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A.E.C. RESEARCH AND DEVELOPMENT REPORT

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**AMES
LABORATORY
IOWA STATE
COLLEGE**

**METALLURGY
SEMI-ANNUAL SUMMARY RESEARCH REPORT
JANUARY-JUNE, 1957**

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U N I T E D S T A T E S A T O M I C E N E R G Y C O M M I S S I O N

SEMI-ANNUAL SUMMARY RESEARCH REPORT IN METALLURGY

For January - June, 1957

by

Ames Laboratory Staff

December 20, 1957

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

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submitted by the Group leaders of
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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 Studies on the Separation of Hafnium from Zirconium (1)*

In the preparation of an aqueous solution of zirconium from commercial ZrCl_4 , HCl is formed and considerable heat is generated. This combination can result in a lack of reproducibility in acid and salt concentrations in making up the starting solution. Methods are being studied for preparation of this solution with the objective being the development of better control of the heat evolution and final salt and acid concentrations.

The acid, zirconium and thiocyanate concentrations in the aqueous phase are interrelated in the transfer of zirconium and hafnium to a particular organic phase. Practically 100 per cent of an essentially neutral solution of the oxychlorides can be transferred to cyclohexanone with a thiocyanate to zirconium ratio of three to one. Such an aqueous solution is readily prepared from crystallized and washed $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$. Means are being studied for preparing such a solution without going through the crystallization process.

One method of producing $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ in steps from ZrCl_4 follows the assumed reactions:

and

Part of the product, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, is recycled to react with more ZrCl_4 while the remainder is employed in making the aqueous solution desired for liquid-liquid extraction. The second

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

reaction is carried out by simply adding a limited amount of water to the $\text{ZrOCl}_2 \cdot 3\text{H}_2\text{O}$. By preparing the solution as indicated, very little HCl is present in the final product and the heat effect of solution of ZrCl_4 is spread. The HCl is liberated from solid reactants so that the rate of its evolution is readily controlled. The HCl could also be recovered for use in subsequent processing or as a by-product.

In separation tests employing the above mentioned organic solution of zirconium and hafnium, it appears that better separation factors are obtained on back extraction with aqueous sulfuric acid solutions than with other acids tested.

1.2 Pyrometallurgical Separation of Uranium from Thorium (6)

Study of the equilibrium phases which exist in magnesium-rich alloys of the Mg-Th-U system was continued during this report period. Principal emphasis was placed on the determination of the solubility of uranium in magnesium, magnesium-16 wt % thorium, magnesium-35 wt % thorium, and magnesium-45 wt % thorium solutions. Experimental apparatus and procedures were described in the previous semi-annual report (ISC-835). The data obtained for pure magnesium, and magnesium-35 wt % thorium are shown in Fig. 1. Data previously obtained by processing magnesium-35 wt % thorium alloys in tantalum crucibles are also plotted for comparison. A similar plot of data for the solubility of uranium in magnesium-16 wt % thorium solutions closely followed that for the solubility of uranium in pure magnesium at temperatures above 775°C while at lower temperatures it showed somewhat less curvature. These data as well as those for magnesium-45 wt % thorium are not shown in Fig. 1. However, smoothed values for the solubility of uranium in all four solutions obtained from these curves are summarized in Table I. The solubility of uranium in these liquids at 650°C is 0.002, 0.004, 0.007, and 0.008 wt % respectively. The solubility at 1132°C in each case is 0.17, 0.14, 0.14, and 0.19 wt % respectively. The accuracy of these values is estimated to be ± 0.003 wt % at 650°C and ± 0.02 wt % at 1132°C . The solubility values for uranium in magnesium-45 wt % thorium are tentative. In this case, the solution had been contaminated by iron which may affect the uranium solubility to some extent. Consequently the solubility of uranium in the 45 wt % thorium solution will be redetermined.

Fig. 1 - Solubility of uranium in magnesium "o" and magnesium-35 wt % thorium "+" solutions as a function of temperature. The points indicated by squares "□" represent results on the solubility of uranium in magnesium-35 wt % thorium solutions processed in tantalum crucibles.

Table I

Smoothed values of the solubility of U in Mg and in Th-Mg solution obtained from plots of $\log Nu$ vs. $1/T$

Temp °C	Pure Mg		Mg - 16 wt % Th ⁹⁰ solution		Mg - 35 wt % Th solution		Mg - 45 wt % Th solution	
	N X 10 ⁷	wt% X 10 ⁴	N X 10 ⁷	wt% X 10 ⁴	N X 10 ⁷	wt% X 10 ⁴	N X 10 ⁷	wt% X 10 ⁴
585					50	40	70	40
650	20	20	40	40	100	70	140	80
700	70	70	100	80	160	110	220	130
750	140	140	180	150	240	160	350	200
800	240	230	270	230	360	240	510	300
850	350	340	400	330	500	340	710	410
900	500	490	550	460	680	460	990	580
950	660	650	730	610	900	610	1320	770
1000	890	870	930	780	1180	790	1710	1000
1050	1160	1140	1170	980	1500	1010	2200	1290
1100	1480	1450	1460	1230	1890	1270	2780	1620
1132	1700	1670	1640	1380	2150	1440	3180	1860

Analyses of all the samples were performed by an ammonium thiocyanate spectrophotometric method. The values for many of the samples of magnesium-35 wt % thorium were further checked by fluorometric analysis. The fluorometric analyses gave somewhat higher values for the solubility of uranium in this solution. In general the values were 0.005 wt % higher than those obtained by the spectrophotometric method of analysis. Samples taken in the temperature range from 625°C to 900°C were checked. These results are not plotted in Fig. 1, but are considered a good confirmation of the data obtained by the spectrophotometric method.

Assuming a straight line relationship for the pure magnesium data shown in Fig. 1, a least squares treatment neglecting the lower two points gives

$$\log N = -(0.424 \pm 0.002) \left(\frac{10^4}{T} \right) - 0.689 \pm 0.017.$$

For the magnesium-35 wt % thorium data shown in Fig. 1 a least squares treatment neglecting the samples processed in tantalum crucibles gives

$$\log N = -(0.3624 \pm 0.005) \left(\frac{10^4}{T} \right) - 1.0786 \pm 0.0044.$$

The limits in both equations represent the probable error for the constants concerned. The extrapolation with the equation for magnesium to 650°C gives the mole fraction of uranium to be $(51 \pm 6) \times 10^{-7}$. The curve as drawn in Fig. 1 indicates the mole fraction to be approximately 20×10^{-7} . Although these two values lie within the estimated accuracy of the data, the deviation from a linear relationship as represented by the curve is probably significant; since this same trend was observed in a previous investigation as well as in the 16 wt % thorium solution. The deviation from linearity at low temperatures was less pronounced for the magnesium-16 wt % thorium solution while the data for magnesium-35 and 45 wt % thorium solutions appeared to fit a straight line relationship over the entire temperature range studied.

1.3 Precipitation of Thorium as Thorium Dihydride from Thorium-Magnesium Solutions (6)

The precipitation of thorium as thorium dihydride from thorium-magnesium solutions has been investigated over the temperature range of 665°C to 810°C. It has been shown that

thorium can be precipitated as thorium dihydride by equilibrating the thorium-magnesium solutions (containing 35 to 42 wt % Th) with hydrogen gas at one atmosphere pressure. The concentration of thorium in the liquid phase for the reactions carried out at one atmosphere hydrogen pressure over the specified temperature range is given by the following relation

$$\log_{10} N = \frac{-4609 \pm 209}{T} + 2.824 \pm 0.208,$$

where N_{Th} represents the mole fraction of thorium in the liquid phase. The above equation was determined by a least squares treatment of the experimental data, and the limits in the equation represent the probably error for the constants. It can be seen that the concentration of thorium remaining in the liquid phase at equilibrium decreases as the reaction temperature is lowered. The concentration of thorium in the liquid, calculated from the above expression, is 25.03 wt % at 800°C and 8.11 wt % at 675°C.

A more complete separation might be achieved by permitting the charge to freeze under an atmosphere of hydrogen. In this case the less dense magnesium rich dendrites would be expected to float to the top of the melt and as the remaining liquid tends to increase in thorium content further precipitation of ThH_2 would be expected. Although complete precipitation of the thorium from the liquid solution was not realized, it is felt that a reaction of this nature might be employed as a method for purifying crude thorium.

A detailed report on the precipitation of thorium dihydride from thorium-magnesium solutions is being prepared.

2. Preparation of Pure Compounds

2.1 Preparation of $ThCl_4$ (5)

Pure thorium tetrachloride is necessary for the preparation of pure thorium metal by reduction with magnesium. A crude thorium tetrachloride can be prepared by chlorination of thorium oxide and carbon mixtures. A complete purification from excess carbon and thorium oxide should be achieved by vaporization of the thorium tetrachloride. This vaporization was attempted under vacuum to reduce the temperature necessary for rapid vaporization.

