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**AMES LABORATORY
RESEARCH AND DEVELOPMENT REPORT
U.S.A.E.C.**

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Metals, Ceramics and Materials (UC-25)
TID - 4500, December 15, 1960

UNITED STATES ATOMIC ENERGY COMMISSION

Research and Development Report

ANNUAL SUMMARY RESEARCH
REPORT IN METALLURGY

July 1959 - June 1960

by

Ames Laboratory Staff

December 1960

Ames Laboratory
at
Iowa State University of Science and Technology
F. H. Spedding, Director
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ANNUAL SUMMARY RESEARCH REPORT IN METALLURGY

For the Period July 1959 through June 1960

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

Previous research reports in this series are:

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ISC-300	ISC-1050
	IS-17

METALLURGY

(Annual Report, July 1959 - June 1960)

Under the direction of F. H. Spedding, H. A. Wilhelm,

O. N. Carlson, P. Chiotti, W. L. Larsen,

R. E. McCarley, D. T. Peterson and

J. F. Smith

1. Metal Preparation and Purification Studies

1.1 Vanadium

1.1.1 Iodide Refining (O. N. Carlson and C. V. Owen)

The optimum conditions for maximum growth rate of iodide vanadium were established as 800-850°C for the feed temperature and 1200-1300°C for the filament temperature. A comprehensive study was made of the impurity transfer from feed to filament under these conditions. The transfer of interstitial impurities was investigated by varying the oxygen, carbon and nitrogen content of the starting material. Crude vanadium varying in these impurities was used in a number of crystal bar experiments. The results for carbon and oxygen, presented in Table I, show that these impurities are partially removed from vanadium by iodide refining. The final carbon value appears to be independent of the concentration in the feed whereas the oxygen content depends somewhat upon the amount present in the initial material.

Two methods were used to prepare crude vanadium of a purity suitable for use as the feed material. Vacuum arc melting was found

Table I

Transfer of Carbon and Oxygen from Vanadium Feed to Hot Filament

w/o O in Feed	w/o O in Bar	w/o C in Feed	w/o C in Bar
0.06	0.004	0.11	0.020
0.4	0.033	0.12	0.009
0.6	0.020	0.14	0.007
2.6	0.027	0.15	0.020
3.7	0.031	0.17	0.012
4.0	0.050	0.21	0.006
4.9	0.052	0.23	0.003
5.9	0.062	0.25	0.018
7.5	0.039	1.0	0.034
9.5	0.047	2.8	0.013
10.0	0.038	3.6	0.015
10.0	0.130	4.9	0.016
11.3	0.180	6.2	0.020
		7.2	0.016
		8.3	0.010

w/o = weight percent

to reduce the oxygen content of calcium-reduced vanadium from 0.15 w/o to 0.04 w/o. Upon iodide refining of this material vanadium containing 0.004 w/o oxygen was obtained. Crude vanadium containing 0.5 w/o yttrium was also tried as the feed material. Since yttrium has a high affinity for oxygen and is not transferred by the iodide process it was added to vanadium in an attempt to scavenge the oxygen from the vanadium matrix thus preventing the formation of a volatile oxyiodide. No evidence was found that oxygen can be held back in this way.

The transfer of metallic impurities in iodide refining of vanadium was also investigated. An arc-melted alloy containing metallic elements usually found either in calcium-reduced or iodide vanadium was used in this study. Approximately 0.1 w/o each of nickel, silicon, copper, iron, chromium, and titanium was added to the vanadium feed. The results of these experiments are summarized in Table II. It will be noted that nickel, aluminum, silicon, copper and titanium are partially transferred while iron and chromium are carried over quantitatively. Yttrium is not transferred under the conditions of the experiment.

