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SEMI-ANNUAL SUMMARY RESEARCH REPORT IN METALLURGY

For January - June, 1956

by

Ames Laboratory Staff

January 8, 1957

Ames Laboratory  
at  
Iowa State College  
F. H. Spedding, Director  
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2

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## TABLE OF CONTENTS

METALLURGY

	<u>Page</u>
1. Purification and Separation Studies. . . . .	7
1.1 Treatment of Ores and Separation of Niobium and Tantalum . . . . .	7
1.2 Studies on the Separation of Hafnium and Zirconium. . . . .	9
1.3 Pyrometallurgical Separation of Uranium From Thorium and From Thorium-Magnesium Eutectic. . . . .	10
1.4 Separation of Thorium From Thorium-Magnesium Eutectic by Precipitation as Thorium-Hydride . . . . .	14
2. Preparation of Pure Compounds. . . . .	15
2.1 Preparation of Thorium Tetrachloride . . . . .	15
2.2 Preparation of Yttrium Trifluoride . . . . .	15
2.3 Preparation of a Compound of Niobium Suitable for Alloy Formation by Bomb Co-reduction . . . . .	16
2.4 Preparation of Pure $V_2O_5$ . . . . .	18
3. Metal Preparation Studies. . . . .	19
3.1 Preparation of Vanadium Metal. . . . .	19
3.2 Preparation of Niobium Metal . . . . .	19
3.3 Preparation of Thorium Metal . . . . .	20
3.4 Preparation of Yttrium Metal . . . . .	20
3.5 Preparation of U-10 w/o Nb Alloy . . . . .	21
4. Alloy Systems. . . . .	21
4.1 Thorium-Zirconium System . . . . .	21
4.2 Thorium-Hafnium System . . . . .	22
4.3 Uranium-Niobium System . . . . .	22
4.4 Tantalum-Zirconium System. . . . .	22
4.5 Zinc-Zirconium System. . . . .	23
4.6 Tantalum-Vanadium Alloy System . . . . .	24
4.7 Thorium-Hydrogen Phase System. . . . .	25
5. Metal Coatings and Corrosion . . . . .	25
5.1 Corrosion of Binary Alloys of Some Refractory Metals . . . . .	25
6. Solid State Investigations . . . . .	25
6.1 Structure of Aluminum-Vanadium Intermetallic Compounds. . . . .	25
6.2 Study of the Allotropic Transformations in Uranium . . . . .	26
6.3 Structure of Delta Uranium-Zirconium . . . . .	28

## TABLE OF CONTENTS (Continued)

	<u>Page</u>
6.4 Electronic Specific Heats of the Sodium Tungsten Bronzes . . . . .	28
6.5 Measurement of Elastic Constants of Metal Single Crystals . . . . .	30
6.6 Structure of Thorium-Magnesium Intermetallic Compounds . . . . .	31
7. Other Investigations . . . . .	31
7.1 Vacuum Fusion Analysis of Metals . . . . .	31
7.2 Low Melting Alloy Studies . . . . .	32
APPENDIX I: LIST OF REPORTS FROM THE AMES LABORATORY . . . .	33
1. Reports for Cooperating Laboratories . . . . .	33
2. Publications . . . . .	35
APPENDIX II: LIST OF SHIPMENTS . . . . .	38
APPENDIX III: . . . . .	42

## SEMI-ANNUAL SUMMARY RESEARCH REPORT IN METALLURGY

For the period January - June, 1956

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Previous research reports in this series are:

ISC-35  
ISC-41  
ISC-56  
ISC-69  
ISC-74  
ISC-76  
ISC-79  
ISC-113  
ISC-130  
ISC-133  
ISC-137  
ISC-171  
ISC-193  
ISC-220  
ISC-248  
ISC-290  
ISC-300  
ISC-323  
ISC-339  
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ISC-423  
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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 Treatment of Ores and Separation of Niobium and  
Tantalum (1)\*

The study of methods for the opening of ores containing niobium and tantalum has been concentrated on a method employing aqueous hydrofluoric acid and a method employing fused sodium hydroxide. The latter method has perhaps a little broader application in that it is quite satisfactory for most ores containing niobium and tantalum, while the hydrofluoric acid is best suited to the columbite-tantalite concentrate type ores that do not contain quantities of yttrium and rare earths to be recovered.

A number of columbite ore concentrates have responded satisfactorily to treatments by 70% commercial hydrofluoric acid alone and to treatments by mixtures of this hydrofluoric acid and concentrated sulfuric acid. In general 150 ml of the 70% hydrofluoric acid is adequate to open 100 grams of a columbite ore concentrate containing roughly 60%  $\text{Nb}_2\text{O}_5$  and 10%  $\text{Ta}_2\text{O}_5$ . It has also been found that 100 ml of the 70% hydrofluoric acid combined with 50 ml of concentrated sulfuric acid is equally effective in treating a 100 gram batch of the same type of ore.

In the procedure, the HF is contacted with the ore in a polyethylene container. The reaction is slowed down at first by means of a water-cooled copper coil that is in the reaction container. This prevents boiling of the solution which would tend to lose HF before it had a chance to react with the ore. If HF and  $\text{H}_2\text{SO}_4$  are used to open the ore, the HF is first added to the ore and then the  $\text{H}_2\text{SO}_4$  is added slowly. The cooling coil is employed here also. The time necessary to get essentially complete reaction of the ore depends on the temperature maintained

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

in the mixture, the amount of agitation or mixing during the reaction time and the fineness of grind of the ore. For ore that passed a seventy mesh screen, the reaction was essentially complete in less than eight hours with agitation at room temperature. Increasing the temperature shortens the time necessary for the reaction.

The niobium and tantalum are extracted from the reaction product by means of an organic solvent such as hexone. The result is an organic solution of the niobium and tantalum and minor amounts of impurities; most of the iron, manganese, titanium, etc., from the ore treatment remains in the non-organic phases. The small amounts of these impurities that do follow the niobium and tantalum can be back-extracted into a small amount of an aqueous phase. An aqueous scrub 6-molar in sulfuric acid is quite efficient in removing these impurities without removing objectionable amounts of niobium and tantalum from the organic.

The resulting organic phase can then be employed in counter-current or batch type liquid-liquid extraction for separation of the niobium from the tantalum. The aqueous phase employed in these liquid-liquid separation studies has contained either  $H_2SO_4$  or  $HCl$ . The dilute  $H_2SO_4$  has been found to serve well in a system employing hexone as the organic phase. By simple batch extractions, a good fraction of the niobium from a sample has been recovered spectrographically free of tantalum and most of the tantalum recovered spectrographically free of niobium.

Opening of niobium and tantalum ore concentrates with sodium hydroxide involves heating the mixture, which consists of roughly equal weights of the ore and  $NaOH$ , for about a half-hour at a temperature of roughly  $650^\circ C$ . The product of this treatment is leached sparingly with water to remove excess  $NaOH$  with some of the silicon, tin, aluminum and other impurities. The residue is then leached by heating with dilute (1:1) sulfuric acid and then adding a little iron powder. After the reaction has subsided, water is added and the white acid oxides are recovered by decantation and filtration.

These acid oxides are dried at  $200^\circ C$  and then treated with 70% aqueous  $HF$  to give a solution from which the niobium and tantalum are extracted by means of an organic solvent. From this point on, the purification and subsequent separation of the niobium from the tantalum is carried out by a liquid-liquid extraction process as described above, following opening the ore with aqueous  $HF$ .

There appear to be possible advantages in the caustic fusion process in that the hydrogen fluoride-acid oxide concentration

ratio can be readily controlled in the system for the subsequent separation. The caustic fusion has given almost quantitative reaction with the ore in a very short time. The amount of hydrofluoric acid required in preparing the solution of the acid oxides is generally less in the caustic process, which tends to offset part of the cost of the caustic.

### 1.2 Studies on the Separation of Hafnium and Zirconium (1)

Exploratory work on the separation of hafnium from zirconium was continued with no new system for separation being evolved that appeared promising at the time. This phase of the work is continuing. Experiments were made to determine the effects of zirconyl chloride concentration on liquid-liquid extraction in the Primene-thiocyanic acid system. The amount of material transferred to the organic solvent phase was not proportional to the amount of zirconium in the aqueous phase, as reducing the concentration of zirconyl chloride to one-sixteenth of the original only cut the transfer in half. This indicated a lack of equilibrium between the aqueous and organic which would probably make the system ineffective for a continuous counter-current process.

