂O₅. These facts led to the trying of a calcium-magnesium reducing mixture. The mixture yielded no biscuit, as nothing appeared to have melted. So a booster of KClO₃ was added to the next charge. Enough booster to add over twenty kilogram calories of heat per mol of Nb₂O₅ did not improve the product.

Antimony with a closest-approach-of-atoms figure of 2.898 Å^o as compared to niobium's 2.845 Å might offer some possibility of forming a low melting alloy with niobium. Antimony is considerably lower boiling than aluminum, but it is not reactive enough to be a

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reducing agent. Metallic antimony was added to a charge using only calcium as a reducer. No melting, no biscuit, essentially no metallic niobium product resulted from this experiment.

In order to try to separate the aluminum from the niobium, a sample of aluminum-niobium alloy was heated in the induction furnace under reduced pressure. A biscuit heated to 1800°C for 30 minutes lost no weight, so it was heated to 1900°C for 30 minutes and lost 4.4% of its weight. A third heating, this time at 1900°C for 90 minutes, resulted in an additional weight loss of 3.4%, a total weight loss of 7.8%. Calculated from the charge, the aluminum content of the sample should have been 22 weight per cent. So most of the aluminum remained in the alloy at this temperature. A sample is being analyzed for more accurate determination of aluminum content. Further work is to be done in attempting to remove the aluminum from the alloy; this might be possible by pulverizing the alloy, pressing into bars and sintering, then heating the bars at reduced pressure by their electrical resistance to a higher temperature.

3.5 Vanadium Metal Preparation Studies (1,2)

The preparation of vanadium metal is now being studied. Work in this Laboratory a few years ago showed that good quality vanadium metal could be obtained by the reduction of V_2O_5 with calcium metal if a booster of sulfur and calcium coreacted. Elsewhere it was shown that the metal could be obtained with an addition of iodine to the charge. In these cases of bomb reductions the calcium additions to the charges were far in excess of stoichiometric amounts in order to get yields of as much as 80 per cent of theoretical vanadium metal. The cost of good quality calcium metal adds considerable to the cost of vanadium metal by this bomb reduction process. The revision of studies on vanadium preparation is being directed toward factors that would possibly reduce the cost of metal and retain or improve on the quality of metal obtained by current processes. At present variables such as bomb liner materials, boosters and the possibility of reducing a lower oxide or other compounds of vanadium are a part of the revised investigation.

3.6 Reduction of Uranium Oxides (1)

Some exploratory work was again undertaken on the reduction of uranium oxides. A mixture of 30 g. of uranium trioxide and 10 g. of magnesium with 40 g. of barium chloride for flux was heated in a graphite crucible under helium. A reaction appeared to take place, but metallic uranium was not readily separable after heating to 1200°C. The use of an equivalent amount of uranium dioxide, magnesium and 80 g. of barium chloride was similarly unsuccessful. Replacing the magnesium with calcium was likewise of no help.

A mixture of 27 g. of uranium dioxide, 6.5 g. of sulfur and 24 g. of calcium was fired in a calcium oxide lined bomb. About 10.3 g. of uranium in the form of small beads was recovered from the bomb. A second bomb was charged with a mixture of 54 g. of uranium dioxide, 6.4 g. of sulfur, and 36 g. of calcium. The uranium recovered from the bomb in the form of coarse particles weighed 18.7 g. The quality of this metal was questionable.

It was thought that better results might be obtained with the reduction of UOS, uranium oxysulfide, instead of with the mixture of uranium dioxide and sulfur. It was reported that UOS could be prepared by heating uranium dioxide in sulfur vapor but an experiment to test this did not yield the desired product.

Efforts to reduce oxides of uranium with the aluminum-calcium mixture employed successfully with Nb_2O_5 have not yet yielded satisfactory metal.

3.7 Preparation of Vanadium Fluoride (2)

Vanadium fluoride is of interest in the vanadium metal preparation. It is thought that by using the fluoride, a high quality, ductile, vanadium metal could be obtained when the fluoride is reduced with calcium or possibly magnesium. In the bomb reduction, good slag separation should be obtained, since calcium fluoride or magnesium fluoride would be formed. These fluorides are relatively low melting (about 1400°C) in comparison with the oxides which are formed when the oxide is reduced with calcium or magnesium.