An inconel unit with a capacity to produce about five pounds of crystal bar vanadium per run was constructed. The retort was three feet long by one foot in diameter with a wall thickness of 0.25 inch. Metal gaskets were employed as vacuum seals on the large retort in an effort to eliminate condensation of vanadium iodide on the water-cooled surfaces, which was encountered with the small retort. A vacuum-tight closure was maintained at head temperatures of 600°C by means of a platinum gasket. Bars of iodide vanadium weighing

Table II

Metallic Impurity Transfer from the Vanadium Feed at 800°C to the
Iodide Bar at 1300°C

Element	w/o in Feed	w/o in Bar	Percent Transferred
Al	10.0	0.17	2
Cr	0.10	0.1	100
	0.08	0.1	100
Cu	0.12	0.020	16
	0.12	0.036	30
Fe	0.07	0.05	79
	0.06	0.07	100
Ni	0.13	0.007	5
Si	0.13	0.017	13
Ti	0.05	0.006	12
	0.09	0.010	11
Y	0.50	not detected	0

approximately four pounds were produced in a twenty-four hour growth period. Chemical analysis showed that the purity of this metal was 99.9% vanadium which is comparable to metal produced in the smaller units.

Vanadium sponge produced by the direct reduction of V_2O_5 with carbon was evaluated as a possible feed material. The results of this study showed that equivalent growth rates were obtained using sponge and the metallic impurities were somewhat lower. The oxygen content

was consistently higher in this metal than in that obtained from the bomb-reduced feed, however.

1.1.2 Purification of Vanadium by Calcium Deoxidation

(D. T. Peterson)

Electron beam melted vanadium which contained 870 ppm of oxygen was deoxidized by treatment with calcium vapor at 1000, 1100 and 1200°C. The oxygen contents of specimens deoxidized for a long time at each temperature were 25, 30 and 15 ppm respectively. The hardness of the metal decreased from 123 DPH before deoxidation to 73 DPH afterward. The kinetics of deoxidation are being investigated more completely but this method of purification appears to be quite effective in reducing the oxygen content of vanadium.

1.2 Niobium (Columbium)

1.2.1 By Carbon Reduction of Nb₂O₅ (H. A. Wilhelm and E. R. Stevens)

Work was continued on the reduction of Nb₂O₅ by carbon. The charge for each reduction was prepared according to the general formula:

Several series of reductions were run. In one series the values of Z were -0.4, -0.3, -0.2, -0.1, 0, +0.1, +0.2, +0.3 and +0.4. The reductions of this series were run simultaneously and the results are found in Table III. The charges were heated at a top temperature of 2000°C for a time which was necessary to allow the pressure of the system to return to its initial pressure of about 1μ. This time was approximately three hours.

Table III

Sample #	Equation for Charge	Z	Hardness R_A	Workability (cold)	Analyses (PPM)		
					Oxygen	Carbon	Nitrogen
ES-4-23	$Nb_2O_5 + (5+Z)C$	-0.4	84	No Roll	4590	159	3064
ES-4-24	" "	-0.3	80	No Roll	3450	173	2055
ES-4-25	" "	-0.2	76	No Roll	3500	170	2850
ES-4-26	" "	-0.1	68	No Roll	2825	93	4099
ES-4-27	" "	0	59	Rolled; no edge-crack	570	251	5562
ES-4-28	" "	+0.1	58	No Roll	215	4153	6910
ES-4-29	" "	+0.2	58	Rolled; edge-cracked	185	11824	6598
ES-4-30	" "	+0.3	57	No Roll	250	1.85%	8031
ES-4-31	" "	+0.4	60	No Roll	210	2.35%	5029

Table IV

Sample #	Temperature of Reduction	Final Pressure at Temperature	Hardness R_A	Workability (cold)	Analyses (PPM)		
					Oxygen	Carbon	Nitrogen
ES-4-63	2000°C	0.15×10^{-3} mm Hg	48	Rolled; edge-cracked	30	5761	241
ES-4-56	1900	0.16×10^{-3}	57	Rolled; no edge-crack	1000	178	369
ES-4-57	1800	0.26×10^{-3}	73	No Roll	6000	111	219
ES-4-61	1700	0.31×10^{-3}	68	No Roll	3000	137	441
ES-4-70	1600	0.50×10^{-3}	55	Rolled; edge-cracked	730	6575	194

Another series of reductions was run to determine the minimum top temperature at which Nb_2O_5 can be reduced to essentially pure Nb. The reductions were made in a system capable of attaining a pressure of approximately 1×10^{-6} mm Hg. To insure a representative charge for each of these reductions, a bulk mixture of Nb_2O_5 and carbon (Z = 0 in formula above) was prepared and an appropriate sample was taken for each reduction. The top finishing temperatures which were investigated were 2000°, 1900°, 1800°, 1700° and 1600°C. For each case the specific top temperature was finally maintained until the pressure of the system attained a constant low pressure. The results for these experiments are presented in Table IV. These data indicate that it may be possible to allow the reduction to take place at approximately 1700°C or lower and then raise the temperature up to 2000°C where there appears to be volatilization of an oxide of niobium. There is a possibility, however, that charge uniformity is difficult to maintain. Work will continue on this project during the next period.