A considerable purification was achieved but some thorium oxide and carbon were carried over into the product. Since both of these materials are practically non-volatile at 800°C, they must have been carried as particulate material by thorium tetrachloride vapor.

An investigation of the separation of a volatile solid from a finely divided non-volatile substance by vaporization was started. For convenience, ammonium chloride was chosen as the volatile solid and silicon carbide, nominal 600 mesh, as the non-volatile impurity. The results which have been obtained indicate that at low pressures, below 500 microns, very poor separations are achieved even at extremely low rates of vaporization. The purification is improved by decreasing the rate of vaporization and by increasing the pressure in the vaporization apparatus. The effect of pressure on the rate of vaporization and the effect of pressure and rate on the purification is being determined.

2.2 Preparation of Rare Earth Fluorides (2,7)

About 4 kg of erbium oxide was converted to erbium fluoride by reaction with anhydrous HF gas at 600°C for 10 hours. A platinum tray was used as the containing vessel. The conversion, based upon weight changes only, was approximately 99 percent.

In the preparation of yttrium fluoride, experiments were conducted to determine the hydrofluorination conditions which yield the highest purity YF_3 . Since no quantitative method has been developed for direct measurement of the oxide content in fluoride, the quality of a given batch of fluoride was determined by the evaluation of the quality of the metal prepared from that fluoride. A relative method of evaluating the oxide in the fluoride has been developed by the Ames Laboratory spectrographic group and has also been employed in these studies. The fluoride is ignited by an arc in an argon atmosphere and a ratio is determined between the intensity of the argon line and the oxygen line being supplied by unconverted oxide present in the fluoride. The lower the intensity ratio, the less oxygen present.

The methods studied for preparing YF_3 were: (1) hydrofluorination of yttrium oxalate or oxide at 600°C, (2) periodic rotation of yttrium oxide heated at elevated temperatures in an HF stream, and (3) precipitation of $YF_3 \cdot 1/2 H_2O$ from aqueous solution followed by thermal decomposition of the hydrate in a stream of HF gas.

Yttrium oxalate tri-hydrate was placed in a stationary bed furnace and hydrofluorinated for 6 hours at 600°C. The fluoride obtained had an intensity ratio of 0.50, as determined by spectrographic analysis. After blending and rehydrofluorinating this material for an additional 6 hours at 600°C, no change in the intensity ratio was noted. The by-product, oxalic acid, was removed in this reaction by volatilization.

A series of experiments were made in which yttrium oxalate was calcined at various temperatures. This was done to determine what effect calcining temperature has upon the rate and efficiency of fluoride conversion. The oxides were all hydrofluorinated simultaneously so that no variable was introduced during this operation. Best conversion to fluoride was obtained on oxide which had been prepared at a calcining temperature between 800 and 900°C.

A method involving periodic rotation of the Y_2O_3 during hydrofluorination was investigated and is believed to be superior to the stationary bed treatment. It was found that hydrofluorination of the oxide in a stationary tray at 600°C required prolonged treatment in an HF stream. With intermittent removal of the fluoride, grinding, mixing and replacement in the furnace, good conversion could eventually be obtained. This suggested that agitation during the HF treatment would be beneficial.

Finely divided yttrium oxide was placed in an inconel tube which was inserted into the hydrofluorinating unit. The furnace was heated slowly to 800°C and held at that temperature for 3 hours with periodic rotation of the tube and its contents. Thus in a 9-hour cycle good conversion to the fluoride was obtained. The spectrographic intensity ratios of fluoride prepared in this manner range from 0.25 to 0.42, the best values obtained on any fluoride prepared to date.

Yttrium trifluoride hemihydrate, $YF_3 \cdot 1/2 H_2O$, was precipitated from a hot hydrochloric acid solution of Y_2O_3 by the addition of liquid anhydrous hydrogen fluoride. The hemihydrate was dehydrated at various temperatures in an anhydrous HF stream. It was found that if temperatures lower than 500°C were used to thermally decompose the hydrated fluoride, the quality of the metal prepared from that fluoride was unsatisfactory. Metal prepared from "wet process" fluoride dehydrated at 600°C was equivalent to that prepared from the dry process material but did not appear to be superior in quality.

In one experiment approximately 10 grams of YF_3 , which had been prepared by treatment of Y_2O_3 with anhydrous HF , was maintained in a bromine trifluoride atmosphere at $600^\circ C$ for 1 hour. Analyses of the YF_3 before and after treatment with the BrF_3 indicated that no detectable change in oxygen content had occurred.

3. Metal Preparation Studies

3.1 Preparation of Vanadium Metal (2,1)

Crystal bar vanadium has been prepared in quantities of about 100 grams per run. Some of the conditions which give greatest growth rate and highest purity have been determined. The temperature of the Inconel retaining vessel and of the vanadium feed material should be maintained at approximately $800^\circ C$ since at this temperature VI_4 forms readily and has an appreciable vapor pressure. A filament temperature of about $1100^\circ C$ was found to give maximum growth rate in the apparatus being used. Higher filament temperatures may be desirable but this would result in over-heating of the feed material above the $800^\circ C$ optimum by radiation from the hot filament. In order to study the effect of higher filament temperatures a different type of furnace for controlling the temperature of the feed material will be required. Another significant factor found to be influential in determining growth rate has been internal pressure. If the total pressure in the system exceeds 1.5 millimeters of mercury the growth rate is exceedingly slow. Control of internal pressure is accomplished by controlling the rate of iodine addition.

Some variation in the purity of the final product is known to result from variation in the starting material. Most metallic impurities and silicon present in the starting material are transferred to the final bar in about the same proportions. The non-metallic impurities, carbon, nitrogen and oxygen, can be fairly well excluded from the final metal although carbon is transferred in proportion to the amount of carbon present in the feed material. Low oxygen and nitrogen content in the final metal appears to depend upon the successful exclusion of leaks from the system.

A larger reaction vessel, designed to produce one-pound quantities of crystal bar vanadium in a single operation is now under construction. This scale of operation has become necessary because of the increased laboratory requirements for high purity vanadium in alloy studies and other research problems.

Work on the carbon reduction of vanadium oxides has given metal with some residual oxygen and carbon. The metal so far produced has not been ductile. Using V_2O_5 , the mixture of carbon and oxide is heated under an inert atmosphere during the initial, somewhat eruptive reaction which gives a lower oxide. After this reaction has subsided, the charge is heated to 950°C before the inert atmosphere is removed. Subsequent reactions carried out by increasing the temperature under vacuum pumping conditions. The reaction appears to be completed by holding at about 1550°C . The resulting sponge metal is subsequently arc-melted. Variations in carbon to oxide ratio are being studied.

3.2 Preparation of Niobium Metal (1)

Previous work indicated that the reduction of Nb_2O_5 with carbon occurs mainly by the following equation:

Data in the previous report showed that soft, ductile metal can be produced by mixing essentially stoichiometric quantities of Nb_2O_5 and carbon, but that a slight deviation from stoichiometry yielded metal which was hard and non-ductile. Also, it was reported that there were possibilities of adding a "scavenger agent" to the reduction. This "scavenger" was added to charges which were deficient in carbon and its function was to form a volatile oxide from any remaining oxygen in the metal. The first test for a "scavenger" employed silicon metal which has a volatile oxide at the temperatures and pressures of the reduction process. However, attention has been directed toward the use of oxides as additives because of their availability, price, and purity. SiO_2 and TiO_2 with carbon have been tested for use as the "oxygen scavenger". Although SiO_2 with carbon in the charge seems to improve the quality of the metal, the use of elemental silicon has given better results to date. Most of the work on the addition agent study for this period has been done with TiO_2 .

The idea can be described in the following manner. Sufficient carbon is mixed with Nb_2O_5 and TiO_2 to insure reduction of TiO_2 and incomplete reduction of Nb_2O_5 . The titanium product at a higher temperature, it is assumed, reacts with the remaining oxygen of the Nb_2O_5 and forms a volatile titanium oxide, which should leave essentially oxygen-free Nb metal as the product. It is not known how the reaction proceeds, chemically, or that the net result is that assumed above but the charges are made according to the following equation:

Experiments were made varying the Z and Y quantities in the charges. The resulting metal was then analyzed and tested. From the data obtained it appears that ductile niobium can be prepared quite readily by proper additions of TiO_2 and carbon to the charge containing Nb_2O_5 . The oxygen contents of the products in a series of tests were all less than 500 ppm. A small amount of titanium usually remains in the niobium metal when TiO_2 is employed as the additive.

No concrete explanation has been established concerning the amount of titanium or TiO_2 that must be used in the charge to scavenge the oxygen from Nb metal. The presence of titanium in the charge appears to be much more effective in oxygen removal than niobium itself. Work is continuing on this problem.

3.3 Preparation of Thorium by the Iodide Process (3)

Some minor changes in the method of heating the Pyrex deposition bulb have improved the output of the apparatus and the techniques appear now to be nearly if not completely satisfactory.