It has been found that a mixture of vanadium pentoxide and ammonium bifluoride (solid) when allowed to sit overnight react to form a golden yellow product. The identity of this compound has not yet been established. If this is an ammonium-vanadium fluoride complex, it may be possible to drive off the volatile ammonium fluoride or bifluoride, and obtain the desired vanadium fluoride in a relatively pure form.

It has also been observed that the formation of the golden yellow compound does not occur when ammonium bifluoride and vanadium trioxide are mixed and allowed to stand.

4. Other Metal and Alloy Studies

4.1 Uranium-Magnesium Alloys (6)

Work on the uranium-magnesium system was concluded during this period. A final report, ISC-377, will be available in the near future.

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The chief difficulty encountered in the study of this system was the contamination of the alloys by impurities from various crucible materials used during their preparation. This resulted in the appearance of extraneous phases in the microstructures. The use of high purity magnesia to which 10 weight per cent MgF_2 was added proved to be a satisfactory crucible material. These crucibles were non-porous to magnesium-rich melts over the temperature range studied.

No intermetallic compounds are formed in this system. The two metals are practically immiscible in the temperature range between room temperature and 1255°C . The solubility of uranium in magnesium was determined by heating the two metals in contact with each other in magnesia crucibles to the desired temperature, quenching, and then analyzing the magnesium-rich portion for uranium content. Heating was done under three atmospheres of helium pressure. Magnesium was also sealed inside small uranium bombs for solubility determinations at temperatures below the melting point of uranium.

The compositions of the two liquids that co-exist under a pressure of three atmospheres at 1150°C are approximately 0.16 weight per cent uranium in magnesium and 0.004 weight per cent magnesium in uranium. The solubility of uranium in magnesium decreases to nearly 0.05 per cent at 675°C and to about 0.0005 per cent at 650°C . Uranium has little or no effect on the melting point of magnesium, and magnesium likewise has little effect on the melting point or transformations of uranium.

The final liquidus line of the magnesium-rich end of the system at three atmospheres pressure was obtained by a statistical treatment of the solubility data obtained. The final results are given in the following table.

Solubility of Uranium in Magnesium at Various Temperatures

Temperature $^\circ\text{C}$	Weight Per Cent Uranium
650	0.0005
660 $\pm$ 5	0.008 $\pm$ 0.006
695 $\pm$ 15	0.055 $\pm$ 0.028
775 $\pm$ 10	0.061 $\pm$ 0.024
845 $\pm$ 10	0.069 $\pm$ 0.024
920 $\pm$ 10	0.074 $\pm$ 0.026
980 $\pm$ 5	0.101 $\pm$ 0.036
1030 $\pm$ 5	0.098 $\pm$ 0.028
1090 $\pm$ 15	0.112 $\pm$ 0.065
1135 $\pm$ 5	0.124 $\pm$ 0.051
1225 $\pm$ 20	0.190 $\pm$ 0.040

4.2 Uranium-Niobium Alloys

a. Properties of Uranium-Niobium Alloys (3)

A new series of uranium-niobium alloys covering a range from 0.25 to 40 weight per cent niobium has been prepared. These alloys are being used in an investigation of the region of the constitutional diagram near the transformations in uranium.

The uranium-rich alloys can be rolled cold after an annealing treatment and alloys containing 15 or 20 per cent niobium can be swaged hot but some compositions are difficult to fabricate by any process. Partly because of this situation, much of the work has been done with pieces of ingot.

Dilatometric measurements have shown that the addition of niobium lowers the beta to gamma transformation sharply and raises the alpha to beta transformation slightly. Graphs for most of the alloys show additional anomalies that are not understood and make interpretation difficult.