It has been reported that hafnium hydroxide is more soluble than zirconium hydroxide in strongly basic solutions. To test this a quantity of zirconyl chloride solution was treated with a large excess of 5-molar potassium hydroxide. The filtrate yielded a second precipitate when acidified with hydrochloric acid and made basic again with ammonium hydroxide. This precipitate contained 11% hafnium compared with 2% in the starting material. However, as there was only about 0.035 g. of oxide dissolved in 100 ml of filtrate, this did not materially lower the hafnium content of the main precipitate.

It is known that activated silica gel will preferentially adsorb hafnium from solutions of zirconium tetrachloride in methanol. It was thought that the adsorption might be more selective from mixtures of methanol with another organic serving as solvent. It was found, however, that the adsorption from solutions of zirconium tetrachloride in hexone or mixtures of hexone and methanol was less selective than the adsorption from undiluted methanol.

Some experiments were made with 1.0 molar zirconium tetrafluoride dissolved in 2.0 molar hydrofluoric acid. There was the possibility that some organic solvent could be found which would preferentially transfer hafnium from such a solution. Of the various types of solvents tried only amines were found to give

any transfer when shaken with the fluoride solution. A 25 volume % solution of Primene 81R in hexone gave considerable transfer, but with only a slight enrichment of hafnium in the organic phase.

A few experiments were made with the recrystallization of potassium fluozirconate. It has been reported that this salt is much more soluble in hot water than in cold and also that the hafnium salt is more soluble than the zirconium salt. By cooling a solution of potassium fluozirconate saturated at 100°C to room temperature, the hafnium content of the mother liquor was increased from 1% to 5%. However, due to the slight solubility of the salt at room temperature, only about 15% of the hafnium was removed from the crystals.

### 1.3 Pyrometallurgical Separation of Uranium From Thorium and From Thorium-Magnesium Eutectic (6)

Thorium as well as thorium-magnesium eutectic (35.0 + 1 w/o Th) have been suggested as blanket materials for power reactors. The capture of neutrons by thorium results in the production of the fissionable isotope uranium-233. Consequently the separation of uranium from the blanket material is of interest.

Previous work has shown that uranium is only sparingly soluble in magnesium, [P. Chiotti, G. A. Tracy, and H. A. Wilhelm, "Uranium-Magnesium System," J. Metals, Trans., 8, No. 5, 562-67, (1956) 7]. The solubility of uranium in magnesium is 0.14 + 0.05 w/o at 1135°C and drops to 0.05 + 0.03 w/o at 675°C, and to about 0.005 w/o at 650°C. The solubility of magnesium in uranium is of the order of 0.004 w/o at 1135°C. It has also been observed that uranium-chromium eutectic, (5.2 w/o Cr, m.p. 860°C) forms an immiscible liquid with magnesium at 900°C, [Report ISC-607, (1955) 7], with little or no uranium or chromium going into the magnesium layer. These observations along with the known alloying behavior of the other components involved suggested the possibility of separating uranium from a thorium-magnesium blanket simply by melting the blanket material containing uranium and letting the uranium settle to the bottom of the melt, or possibly by heating the blanket material to the melting point of uranium and separating the uranium as a separate liquid layer. Since at higher temperatures the solubility of uranium in the magnesium-rich layer might be too high, the addition of enough chromium to form uranium-chromium eutectic might permit separation of uranium as the liquid eutectic at temperatures near the melting point of this eutectic, namely 860°C. Similar procedures might also be applied to thorium containing uranium.

The present investigation has been primarily concerned with the study of equilibria involving thorium-magnesium-uranium, and thorium-magnesium-uranium-chromium, in which magnesium is the major constituent.

In general the components to be studied were heated in tantalum crucibles. Previous experience has shown tantalum to be a suitable crucible material.

Two procedures were employed in studying the solubility of uranium in thorium-magnesium eutectic. The first consisted of charging a small tantalum crucible, 1" in diameter and 3 1/2" long, with a few clean uranium shavings and massive magnesium and thorium in approximately the correct ratio to form the eutectic. A tantalum cap was welded on the open end of the crucible under an argon atmosphere. The tantalum crucible was then encased in a welded stainless steel bomb. This assembly was heated to above the eutectic melting temperature for several hours in a rotating resistance furnace to insure thorough mixing of the charge. The mixed charge was then held at the same temperature with the crucible in a vertical position for several hours to permit separation of any undissolved uranium. The charge was then furnace cooled to room temperature.

A second procedure consisted of charging a tantalum crucible with a dilute thorium-uranium alloy prepared by arc-melting. Sufficient magnesium was added to form the 35 w/o thorium-magnesium eutectic. This charge was then processed in the manner described above.

Samples containing in addition enough chromium to form uranium-5.18 w/o chromium eutectic were prepared in a similar manner.

The results of chemical analyses of a number of Th-Mg-U mixtures heated at various temperatures are given in Table I. The charge was mixed at temperature by rotating the furnace end-wise back and forth through an arc of approximately 180°. One complete cycle required 1 2/3 minutes. After mixing, the charge was permitted to settle with the furnace in an upright position. After settling the samples were furnace cooled. The charge was removed, cut in two lengthwise, and one of these pieces was then cut into three sections. The top, middle and bottom sections were analyzed for uranium. The analyses of these three sections for the first series of thirteen alloys showed that most of the uranium was concentrated in the bottom section or bottom third of the alloy. The scatter in the analytical results was too great to indicate any significant difference in the concentration of uranium in the middle and top sections.

Table I  
Solubility of Uranium in Magnesium-Rich  
Liquid Magnesium-Thorium Alloys

Typical Charge	No. of Charges Processed	Mixing Time and Temp.	Settling Time and Temp.	Average Chemical Analyses
U shavings 1.3 g.	13	1 1/2 to 2 hrs. 1000°C	1 to 2 hrs. 800°C	w/o U (Top Section) 0.005 $\pm$ 0.002
Th (Massive) 26.0 g.			Furnace cooled	w/o U (Middle Section) 0.008 $\pm$ 0.004
Mg (Massive) 46.0 g.				
Th-2.25 w/o U (Arc-Melted Alloy) 24 g.	5	1 to 1 1/2 hrs. 1000°C	1 to 1 1/2 hrs. 800°C	w/o U (Top and Middle Sections) 0.009 $\pm$ 0.007
Mg (Massive) 44 g.			Furnace cooled	w/o Th (Top and Middle Sections) 34.3 $\pm$ 1.2
U (Massive) 26.3 g.	2	2 hrs. 900°C	1 hr. 800°C	w/o Th (Bottom U-Rich Layer) 0.28 $\pm$ 0.08
Th (Massive) 19.6 g.				
Mg (Massive) 44.6 g.		10 min. 1200°C	Furnace cooled	w/o Th (Mg-Rich Layer) 29.2 $\pm$ 0.4

In the second series of alloys the uranium and thorium were added as an arc-melted alloy. After processing, chemical analyses showed a fairly uniform distribution of thorium throughout the charge while the uranium was concentrated at the bottom of the charge. These results were confirmed by metallographic examination. The microstructures showed primarily Th-Mg eutectic with fine particles of uranium at the bottom of the charge.

Heating at temperatures just above the melting point of uranium resulted in the formation of two liquid layers giving a sharp boundary between the magnesium-rich layer and the uranium-rich layer. Two samples processed in this manner, see Table I, showed that the thorium remains primarily in the magnesium-rich layer and only a small amount goes into the uranium-rich layer. A gravimetric method was used in analyzing for thorium in the uranium layer and the value of 0.28 w/o Th is believed to represent an upper limit. However, other samples have been prepared and these results will be checked further.

The addition of chromium in the correct proportion to tie up the uranium present as U-5.18 w/o Cr eutectic is also being investigated. Microscopic examination shows a clean-cut separation of the liquid eutectic from the rest of the charge. Chemical analyses of the two liquid phases are in progress. This procedure has the advantage that processing temperatures need not exceed 900°C, but has the disadvantage of yielding a uranium-chromium alloy instead of essentially pure uranium. No pyrometallurgical method is known whereby the chromium can be readily separated from the uranium.

The experimental data obtained show that uranium is only very sparingly soluble in liquid thorium-magnesium eutectic, 50 to 90 ppm, at temperatures near the melting point of the eutectic. Consequently it should be possible to reduce the concentration of U-233 in a thorium-magnesium eutectic blanket by heating to above the melting point of the eutectic and permitting the uranium to concentrate at the bottom of the melt. This concentrate can be further separated into a uranium-rich liquid layer by heating to above the melting point of uranium or to about 1200°C. An alternative would be to add an appropriate amount of chromium and separate the uranium as the uranium-chromium eutectic in the same manner by heating to the melting point of the uranium-chromium eutectic.