3.4 Preparation of Yttrium Metal (2,7)

Additional studies have been made on the preparation of yttrium metal by reduction of YF_3 with calcium to form a low melting Y-Mg alloy. The effect of the quality of the ingredients used upon the quality of metal obtained was investigated. The primary sources of oxide in the metal appear to be the fluoride and the calcium, with an indeterminate amount introduced in handling operations.

Experiments with a segregated reduction charge were successful and indications are that it is superior to a homogeneously mixed charge for this reaction. Granular calcium and magnesium, intimately mixed, were placed in the bottom of the zirconium reaction vessel. A mixture of YF_3 and CaCl_2 was then added. When the reaction was carried out in this manner, the slag-metal separation was excellent and good recovery of the yttrium-magnesium alloy was obtained. Massive calcium and magnesium can be employed in this way if they are first melted together forming a calcium-magnesium alloy block. The fluoride-chloride salts are then added and the reaction is carried out.

Conditions for removal of calcium and magnesium from the alloy by vacuum sublimation were studied in considerable detail. It was found that magnesium can be readily removed to less than 500 ppm by heating to 1000°C for 8 hours under a pressure of 0.1 micron. Calcium is not removed completely under these conditions however, with 0.2% Ca or more remaining. Removal of calcium is more complete upon heating at 1100°C for 8 hours; the residual calcium then varies from 300 to 1000 ppm.

The removal of calcium and magnesium from the alloy is most easily accomplished by first crushing the brittle alloy. In doing this the formation of some fine particles is inevitable. Some of these "fines" which passed through a 20 mesh screen were "demagged". The per cent of bromine insoluble was determined for the finer material and was found to be higher by a factor of ten than for the larger particles.

4. Alloy Systems

4.1 Thorium-Zirconium System (2)

The investigation of the thorium-zirconium alloy system has been completed and the work is described in detail in the M.S. thesis of E. D. Gibson entitled "Investigation of the Thorium-Zirconium System with Emphasis on High Temperature X-ray Techniques". This thesis is available from the Iowa State College Library. The work has also been described in a paper entitled "Thorium-Zirconium and Thorium-Hafnium Alloy Systems" by E. D. Gibson, B. A. Loomis and O. N. Carlson which has been accepted for publication in the 1958 Transactions of the American Society for Metals.

4.2 Thorium-Yttrium System (2)

A study of the thorium-yttrium system has been initiated and a 50 wt % Th-Y alloy prepared. The alloy was examined microscopically in the as-arc-melted condition revealing a one phase structure. Before a more comprehensive study was carried out on this system an attempt was made to purify yttrium metal by vacuum distillation. Yttrium metal prepared in this Laboratory containing about 0.25% oxygen and 0.5% zirconium was distilled at a temperature of about 2000°C from a tantalum vessel. Approximately 50 grams of yttrium was collected on the condenser. This metal was free of zirconium but contained about the same amount of oxygen as the original material.

4.3 Tantalum-Zirconium System (3)

The upper boundary of the decomposition loop has now been established by measurements of electrical resistance over the range from 1000°C to 1800°C. The crossing of the boundary makes itself evident by a change in the slope of the curve. Results obtained by these measurements agree well with the x-ray and metallographic data obtained previously.

Resistance-temperature measurements at lower temperature have established that the eutectoidal horizontal terminates on the tantalum-rich side at about 94% tantalum. Some difficulty is still being encountered in determining the composition of the eutectoid.

4.4 Zinc-Zirconium System (6)

The zinc vapor pressures over a number of zinc-zirconium alloys have been measured and the results are summarized in the accompanying Tables II and III. These data will be used in making other calculations on the thermodynamic properties of these alloys.

4.5 Tantalum-Vanadium System (2)

The study of the tantalum-vanadium system is nearing completion and a terminal paper is now being written on this work. The structure and composition of the intermediate phase in this system has not been fully determined although recent work has indicated that the compound can be indexed satisfactorily on the basis of a hexagonal structure. Further work is being done to confirm this and to refine the lattice parameters. The reflections from the hexagonal cell appear to be closely related to those of the body-centered cubic phase from which it precipitates.

4.6 Thorium-Hydrogen System (5)

The apparatus for determining pressure composition isotherms for the thorium-hydrogen system was modified to eliminate temperature gradients in the sample and to allow more accurate measurement of the sample temperature. These changes did not affect the variation of the hydrogen pressure with sample composition in the composition range where thorium was in equilibrium with thorium dihydride. This pressure variation was found to be different for samples of crystal bar thorium and Ames thorium. The explanation would seem to be that the impurities in the thorium are responsible for this pressure variation. The effect of impurities added in known amounts to thorium on the pressure-composition isotherms will be investigated to obtain a more complete understanding of this phenomenon.

Table II

Log vapor pressure of zinc for several zinc-zirconium
compositions and temperatures

w/o Zr	Temp. (°C)	$10^4/T$ (K°)	Log ₁₀ Pressure Atmos- pheres	Temp. (°C)	$10^4/T$ (K°)	Log ₁₀ Pressure Atmos- pheres
1.08	669	10.613	-1.368	814	9.198	-0.452
	707	10.200	-1.090	853	8.879	-0.252
	757	9.707	-0.784	884	8.642	-0.106
	794	9.370	-0.569	917	8.402	+0.031
	836	9.016	-0.347	949	8.182	+0.165
4.0	799	9.330	-0.580	875	8.69	-0.165
	843	8.960	-0.334	914	8.42	+0.008
8.74	651	10.823	-1.470	866	8.780	-0.229
	704	10.235	-1.129	885	8.636	-0.136
	757	9.709	-0.794	932	8.299	+0.054
	814	9.200	-0.478	983	7.962	+0.271
12.24	595	11.518	-1.974	773	9.558	-0.710
	627	11.109	-1.649	826	9.098	-0.446
	671	10.595	-1.343	868	8.766	-0.259
	688	10.408	-1.226	904	8.492	-0.085
	707	10.202	-1.101	947	8.198	+0.102
	740	9.870	-0.899			
15.0	854	8.873	-0.306	943	8.230	+0.068
	897	8.547	-0.118			

Table II (Continued)

w/o Zr	Temp. (°C)	$10^4/T$ (K°)	Log ₁₀ Pressure Atmos- pheres	Temp. (°C)	$10^4/T$ (K°)	Log ₁₀ Pressure Atmos- pheres
19.0	543	12.246	-2.699	755	9.730	-0.799
	583	11.680	-2.200	802	9.301	-0.546
	641	10.939	-1.649	870	8.747	-0.260
	692	10.356	-1.242	910	8.452	-0.050
	726	10.004	-0.984	970	8.046	+0.186
23.73	957	9.709	-0.790	921	8.375	-0.007
	802	9.302	-0.554	946	8.200	+0.105
	845	8.945	-0.371	958	8.115	+0.135
	885	8.636	-0.145			
24.7	728	9.988	-0.981	822	9.131	-0.451
	744	9.831	-0.864	856	8.856	-0.287
	761	9.669	-0.767	877	8.684	-0.188
	781	9.486	-0.655	900	8.524	-0.084
	798	9.335	-0.462	924	8.353	+0.012
25.0	583	11.680	-2.176	770.6	9.580	-0.706
	609.6	11.328	-1.924	799.6	9.321	-0.555
	647.0	10.867	-1.568	838.0	8.999	-0.361
	678.6	10.506	-1.338	872.4	8.729	-0.210
	704.6	10.227	-1.134	918.0	8.395	-0.019
	730.4	9.964	-0.943			

Table II. (Continued)

w/o Zr	Temp. (°C)	$10^4/T$ (K°)	Log ₁₀ Pressure Atmos- pheres	Temp. (°C)	$10^4/T$ (K°)	Log ₁₀ Pressure Atmos- pheres
35.0	653.0	10.797	-2.434	843.6	8.954	-0.827
	681.0	10.480	-2.140	859.6	8.828	-0.701
	724.0	10.028	-1.757	896.4	8.550	-0.441
	740.0	9.869	-1.636	933.0	8.291	-0.244
	762.2	9.654	-1.448	961.0	8.100	-0.095
	798.0	9.335	-1.176			
50.0	675.4	10.542	-2.538	872.4	8.729	-0.984
	732.0	9.948	-1.980	922.6	8.363	-0.661
	775.4	9.537	-1.636	953.0	8.155	-0.458
	830.0	9.065	-1.275			
69.0	667.0	10.636	-4.150	775.4	9.537	-2.712
	714.4	10.126	-3.459			
71.0	757.6	9.701	-2.929	861.2	8.815	-1.717
	766.6	9.617	-2.820	906.0	8.480	-1.351
	822.0	9.131	-2.192			

Table III.

The boiling points of several zinc-zirconium alloys

Alloy Composition (w/o Zr)	Boiling Point (°C)
pure zinc	907
1.08	910
4.0	914
8.74	917
12.24	923.7
15.0	924.5
19.0	924
23.73	924.5
24.7	924
25.0	925
35.0	980
44.0	1040
50.0	1040
69.0	----

The solubility of thorium dihydride in thorium metal is being determined at a number of temperatures. The method being used is to saturate a sample of thorium with hydrogen at a given temperature, remove any excess thorium hydride from the surface and analyze the saturated portion for hydrogen. The analytical method used for hydrogen was a warm extraction of the hydrogen at 800°C. The solubility of thorium dihydride in Ames thorium is given in the accompanying table.