Melting point determinations show that the solidus line rises steadily with increasing niobium content up to about 50 per cent niobium. The 50 per cent alloy begins to melt at about 1825°C. Alloys between 50 and 80 per cent niobium are difficult to melt and no data have been obtained on them.

b. Preparation of Uranium-Niobium Alloys by Bomb Reduction (2)

Experimental bomb reductions have been carried out in a study of methods for preparing a 5 per cent niobium in uranium alloy. Good homogeneous alloys have been prepared by adding niobium powder to the bomb charge. Equally successful results have been obtained by adding niobium pentoxide or niobium pentachloride to the bomb charge. Little difference could be observed in the quality of the alloy prepared by the three different additions; however, the use of niobium oxide or of niobium powder gave best yields and control of composition. These small scale bomb reductions were made with UF₄ and calcium metal.

4.3 Niobium-Vanadium Alloys (2)

Work on this system has been nearly completed and a final report is being written. Niobium and vanadium have been shown to form a complete series of solid solutions. No evidence of a second phase was found for this system above 650°C. The solidus curve has a long, nearly flat minimum extending from about 10 to 50 per cent niobium with the minimum temperature at about 1805°C near the composition of 35 weight per cent niobium. The liquidus curve lies very close to the solidus curve throughout the system.

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Alloys prepared from niobium powder were brittle and could not be cold rolled whereas those prepared from niobium sheet were much softer and ductile. This difference is believed to be due to impurities in the niobium powder. Alloys prepared from sheet niobium were reduced as much as 90 per cent in thickness by cold rolling without serious edge cracking.

Corrosion tests were made on the 5, 10 and 50 per cent niobium alloys, niobium sheet and vanadium sheet. After 375 hours in 178°C distilled water there was little change in the appearance of the alloys and weight changes were all within experimental error (0.0003 grams).

Similar tests were then carried out at 250°C for 60 hours. Except for the vanadium specimen which was covered with a black film, the specimens were only slightly tarnished. A further test at 330°C for 60 hours produced a black film on all specimens but none had disintegrated. The vanadium and the 5 per cent niobium alloy showed most attack.

4.4 Aluminum-Vanadium Alloys (2)

Continuing the investigation of the Al-V system, intensity calculations were made for the intermediate phase, δ (Al-V), in order that a possible formula could be chosen by comparison with the relative intensities of a powder photograph.

The microscopic investigation showed that an isotropic one-phase region existed near 56 per cent vanadium. The x-ray photographs of alloys in this range indexed as a body-centered-cubic cell with $a_0 = 9.207 \text{ \AA}$. Since single crystal data were not available, no unique space group determination could be made. However, it was known that the structure must conform to some sort of a superlattice since a_0 was exactly three times as long as a_0 for the saturated solid solution of Al in vanadium (V), and the strong lines of δ (Al-V) were the body-centered lines of (V).

A survey of the literature suggested that δ (Al-V) belonged to the γ -Brass type of structure of which there are 32 known representatives. The cell contains 52 atoms and belongs to the space group $T_d^3 - I 43m$. Symmetry considerations would permit only three possible formulae: Al_9V_4 , Al_8V_5 , and Al_7V_6 . Also the space group permits two possible arrangements of Al_8V_5 . One arrangement corresponds to that shown by Al_8Cr_5 which has a distorted γ -Brass structure, and the other arrangement corresponds to that of Zn_8Ag_5 .

A powder photograph was obtained from a 58 per cent vanadium alloy for comparison between the calculated intensities and the observed intensities. The numerical intensities were calculated by an approximation method used by Bradley and Thewlis in the original structure determination of γ -Brass. The structure that

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was isomorphous with Zn_8Ag_5 gave the best fit of the calculated to the observed powder intensity of a 58 per cent vanadium alloy.

Alloys were also made up in the range of 15 to 28 per cent aluminum in order to determine the exact composition of β (Al-V). Microscopic examination of these alloys indicated that Al_6V was the probable formula for β (Al-V). As has been previously reported the compound has been indexed as hexagonal with $a_0 = 7.718 \text{ \AA}$ and $c_0 = 17.15 \text{ \AA}$.

By use of a single crystal of β (Al-V) relative intensities were calculated of spots on a pattern obtained by the precession camera. The intensity calculations were used to make a Patterson projection in an effort to determine the structure of the β (Al-V) phase.