#### 1.4 Separation of Thorium From Thorium-Magnesium Eutectic by Precipitation as Thorium-Hydride (6)

The separation of thorium from magnesium-rich alloys is of interest for several reasons. Thorium may be used as a blanket material for power reactors. A proposed method for separating uranium-233 from the thorium involves dissolution of the thorium in magnesium and the precipitation of the uranium from the melt. Likewise if thorium-magnesium eutectic is used as a blanket material, uranium-233 can be precipitated simply by melting the blanket material. It might further be necessary to reclaim the thorium from the magnesium due to the build up of radioactive impurities in the magnesium, or simply to reclaim the thorium so that it can be reused as a blanket material in pure form.

Although the magnesium can be removed by distillation, it would be advantageous to concentrate the thorium and reduce the amount of magnesium to be distilled. Consequently the possibility of precipitating thorium from a magnesium melt with hydrogen is being investigated.

Such a separation might also be of interest in the production of thorium, particularly in reduction processes yielding a magnesium-rich alloy.

The dihydride of thorium has a dissociation pressure of less than one atmosphere at 700°C. Thorium-magnesium eutectic (35 + 1 w/o Th) contained in a magnesia crucible inside of a stainless steel chamber has been brought into contact with hydrogen at one to three atmospheres pressure at 700°C. Under these conditions much of the thorium was precipitated as the hydride; however, the precipitation was not complete. Chemical analyses of the top portion of several melts reacted in this manner show the residual thorium to be in the range of 10 to 20 w/o. The amount of thorium remaining in the melt was found to decrease as the time in contact with hydrogen was increased. The results obtained indicate that stirring of the melt will be necessary in order to attain equilibrium in a reasonable period of time.

Attempts have also been made to determine the solubility of the hydride in magnesium by bringing magnesium in contact with the hydride at 675°C. The amount of thorium dissolved in the magnesium was found to be much less than 10 w/o. Further experiments and analyses are in progress.

Alterations in the apparatus are being made so that the charge may be agitated in order to speed up the attainment of equilibrium.



## 2. Preparation of Pure Compounds

### 2.1 Preparation of Thorium Tetrachloride (5)

The horizontal tube chlorination reactor was completed and several trial runs were made. The reactor worked satisfactorily and produced thorium tetrachloride of 68.8 per cent thorium assay at a rate of about 5 pounds of product per hour. The only trouble encountered in these tests was plugging of the charge feeding mechanism. This part of the reactor will have to be redesigned to remedy the plugging problem. After this change has been made, more chlorination runs will be made to evaluate the apparatus and collect necessary operating data. ✓

The continuous vacuum sublimation still for purification of thorium tetrachloride was improved by building a cyclone separator into the system. The thorium oxide and carbon were removed from the thorium tetrachloride gas before it was condensed, thus producing a purer product. The rate of sublimation could be increased by a factor of 2 to 3 while maintaining the same product purity as was obtained without the separator. Development will be continued to achieve even higher purification in this apparatus.

### 2.2 Preparation of Yttrium Trifluoride (2,7)

Yttrium fluoride was prepared by heating the oxide to 575°C for 8 to 16 hours in a stream of anhydrous hydrogen fluoride. The oxide was placed in inconel trays in a stationary bed furnace and the HF was passed over it. Conversions of 97 to 99.5% of theoretical were obtained as estimated from the weight change observed after hydrofluorination. Examination of the fluoride by means of a petrographic microscope also gave qualitative correlation between the poorer and better grades of fluoride, but the method did not appear to be sufficiently sensitive to give a quantitative estimate of the purity of the fluoride. At the present time there is no completely satisfactory method of determining the amounts of unconverted oxide or oxyfluoride remaining in the fluoride. The method employed has been to reduce the fluoride to the metal and to determine the purity of the final product. By keeping other variables in the reduction step constant a comparison of batches of fluoride can be made.

Recent experiments indicate that periodic rotation of the bed improves the quality of the fluoride prepared. Also higher temperatures during hydrofluorination show some indications of higher fluoride conversion.

Some yttrium trifluoride was prepared by dissolving yttrium oxide in 6N HCl and filtering off insolubles. The acid solution was neutralized with  $\text{NH}_4\text{OH}$  and the precipitate of  $\text{Y}(\text{OH})_3$  washed several times with distilled water. The hydroxide was heated to  $700^\circ\text{C}$  overnight in order to calcine to the oxide and also to remove any  $\text{NH}_4\text{Cl}$  present. This oxide was hydrofluorinated for 6 hours at  $575^\circ\text{C}$  in a stationary bed furnace. The resulting fluoride was reduced with calcium. Chemical analysis and microscopic examination of the Y-Mg alloy and of the final metal revealed the presence of the usual amounts of oxide inclusions.

About 2 kg of  $\text{YF}_3$  was prepared by condensing HF gas and dripping it into a hot solution of  $\text{YCl}_3$ . The precipitate was filtered and dried at  $150^\circ\text{C}$  and then dehydrated in an HF atmosphere at 250 to  $400^\circ\text{C}$ . Metal obtained from this fluoride was comparable to that obtained from dry process fluoride.

### 2.3 Preparation of a Compound of Niobium Suitable for Alloy Formation by Bomb Co-reduction (1)

The particular alloy of interest in connection with this study was one consisting of 10 weight per cent niobium in uranium. The simple halide compounds of niobium appeared to be too volatile for use in the charge while the oxide of niobium would probably introduce objectionable amounts of oxygen in the charge. The possibility of forming a double fluoride of an alkali metal and niobium, it was hoped, might give a compound of niobium suitable for use in bomb co-reduction.

A series of small scale preparations of the potassium fluoride complexes of niobium were effected by both the wet (aqueous HF) method and the dry (bifluoride fusion) method. In ten experiments by the wet method, the actual stoichiometry relative to weight relations indicated a compound intermediate to the formulas  $\text{K}_2\text{NbOF}_5$  and  $\text{K}_2\text{NbF}_7$ . Fluorine analysis of these samples ranged from 36.21% - 36.55%. However, at the fusion temperature of  $700^\circ\text{C}$  in air, excessive white fumes were evolved indicating some instability under the conditions. This probably accounts for the variation in fluorine content. Sufficient  $\text{K}_2\text{NbOF}_5$  was prepared by both methods to supply charges for bomb reductions involving up to 3 pounds of uranium. In all cases the results were poor with only partial metal and slag separation. However, the salt prepared by the ammonium bifluoride fusion appeared to yield a greater percentage of massive alloy than the wet process. The potassium-niobium salt appeared unsatisfactory for this co-reduction problem.

The possibility of preparing a desirable sodium fluoride complex of niobium was investigated. The sodium salt ( $\text{Na}_2\text{NbOF}_5$ ) was prepared by reacting a mixture of  $\text{NaF}$ ,  $\text{Nb}_2\text{O}_5$  and  $\text{NH}_4\text{HF}_2$  and by reacting a mixture of  $\text{NaF}$ ,  $\text{Nb}_2\text{O}_5$  and  $\text{HF}$ .

Bomb reductions on samples of the salt prepared by both methods were effected, and these gave very satisfactory reductions. For the dry ( $\text{NH}_4\text{HF}_2$  fusion) method, 20 preparations carried out varied from 1-2% difference from the stoichiometric weight obtained, based on the formula  $\text{Na}_2\text{NbOF}_5$ . It was found that an excess of 50%  $\text{NH}_4\text{HF}_2$  was sufficient to give a maximum salt conversion for the particular conditions and reaction vessel employed. Larger scale preparations were made in a platinum lined nickel boat with a capacity to prepare 5000 grams of  $\text{Na}_2\text{NbOF}_5$  batchwise. Three of these larger scale preparations were carried out and the average variation in composition from the theoretical weight based on the formula  $\text{Na}_2\text{NbOF}_5$  was 1.51%. Ten experimental co-reductions were made with this salt and all resulted in good slag and metal separation with above 95% yield of massive alloy.

In the wet method of preparation for  $\text{Na}_2\text{NbOF}_5$  the results of using 70% and 48%  $\text{HF}$  were compared. The 70%  $\text{HF}$  treatment consistently yielded a somewhat transparent or white solid having a melting point of about  $700^\circ\text{C}$ . In contrast the 48%  $\text{HF}$  treatment gave rise to a fused compound similar in appearance to the bifluoride fusion product. In all the attempted preparations on a small scale, the deviations in weight of product based on the formula  $\text{Na}_2\text{NbOF}_5$  varied from 0.6 - 1 gram in 25 grams of total compound.