Solubility of thorium dihydride in thorium

Temperature	Solubility Limit Atomic Percent
198	0.54
305	1.4
405	4.9
552	8.5
616	12.9
685	17.0
820	25.3

These results agree with the solubility limits obtained from pressure composition isotherms. The solubility in crystal bar thorium and in thorium to which carbon has been added will be determined.

4.7 Tantalum-Niobium System (3)

The investigation of this system was completed during this period and a final report written. The report has been accepted by the American Society for Metals for presentation at the Metal Congress in November. The phase diagram shows a continuous series of solid solutions at all temperatures but no other features. Exploration by electrical resistance measurements from room to high temperatures failed to reveal any anomaly.

4.8 Thorium-Molybdenum System (3)

Melting point data have indicated that the composition of the eutectic lies between 70% and 90% thorium. Previous work had established that the eutectic temperature is about 1400°C. The approximate composition has been checked by metallography.

4.9 Zirconium-Nickel System (3)

Melting point measurements show a eutectic point close to 17% nickel and 975°C. The eutectic horizontal terminates at about 2% nickel. Both pieces of information are corroborated by metallography. The first compound is at 24% nickel, corresponding to NiZr_2 , according to melting point and x-ray measurements. X-ray results point to practically no solubility of nickel in zirconium at room temperature. The zirconium-rich alloys can be fabricated up to 5% nickel and wires made from them are being investigated by resistance-temperature measurements.

4.10 Thorium-Tantalum System (3)

An investigation of the thorium-tantalum system was started late in the reporting period. Several of the high tantalum alloys have been prepared in the tungsten electrode arc furnace. Those in the intermediate composition range are difficult to make homogeneous.

4.11 The Uranium-Hafnium System (5)

Samples of uranium-hafnium alloys of various compositions were heat-treated for 72 hours and quenched into water from 625°C, 685°C and 756°C. These temperatures bracket the temperatures at which thermal arrests had been observed. Microscopic examination of these samples were hindered by difficulty in obtaining satisfactory etched surfaces. The samples quenched from below the alpha-beta transformation were all two phase alloys and no indication of an intermediate phase was observed. Additional uranium-rich alloys were prepared to permit more detailed investigations of the high uranium end of the phase diagram.

4.12 Yttrium-Titanium Alloy System (2)

A study of the yttrium-titanium system was initiated for the purpose of determining the phase relationships, corrosion resistance and mechanical properties of the alloys at room temperature and above. Alloys were prepared from Grade A titanium sponge obtained from the Crane Company and from yttrium sponge prepared in this Laboratory.

The titanium allotropic transformation lies on a temperature horizontal at 880°C for alloys of composition lying between 15 and 95 wt % titanium. This is approximately 10 degrees below that for the unalloyed titanium. There is a eutectic horizontal in the system extending from approximately 10 wt % titanium to 95 wt % although the exact limits of terminal solid solubility at the eutectic temperature have not been established. The eutectic temperature was determined to be 1330°C by a method employing an optical pyrometer which is sighted on a small hole drilled into a bar of the alloy specimen. First evidence of melting observable in the hole during heating was taken as the solidus temperature. The melting point of the titanium used in this investigation was determined to be 1630°C by this method and of yttrium, 1465°C .

4.13 Molybdenum-Rhenium System (3)

An investigation of this system in which alloys were prepared by the methods of powder metallurgy was suspended for several years because of pressure of other work. This problem is being taken up again and this time the alloys will be prepared by co-melting of pieces cut from sheets of the component metals.

4.14 Vanadium-Chromium System (2)

As reported in ISC-835 chromium-vanadium alloys exhibited promising corrosion resistance to high temperature steam (300°C) and to air oxidation at 500°C . An investigation of the vanadium-chromium system was undertaken to establish the phase diagram and to determine the degree of ductility of some of the intermediate compositions. Vanadium and chromium form a complete series of solid solutions with a minimum in the solidus occurring at 70 at % Cr and at 1750°C . The solidus data, as determined by the optical pyrometer method described in the preceding section, are plotted in Fig. 2. Hardness versus composition of the vanadium-chromium alloys is shown in the graph in Fig. 3. The hardness approaches a maximum at about 50 percent. Interestingly, vanadium with a hardness of $R_A-42.5$ can be cold rolled extensively whereas chromium, which is of lower hardness, R_A-39 , has no ductility at room temperature. None of the alloys containing greater than 10% chromium exhibit any degree of ductility as evidenced by their inability to be cold rolled.

Fig. 2 - Plot of melting temperatures (solidus) vs composition for V-Cr alloys.

Fig. 3 - Hardness vs composition for V-Cr alloys.

5. Corrosion Studies

5.1 Corrosion Properties of Some of the Refractory Metals Upon Alloying with Yttrium. (2,7)

Alloys containing additions of small amounts of yttrium to tantalum, niobium, molybdenum, titanium, vanadium and zirconium were continued in corrosion tests during this report period. Results of preliminary tests up to a maximum of 21 days were reported in ISC-835. Some of the more stable alloys were tested for a total of 42 days in air at 500°C and for 60 days in water at 300°C. These data have been compiled in Table IV. Chromium containing 0.5 and 1 wt % yttrium appears to exhibit slightly improved oxidation resistance at 500°C.

A survey of the yttrium base binary alloys of yttrium-niobium, yttrium-chromium and yttrium-titanium has recently been initiated. Alloys have been prepared and examined microscopically but no corrosion data have been obtained.

Table IV

Alloy Composition at %	Water Corrosion at 300°C after 60 days Grams weight change*	Air oxidation at 500°C after 42 days Grams weight change
Pure Cr	0.0030	0.0006
Cr-0.5% Y	0.0010	0.0001
Cr-1.0% Y	0.0010	0.0002
Nb-0.5% Y	0.0010	Failed
Nb-1.0% Y	0.0007	"
Nb-7.9% Y	-0.0012	"
Mo-0.5% Y	0.0010	Failed
Mo-1% Y	0.0001	"
Ta-1% Y	0.0010	Failed
Ta-2.8% Y	----	"
Ti-0.5% Y	0.0000	0.0010
Ti-1.0% Y	-0.0001	0.0011
Ti-5.5% Y	0.0001	0.0033
V-0.5% Y	-0.0003	0.0122
V-1.0% Y	0.0005	0.0107

* Each specimen tested had an area of approximately 2.5 cm² and weighed 1-2 grams.

Table IV (Continued)

Alloy Composition at %	Water Corrosion at 300°C after 60 days Grams weight change*	Air Oxidation at 500°C after 42 days Grams weight change
Zr-0.5% Y	0.0590	Failed
Zr-1.0% Y	Powder	"
Zr-5.3% Y	Powder	"
V-46% Cr-6% Y	0.0004	0.0050
V-15% Cr-4% Y	0.0007	0.0090

* Each specimen tested had an area of approximately 2.5 cm² and weighed 1-2 grams.

6. Solid State Investigations

6.1 Structure of Aluminum-Vanadium Intermetallic Compounds (4)

The structure of the α -phase compound in the vanadium-aluminum system has recently been determined by Miss P. J. Brown.¹ This structure has the space group symmetry O_h^{17} --Fd3m and has vanadium atoms in the 16c positions and aluminum atoms in the 96g, 48f, and 16d positions. An interesting feature of the structure is the large volume available at the 8b positions in the structure. Brown's data indicated that the crystals from which she obtained intensity data had 10% or less of the 8b sites occupied by aluminum atoms. The present work corroborates Brown's structure determination in detail, but the crystals investigated at this Laboratory were found to have ~50% aluminum occupancy of the 8b sites. Thus comparison of the two sets of data indicates that the α -phase can exist over a range of composition and that the composition variation arises from the degree of occupancy of the 8b sites. Composition limits of VA_{10} and V_2Al_{21} may be inferred.

¹P. J. Brown, Acta Cryst. 10, 133 (1957).

Crystals of the α -phase compound were prepared by holding a vanadium-aluminum alloy (6 wt % vanadium) at $665 \pm 3^\circ\text{C}$ for two weeks under a helium atmosphere.¹ The alloy was then quenched in oil, cleaned, and the aluminum matrix dissolved in 1N HCl. Suitable crystals were manually separated from the residue. Symmetry was confirmed by layer line patterns taken with Weissenberg and precession cameras. Intensity data were taken with a G-M tube attached to a Weissenberg camera and $\text{CuK } \alpha$ radiation was employed. The intensities for equivalent reflections agreed within 5% after corrections were made for Lorentz and polarization factors. The data were processed on an IBM-650 computing machine using the Least Squares II program written by Dr. M. E. Senko of the I. B. M. Research Center, Poughkeepsie, N. Y. This program refines both the structure parameters and the temperature factors for each set of atoms. Refinement of the structure was done with the 8b positions 0%, 25%, 50%, 75%, and 100% occupied. Figure 4 shows a plot of the reliability factor, $R = \sum |F_o| - |F_c| / \sum |F_o|$, obtained from the calculations. The most intense reflection, (880), was omitted when computing R to avoid scaling errors. The magnitudes of F_o and F_c are shown in Table V; the tabulated F_c is based on the structure with 8b sites 50% occupied. There is excellent agreement between the three structure parameters obtained by the least squares refinement and those obtained by Brown.