4.5 Uranium-Molybdenum Alloys (3)

A limited investigation is under way for the purpose of obtaining information on the behavior of alloys of uranium containing 8 to 15 per cent molybdenum. The first published constitutional diagrams indicated that the gamma phase persisted to room temperature within this limited range, but this conclusion has not been accepted by all metallurgists.

As resistance-temperature measurements can show whether an alloy is undergoing change with time, they are being used to determine whether an alloy in the gamma state will revert to the alpha state at any temperature. The 10 per cent molybdenum alloy, the only one tested as yet, appears to revert to the low temperature form in a matter of hours at 450°C and undoubtedly would do so more slowly at a much lower temperature.

In the equilibrium state, the 10 per cent alloy shows a marked discontinuity in resistance at 570°C .

4.6 Casting Uranium onto Uranium-Niobium Alloy (2)

The investigation of methods of bonding uranium to the corrosion resistant 7.5% niobium-uranium alloy by direct casting of uranium onto alloy disks has been continued. By first electrodepositing a thin copper film on the alloy surface good continuous bonds have been obtained. The coated alloy is preheated to 850°C - 900°C and molten uranium is poured onto it. By raising the bonding temperature to 1180°C (just below the melting temperature of the alloy) a good continuous bond can be formed. The conditions appear to be quite critical, however.

4.7 Coating Uranium (6)

Some work was done in an attempt to improve the aluminum coat obtained when it is electroplated from the $AlCl_3$ -NaCl molten salt

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bath. Imposing an alternating current over the regular direct current with variations in the ratio of the direct current to the alternating proved to be of little effect in improving the thickness of the Al coat. The alternating current was either equal to or up to three times greater in value than the direct current used.

Copper plating on uranium with copper cyanide plating baths was employed in an attempt to improve the adherence of the copper to uranium. The copper coat deposited from a cyanide bath was then built up further by copper deposited from the copper sulfate bath. Corrosion testing in boiling water showed that copper coats plated from cyanide alone, sulfate alone, and combinations of the two were all porous and provided little protection for the uranium.

Attempts were then made to find some method of decreasing the permeability of the copper coat by first putting a zinc coat on the uranium, then electroplating a copper coat over the zinc, and applying some form of annealing, buffing, or dipping in other liquid metals to seal the whole coat.

Uranium samples were polished, cleaned anodically, and washed in acetone. They were then coated with zinc either by electro-deposition or by dipping in molten zinc. The latter proved to be the best way to apply zinc. The electrodeposited zinc was very non-adherent. The temperature of the zinc metal bath ranged from 440°C up to 508°C . The samples were dipped for various lengths of time up to five minutes. These samples were then plated with copper of various thicknesses of up to 3 mils. Current densities of 15-30 amps/ft² were used.

Samples prepared in the above manner were then annealed in several ways. A molten lead bath using a surface flux of equal molar ratios of KCl, LiCl, and NaCl was used. Annealing at temperatures both above and below the melting point of Zn (419.6°C) were used. Some lead stuck to the copper coats and the annealing treatment appeared to have a detrimental effect on the copper. The treatment showed that the zinc was not completely adherent to the copper. Samples were also annealed in a molten salt bath of the equal molar ratio KCl-LiCl-NaCl flux at 440°C . The flux apparently enters flaws in the copper-zinc coat and reacts with the uranium underneath. After five minutes in the bath, the whole copper coat was undercut. Similar results were obtained when a bath of 42 mole per cent KCl, 58 mole per cent LiCl was used to anneal samples up to 562°C . The zinc and copper form intermetallic phases or compounds when the samples are heat treated. Whether separation of the coat is due to compound formation or undercutting by the fused salt is uncertain. At any rate, the heat treatment proved detrimental to the corrosion resistance of the composite coat as corrosion samples failed in from 11-96 hours in boiling water. Unannealed samples are not undercut by boiling water after 192 hours but do show some pitting.

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Some of the KCl-LiCl salt mixture was used with a small amount of CuCl to see if copper could be deposited by chemical means on the zinc. Copper was deposited, but it proved to be rather scattered and non-adherent. It appeared to have the same effect on regular copper-zinc coats when the above bath was used for annealing as the regular LiCl-KCl bath.