1.2.2 Purification of Niobium by Iodide Refining (R. E. McCarley and W. Tadlock)

This work was continued with efforts to lower the concentration of oxygen incorporated in the crystal bar niobium during the iodide refining. Several reactions were performed in which niobium alloys containing 1-3 w/o yttrium were used as feed metal. This approach was tried since the heat of formation of yttrium oxide is sufficiently large that yttrium was expected to function as an oxygen getter in the presence of niobium. The properties of yttrium triiodide are also

favorable for this purpose. Thus, the relatively high melting point and low vapor pressure of YI_3 at the reaction temperature are desirable in order to maintain conditions conducive to good filament growth. However, results of these experiments were very unsatisfactory. The oxygen concentration in the crystal bar obtained from the Nb-Y alloy feed was comparable to that previously obtained using only Nb feed. In the light of these results, and the additional effort needed to prepare and recover the alloy feed, the method was dropped from further consideration.

Additions of anhydrous barium chloride to the reaction vessel were also made, since it had been reported by Rolsten⁽¹⁾ that this material was effective for the reduction of oxygen transfer to the crystal bar. Results of these experiments are given in Table V.

Table V

Effect of $BaCl_2$ Additions on Oxygen Transfer from Feed to Crystal Bar

Reaction Temp. °C	<u>O₂ Conc., ppm</u>		<u>BaCl₂ used</u> grams
	<u>Feed</u>	<u>Xtal Bar</u>	
500	730	960	10
500	160	260	5
600	120	310	50
600	145	310	0
610	145	440	30

(1)R. F. Rolsten, Trans. Met. Soc. AIME 215, 478 (1959)

The data obtained in this work fail to support the observation made by Rolsten. There was, however, a major difference in the oxygen concentration of the feed metal used in this work and that of Rolsten who used metal of 0.3 to 0.4 w/o oxygen. Clearly there must be a source of oxygen other than that in the feed, which has contaminated the crystal bar metal and actually increased the oxygen concentration above that of the feed. The desired observation was thus completely obscured. Assuming that the unidentified source of oxygen was small, the same results may not have been noted for feed of high oxygen content. Experiments are in progress to identify and exclude miscellaneous sources of oxygen in these systems.

Preliminary observations on the outgassing operation have shown that oxygen is actually removed from the feed in this step. For example, two samples of feed metal, each initially containing 145 ppm oxygen, after outgassing for 24 hours at 800° and 2×10^{-5} mm in a vycor vessel, were found to contain 68 and 40 ppm oxygen. At the same time the nitrogen content of these samples was increased from 512 ppm initially to 1115 and 1091 ppm after outgassing. In view of these results, the outgassing procedure appeared to be favorable for maintenance of the low oxygen concentration in the feed metal. Work is now underway to detect and eliminate oxygen which may be introduced into the crystal bar vessel along with the iodine after the outgassing operation.

Since the previous report in this series (IS-17) a new modification of the crystal bar vessel has been employed. The modification concerns only the method for retaining the feed metal in the vessel. A molybdenum

bucket which fits snugly within the vycor vessel has been used to retain the feed metal on the outer walls, while a molybdenum screen retained the metal on the inner side near the filament. This arrangement was designed to reduce the possible reaction of the feed metal with the walls of the vycor vessel. However, in the experiments in which this arrangement has been used, it was determined that the nitrogen content of the crystal bar metal was below the limits of detection. This corresponded to less than 10 ppm nitrogen in the refined metal and a purification factor of up to 1000 relative to nitrogen content in the feed. Apparently the molybdenum is a very effective getter for nitrogen, which may be liberated from the niobium feed during the course of the refining process.