That the compounds formed or the completeness of conversion by the wet and dry method were not identical was tested by allowing the product obtained from the dry fusion method to stand for 24 hours in a 70%  $\text{HF}$  solution. The resulting salt was then reheated and fused at  $750^\circ\text{C}$ . A gain in weight of 4% in the salt resulted. Bomb reductions effected with salt by either method were very satisfactory and no difference in yield or purity of alloy was noted. However, the wet process is advantageous from the standpoint of cost and ease of effecting a preparation of the supposed compound  $\text{Na}_2\text{NbOF}_5$ .

The major difficulty encountered in the preparation of the salt  $\text{Na}_2\text{NbOF}_5$  was that the product weight of the final salt varied from 1-3% of the amount of  $\text{Na}_2\text{NbOF}_5$  required theoretically by the reactants. This led to uncertainties in the actual amount of niobium present in each salt preparation, which would give rise to some possible error in the composition of the 10% niobium binary with uranium if calculations are based on that formula.

The variation may be attributed to the four following points:

- (1). Pyrohydrolysis of the compound during preparation.
- (2). Possible volatility of compounds formed by side reactions such as  $\text{NbF}_5$  and  $\text{NbOF}_3$ .
- (3). Impurities or occluded and hydrated water present in the basic constituents of  $\text{NaF}$ ,  $\text{Nb}_2\text{O}_5$ , and  $\text{HF}$  utilized in preparation of the salt.
- (4). The compound prepared is not of the formula  $\text{Na}_2\text{NbOF}_5$ .

Drying rate curves and analytical results obtained on the  $\text{NaF}$  and  $\text{Nb}_2\text{O}_5$  indicated no water or significant impurities present. Evaporation of the  $\text{HF}$  (70%) to dryness showed only a very small residue present.

Different ratios of moles of  $\text{NaF}$  per mole  $\text{Nb}_2\text{O}_5$  were utilized in a study on the preparation of a desirable salt. From analysis of products formed it was concluded that at and above a ratio of 2 moles  $\text{NaF}$  per  $\text{Nb}_2\text{O}_5$  a homogeneous fused solution exists. Analysis of the stoichiometry indicated that one compound closely approximates the formula  $\text{NaNbOF}_4$ . Bomb reductions of this salt gave satisfactory results with a 97.5% yield. Preparations carried out with the 3 $\text{NaF}$  ratio closely approximated the formula  $\text{Na}_3\text{Nb}_2\text{F}_{13}$ , which also produced a 97.5% yield in the subsequent bomb reductions. Results from other experiments showed that increased addition of  $\text{NaF}$  decreases the volatility of the niobium from the fluoride.

Conclusions drawn from data gathered indicate that the major deviations in the stoichiometry is pyrohydrolysis without loss of niobium at elevated temperatures in air. This difficulty was removed satisfactorily by not fusing the salt at  $700^\circ\text{C}$ . Drying at  $500^\circ\text{C}$  was found satisfactory in the preparation of the salt by the wet process.

#### 2.4 Preparation of Pure $\text{V}_2\text{O}_5$ (1)

Some work has been done in an attempt to prepare high purity  $\text{V}_2\text{O}_5$  from the impure red-cake by-product from uranium production. It appears that purification is best effected by first putting the  $\text{V}_2\text{O}_5$  in aqueous solution. Some of the compounds that facilitate the solution formation are  $\text{NH}_4\text{OH}$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaOH}$ ,  $\text{Na}_2\text{O}_2$ ,  $\text{H}_2\text{SO}_4$  and oxalic acid.

When the pentoxide is dissolved in oxalic acid, the vanadium is reduced to a valance of four. The addition of ammonium hydroxide will precipitate a compound. When this is roasted,  $\text{V}_2\text{O}_4$

is obtained. No clear-cut purification is obtained, however, by this treatment and, furthermore, to make the process economical some of the oxalic acid should be recovered.

When a sodium-vanadium solution is acidified with a mineral acid to a pH of 2-3 a red cake precipitate is obtained. This has not given sufficient purification over the original technical grade vanadium pentoxide to be attractive. The purest product by any method yet found, is to add a saturated ammonium chloride solution to a basic vanadium solution. This precipitates ammonium vanadate and when this precipitate is roasted high purity  $V_2O_5$  can be obtained.

### 3. Metal Preparation Studies

#### 3.1 Preparation of Vanadium Metal (2)

Work has been continued on the preparation of vanadium metal by the thermal decomposition of the iodide on a hot tungsten filament. Several small crystal bars have been grown during this report period. These bars were generally 20 to 30 grams in weight, but contained undesirable amounts of Fe, Cr and Si impurities. The equipment used in these experiments imposed severe limitations on the maximum size and ultimate purity of the final product. Therefore a new apparatus was constructed which was designed to eliminate problems encountered in maintaining a vacuum on the chamber and to increase the size of the bar which can be grown. Recently bars of 1/8" in diameter have been grown in this apparatus. Evaluation of the purity has not been completed although the microstructure of some of this material appears to be almost free from inclusions.

Continued studies on the bomb reduction of  $VF_3$  with calcium have shown that a massive vanadium biscuit can be obtained. Chemical analysis of this metal showed the following major impurities to be present: 0.1% C, 0.05 to 0.15%  $N_2$ , and 0.1% Si. This metal was extremely brittle possessing a hardness of  $R_A$  57. Because of the poor quality of the metal obtained, work on the reduction of  $VF_3$  has been discontinued.

#### 3.2 Preparation of Niobium Metal (1)

The carbon reduction of  $Nb_2O_5$  has been studied further. The experimental set up has been overhauled to prevent carbon from the insulation getting into the charge. In some experiments it was shown that small amounts of this material had contacted the charge and given inconsistent results. Furthermore, techniques for

thorough mixing of the reactants, which is very desirable for the solid-solid reaction, have been employed. The mixed powdered solids are converted into a paste by addition of a suitable liquid. Stirring the paste rather than the dry powders seems to be much more effective in the preparation of a desirable blend. The liquid is then dried out and the charge heated for the reaction.

### 3.3 Preparation of Thorium Metal (5)

Studies on the preparation of thorium metal were suspended during this period because of a lack of sufficient pure thorium tetrachloride and of personnel.

### 3.4 Preparation of Yttrium Metal (2,7)

As previously reported, an yttrium-magnesium alloy can be prepared by heating yttrium fluoride, calcium, magnesium and calcium chloride in a MgO, zirconium or titanium metal crucible to 1000°C in a helium or argon atmosphere. The Y-Mg alloy obtained from the reaction is in a massive form at the bottom of the reaction crucible with a slag layer above.

The magnesium and calcium are removed from the alloy (demagging) by breaking the brittle alloy into 1/2 inch diameter pieces and heating slowly in a zirconium metal crucible in vacuo to temperatures of 1100°C or higher. This yields a bright metallic sponge which is readily arc-melted into button or ingot form. This work has been described in ISC-744.

Several investigations relevant to the reduction and demagging operations have been carried out during this period. The effect of varying the amount of magnesium and the excess calcium upon the nature of the alloy was studied. Reductions were performed in which magnesium additions of 15, 17 and 20% were used and in which the calcium excess was varied by 5, 10 and 20% of the stoichiometric amount. X-ray powder patterns of Y-Mg alloys identified yttrium as one of the phases in the alloy. Lines from an unidentified phase presumed to be an intermetallic compound were also present in the patterns.

Back reflection x-ray photographs were also taken of three yttrium samples which were obtained from yttrium metal prepared in zirconium, titanium and magnesia reaction crucibles. The following values were obtained: yttrium prepared in zirconium,  $a = 3.659$ ,  $c = 5.747$  Å; Y prepared in titanium,  $a = 3.657$ ,  $c = 5.764$  Å; and Y prepared in MgO,  $a = 3.655$ ,  $c = 5.746$  Å. No particular interpretation has been given to these variations.

The melting point of yttrium which was prepared in a zirconium crucible and contained about 1% Zr was determined. It was found to be 1485°C.

Some work has been done on the identification of inclusions generally observed in the microstructure of yttrium metal. Inclusions were removed from the surface of a polished metal sample by means of a probe and examined by means of powder x-ray diffraction techniques. The major constituent was identified as  $Y_2O_3$ . Lines from another unidentified phase were also present. This phase is presumed to be YOF.

### 3.5 Preparation of U-10 w/o Nb Alloy (1,2)

A study was made of the preparation of a U-10 w/o Nb alloy by the bomb reduction of a suitable form of niobium and uranium tetrafluoride with calcium. A series of reductions were tried in which  $Nb_2O_5$ , Nb metal powder,  $NbCl_5$ ,  $K_2NbOF_5$  and  $Na_2NbOF_5$  were added to the reduction charge. A compound with the probable formula of  $Na_2NbOF_5$  proved to be most satisfactory as the source of Nb. Chemical analysis and density determinations showed the composition of the co-reduced alloy to be  $10 \pm 0.5$  w/o Nb. Fifteen pounds of alloy were melted in BeO and cast into a graphite mold. This work has been described in report ISC-743.