Another molten metal bath which is being used is mainly magnesium. Into this bath other materials are put with the hope that they will diffuse into the uranium. The materials which have been used in this manner recently include nickel, zirconium and silicon.

The samples have been treated by dipping in the bath for periods of time ranging from four minutes up to two hours, at temperatures from 600°C to 850°C. Prior to dipping in the metal bath the samples were polished on 240 grit silicon carbide paper, degreased in trichloroethylene, then either alternately dipped in 1:1 nitric and concentrated hydrochloric acid, or anodically treated in a 5:3:1 solution of sulfuric acid, water and glycerine. In either case it was difficult to obtain consistent uniform wetting of the surface by the molten metal bath. Further work is being done on this problem.

4.8 Rare Earth Metallurgy

(Reported in ISC-394.)

4.9 Uranium-Thorium-Magnesium Alloys (5)

The preliminary investigation of the solubility of uranium in thorium-magnesium eutectic alloy was completed. The thorium-magnesium alloy was heated in contact with uranium metal for 36 hours at temperature, then quenched to room temperature and analyzed for uranium. The results of the investigation are given in the following table.

Solubility of Uranium in Thorium-Magnesium Eutectic Alloy

Temperature	Per Cent Uranium by Weight
650°C	0.06
700°C	0.12
750°C	0.15
800°C	0.4
850°C	0.4
900°C	0.9
950°C	0.6
985°C	0.5

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The experimental errors in the tests are quite large and the values are probably somewhat high so the results are to be taken as indicating merely the low solubility of uranium in the liquid alloy.

4.10 Uranium-Zirconium-Niobium Alloys (2)

A preliminary survey of some uranium-rich alloys containing zirconium and niobium revealed promising corrosion resistance in most of the alpha annealed alloys containing a minimum addition of 5 weight per cent niobium when tested in boiling distilled water. Five of these alloys with the best corrosion rates in boiling water were given a test in a 178°C autoclave. Of those tested, only the 16.7% Zr-10% Nb alloy was intact after 100 hours. A series of alloys containing 1% increments of zirconium and niobium up to 5 weight per cent of each element was prepared by arc-melting. These were homogenized at 850°C for 2 hours, alpha annealed at 400°C for 16 hours and furnace cooled. Corrosion, microscopic and hardness tests were made on this series of both the annealed and gamma quenched state. All alloys except the 1 per cent Nb-1 per cent Zr alloy stood up in a short time (36 hours) autoclave test (178°C H₂O) in the gamma quenched condition. As was expected all of the alloys in the annealed condition disintegrated completely in the same test.

Hardness data were also taken on the alloys in this series. The zirconium shows a slight tendency to harden uranium in the alpha annealed state and imparts an increased hardness also in the gamma quenched state. Niobium increases considerably the hardness in the alpha annealed condition but in the gamma quenched state the effect is much less.

Microscopic examination of the annealed series revealed solid precipitation in the ternary alloys, resembling that found in uranium-zirconium binary alloys. The 1 per cent Zr-1 per cent Nb alloy has a hypoeutectoid structure. In the gamma quenched condition all alloys appear to have been quenched from a one phase region.

4.11 Tantalum-Vanadium Alloy System (2)

Work was begun on the Ta-V system. Alloys of 5, 25 and 50 nominal weight per cent were prepared by arc-melting of bomb reduced vanadium with Fansteel tantalum sheet. The as-arc-melted alloys had the following R_A hardness:

100 % V	-	R _A	61
5 % Ta-V			65
25 % Ta-V			71.5
50 % Ta-V			74

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Metallographic examination showed all alloys to be single phase in the arc-melted condition indicating an extensive range of solid solubility.

4.12 High Temperature X-Ray Structure of Vanadium (6)

Samples of vanadium were run in the high temperature x-ray diffraction equipment. The samples were heated in a helium atmosphere to reduce vaporization during the high temperature measurements. The extrapolated lattice constant of vanadium at room temperature was 3.028 and at 1450°C was 3.087 angstrom units. A temperature of 1685°C was reached with only b.c.c. reflections being present. At temperatures above 1450°C only the 110 reflection remained.