1.2.3 Purification of Niobium Metal by Calcium Deoxidation

(D. T. Peterson)

Niobium metal which had been prepared by carbon reduction of niobium pentoxide so as to result in a high oxygen content product was deoxidized by treatment with calcium vapor at 1200°C. No oxygen analyses have been obtained but the hardness of the metal was lowered from 238 DPH to 115 DPH. The decrease in hardness indicates a significant removal of oxygen from the metal.

1.3 Thorium

1.3.1 Purification of Thorium by Iodide Refining (W. L.

Larsen and P. E. Palmer)

A metal system for the purification of thorium by iodide refining has been constructed and successfully operated. It has a greater production rate and more durability than the Pyrex apparatus previously used.

In view of the success of other means of thorium refining and the commercial availability of iodide thorium, further work on the development of equipment for purifying thorium by this process will be discontinued. Thorium will be refined only as may be needed for alloy investigations.

1.3.2 Purification by Calcium Deoxidation (D. T. Peterson)

Exposure of thorium containing thorium oxide inclusions to calcium vapor at 1000°C resulted in the growth of a calcium oxide layer on the outer surface of the thorium and the disappearance of the thorium oxide particles in the thorium metal. The reaction occurred by diffusion of the oxygen in solution in the thorium to the surface where it reacted with calcium vapor. To maintain the equilibrium concentration of oxygen in the thorium, the thorium oxide inclusions dissolved in the metal beginning at the outer surface. The kinetics of the reaction were investigated and the rate of growth of the thorium oxide free rim in the thorium was found to follow the parabolic rate law. The oxygen content in thorium in equilibrium with calcium oxide and saturated calcium vapor was determined at 1000°, 1100° and 1200°C and found to be 16, 26 and 72 ppm respectively. The solubility limit of oxygen in thorium was determined at the same temperatures and found to be 35, 52 and 90 ppm respectively. The diffusion coefficients of oxygen in thorium were calculated at these temperatures.

This reaction appears to be an excellent way of lowering the oxygen content of thorium metal. Thorium containing up to 1300 ppm of oxygen can be treated and probably much higher concentrations could also be

tolerated in the starting metal. Oxygen contents of 16 ppm have been obtained and lower oxygen contents could probably be achieved. The purity of the thorium with respect to other impurities is not significantly changed. Calcium metal is not appreciably soluble in thorium and no change in the calcium content of the metal as a result of deoxidation was observed. Carbon and nitrogen were not removed from the thorium and indeed if the thorium is in contact with liquid calcium these impurities may be transferred to the thorium. However, if only calcium vapor were in contact with the thorium, no transfer of carbon or nitrogen would occur because both calcium carbide and nitride are nonvolatile at 1200°C. Deoxidation had no significant effect on the hardness or ductility of thorium and, in all of the specimens which were examined, the hardness of the deoxidized rim was identical to that of the undeoxidized core.

1.3.3 Preparation by Mg Reduction of ThCl_4 (D. T. Peterson)

Several minor modifications of the purification and reduction procedure described previously⁽²⁾ have resulted in significant improvement in the purity of the thorium product. The amount of excess magnesium used in the reduction was decreased and solid pieces of special purity magnesium were substituted for the coarse ground magnesium used previously. These changes have resulted in the preparation of thorium containing 50 ppm of carbon and 24 ppm of nitrogen. The lowest oxygen content which has been achieved is 180 ppm but this is

(2) U. S. Atomic Energy Commission Report IS-17, Iowa State University, Ames, Iowa (1960).

now of little concern since a method of lowering the oxygen content to 16 ppm has been discovered. The softest thorium which has been produced by this method has a hardness of 35 DPH and was too soft to measure on the R_E scale. Plans are being made to produce thorium by this method on a several kilogram scale.

1.4 Yttrium Metal (O. N. Carlson, F. A. Schmidt and J. A. Haefling)

Major emphasis during this period was on improving the purity of yttrium metal. The purification of the Y-Mg alloy by a fused salt extraction has been described in detail.⁽³⁾ The method was scaled up to a 30-lb scale facilitating the preparation of several pounds of yttrium metal of 99.9% purity. Several other methods of preparing the Y-Mg intermediate alloy were also investigated.