<u>Position</u>	<u>Brown</u>	<u>These Data</u> <u>(8b, 50% occupied)</u>
96 g (xxz)	x = 0.0654	x = 0.0644
	z = 0.3009	z = 0.3009
48 f (x00)	x = 0.1407	x = 0.1408

A lattice parameter of 14.516 Å was obtained from data taken on a back-reflection Weissenberg camera; Brown obtained 14.492 Å. The difference in the two values is in the direction which might be expected from the indicated difference in aluminum content.

¹ Heating the same alloy at 673°C produced crystals having monoclinic symmetry.

Fig. 4 - Values of the reliability factor, R , obtained as a function of the degree of filling of the 8b positions.

Table V.

Magnitudes of Observed and Calculated Structure Factors for $\alpha(\text{Al-V})$

hkl	F _o	F _c	hkl	F _o	F _c	hkl	F _o	F _c	hkl	F _o	F _c
(000)	-	158.2	5,11,1	6.0	5.8	10,10,2	9.2	9.7	6,14,4	<2.0	3.0
220	3.5	4.6	5,13,1	7.1	7.1	10,12,2	<2.1	0.8	6,16,4	4.9	5.0
260	18.7	19.4	5,15,1	<1.9	0.7	10,14,2	19.3	18.3	884	11.2	9.6
2,10,0	12.7	11.6	5,17,1	3.8	6.0	12,12,2	4.7	3.1	8,10,4	4.2	3.8
2,14,0	11.8	11.2	771	<1.7	0.8	12,14,2	<2.1	0.7	8,12,4	10.6	11.3
2,18,0	6.8	5.5	791	7.1	6.2	333	<2.2	0.6	8,14,4	2.7	2.9
400	11.8	11.4	7,11,1	3.0	3.7	353	24.9	33.6	10,10,4	12.1	10.0
440	18.6	19.6	7,13,1	6.1	5.0	373	10.3	9.2	10,12,4	13.0	10.5
480	15.4	15.3	7,15,1	19.7	19.5	393	13.9	15.3	10,14,4	4.4	2.9
4,12,0	17.7	15.6	991	9.1	9.9	3,11,3	26.8	33.2	12,12,4	20.3	16.4
4,16,0	11.3	9.4	9,11,1	8.3	7.6	3,13,3	<2.2	1.8	555	15.8	15.8
660	18.3	18.5	9,13,1	<1.9	0.2	3,15,3	<2.0	0.9	575	7.8	7.3
6,10,0	<2.4	1.0	9,15,1	9.6	9.5	3,17,3	<1.9	2.2	595	15.5	14.4
6,14,0	10.4	8.1	11,11,1	<1.9	0.3	553	2.7	2.2	5,11,5	18.9	18.3
800	<1.7	0.3	11,13,1	2.7	3.4	573	11.1	10.6	5,13,5	<2.0	2.1
880	47.0	66.5	222	9.5	10.2	593	7.1	7.5	5,15,5	7.8	7.2
8,12,0	3.4	0.4	242	5.3	6.4	5,11,3	<2.2	0.4	775	4.3	4.7
8,16,0	2.7	1.8	262	28.4	40.9	5,13,3	11.4	9.3	795	2.5	2.2
10,10,0	13.4	11.0	282	14.7	15.0	5,15,3	<1.9	1.7	7,11,5	3.5	2.8
10,14,0	8.9	6.1	2,10,2	24.3	27.4	5,17,3	7.9	8.2	7,13,5	14.7	14.4
12,0,0	9.1	10.4	2,12,2	10.2	9.1	773	<2.0	0.1	7,15,5	<1.9	1.0
12,12,0	11.0	12.0	2,14,2	4.0	3.9	793	3.8	3.3	995	5.1	6.5
111	9.6	12.9	2,16,2	8.4	8.7	7,11,3	<2.2	1.3	9,11,5	7.6	7.5
131	6.9	5.4	2,18,2	6.4	6.6	7,13,3	<2.1	2.5	9,13,5	13.9	12.9
151	<1.7	1.6	442	13.8	13.8	7,15,3	<2.0	0.7	9,15,5	<1.9	0.7
171	20.3	25.3	462	5.3	5.4	993	9.0	8.2	11,11,5	20.5	21.0
191	5.5	5.6	482	5.5	5.7	9,11,3	2.5	1.6	11,13,5	2.7	2.7
1,11,1	<1.9	1.2	4,10,2	13.7	13.5	9,13,3	9.2	8.1	666	27.4	33.9
1,13,1	<2.1	0.3	4,12,2	7.3	6.5	9,15,3	5.8	4.9	686	13.2	13.5
1,15,1	<1.9	0.9	4,14,2	<2.2	2.4	11,11,3	<2.0	2.3	6,10,6	24.1	26.2
1,17,1	8.5	6.8	4,16,2	6.1	5.9	11,13,3	14.2	11.7	6,12,6	<2.0	0.4
331	6.3	7.2	662	4.9	3.1	444	33.3	43.5	6,14,6	4.4	2.5
351	13.7	15.6	682	4.3	4.1	464	4.9	5.1	6,16,6	2.7	2.5
371	<1.5	0.2	6,10,2	5.6	6.1	484	14.0	13.0	886	<2.2	1.0
391	5.2	5.8	6,12,2	6.6	7.2	4,10,4	18.4	18.3	8,10,6	9.2	9.7
3,11,1	8.7	8.6	6,14,2	23.2	22.9	4,12,4	26.1	25.6	8,12,6	2.8	3.4
3,13,1	13.1	13.2	6,16,2	7.4	6.8	4,14,4	2.7	2.1	8,14,6	13.7	13.1
3,15,1	<1.9	1.6	882	<2.1	1.1	4,16,4	4.6	4.8	10,10,6	19.1	18.5
3,17,1	5.6	5.9	8,10,2	9.7	10.2	664	5.7	5.7	10,12,6	7.1	6.3
551	17.6	19.7	8,12,2	4.8	3.7	684	4.9	5.2	10,14,6	3.8	3.2
571	<1.8	1.7	8,14,2	8.6	7.9	6,10,4	4.2	3.3	12,12,6	<1.9	1.0
591	3.4	3.0	8,16,2	<1.6	1.2	6,12,4	<2.3	1.7			

The temperature factors are related to the vibrational amplitudes and hence to the strength of the bonds. The temperature factor values are consistent with the bond strengths indicated by interatomic distances given by Brown. The values,

<u>Set</u>	<u>Temp. Factor ($\text{\AA}^2$)</u>
16 c (V)	0.12
96 g (Al)	0.52
48 f (Al)	0.39
16 d (Al)	1.35
8 b (Al, 50%)	1.53,

show that the vanadium atoms are most localized due to their greater mass and strong bonding. Similarly, the aluminum atoms in the 96g and 48f sets which are coordinated to vanadium are more localized than the aluminum atoms in the 16d and 8b sets which are not bonded directly to vanadium. Finally, the aluminum atoms in 8b with no bonds shorter than 3.1 Å have the most vibrational freedom and hence the lowest bond energy, and these are the atoms which do not seem necessary for stability of the structure.

Since the crystals used in this investigation and those used by Brown were all grown on the aluminum rich side of the compound, the difference in composition quite probably indicates a slope in the phase boundary as a function of temperature.

6.2 Study of the Allotropic Transformation in Uranium (6)

A report, ISC-893, "Characteristics of the Solid State Transformations in Uranium," by H. Klepfer and P. Chiotti, gives the experimental details and results of an investigation of the allotropic transformations in uranium. A previous report, ISC-837, summarized the results on the lattice constant values obtained by x-ray diffraction techniques from room temperature to the melting point of uranium. Consequently, only a brief summary of ISC-893 is given below.

Measurements of the changes in electrical resistance, sonic activity and x-ray diffraction patterns of uranium on heating through both transformations were employed to obtain information on the characteristics of these transformations.

Changes in the electrical resistance accompanying the transformations in high-purity uranium indicate a certain degree of reversibility in crystalline orientation of the allotropic forms involved. No sonic activity was detected on heating or cooling through the transformations; however, sonic activity was clearly detected on cooling below 600°C which was attributed to deformation by twinning. It was interesting to note that no sonic activity was detected during initial heating or on reheating from room temperature to above 600°C. Rapid thermal cycling through the transformations raised the temperature at which twinning could be detected, produced a small but detectable increase in the electrical resistivity of the newly formed alpha phase, and lowered the temperature at which transformation was detectable for both transformations. These effects are believed to be due to lattice hardening.