5. Miscellaneous

5.1 Metal Displacement Reactions (5)

Preliminary work on the displacement of magnesium by calcium in chloride melts is under way. Conditions necessary to obtain a satisfactory separation at the salt phase and metal phase are being established. Sampling and analytical techniques are being checked for accuracy and reliability.

5.2 Lithium Studies (1)

Lithium isotope separation studies are awaiting suitable analytical procedures, as any exploratory work on separation depends largely on good analyses.

5.3 Solubility of Uranium-Chromium and Uranium-Iron Liquid Alloys in Liquid Thorium-Magnesium Eutectic (5)

The solubility of uranium-chromium and uranium-iron alloys in thorium-magnesium eutectic alloys was determined by heating the two alloys at temperature, quenching to room temperature and analyzing the thorium-magnesium alloy for uranium and chromium or iron. The results are given in the following tables.

Solubility of Uranium-Chromium Alloy in Thorium-Magnesium Eutectic Alloy

Temperature	Per Cent Uranium by Weight	Per Cent Chromium by Weight
900°C	0.26	----
950°C	0.5	0.03

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Solubility of Uranium-Iron Alloy in Thorium-Magnesium
Eutectic Alloy

Temperature	Per Cent Uranium by Weight	Per Cent Iron by Weight
800°C	0.13	0.07
850°C	0.58	0.08
900°C	0.87	0.4
950°C	0.5	0.3
1000°C	0.58	0.1

It is apparent that the presence of chromium or iron does not increase the solubility of uranium in the eutectic alloy (see part 4.9 above).

5.4 Corrosion of Tantalum, Zirconium and Niobium by Liquid Thorium-Magnesium Alloys (5)

An investigation of the corrosion of tantalum, zirconium and niobium by liquid thorium-magnesium alloys at 1000°C was continued during this period. Small crucibles were made of the metal to be tested, filled with the thorium-magnesium alloy, sealed by welding in an inert atmosphere, and, in turn, sealed in stainless steel crucibles to prevent oxidation. These crucibles were held at 1000°C in a muffle furnace for the desired periods of time. They were then opened, sectioned perpendicular to the sidewalls and examined under a microscope. The thickness of the remaining metal was measured by means of a calibrated eyepiece of a Tukon hardness tester. Results obtained for tantalum and niobium are given in the following tables.

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

Time	Thickness of Ta Sheet
0 days	0.0058 inches $\pm$ 0.0001
30 days	0.0051 inches $\pm$ 0.0001
60 days	0.0051 inches $\pm$ 0.0001
120 days	0.0049 inches $\pm$ 0.0001

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

Time	Thickness of Nb Sheet
0 days	0.0053 inches $\pm$ 0.0001
20 days	0.0048 inches $\pm$ 0.0001
40 days	0.0051 inches $\pm$ 0.0001

The tests show that tantalum and niobium are quite inert to the thorium-magnesium liquid alloy at 1000°C. Zirconium reacted excessively with this alloy.

5.5 Etching of Metals by Ionic Bombardment (3)

A more serious investigation of the usefulness of ionic bombardment as a means of etching metallographic specimens was undertaken during the quarter. In the ionic bombardment method, the specimen is made a part of the cathode in an electrical discharge tube operating at a low pressure of gas--argon in these experiments. Preliminary tests made during the 18 months since the apparatus was constructed had given encouraging results but did not lead to a definite decision as to the value of the method. The recent work indicates that etching by this method does give better results than any chemical or electrochemical procedure used to date on thorium and most thorium alloys. Superior results were obtained on uranium also. Etching of common metals by ionic bombardment has been tried in only a few instances. Results on brass indicate that the method gives surfaces as satisfactory but not better than chemical etching. The etching of a pearlitic steel was less satisfactory than may be obtained by chemical methods.

5.6 The CaO-CaF₂ System (1)

Work has been started on the CaO-CaF₂ system, aimed at locating the liquidus line in the high CaF₂ region and locating the solid solution range if any in the high CaF₂ region. The portion of this liquidus line is important in the bomb reduction of fluorides with calcium when oxide is present to give a slag of CaF₂ containing CaO. The CaF₂ in CaO-rich mixtures is important for consideration in connection with the addition of CaF₂ in making CaO crucibles. The method used to determine the liquidus has been the taking of cooling curves on mixtures of known compositions. Samples were heated through melting by induction in graphite crucibles employing chromel-alumel thermocouples and on automatic temperature recording device to obtain the heating and cooling curve data.