## 4. Alloy Systems

### 4.1 Thorium-Zirconium System (2)

Examination of the Th-Zr alloy system by high temperature x-ray techniques was continued during this period. A determination of the boundary in the Th-Zr system between the F.C.C. + B.C.C. region and the B.C.C. solid solution was made using a vanishing phase technique with the (111) F.C.C. x-ray reflection as an indication of phase disappearance. The temperature was slowly raised and lowered through the transformation. The alloys which have been run to date and their transformation temperature are as follows:

Table II

Upper  $\alpha + \beta$  Boundary in Thorium-Zirconium Alloys

Alloy Composition w/o Zr	Transformation Temperature °C
12	990
25	908
30	910
40	894
50	750
75	760

#### 4.2 Thorium-Hafnium System (2)

The investigation of the thorium-hafnium system was completed during this period and a phase diagram was proposed. The thorium-hafnium system was investigated by electrical resistance, thermal, microscopic, and x-ray methods. On the basis of data obtained from these investigations, eutectic, eutectoid, and inverse peritectic reactions are postulated in this alloy system. The eutectic reaction occurs at  $1450^{\circ} + 15^{\circ}\text{C}$  and 25.74% hafnium, the eutectoid reaction at  $1295^{\circ} + 15^{\circ}\text{C}$  and 8.95% hafnium, and the inverse peritectic reaction at approximately  $1600^{\circ}\text{C}$  and about 96% hafnium. The solid solubility limit of hafnium in alpha thorium at room temperature is 4.9%. There is little if any solubility of thorium in alpha hafnium at ambient temperatures.

#### 4.3 Uranium-Niobium System (3)

The investigation of this system is approaching completion. At the close of the reporting period, a few details of the phase diagram are being checked for accuracy.

A procedure has been found for eliminating the inhomogeneity of the cast alloys of intermediate composition. Although these alloys cannot be rolled or swaged, they can be pressed hot to a reduction in thickness of 30 per cent. Then, subsequent heating at  $50^{\circ}$  to  $100^{\circ}\text{C}$  below the melting point produces a microscopically homogeneous alloy. Specimens treated in this manner have been used in a redetermination of the solidus line and also in a revision of the lattice parameter-composition curve of alloys quenched from the gamma conditions. Points obtained with filings from the homogenized alloys differ less than anticipated from the corresponding points determined from unhomogenized alloys.

Positions of the solvus lines bounding the alpha-uranium-rich and niobium-rich solid solutions, respectively, are being examined by x-ray and metallographic methods. The solubility of niobium in alpha uranium may be less than has been estimated.

#### 4.4 Tantalum-Zirconium System (3)

Because of the extended horizontal, or nearly horizontal, portion of the solidus line in this system, the diagram was assumed, at first, to contain a eutectic. Additional study has shown that diagram-wide solid solubility actually exists immediately below the solidus, but that this solid solution decomposes upon cooling. The existence of a decomposition loop at intermediate compositions is in agreement with the unexpectedly high solubilities at elevated temperatures described in the previous report.



The boundary of the loop is being determined by x-ray and metallographic analysis. Alloys in the form of small diameter wires are quenched in helium from a series of temperatures and the lattice parameter of each phase determined. Comparison of these parameters with a lattice parameter-composition curve for the solid solution of tantalum and beta zirconium gives the composition of the two phases in the alloy. Metallographic results, although limited, agree with the x-ray findings.

#### 4.5 Zinc-Zirconium System (6)

The existence of five intermetallic phases have been observed in the zinc-zirconium system. Vapor pressure measurements indicate that alloys containing up to 41 w/o zirconium have a zinc vapor pressure of one atmosphere at 920°C. However, some recent data have cast doubt on the vapor pressure measurements on alloys in the composition range between 31 and 41 w/o zirconium. The x-ray powder patterns of all except one of these phases (ZrZn) are complex.

The compound ZrZn (58.25 w/o Zr) has a simple cubic lattice with  $a_0 = 3.336 \text{ \AA}$ . This compound melts incongruently at 1050°C.

The compound ZrZn<sub>2</sub> (41.1 w/o Zr) is face centered cubic with  $a_0 = 7.396 \text{ \AA}$ . This compound has been previously identified by Pietrokowsky, J. Metals, Trans. section 6, 219 (1954).

The microstructure of alloys in the composition range near 31.7 w/o zirconium (ZrZn<sub>3</sub>) show a twinned single phase structure. The x-ray powder patterns of this phase are very complex and attempts to index the numerous reflections have been unsuccessful. This compound when heated under its own vapor pressure, is believed to melt incongruently at 1100°C.

There is some doubt whether one or two compounds exist in the composition range 18.9 w/o zirconium (ZrZn<sub>6</sub>) and 12.24 w/o zirconium (ZrZn<sub>10</sub>). A single crystal obtained from an alloy of an intermediate composition showed hexagonal symmetry with  $a_0 = 8.02 \text{ \AA}$  and  $c_0 = 7.31 \text{ \AA}$ . Metallographic and thermal data show a definite peritectic horizontal at 750°C and a less definite peritectic horizontal at 850°C. The existence of two compounds in the composition range in question could explain these results.

Another compound of still higher zinc content is face center cubic with  $a_0 = 14.11 \text{ \AA}$ . Space group considerations indicate that its composition corresponds to ZrZn<sub>14</sub> (9.06 w/o Zr) instead of ZrZn<sub>15</sub> (8.51 w/o Zr) as previously reported. This compound decomposes peritectically at 550°C.

4.6 Tantalum-Vanadium Alloy System (2)

The investigation of the tantalum-vanadium system has continued. The solidus was redetermined for several alloys and they are now considered to be more accurate than values reported for the same alloys in the previous report (ISC-708).

Table III

## Solidus Points for Ta-V Alloys

Composition w/o V	Solidus Temp. °C
100	1885 + 15
79	1830 $\pm$ 15
70	1815 $\pm$ 15
60	1855 $\pm$ 15
40	1880 $\pm$ 15
30	2010 $\pm$ 15
20	2190 $\pm$ 20
Pure Ta	2995 $\pm$ 50

The structure of the intermediate phase has not been satisfactorily determined. Due to difficulties in attaining complete equilibrium in alloys near the composition of the compound it has been impossible to estimate the composition precisely either from microstructure or from x-ray diffraction data. After considerable search for a suitable etchant for alloys in the intermediate region of this system, an electrolytic etch of 60 g. H<sub>2</sub>O, 180 g. acetic acid and 50 g. CrO<sub>3</sub> was found which successfully differentiated regions of compound from that of the body centered cubic solid solution. Present estimates from microscopic evidence place the composition of the intermediate phase at 60 w/o Ta + 5%. This corresponds most simply to the formula, TaV<sub>2</sub>, at 64% Ta.

The identification of the structure of the intermediate phase was hindered by the failure to obtain a single crystal for use in x-ray studies. Several unsuccessful attempts were made to select a single crystal of the compound by fragmentation of the alloy. Preferential chemical dissolution methods also failed due principally to the tendency for the compound phase to dissolve leaving crystals of the solid solution matrix behind.

#### 4.7 Thorium-Hydrogen Phase System (5)

A study has been started of the effect of hydrogen on the properties of thorium metal. The first phase of this work was determination of the solubility of hydrogen in thorium metal at various temperatures. An apparatus for introducing hydrogen into thorium samples and measuring the equilibrium hydrogen pressure has been built. A system has been built in which the hydrogen content of thorium samples can be determined. After the solubility of hydrogen in thorium has been established, the effect of various hydrogen contents on the principal mechanical properties of thorium will be determined.

### 5. Metal Coatings and Corrosion

#### 5.1 Corrosion of Binary Alloys of Some Refractory Metals (2)

A survey of the phase relationships and corrosion properties of binary alloys prepared from the refractory metals in Groups Va and VIa is now underway. Arc-melted alloys having compositions 40 and 60 w/o were prepared of each of the following binary combinations: Ta-W, Ta-Mo, W-Mo, Nb-W, V-Mo, Nb-Mo, V-Cr, Mo-Cr and V-W. These were homogenized at 1300°C to 1800°C for 8 hours, the temperatures selected depending upon the particular alloy being homogenized. These are currently being annealed at 900°C for a 15-day period to determine whether any of these alloys form an intermediate phase such as occurs in the Ta-V system described in an earlier section of this report. Microscopic examination of the annealed samples and corrosion tests in high temperature air and water are now planned.