The allotropic transformations in uranium proceed isothermally, but the extent of isothermal transformation is a function of temperature over a definite temperature range. The isothermal transformation initially appears to involve bursts of transformation activity, and proceeds slowly in its later stages to an apparent end of transformation. A small, subsequent change in temperature, within the transformation region, results in another high initial transformation rate which decays rapidly and then again slowly approaches an apparent end of transformation.

In general, the experimental results indicate that the allotropic transformations in uranium proceed by the growth of coherent nuclei. The characteristics of the transformations are similar to those for typical martensitic transformations, except for the isothermal kinetic features. Arguments have been proposed for these non-typical kinetic features.

6.3 Electronic Specific Heat of Sodium Tungsten Bronze (Na_xWO₃) (4)

The heat capacity of sodium tungsten bronze (Na_xWO₃) has been measured over the temperature range 1.8-4.2°K for various

concentrations of sodium. An approximation to the density of states curve for the conduction band was obtained from the experimental data. It was found that the lattice contribution to the heat capacity was appreciably affected by the thermal history of the sample while the electronic contribution was relatively unaffected.

At sufficiently low temperatures the heat capacities of simple metals can be written as a sum of two terms, one linear in absolute temperature and the other cubic:¹

$$C = T + T^3. \quad (1)$$

The cubic term is associated with the lattice vibrations and, if C is the molar heat capacity, the coefficient β is given by

$$\beta = (12/5) \pi^4 n R (1/\theta_D)^3 \quad (2)$$

where R is the gas constant, θ_D is the Debye characteristic temperature and n is the number of atoms per formula weight. This equation is not rigorous in the case of the sodium tungsten bronzes since it does neglect the optical vibrational modes, but the equation does provide a parameter to associate with the lattice vibrations. This parameter should have significance for the purposes of this investigation unless there were an appreciable contribution by the optical modes to the heat capacity term which is linear in temperature. Since the energy contributions of the optical modes are frequently represented by Einstein functions, there seems to be no basis for expecting such a contribution.

The linear term should be due to the free electrons in the metal, and, in the so-called 'one-electron' approximation, is given by

$$\gamma = \pi^2 k^2 V_m N(\mathcal{E}_F)/3 \quad (3)$$

where k is Boltzmann's constant, $N(\mathcal{E}_F)$ is the density of energy states per unit volume evaluated at the Fermi level, and V_m is the molar volume. $N(\mathcal{E}_F)$ is placed on a per unit volume basis

¹A. H. Wilson, "The Theory of Metals" (Cambridge University Press, 1954), 2nd Ed., pp. 133-150.

rather than on the more customary per unit mass or per atom basis because the volume is relatively insensitive to changes in sodium concentration. It should be noted that this treatment neglects exchange and correlation contributions, but to a first approximation these effects cancel one another.¹

The bronze samples for this study were prepared by cathodic reduction of a sodium tungstate-tungsten(VI) oxide melt. It has been found empirically that the concentration of sodium in the bronze depends on the tungsten(VI) oxide concentration and that, as the latter is decreased from 50 to 20 mole per cent, x changes from 0.56 to 0.92. Attempts to grow samples outside this concentration range by this method of cathodic reduction were unsuccessful.

The sodium concentration of the samples was measured by an x-ray determination of the lattice parameter. It has been found by several investigators² that Vegard's law holds throughout the cubic range of the bronzes. The following linear relation between lattice parameter, a_0 , and sodium concentration was used in this study,

$$a_0 = 0.0820x + 3.7845. \quad (4)$$

The calorimeter was of standard design and has been described in a previous report (ISC-835). Bronzes having x equal to 0.56, 0.65, 0.73, 0.81 and 0.89 were measured. These data are plotted in Fig. 5 as C/T versus T^2 . The quantities which were obtained from these data are given in Table VI.

¹E. P. Wigner, Trans. Faraday Soc. 34, 678 (1938);
D. Pines, "Solid State Physics" (Academic Press, New York, 1955),
Vol. I, p. 368.

²B. W. Brown and E. Banks, J. Am. Chem. Soc. 76, 963 (1954).

Fig. 5 - C/T vs. T^2 for five bronzes.

Table VI
Summary of results

Sample	γ (millijoules-mole ⁻¹ -deg ⁻²)	Θ_D (°K)	$N(\epsilon_F)$ (e.v. ⁻¹ -cm ⁻³)
Na _{0.56} WO ₃	1.76 ± 0.02	454 ± 4	1.33 x 10 ²²
Na _{0.65} WO ₃	1.92 ± 0.02	449 ± 3	1.44 x 10 ²²
Na _{0.73} WO ₃	2.05 ± 0.02	497 ± 5	1.53 x 10 ²²
Na _{0.81} WO ₃	2.56 ± 0.03	454 ± 5	1.90 x 10 ²²
Na _{0.89} WO ₃	2.82 ± 0.03	505 ± 6	2.09 x 10 ²²

The lines in Fig. 5 were fitted to the experimental points by the method of least squares; the electronic heat capacity, γ , and the Debye temperature, Θ_D , were evaluated from the intercept and slope, respectively. The deviations quoted are probably errors calculated from the scatter of points about these lines. The densities of energy states at the Fermi level, $N(\epsilon_F)$, were calculated from the electronic heat capacities by Eq. 3.

Errors in a heat capacity determination arising through uncertainties in measurements of the energy supplied to the sample, the mean value of the temperature, the temperature rise of the sample, and the heat capacity of the addenda were estimated to be less than 3 per cent at all temperatures.

The crystalline symmetry of the metallic sodium tungsten bronzes, as shown by x-ray diffraction patterns, does not change with sodium concentration. On this basis, the Brillouin zone geometry is independent of sodium concentration and the curve describing the density of available electronic

energy states as a function of energy should be essentially the same for all sodium concentrations. Of course, this is not rigorous and some variation in the potential field experienced by the electrons must result from variation of the sodium concentration. However, the contribution of the sodium cores to the potential at any point in the lattice can be calculated by Ewald's method;¹ such a calculation² indicates that the potential contribution varies monotonically and, for most points, slowly with sodium concentration if the sodium distribution is random. This slight perturbation would be reflected in the electronic wave functions and might be expected to warp the density of states curve somewhat but would not be expected to change the general contour.

If one neglects this small warpage and assumes that the only change in the density of states curve with sodium concentration is the degree of filling of the available states, an approximate form from the density of states curve over the measured concentration region may be obtained from the experimental data. Since $N(\mathcal{E}_F)$ has been obtained from Eq. 3 for several values of x (refer to Table VI), these values can be used as ordinates for a plot of $N(\mathcal{E})$ versus x . Because of the 1:1 ratio of the conduction electrons to sodium atoms, this is equivalent to a plot of $N(\mathcal{E})$ versus the number of conduction electrons and $N(\mathcal{E})$ may be expressed as a function of electron density:

$$N(\mathcal{E}) = F(n). \quad (5)$$

Now the number of electrons with energy between $\mathcal{E}$ and $\mathcal{E} + d\mathcal{E}$ is given by

$$dn = f(\mathcal{E}) N(\mathcal{E}) d\mathcal{E} \quad (6)$$

where $f(\mathcal{E})$ is the Fermi-Dirac distribution function. At the temperatures in question, $f(\mathcal{E})$ may be taken as unity for all occupied states and substitution of Eq. 5 into Eq. 6 leads to

$$dn/F(n) = d\mathcal{E} \quad (7)$$

¹M. Born and M. Göppert-Mayer, "Handbuch der Physik" (Julius Springer, Berlin, 1933), Vol. 24, Part 2, p. 710.
²J. F. Smith, Phys. Rev. 95, 1369 (1954).

Graphical integration of Eq. 7 by the trapezoidal method provides a convenient method of converting the abscissa in the $N(\mathcal{E})$ versus x plot to an energy scale. Because of the constant of integration the zero point is arbitrary. The data are shown in Fig. 6. This shape of the density of states curve might result from the proximity of the energy surfaces to the Brillouin zone boundaries.

An additional experiment indicates anomalous behavior of the lattice contribution to the low temperature heat capacity. This experiment was simply a remeasurement of the low temperature heat capacity of $\text{Na}_{0.73}\text{WO}_3$ after annealing at 700°C for five days in a sealed quartz container. X-ray analysis showed no change in sodium concentration. The measured values were

$$\gamma = 1.98 \pm 0.02 \text{ millijoule-mole}^{-1}\text{-deg}^{-2}$$

$$\text{and } \theta_D = 589 \pm 10^\circ\text{K.}$$

The electronic contribution to the heat capacity is lower by 3.4 per cent than the value before annealing and the significance is dubious in view of the estimated experimental error. However, the Debye temperature increased by more than 18 per cent and this increase must be considered real. This result indicates that the electronic contribution to the heat capacity is relatively insensitive to the thermal history of the sample, but the lattice contribution is appreciably affected.