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Early results are somewhat indefinite due to impurities in the raw materials, but it seems probable from the runs made that calcium oxide reduces the melting point of the fluoride when present in small percentages. The minimum melting point appears to occur somewhere in the neighborhood of 16% CaO 84% CaF₂. These data agree fairly well with data in the literature on part of this system.

5.7 Studies of Liquid-Liquid Extraction (1)

The separation of optically active isomers has been given some attention in the exploratory work on liquid-liquid extraction. The elucidation of fundamental extraction principles is the objective here. It is thought that the steric configurations in solution might be a determining factor in the formation of soluble and extractable complexes.

A few tests have been made to determine the feasibility of separating the optically active isomers of racemic mandelic acid. An aqueous phase containing dl-mandelic acid and brucine has been extracted with benzene in one experiment and in another the extraction was made into tributyl phosphate. The total amounts of the acid transferred to the organic phase differed widely in these two tests; however, the dextro form favored the organic phase in both cases. Single stage extraction data indicate that a multi-stage extractor might be capable of essentially complete separation of the two isomers of dl-mandelic acid. Further work will be done on this problem as time permits.

5.8 Magnesium-Redistillation (2)

Early in this quarter enough calcium had been purified by distillation to meet all outstanding orders and supply the Ames Laboratory for several months, so that operation was closed down. Considerable badly-oxidized magnesium metal was on hand and the calcium stills were then employed in an effort to recover some of the magnesium.

The lower boiling point and higher sublimation pressure of magnesium as compared to calcium made it necessary to vary a number of operating conditions to assure a good yield of good quality magnesium from this material. The starting material was that which was left over from uranium production here during World War II. It had been ground and kept in drums for a number of years in contact with air, so it was too badly oxidized to use directly in bomb reductions.

After varying the conditions of operation sufficiently an over-all yield of 75% magnesium was recovered from 1,608 pounds of the starting material.

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

An investigation was started of the explosions which occur during and after the pickling of uranium-zirconium alloys in nitric acid. These explosions were found to be the rapid oxidation, by air or nitric acid, of a dark grey film formed on the surface of the alloy during pickling. Scratching or jarring the sample was necessary to start the explosion. The film was formed on alloys containing from two to twenty weight per cent zirconium. The film could not be produced on these alloys as arc-melted or when quenched from 725°C but could be formed if the alloy was annealed at 625°C or lower before pickling. Addition of fluoride ion to the pickling bath prevented the formation of this pyrophoric layer. The film was richer in zirconium than the parent metal and contained less uranium. An x-ray powder diffraction pattern of the film has not been identified.