### 6. Solid State Investigations

#### 6.1 Structure of Aluminum-Vanadium Intermetallic Compounds (4)

The structure of the  $\beta$ -phase compound,  $V_4Al_{23}$ , has been previously reported (ISC-708). Current work has been directed toward elucidating the structure of the  $\alpha$ -phase compound. Symmetries of the x-ray diffraction patterns of single crystals indicate the space group symmetry  $O_h^7 - Fd3m$ . A back-reflection Weissenberg camera was used to obtain a precision lattice parameter of  $a_0 = 14.516 \pm 0.003 \text{ \AA}$ .

The density of small single crystals of the  $\alpha$ -phase was measured by the float-sink method in methylene chloride diluted with carbon tetrachloride. The density determined in this way

was 2.950 gm/cm<sup>3</sup>. The theoretical densities of three tentative formulae are: V<sub>2</sub>Al<sub>23</sub>, 3.136 g/cm<sup>3</sup>; VAl<sub>11</sub>, 3.019 g/cm<sup>3</sup>; V<sub>2</sub>Al<sub>21</sub>, 2.902 g/cm<sup>3</sup>. The size of the unit cell and symmetry restrictions preclude other formulae. The measured density is almost certain to be less than the theoretical density, hence the formula V<sub>2</sub>Al<sub>21</sub> is unlikely.

Microspectrophotometric analysis of a representative sample showed the  $\alpha$ -phase to contain 14.06 + 0.09 w/o vanadium. The analysis favors the formula V<sub>2</sub>Al<sub>23</sub> while the density measurement favors the formula VAl<sub>11</sub>. It remains for the structure determination to differentiate between these formulae. Currently a trial structure based on the formula VAl<sub>11</sub> has been constructed, and a reasonable agreement with the Patterson projection, P(x,y), has been found. A Fourier projection of the electron density map,  $\rho(x,y)$  is now being run.

## 6.2 Study of the Allotropic Transformations in Uranium (6)

This investigation includes a study of the kinetics and mechanism of the alpha-beta and beta-gamma transformations in uranium. The temperature dependence of the lattice parameters of the three crystalline forms of uranium and the orientation relationship for the alpha to beta transformation are being measured. The kinetics of the transformation are being studied employing resistivity measurements. From these observations an attempt will be made to determine whether the transformations in pure uranium are of the classical nucleation and growth or of the "martensitic" type.

### 6.2.1 Temperature Dependence of the Lattice Parameters of Uranium (6)

The temperature dependence of the lattice parameters of orthorhombic uranium as reported in the previous report (ISC-709) is in good agreement with the x-ray data reported by Schwartz and Vaughan [C. M. Schwartz and D. A. Vaughan, Battelle Memorial Institute] and the dilatometric data reported by Lehr and Langeron [Pierre Lehr and Jean-Paul Langeron, Comptes Rendus, 241, No. 7, 1130, (1955)]. The temperature dependence of the lattice parameter for the cubic gamma phase previously reported (ISC-641) is thought to be reliable and has not been rechecked during this report period. The data for the beta phase have proved somewhat difficult to obtain, and the thermal expansion and atomic volume for this phase have not been definitely established. Indexing

the beta peaks is difficult due to the large number of possible reflections. In past work this problem has been further complicated by carbide contamination. Several modifications are being made in our apparatus in an attempt to eliminate or reduce the carbon contamination and to improve the alignment of the specimens in the high temperature x-ray diffraction apparatus.

A high vacuum "Evaporion" pump developed by Consolidated Vacuum Corporation, has been installed as part of the high temperature x-ray diffractometer apparatus. Its pumping action is due to electronic ion entrapment and the gettering action of evaporated titanium. This pump has no oil pumping fluid, and metal gasket seals are employed. Installation of the pump has allowed high temperature x-ray runs to be made at a better vacuum, by an order of magnitude, than it was possible to obtain with the previous system. Trial tests were made with pure thorium. Pressures below  $8.5 \times 10^{-7}$  mm of Hg could be maintained at temperatures up to  $1400^{\circ}\text{C}$ , and no carbide contamination was observed. However, after several hours in the beta range, uranium samples still showed some carbide diffraction peaks. This contamination builds up rather slowly and is not expected to seriously hamper future beta lattice parameter determinations.

Presently modifications are being made on the diffractometer apparatus to increase the ease in sample alignment and allow rotation of the sample about an axis parallel to the x-ray beam. The beta phase parameter studies will continue upon completion of these modifications.

#### 6.2.2 Transformation Kinetics and Orientation Relationships (6)

Electrolytically deposited uranium crystals (50 to 100 ppm total impurity) obtained from the Argonne National Laboratories show by their Laue x-ray patterns to be bicrystals of a definite orientation. Attempts are being made to determine the relative orientation of the alpha and beta phases on transformation in these crystals using high temperature Laue x-ray techniques. Back-reflection and cylindrical Laue patterns of these bicrystals have been obtained at temperatures up to  $700^{\circ}\text{C}$ . The experimental techniques are being improved and the interpretation of the patterns is being studied. ✓

Some information on the alpha-beta transformation characteristics is being obtained by following the changes in the electrical resistivity as a function of time at various temperatures in the transformation region. The shape of the resistivity breaks and the length of the incubation and transformation periods at

various temperatures should give information about the nature of the transformation process. Trial experiments have been made with small single crystals. The data obtained are insufficient to permit any conclusions to be drawn. Further experiments will be carried out with single crystals and polycrystalline wire. Various heating programs will be employed.

### 6.3 Structure of Delta Uranium-Zirconium (5)

The determination of the structure of this compound, previously called epsilon uranium-zirconium, has not been successful. A number of methods of refining the parameters in the trial structure have been used, but have not resulted in better agreement between the calculated and observed diffraction intensities. Microscopic examination of one-phase delta alloys after chemical etching and after cathodic etching did not show the optical anisotropy reported for this phase. Further structure work and microscopic examination will be done.

### 6.4 Electronic Specific Heats of the Sodium Tungsten Bronzes (4)

A calorimeter for measuring specific heats in the range 1°-4°K has been constructed. Low temperature specific heats of metals are normally fit to the formula,  $c = \gamma T + \beta T^3$ , where  $\gamma$  is the electronic specific heat. A calibration run on the electronic specific heat of Cuprovac copper (99.99% purity) has been made. The plot of values of  $C/T$  versus  $T^2$  is shown in the accompanying figure. The recent data of Corak, et. al. are also plotted for comparison. The data yield a value of  $1.67 \times 10^{-4}$  cal mole<sup>-1</sup> deg<sup>-2</sup> for the electronic specific heat of copper. This value is compared with that of other investigators in Table IV. (See Fig. 1)

Table IV

$\gamma$	Reference
$1.67 \times 10^{-4}$	this investigation
$1.64 \times 10^{-4}$	Corak et. al. (Phys. Rev. <u>98</u> , 1699 (1955))
$1.73 \times 10^{-4}$	Rayne (Phys. Rev. <u>95</u> , 1428 (1954))
$1.78 \times 10^{-4}$	Kok and Keesom (Physica <u>3</u> , 1035 (1936))
$1.80 \times 10^{-4}$	Estermann et. al. (Phys. Rev. <u>81</u> , 582 (1952))