1.4.1 Preparation of High Purity Y-Mg Alloy by Fused Salt Extraction

All of these experiments were carried out in tantalum crucibles to minimize metallic contamination of the yttrium metal. The Y-Mg alloy was prepared in the usual manner by the reduction of YF_3 with calcium in the presence of magnesium metal. This was followed by a refining step in which the Y-Mg alloy was contacted with a $YF_3:CaCl_2$ fused salt mixture at 900-950°C. In several experiments a second extraction with YCl_3 was performed. Yttrium metal containing 150 to 300 ppm oxygen, 10 ppm nitrogen, 100 ppm carbon, and 50 ppm fluorine

(3) O. N. Carlson, J. A. Haefling, F. A. Schmidt and F. H. Spedding, J. Electrochem. Soc. 107, 540 (1960).

was consistently prepared by this method. Total metallic impurities, consisting mostly of iron and nickel, varied from 300 to 800 ppm.

To facilitate preparation of larger amounts of high purity yttrium metal a tantalum-lined reduction vessel was constructed. A pot with a capacity to produce 30 pounds of yttrium metal per batch was fabricated and several reductions were made in this apparatus. The resulting yttrium metal was of comparable analytical purity to that obtained in the smaller experiments described above.

1.4.2 Decreasing the Iron and Nickel Content of Yttrium

Efforts were also made to prepare yttrium metal that was low in iron and nickel. These impurities are introduced into the YF_3 during hydrofluorination. Analysis of the YF_3 shows that 100 to 200 ppm of iron is present and about 50 ppm of nickel. Particular attention was devoted to the removal of iron and nickel from the $\text{YF}_3\text{-CaCl}_2$ fused salt mixture prior to reduction to the metal. Two methods employed were (1) electrolysis and (2) displacement with a more active metal. The iron content of the $\text{YF}_3\text{-CaCl}_2$ salt mixture was decreased from 150 to 75 ppm and the nickel content lowered from 50 to 15 ppm by passing a current through the fused salt. The second method, involving stirring of the molten salt mixture in contact with yttrium or titanium, resulted in substantial decrease in the iron and nickel content. Yttrium metal prepared by reduction of the purified $\text{YF}_3\text{-CaCl}_2$ mixture contained about 50 ppm iron and 20 ppm nickel.

1.4.3 Reduction of Y Salts with Zn-Ca and Zn-Mg Alloys

Attempts were made to prepare the Y-Mg alloy by direct reduction of Y_2O_3 . Such an alloy would probably have a high oxygen content but

could then be purified by the refining technique described above.

Although thermodynamic data indicate that magnesium metal will not reduce Y_2O_3 the use of a Mg-Zn alloy reductant was tried since yttrium and zinc form a stable intermetallic compound with a high heat of formation. No reduction of yttrium oxide was obtained with the Zn-Mg alloy; however, a Zn-Ca reductant gave some reduction although the yields were low (25% of theoretical) and the oxygen content of the final yttrium was

very high. Highest yields were obtained with Zn-5 w/o Ca alloy.

As has been reported previously, metal yields of less than 20 w/o are obtained by the reduction of YF_3 with magnesium. Attempts were made to reduce YF_3 with the Zn-Mg alloy in an effort to obtain higher yields of yttrium by taking advantage of the stability of the Y-Zn product. A series of reductions was carried out in a tantalum vessel at $900^\circ C$ with stirring for one hour using various magnesium-zinc alloys as reductants.

Fig. 1. Effect of Mg concentration in the Zn-Mg reductant on yttrium metal yields obtained by reduction of YF_3 .

Sufficient Zn-Mg alloy was used in each experiment to reduce 134g. of YF_3 assuming magnesium was the reductant. One experiment employing pure zinc as the reductant yielded no measurable amount of yttrium metal. Yttrium metal recoveries of 70% were obtained using a Zn-2.5 w/o Mg alloy reductant. A plot of yttrium metal obtained versus composition of the Zn-Mg alloy is presented in Fig. 1. In the high-magnesium range the yttrium metal yields were

determined by weight changes occurring in the alloy and salt phases as a result of the reduction reaction. In the low-magnesium range the alloy and slag did not separate cleanly thus making it difficult to obtain accurate weight changes. The yields in this range were determined from chemical analysis of the final alloy.

1.4.4 Reclaiming of Yttrium Metal Scrap

A method for reclaiming yttrium scrap metal has been developed.