It should be noted that the sample, $\text{Na}_{0.81}\text{WO}_3$ was heated to 600°C for two days in the process of cleaning the sample. This is tantamount to annealing and was done before there was any suspicion that annealing would have an effect. Furthermore, the three samples having approximately the same Debye temperature were prepared about two years prior to measurement while the two samples with high Debye temperatures were recent preparations. All samples were prepared by the same technique and by the same person. Variation in reagent purity is possible, but currently it is believed that time is more suspect than purity. Some type of ordering phenomenon might explain these results. However, the fact that the electronic contribution to the heat capacity is not markedly affected by the past history of the sample lends credence to the construction of the density of states curve shown in Fig. 6. The shape of this curve should be susceptible to test by soft x-ray spectroscopy.

Fig. 6 - Density of states curve for Na_xWO_3 in the range $0.56 < X < 0.89$.

6.4 Measurement of Elastic Constants of Metal Single Crystals (2,4)

Measurements of the elastic constants of single crystals of metallic beryllium as a function of temperature are in progress. These determinations are being made by measuring ultrasonic pulse velocities through the pulse-echo technique. Preliminary figures for four of the five elastic moduli have been determined at room temperature:

$$c_{11} = 28.81 \times 10^{11} \text{ dyne/cm}^2$$

$$c_{33} = 34.57 \times 10^{11} \text{ " " "}$$

$$c_{44} = 15.96 \times 10^{11} \text{ " " "}$$

$$c_{12} = 2.55 \times 10^{11} \text{ " " "}$$

An investigation of the single crystal elastic constants of high purity thorium metal has been completed. Values for the elastic constant c_{11} , c_{12} and c_{44} of thorium were determined for the temperature range from 80 to 370 degrees K by ultrasonic measurements on single crystals. Two crystals were prepared by the strain-anneal method. One crystal was cut in the form of a circular plate about 0.7 inch in diameter and 0.06 inch thick with the $\langle 111 \rangle$ direction of the crystal perpendicular to the sample face. Measurements on this crystal by a resonance method gave values for the stiffness coefficient Q in the $\langle 111 \rangle$ direction. This stiffness coefficient is a function of all three elastic constants:

$$Q \langle 111 \rangle = \frac{c_{11} + 2c_{12} + 4c_{44}}{3}$$

The other crystal was in the form of a plate 0.28 inch thick, 0.5 inch wide and 1.0 inch long. The direction perpendicular to the largest face was found to lie between the $\langle 111 \rangle$ and $\langle 100 \rangle$ directions and close to the (011) plane. The cosines of this direction were determined accurately. Measurements of the velocities of the longitudinal mode and the two shear modes that could be propagated in this direction were obtained by the ultrasonic pulse-echo technique. Values for the elastic constants were calculated from the direction cosines and the velocity measurements, using a perturbation solution of the equations of motion in a skew direction as outlined by Neighbours and Smith.¹

¹J. R. Neighbours and C. S. Smith, Appl. Phys. 21, 1338 (1950).

These elastic constants were used to calculate values for the stiffness coefficient in the $[111]$ direction and these values were compared with the results obtained from the resonance method. The differences were assumed to be caused by systematic transit time errors inherent in the pulse-echo method. Allowance for these systematic errors was made by applying small corrections to the measured echo transit times, in proportion to the magnitudes of the times. The corrected transit times were used to calculate velocities from which values were obtained for the elastic constants. At 300 degrees K, $c_{11} = 7.53 \times 10^{11}$ dyne-cm⁻², $c_{12} = 4.89 \times 10^{11}$ dyne-cm⁻² and $c_{44} = 4.78 \times 10^{11}$ dyne-cm⁻². The maximum uncertainty in these values is about one percent. A value of compressibility of 17.3×10^{-15} cm²-dyne⁻¹ and a value of the anisotropy term,

$$\frac{2c_{44}}{c_{11} - c_{12}},$$

of 3.62 were calculated from the elastic constants.

Single crystals of copper, nickel and of copper-nickel alloys having nominal compositions of 10, 20, 30, 40, 50 and 60 wt % were prepared and their orientations determined. The measured longitudinal velocities appear to increase linearly for those alloys studied for a $[100]$ direction from 4.2×10^5 cm/sec for pure copper to 5.1×10^5 cm/sec for pure nickel.

6.5 Low Temperature Properties of Vanadium (2)

The brittle-ductile transition in vanadium metal reported in the preceding report (ISC-835) was examined further during this period. Tensile tests were carried out on standard 0.252 inch diameter tensile specimens prepared from bomb-reduced vanadium. These tests were performed at temperature intervals between -120°C and room temperature. A change from brittle to ductile fracture was found to occur between -55 and -70°C from tests made at a strain rate of 2×10^{-4} in/in per second.

The effect on the brittle-ductile transition of the addition of several elements which are known to have limited or extensive solid solubility in vanadium, was investigated and the results are shown in Table VII. The transition temperature for each alloy was determined from a series of tensile tests.

Table VII

Effect of alloying additions on transition temperature of vanadium

Composition Wt %	Transition Temperature °C
Bomb reduced vanadium	$-65^{\circ} \pm 10^{\circ}$
V-0.5% Cr	$-45^{\circ} \pm 10^{\circ}$
V-0.5% Ta	$-15^{\circ} \pm 10^{\circ}$
V-0.5% Mo	$-35^{\circ} \pm 10^{\circ}$
V-0.5% Ti	$-65^{\circ} \pm 10^{\circ}$
V-0.5% Zr	$-55^{\circ} \pm 10^{\circ}$
V-0.5% Th	$-65^{\circ} \pm 10^{\circ}$

From the data presented above it is apparent that small additions of titanium, zirconium and thorium have little effect upon the transition temperature whereas additions of chromium, tantalum and molybdenum raise the transition temperature significantly.

The lattice constant of bomb reduced and of higher purity crystal bar vanadium was determined as a function of temperature through the transition range. For bomb reduced vanadium a_0 decreases linearly from 3.0277 Å at 26°C to 3.0240 Å at -124°C with no discontinuity observed in passing through the transition temperature. For crystal bar the lattice constant varied from 3.0213 Å at -4°C to 3.0123 Å at -189°C with a change in slope occurring at -75°C.

7. Other Investigations

7.1 Vacuum Fusion Analysis of Metals (5)

The development of the nickel bath technique for vacuum fusion analysis of yttrium metal was continued. The percentage of added oxygen which was recovered from three samples was 95.2 percent. A number of analyses were performed on three lots of yttrium which had been analysed for oxygen by a spectroscopic method. The results by vacuum fusion were approximately 50 percent higher than the spectroscopic results. Additional standards containing known additions of oxygen are being prepared to determine more precisely the recovery which is obtained in the vacuum fusion analysis for oxygen using a nickel bath.

7.2 The Reaction of Calcium with Barium Chloride (5)

The reaction of calcium with barium chloride is being studied at 900°C. The metal and salt phases are immiscible at this temperature and the composition of the phases which exist at equilibrium is being determined by analysis of quenched samples. The samples of each phase are analyzed for calcium, barium, chloride ion and free metal. As a first approximation, the equilibrium is being treated by use of the law of mass action using concentrations for activities. The calculated equilibrium constants change with composition which indicates that these solutions are non-ideal in behavior. The solubilities of the metal in the salt phase also changes with composition. An attempt is being made to explain these results by postulating that calcium ions in the liquid salt cluster about the dissolved metal atoms.

7.3 Fabrication Properties of Yttrium Metal (2,7)

An investigation of the fabrication properties of yttrium metal was initiated to determine the cold working characteristic of the metal and of the effect of impurities upon this property. The study was begun with a qualitative observation of the cold rolling properties of the metal and several observations were noted. The metal in the arc melted condition exhibits a degree of ductility depending somewhat upon the original thickness of the section to be rolled. The metal work-hardens rapidly with the major increase in hardness occurring within the first ten per cent reduction. Several different specimens

varying in oxygen, calcium and magnesium content as well as other impurities were evaluated as to their ability to be cold rolled to determine whether a particular impurity was responsible for the rapid work-hardening and lack of ductility of the metal. To date no significant difference has been noted in the rolling character of the various specimens.

A study of the recovery and recrystallization temperatures of yttrium has also been made. A thin section of an arc melted ingot was cold rolled to 91% reduction thickness. Sections from the resulting sheet were vacuum annealed at various temperatures from 200°C to 900°C for a period of one hour. Microhardness measurements were taken after each annealing treatment and a recrystallization and recovery curve has been drawn from these data as shown in Fig. 7. There is a pronounced decrease in hardness after annealing at 400 - 500°C and a small anomalous increase around 800°C. Microscopic examination of the annealed specimens indicate that recovery probably occurs around the 500°C temperature and that the recrystallization temperature is near 750°C. A more detailed microscopic examination of the recrystallized grain structure will be made later following the development of a suitable polishing and etching technique to reveal the true structure of the annealed specimens.