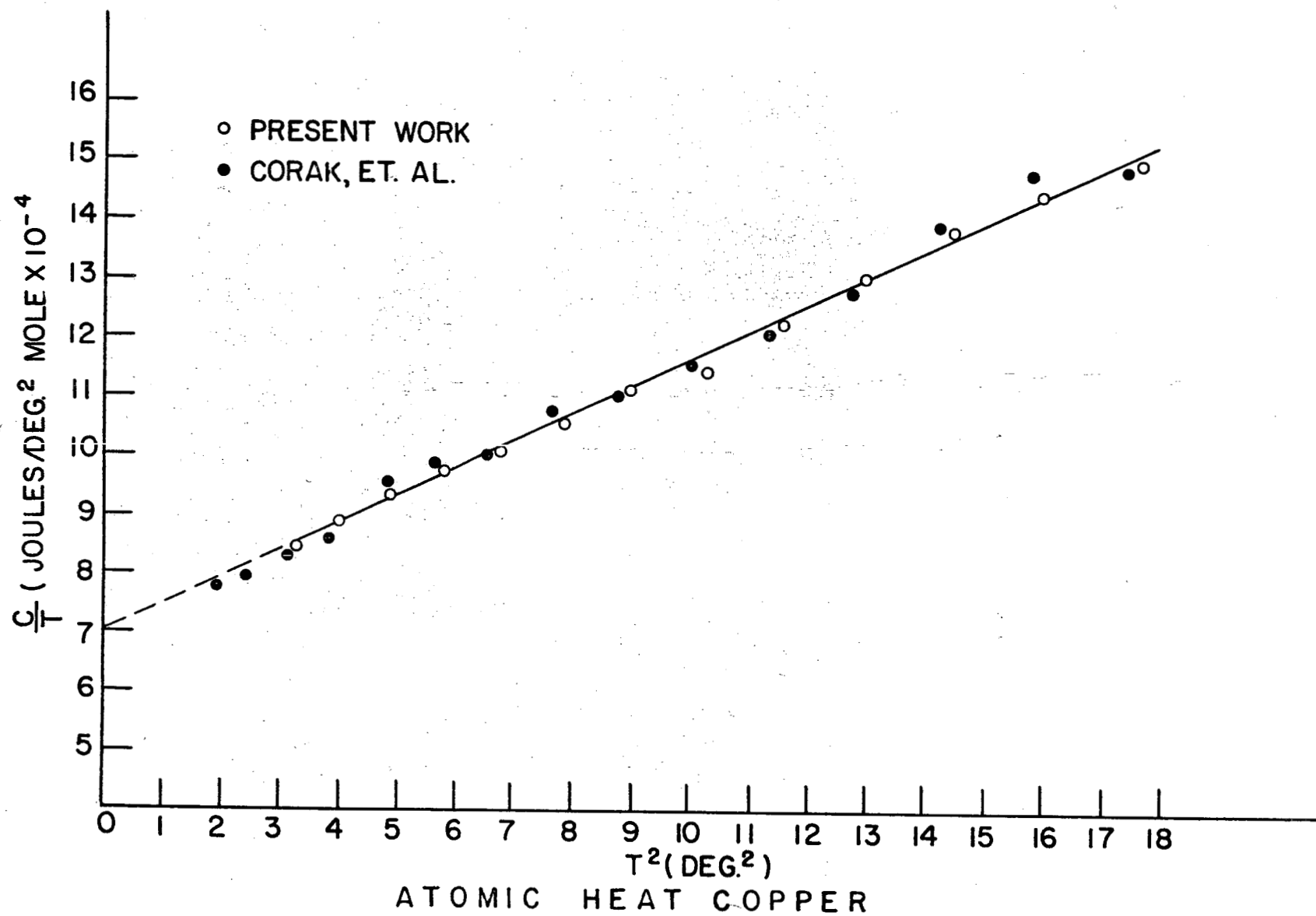


Fig. 1 - A Plot of the Heat Capacity/Degree vs. T² for Copper.

The agreement of values indicates the reliability of the calorimeter design. Initial measurements of the electronic specific heat of the sodium tungsten bronze,  $\text{Na}_{0.81}\text{WO}_3$ , are now in progress.

#### 6.5 Measurement of Elastic Constants of Metal Single Crystals (2)

The problem of determining elastic constants of small metal single crystals has been pursued by construction of apparatus to perform the measurements. Suitable crystals were grown, their orientation determined, sectioned as desired and several trial determinations of sound velocities were performed on these crystals.

After some experimentation, a suitable radio frequency generator has been constructed which will produce output voltages of between 20 and 100 volts at frequencies between 1.8 and 13 megacycles. This generator is used to drive small quartz or barium titanate crystals in longitudinal or shear modes of vibration. These driver crystals are then coupled to a sample, with resulting resonances occurring as the frequency is varied. These resonances are a function of the impressed frequency, sample thickness, and sample density.

Detection of longitudinal mode resonances was done using the Debye-Sears method of passing a sound beam through a liquid, and observing the resulting density variations by an optical diffraction technique. The sample was suspended on the liquid surface, with the driver crystal placed on the sample. At resonance, a stronger sound wave passed through the liquid and could be detected optically.

Detection of shear mode resonances by observing the output of the generator has been unsuccessful, as have experiments in passing the shear vibrations through an optically transparent solid and detecting them by the Debye-Sears method. Tests are to be made using two crystals and electronic detection for shear measurements, as well as to see how small a sample will work using the pulse-echo technique.

Single crystal growth experiments have been tried on nickel, copper, nickel-copper alloys, and thorium metal, using a vacuum furnace and the Bridgman technique of growth from the liquid. Reaction of thorium with the crucible materials seemed to prevent large grain formation, but single crystals were obtained of the other metals. Attempts were made to grow zirconium crystals by the phase change and strain anneal methods. Large beta grains could be produced, but these changed to oriented alpha fine grains during slow cooling.



Techniques were developed for cutting and polishing the nickel-copper crystals and several  $\langle 111 \rangle$  oriented single crystal nickel samples were prepared. These samples were used in evaluating the effect of method and sample size on the longitudinal velocity measurements. The following data were obtained:

Table V

Sound Velocities in  $\langle 111 \rangle$  Oriented Nickel Single Crystal Plates

Sample Dimensions		Measuring Method	Room Temperature Sound Velocity inches/second
Diameter Inches	Thickness Inches		
1.0	0.3094	Debye-Sears Resonance	$2.476 \times 10^5$
1.0	0.3094	Pulse echo- Sperry Reflectoscope	$2.46 \times 10^5$
1.0	0.0615	Debye-Sears Resonance	$2.474 \times 10^5$
		Same, remounted sample	$2.476 \times 10^5$
1.0	0.0303	Debye-Sears Resonance	$2.473 \times 10^5$
		Debye-Sears Resonance	$2.473 \times 10^5$

These data seem to show that for longitudinal measurements, samples as small as 0.4 inch in diameter and 0.03 inch in thickness will give substantially the same answers as the much larger samples required for the pulse echo techniques.

#### 6.6 Structure of Thorium-Magnesium Intermetallic Compounds (5)

The structure of two intermetallic compounds of the composition Th-Mg<sub>2</sub> has been established. The results of this determination have been submitted to Acta Crystallographica as a Short Communication.

### 7. Other Investigations

#### 7.1 Vacuum Fusion Analysis of Metals (5)

Development of vacuum fusion analytical methods for determining oxygen, nitrogen and hydrogen was continued. Analysis of duplicate samples of lanthanum in a nickel bath and in a platinum bath

indicated that the extraction of the gaseous elements was more complete with the platinum bath. The analytical results on oxygen and nitrogen recovery were less accurate than expected because of the high hydrogen content of the samples. A few preliminary analyses of standard neodymium samples in a nickel bath gave extractions and recoveries very similar to those obtained with lanthanum samples. Preliminary results on yttrium metal showed that a temperature of 1950°C was necessary for rapid extraction of the gas using a nickel bath. Preparation of standard samples of yttrium metal is underway to permit quantitative study of the extraction of gas from yttrium using a nickel bath.

## 7.2 Low Melting Alloy Studies (1)

Work is being continued on a study of aluminum-rich aluminum-thorium-uranium alloys. The study is being conducted to determine the liquidus surface in the aluminum corner of the ternary system to aid in the development of these alloys for possible use as liquid fuels in nuclear reactors.

The methods being used in this study are: (1) thermal analysis of ternary alloys of various compositions, and (2) microscopic examination of polished surfaces of the ternary alloys after thermal analysis.

During the previous period, some difficulty was met due to segregation in the specimen undergoing thermal analysis. A specimen weighing approximately 15 grams was used, with a resistance furnace providing heat to the specimen. At present a 100-gram specimen is being used with self-induction heating. Segregation due to the settling out of the heavier components during solidification of the thermal analysis specimen is largely overcome by using self-induction heating.

Alloys are prepared by co-melting the metals in a refractory crucible in an induction furnace. Ames thorium, production grade uranium and 99.99% pure Alcoa aluminum are used to make the alloys.

Compositions are chosen for thermal analysis specimens to give data that will help to locate binary eutectic valleys originating at the binary eutectics in the two systems, aluminum-thorium and aluminum-uranium. It is assumed that a binary relationship exists between the peritectic compounds  $UAl_4$  and  $ThAl_3$ , and that a binary eutectic exists in this binary system. A binary eutectic valley is assumed to originate from this assumed eutectic and join the two binary valleys originating from the two known binary eutectics, forming a ternary eutectic of aluminum,  $ThAl_3$  and  $UAl_4$ .