The process consists of heating anhydrous MgCl_2 in contact with yttrium metal at 900°C . The reaction is

whereby the YCl_3 extracts oxygen from the Y-Mg alloy. In this way scrap metal containing greater than 3000 ppm oxygen has been successfully reclaimed and yttrium containing less than 500 ppm oxygen obtained. The reaction has been satisfactorily applied to yttrium turnings, sponge or massive pieces. The YCl_3 produced by this reaction can be purified by distillation.

1.4.5 Electron Beam Melting of Yttrium Sponge

Approximately 12 pounds of yttrium sponge was sent to the National Research Corporation, Newtown, Mass. for electron-beam melting. The initial sponge contained 890 ppm oxygen, 60 ppm nitrogen and 1817 ppm fluoride. The fluoride content of the melted ingot had decreased to 95 ppm but the nitrogen and oxygen contents of the ingot had increased during melting, resulting from a vacuum leak that developed in the system during the heating operation.

1.5 Uranium Metal by Carbon Reduction of UO_2 (H. A. Wilhelm
and E. P. Neubauer)

The two major problems of the carbothermic reduction of UO_2 are; (1) that of lowering the quantity of carbon remaining in the product metal and (2) that of obtaining a container which will withstand the attack of the molten metal at the high temperature required for the reduction. A possible solution to carbon contamination may be found in the tendency of free carbide to concentrate near the top of the liquid metal. Rather than doing the liquation in a separate procedure it was hoped that it could be incorporated into a continuous operation of producing and casting the metal. Efforts to date have met with only very limited success, however.

The course of the reduction reaction was followed by collecting the gas evolved at 50 centigrade degree intervals for increasingly higher temperatures. Seventy-five percent of the gas is given off below 1700°C , where the reaction subsides until 2000°C . This may lead to a better understanding of the reaction and possibly throw some light on a means of by-passing the high temperature fusion of the product.

The molten uranium metal at the temperature required in the carbothermic reduction of UO_2 is very reactive, and consequently it has posed a serious problem as to how it can be contained. UO_2 crucibles have been used, but the vapor pressure of UO_2 at the high temperatures is such that the crucible life under vacuum conditions in a graphite environment is very short. Also, the UO_2 crucibles have to be broken

away from the solidified metal each time. A desirable crucible would be inert to the molten uranium and stable in contact with a graphite heater.

In an attempt to improve upon the properties of the UO_2 crucible or to replace it, various mixtures of UO_2 , ThO_2 , ZrO_2 , Y_2O_3 , CaO , TiO_2 and BeO were made into crucibles. In many cases the vaporization problem was overcome, but the molten uranium appeared to attack to some degree every crucible tested. In some instances the contamination of the metal from the crucible was quite appreciable. Further work is to be done in this area.

1.6 Preparation of Tantalum Metal (H. A. Wilhelm and C. B. Hamilton)

The problem of obtaining pure ductile tantalum metal by the carbon reduction of tantalum pentoxide is still under investigation.

An attempt to lower the 2200°C temperature needed to obtain good metal by the addition of silicon metal or silicon dioxide proved unsuccessful. Apparently the silicon metal forms silicon carbide which cannot be oxidized by the tantalum oxide, thus causing a high carbon content in the final metal. Silicon dioxide showed little effect on the reduction, except that it tended to lower the yield of tantalum metal.

A comparison was made between two forms of carbon--an acetylene black and graphite. Both forms gave good yields along with soft metal. However, the graphite gives more compact charges but is less pure.

The graphite powder received from the National Carbon Company had .18% residue on ignition. This residue consisted mainly of iron

with traces of silicon, aluminum, titanium and vanadium. The best results in purifying this graphite powder by a simple process were obtained by washing it in concentrated hydrochloric acid.

A feed material for the resistance heating of pressed bars was made by first heating a mixture of a stoichiometric amount of carbon and tantalum pentoxide to 1600°C to give a product containing mainly carbide and an oxide. Several observations were made in the resistance heating of bars made from this feed material. Care should be taken when heating the bar at temperatures between 1800°C and 1900°C since, if the bar is heated too rapidly, the center will melt before the outside of the bar reacts. The addition of titanium dioxide to the pressed bar does not change the heating characteristics of the bar even when additional carbon is added.