7.4 Distribution of Silver Between Liquid Lead and Liquid Zinc (5)

The distribution of silver between liquid zinc and lead at 500°C is being determined. A tracer technique using Ag^{110} will be used to determine the distribution coefficient. The use of a tracer method will permit the determination of this distribution coefficient at very low silver concentrations. The two liquid metals containing a known amount of silver are equilibrated at 500°C and samples taken by pipeting through a sintered glass filter. In this way, representative samples of the liquid melts should be obtained. The entire sample of each phase was dissolved so that segregation during solidification of the sample would not affect the analysis. The silver was precipitated from these solutions after adding silver nitrate to each solution to make the amounts of silver precipitate equal.

Fig. 7 - Room temperature hardness vs annealing temperature for cold worked yttrium metal. Annealing time one hour at each temperature. Original cold working 91% reduction in thickness.

This made the self-absorption counting correction equal for all samples and assured the same recovery of the silver tracer from all the samples. The silver precipitate was dried and the activity measured with a G-M counting tube and scaler. The distribution coefficient was simply the ratio of the number of counts per minute per gram of the sample from the liquid zinc to the corresponding activity of the sample from the liquid lead. Only a few preliminary results have been obtained. These indicate a value of about 80 for the distribution coefficient at very low silver concentrations.

7.5 Reduction of Vanadium Oxides (1)

An investigation of the reduction of V_2O_5 to V_2O_4 and V_2O_3 with hydrogen and carbon has been initiated. The purpose of this study is to prepare pure V_2O_3 or V_2O_4 which will be used as starting materials for the reduction to vanadium metal with carbon. Since the stoichiometry of the V_2O_5 -carbon reaction is known to be complicated, a thorough study of this reaction at temperatures from 400 to 1000°C has also been initiated.

7.6 Some Studies on Reduction of Fluorides with Mixed Reductants (1)

When mixtures of calcium and magnesium are employed in the reduction of fluorides it should be possible to obtain a slag of calcium and magnesium fluorides having a lower melting point than a slag of only calcium or magnesium alone. Some preliminary work has been done and it is planned to extend this idea with the alloy formation idea to include tests on thorium, yttrium and other fluorides as a means for the preparation of the metals from their fluorides.

7.7 The Carbon Reduction of UO_2 (1)

Further exploratory tests are being made on this reduction process which has been investigated several times in the past. It is possible that with some of the modern equipment, crucible materials and techniques now available, contamination of the uranium obtained at the temperature required for the reaction can be eliminated or materially reduced.

8. Rare Earth Metallurgy

The major part of this material is included in ISC-902.

APPENDIX I: LIST OF REPORTS FROM THE AMES LABORATORY

1. Reports for Cooperating Laboratories

- ISC-687 John Gibson and J. M. Keller. Multi-Band Electrical Conduction.
- ISC-700 D. A. McCutchan and Glenn Murphy. The Stress-Strain Characteristics of Uranium.
- ISC-726 R. M. Henry and D. S. Martin. Comparative Yields of $\text{Fe}^{54}(\gamma, \text{pn})\text{Mn}^{52}$ and $\text{Fe}^{54}(\gamma, 2\text{n})\text{Fe}^{52}$.
- ISC-729 Thomas Hendrickson and J. M. Keller. Ferromagnetic-Antiferromagnetic Phase Transitions.
- ISC-746 Joseph I. Genco, M. Griffel, F. R. Duke and L. D. Jennings. The (C-H) Bond Dissociation Energy in the Methyl Group of Toluene.
- ISC-757 Ames Laboratory Staff. Chemistry. Semi-Annual Summary Research Report. January-June, 1956.
- ISC-758 Ames Laboratory Staff. Physics. Semi-Annual Summary Research Report. January-June, 1956.
- ISC-759 Ames Laboratory Staff. Metallurgy. Semi-Annual Summary Research Report. January-June, 1956.
- ISC-777 Charles Apel and H. J. Svec. Kinetics of the Reaction Between Calcium and Water Vapor.
- ISC-779 Dale Gibbs and H. J. Svec. Kinetics of the Reaction Between Magnesium and Water Vapor.
- ISC-802 Ernest L. Koerner, Jr., Morton Smutz and H. A. Wilhelm. Separation of Niobium and Tantalum by Liquid Extraction.
- ISC-804 G. W. Eakins, B. J. Loupee, W. A. Rhinehart, G. Schupp and E. N. Jensen. A Method for Reducing Time-Jitter in the Output of a Single Channel Analyzer.
- ISC-812 K. A. Gschneidner, D. J. Beerntsen, R. W. Vest, J. A. Kingston and J. F. Smith. Tabulation, Bibliography, and Structure of Binary Intermetallic Compounds. II. Compounds of Beryllium, Magnesium and Calcium.
- ISC-833 Ames Laboratory Staff. Physics. Semi-Annual Summary Research Report. July-December, 1956.

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APPENDIX II: LIST OF SHIPMENTS

<u>Destination</u>	<u>Item</u>
Dr. Gilbert Eggert Sandia Corp. Albuquerque, New Mexico	650 gm zinc-zirconium alloy
University of Minnesota Minneapolis, Minnesota	1 gm hafnium metal
University of Kansas Lawrence, Kansas	25 gm cerium metal
State University of Iowa Iowa City, Iowa	5 gm terbium oxide 2 gm special N ¹⁵ sample
Union Carbide Nuclear Company Oak Ridge, Tennessee	100 gm yttrium oxide 10 gm lanthanum oxide 10 gm neodymium oxide 10 gm samarium oxide 10 gm gadolinium oxide 10 gm dysprosium oxide 5 gm praseodymium oxide 1 gm ytterbium oxide 500 mg holmium oxide 500 mg erbium oxide 250 mg terbium oxide 250 mg thulium oxide 100 mg lutetium oxide 2 kgm dysprosium oxide 1 kgm ytterbium oxide 20 gm samarium metal 20 gm gadolinium metal
General Electric Research Laboratory Schenectady, New York	5 gm holmium metal
Brookhaven National Laboratory Upton, Long Island, New York	1 gm holmium oxide 1 gm thulium oxide 1 gm terbium oxide 1 gm lutetium oxide 4 pieces erbium metal 100 mg thulium metal
Princeton University Palmer Physical Laboratory Princeton, New Jersey	3 gm hafnium oxide
Lansen-Naeve Corp. New York 4, New York	10 gm ytterbium metal

<u>Destination</u>	<u>Item</u>
Oak Ridge Institute of Nuclear Studies Oak Ridge, Tennessee	1 gm holmium oxide 1 gm lutetium oxide
University of Kentucky Lexington, Kentucky	2 gm samarium oxide 2 gm neodymium oxide
Dr. John Owen The Clarendon Laboratory Oxford, England	2 specimens of gadolinium- yttrium alloy
Heavy Minerals Company Chattanooga, Tennessee	1 gm lanthanum oxide 1 gm cerium oxide 1 gm praseodymium oxide 1 gm neodymium oxide 1 gm samarium oxide 1 gm yttrium oxide 1 gm gadolinium 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
University of California Los Alamos Scientific Laboratory Los Alamos, New Mexico	20 gm yttrium oxide 20 gm lanthanum oxide 20 gm praseodymium oxide 20 gm neodymium oxide 20 gm samarium oxide 20 gm gadolinium oxide 5 gm erbium oxide 5 gm ytterbium oxide 3 gm terbium oxide 3 gm dysprosium oxide 3 gm holmium oxide 3 gm thulium oxide 3 gm lutetium oxide
Institut fur Physikalische Chemie an der Technischen Hochschule Vienna, Austria	10 gm hafnium metal
Dr. Frank Benner National Research Corp. Cambridge, Massachusetts	5 samples yttrium metal

<u>Destination</u>	<u>Item</u>
Purdue University Lafayette, Indiana	10 gm cerium oxide
Massachusetts Institute of Technology Cambridge, Massachusetts	2 gm yttrium oxide 2 gm lanthanum oxide 2 gm erbium oxide 3 gm dysprosium metal 1 gm gadolinium metal
Columbia-Southern Chemical Corp. Barberton, Ohio	50 gm xenotime sand
Physikalisches Institut der Technischen Hochschule Munich, Germany	1 gm terbium metal 1 gm holmium metal 1 gm thulium metal
National Bureau of Standards Washington 25, D. C.	2/10 gm each of the following oxides: cerium dysprosium holmium thulium ytterbium thorium
Universitetet Institute for Teoretisk Fysik Copenhagen, Denmark	1 gm dysprosium oxide 1 gm erbium oxide
Dr. Joseph Graca Iowa State College Ames, Iowa	9.7 gm yttrium oxide 13.45 gm erbium oxide 11.17 gm dysprosium oxide 200 ml each of the following 5% solutions: holmium ethylenediamine- tetraacetate yttrium chloride thulium chloride ytterbium chloride terbium chloride holmium chloride cerium chloride dysprosium chloride samarium chloride gadolinium chloride erbium chloride

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