## APPENDIX I: LIST OF REPORTS FROM THE AMES LABORATORY

1. Reports for Cooperating Laboratories

- ISC-288 D. R. Wilder. Sintering Mechanism as Applied to Refractory (Suppl.) Oxides.
- ISC-638 Hobart Cammack and G. L. Bridger. Recovery of Uranium from Slag from the Electric Furnace Production of Phosphorus.
- ISC-644 Ames Laboratory Staff. Metallurgy. Quarterly Summary Research Report. April, May, June, 1955.
- ISC-647 Loren R. McMurray and D. J. Zaffarano. A Possible Method for Beam Extraction from an Alternating Gradient Synchrotron.
- ISC-648 Lawrence S. Ring, Jr., and D. J. Zaffarano. Beta Spectra of Some Short-Lived Nuclides.
- ISC-652 J. W. Murdock and Glenn Miller. Secondary Electron Emission Due to Positive Ion Bombardment.
- ISC-654 R. W. Laity and F. R. Duke. Measurements and Significance of Transport Number in Fused Salts.
- ISC-655 R. A. Lowry and G. H. Miller. Measurement of the Ionization Yield of Low Energy Atomic Particles in Gases.
- ISC-659 George Pulliam and E. S. Fitzsimmons. Reaction of Lanthanum and Cerium with Ceramic Oxides.
- ISC-662 Martin Welt and Morton Smutz. Thorium and Uranium from Monozite.
- ISC-663 C. Adams, D. W. Barnum, R. Bisque, R. I. Bystroff, F. Debbrecht, J. S. Fritz, D. E. German, P. G. Grimes, M. Johnson, W. Lane, A. Moye, J. W. O'Laughlin, J. L. Spooner, S. Sutton, W. Trask, G. Umbreit, E. Wadsworth, S. S. Yamamura, R. E. Yerick and J. Zimmerman. Survey of Masking Agents Used in Quantitative Analysis.
- ISC-666 R. C. Strittmater and G. C. Danielson. Measurement of Specific Heats by a Pulse Method.
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- ISC-671 F. R. Parchen and F. R. Duke. Kinetics of the Exchange Reaction Between Two Oxidation States of Cerium.

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- ISC-678 W. W. Davis and Morton Smutz. Effect of Phosphate Rock Particle Size on Recovery of Uranium from Superphosphate.
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- ISC-685 R. D. Redin and G. C. Danielson. Measurement of Magnetic Field Gradient by the Hall Effect.
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- ISC-693 R. A. Foos and H. A. Wilhelm. Applications of Liquid-Liquid Extraction for the Separation of Zirconium from Hafnium.
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## APPENDIX II: LIST OF SHIPMENTS

<u>Destination</u>	<u>Item</u>
University of California Los Alamos Scientific Laboratory Los Alamos, New Mexico	20 gm erbium metal 20 gm yttrium metal 20 gm lanthanum metal 66 gm neodymium metal 69 gm samarium metal 72 gm gadolinium metal 77 gm erbium metal
Mr. H. A. Boorse Pupin Physics Bldg. New York, New York	1 cylinder lanthanum metal
Atomics International North Am. Aviation, Inc. Downey, California	250 gm thorium metal
General Electric Company General Engineering Laboratory Schenectady, New York	100 mg dysprosium oxide 100 mg terbium oxide 100 mg holmium oxide 100 mg erbium oxide 100 mg ytterbium oxide 100 mg thulium oxide 100 mg lutetium oxide 1 gm lanthanum oxide 1 gm cerium oxide 1 gm praseodymium oxide 1 gm neodymium oxide 1 gm samarium oxide 1 gm gadolinium oxide 1 gm yttrium oxide
Dr. Franz R. Metzger Bartol Research Foundation Swarthmore, Pennsylvania	10 gm special N <sup>14</sup>
Carbide & Carbon Chemical Company Union Carbide & Carbon Corp. Oak Ridge, Tennessee	50 gm pure cerium metal
Dr. Richard A. Ogg, Jr. Stanford University Stanford, California	1 gm N <sup>15</sup>



<u>Destination</u>	<u>Item</u>
General Electric Company ANP Department Cincinnati, Ohio	1 gm cerium oxide 1 gm lanthanum oxide 1 gm praseodymium oxide 1 gm neodymium oxide 1 gm samarium oxide 1 gm gadolinium oxide 1 gm yttrium oxide 100 mg terbium oxide 100 mg dysprosium oxide 100 mg holmium oxide 100 mg erbium oxide 100 mg ytterbium oxide 100 mg thulium oxide 100 mg lutetium oxide
General Electric Company Richland, Washington	1 gm lanthanum oxide 1 gm cerium oxide 1 gm praseodymium oxide 1 gm neodymium oxide 1 gm samarium oxide 1 gm gadolinium oxide 1 gm yttrium oxide 100 mg terbium oxide 100 mg dysprosium oxide 100 mg holmium oxide 100 mg erbium oxide 100 mg ytterbium oxide 100 mg thulium oxide 100 mg lutetium oxide
Dow Chemical Company Midland, Michigan	20 lbs. anhydrous thorium
Dr. J. F. McClendon Albert Einstein Medical Center Philadelphia, Pennsylvania	1 gm special hafnium oxide
Brookhaven National Laboratory Upton, Long Island, New York	20 mg holmium oxide
Dr. Thomas C. Hoering Department of Chemistry University of Arkansas Fayetteville, Arkansas	2 samples N <sup>15</sup>
Battelle Memorial Institute Columbus, Ohio	2 gm terbium metal 2 gm erbium metal 2 gm ytterbium metal 2 gm holmium metal 2 gm praseodymium metal

<u>Destination</u>	<u>Item</u>
Research Laboratories of Colorado, Inc. Newtown, Ohio	1 gm lanthanum oxide 1 gm cerium oxide 1 gm praseodymium oxide 1 gm neodymium oxide 1 gm samarium oxide 1 gm gadolinium oxide 1 gm yttrium oxide 100 mg terbium oxide 100 mg dysprosium oxide 100 mg holmium oxide 100 mg erbium oxide 100 mg ytterbium oxide 100 mg lutetium oxide
Dr. T. J. Bond Department of Chemistry Baylor University Waco, Texas	1 gm neodymium oxide 1 gm dysprosium oxide 1 gm yttrium oxide 1 gm erbium oxide
Dr. Sumner Davis Massachusetts Institute of Technology Cambridge, Massachusetts	1 gm terbium oxide 1 gm holmium oxide 1 gm dysprosium oxide
Yale University New Haven, Connecticut	40 gm gadolinium oxide 10 gm terbium oxide 20 gm holmium oxide 5 gm thulium oxide 20 gm dysprosium oxide 20 gm erbium oxide
The Eagle-Picher Research Laboratories Joplin, Missouri	1 gm lanthanum oxide 1 gm cerium oxide 1 gm praseodymium oxide 1 gm neodymium oxide 1 gm samarium oxide 1 gm gadolinium oxide 1 gm yttrium oxide 100 mg terbium oxide 100 mg dysprosium oxide 100 mg holmium oxide 100 mg erbium oxide 100 mg ytterbium oxide 100 mg thulium oxide 100 mg lutetium oxide

<u>Destination</u>	<u>Item</u>
University of California Scripps Institution of Oceanography La Jolla, California	1 gm lanthanum oxide 1 gm cerium oxide 1 gm praseodymium oxide 1 gm neodymium oxide 1 gm samarium oxide 1 gm gadolinium oxide 1 gm yttrium oxide 100 mg terbium oxide 100 gm dysprosium oxide 100 mg holmium oxide 100 mg erbium oxide 100 mg ytterbium oxide 100 mg thulium oxide 100 mg lutetium oxide
Florida State University Tallahassee, Florida	10 gm praseodymium oxide 10 gm neodymium oxide
Professor Tarhen Huus Institute for Teoretisk Fysik Copenhagen, Denmark	100 mg terbium oxide
Dr. Allen J. VanderWeyden, U.S.A.E.C. Liaison Officer Atomic Energy of Canada, Ltd. Chalk River, Ontario, Canada	2 gm yttrium oxide 2 gm dysprosium oxide 2 gm ytterbium oxide
Dr. Jagdish Shanker Chemistry Division Department of Atomic Energy Government of India Bombay, India	1 gm gadolinium oxide 1 gm dysprosium oxide
U.S.A.E.C. c/o Mallinckrodt Chem. Works Uranium Division St. Louis, Missouri	100 mg holmium oxide 100 mg terbium oxide 100 mg dysprosium oxide 100 mg erbium oxide 100 mg thulium oxide
Argonne National Laboratory Lemont, Illinois	1 sample gadolinium metal 1 sample erbium metal
University of Saskatchewan Betatron Department Saskatoon, Saskatchewan, Canada	25.6394 gm yttrium oxide 50 gm lutetium oxide 50 gm thulium oxide 50 gm terbium oxide 50 gm yttrium oxide 50 gm holmium oxide

<u>Destination</u>	<u>Item</u>
Dr. Fisher c/o Air France Cargo Department New York International Airport Jamaica, Long Island, New York	25 gm neodymium oxide
Anaconda Aluminum Company Columbia Falls, Montana	1 gm hafnium oxide

## APPENDIX III

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