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APPENDIX I: LIST OF REPORTS FROM THE AMES LABORATORY

1. Reports for Cooperating Laboratories

- ISC-271 A New Technique for the Separation of Radiophosphorus from Sulfur, by L. D. McIsaac and A. F. Voigt. UNCLASSIFIED.
- ISC-288 Sintering Mechanism as Applied to Refractory Oxides (Bibliography, 1937-1952), compiled by D. R. Wilder. UNCLASSIFIED.
- ISC-289 The Heat Capacity and Entropy of Thorium from 18° to 300°K, by M. Griffel and R. E. Skochdopole. UNCLASSIFIED.
- ISC-294 Performance of a Pulse Extraction Column, by R. Cohen and G. H. Beyer. UNCLASSIFIED.
- ISC-306 Some Magnetic Properties of Gadolinium Metal, by J. F. Elliott, S. Legvold and F. H. Spedding. UNCLASSIFIED.
- ISC-311 Thermal Diffusivity of Metals at High Temperatures, by P. Sidles and G. C. Danielson. UNCLASSIFIED.
- ISC-312 Calorimetric Apparatus in the Ames Laboratory, by M. Griffel and R. E. Skochdopole. UNCLASSIFIED.
- ISC-316 Rockwell and Vickers Hardness of Ames Thorium, by G. Murphy and E. Arbtin. UNCLASSIFIED.
- ISC-319 Operating Characteristics of a D.C. Magnetic Ion Source, by G. H. Miller, R. A. Lowry and J. E. Osher. UNCLASSIFIED.
- ISC-322 Quarterly Summary Research Report - Physics (October, November, and December, 1952) by the Ames Laboratory Staff. UNCLASSIFIED.
- ISC-323 Quarterly Summary Research Report - Metallurgy (October, November, and December, 1952) by the Ames Laboratory Staff. SECRET.
- ISC-327 Adsorption of Both Components from Binary Solution on Porous Adsorbents, by R. D. Hansen and R. S. Hansen. UNCLASSIFIED.
- ISC-330 A Generalization of the Polanyi Theory of Adsorption from Solution, by R. S. Hansen and W. V. Fackler. UNCLASSIFIED.
- ISC-331 Titration of Weak Bases in Acetic Anhydride Solvent Mixtures, by J. S. Fritz and M. O. Fulda. UNCLASSIFIED.

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- ISC-333 Reaction of Fe(II) with 1,2-Cyclohexanedionedioxime in Acid Solution, by C. V. Banks and E. K. Byrd. UNCLASSIFIED.
- ISC-334 The Kinetics of the Cerium(IV)-Chloride Reaction. The Cerium(IV) Thallous Reaction in the Presence of Chloride, by F. R. Duke and C. E. Borchers. UNCLASSIFIED.
- ISC-335 The Hall Effect in Yttrium, Lanthanum, Cerium, Praseodymium, Neodymium, Gadolinium, Dysprosium, and Erbium, by C. J. Kevane, S. Legvold and F. H. Spedding. UNCLASSIFIED.
- ISC-343 A New Approach to Direct Reading Spectrochemical Analysis, by R. K. Brehm and V. A. Fassel. UNCLASSIFIED.

2. Papers Published in Scientific Journals

- Banks, C. V., D. Klingman and C. H. Byrd
Spectrophotometric Determination of Thorium in Black Sands.
Anal. Chem. 25, 992-993, June, 1953.
- Barson, N. and G. H. Beyer
Performance Characteristics of a Podbielniak Centrifugal
Extractor. Chem. Eng. Prog. 49, 243-252, May, 1953.
- Cohen, R. and G. H. Beyer
Performance of a Pulse Extraction Column. Chem. Eng. Prog.
49, 279-286, June, 1953.
- Daane, A. H., D. H. Dennison and F. H. Spedding
The Preparation of Samarium and Ytterbium Metals.
J. Am. Chem. Soc. 75, 2272-2273, May, 1953.
- Fassel, V. A., A. M. Howard and D. O. Anderson
Conducting Briquet Technique of Spectrographic Analysis.
Analysis of Zirconium Metal as the Oxide.
Anal. Chem. 25, 760-763, May, 1953.
- Godycki, L. R. and R. E. Rundle
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487-495, June, 1953.
- Hiller, D. M. and D. S. Martin
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- Huke, F. B., R. H. Heidel and V. A. Fassel
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J. Opt. Soc. Am. 43, 400-404, May, 1953.

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Radiations from Selenium 75. Phys. Rev. 90, 557-563,
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Electron Deficient Compounds. VII. The Structure of the
Trimethylaluminum Dimer. J. Chem. Phys. 21, 986-992,
June, 1953.

Rundle, R. E.
The Deuterium Effect on Hydrogen Bond Distances in Crystals.
J. Chem. Phys. 21, 937-938, May, 1953.

Wheelwright, E. J. and F. H. Spedding
A Rapid Method for Fractionating Crude Rare Earth Ores
into Mixtures Greatly Enriched with Regard to Particular
Rare Earths. J. Am. Chem. Soc. 75, 2529-2530, May, 1953.

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APPENDIX III

- (1) H. A. Wilhelm
- (2) O. N. Carlson
- (3) B. A. Rogers
- (4) R. W. Fisher
- (5) D. Peterson
- (6) P. Chiotti

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