A "Wet Test" gas meter was used to get a direct volume measurement of gases pumped from the reaction mixture with increasing temperature during a carbon reduction of tantalum pentoxide. Previously an approximate volume was obtained by multiplying the pressure in the vacuum system by the measured length of time at each temperature. The volume of gas evolved vs. temperature of charge curve compared favorably with the curve obtained by the earlier method. Most of the reaction is completed at temperatures well below 2000°C but a temperature of 2200°C or better and a vacuum are required to remove any excess oxygen from the metal.

1.7 Preparation of High Purity Chromium (O. N. Carlson, D. T. Peterson and F. A. Schmidt)

During the period of this report a program was initiated on the

preparation of high-purity chromium metal. Several refining techniques are being explored.

One method consisted of the dissolution and re-precipitation of chromium in molten calcium metal. Commercially pure chromium metal containing 5000 ppm oxygen and 60 ppm nitrogen was sealed in a tantalum crucible with freshly distilled calcium. The tantalum crucible was sealed under an argon atmosphere and placed in a resistance furnace. The bottom of the calcium column was held at 1200°C and the upper portion at 900°C. In this temperature gradient chromium dissolved in the calcium at the higher temperature and precipitated onto the crucible wall at the lower temperature. After a heating period of 36 hours the precipitated chromium was isolated by leaching out the calcium with dilute HNO_3 . The chromium crystals were dried, compacted and arc melted. The resulting metal contained 125 ppm oxygen and 8 ppm nitrogen.

Iodide chromium containing 25 ppm oxygen and 40 ppm nitrogen was also treated in the above manner; the resulting metal contained 30 ppm oxygen and 70 ppm nitrogen after precipitation. This increase in the nitrogen value suggests the possibility of a leak; or it may have been picked up from the calcium.

Attempts were made to purify chromium by deoxidation with calcium metal at elevated temperature. Pieces of commercial chromium were held in contact with molten calcium at a uniform temperature of 1000°C for 72 hours. A second experiment was conducted at 1200°C

for the same length of time. Upon microscopic examination of the chromium treated at 1000°C it was observed that no change had occurred in the microstructure. However, the chromium treated at 1200°C was observed to contain noticeably less of the oxide phase, with the outer edge of the sample virtually free of inclusions.

Attempts were made to find a low melting chromium-rich alloy that could be used in a fused salt extraction step such as has been employed for the Y-Mg alloy. Volatile metals such as bismuth, indium, cadmium, magnesium, antimony and zinc were tried as alloying agents but none were found to lower the melting point of chromium sufficiently.

Chromium trifluoride was prepared for possible use as a fused salt extractant or for direct reduction to the metal. Chromium trioxide was reacted with $\text{NH}_4\text{F} \cdot \text{HF}$ in the presence of an HF atmosphere.

1.8 Studies on Refining of Tungsten (O. N. Carlson and K. Solie)

A study of methods of refining tungsten metal was initiated during this period. High purity tungsten is of interest in the investigation of the brittle-ductile transition in tungsten metal. An electron-beam furnace of a design similar to that described by Calverly⁽⁴⁾ is now under construction for use in zone refining of tungsten. The ductility of tungsten is improved by electrolysis in an aqueous solution of KOH and KNO_3 using the tungsten specimen as the anode. Several specimens were found to be ductile in a bend test following the electrolysis treatment. Further studies are underway to elucidate this surface phenomenon.

(4) A. Calverly, M. Davis and R. L. Lever, J. Sci. Instr. 34, 142 (1957).

2. Phase Equilibria and Thermodynamic Properties of Alloys

2.1 Phase Diagram and Thermodynamic Properties of Thorium-Zinc Alloys (P. Chiotti and K. Gill)

Work on the thorium-zinc system has been completed. The phase diagram has been presented in an earlier report, ISC-1050, and other details in IS-17. The final relations for the zinc vapor pressure over various two phase regions are summarized in Table VI.

Table VI
Zinc Vapor Pressure as a Function of Temperature for Four of the
Solid Two-Phase Regions of the Thorium-Zinc System
 $\log_{10} P \text{ atm.} = aT^{-1} + b$

Equilibrium Phases	a	a*	b	b*	Temp. Range °K
Th-Th ₂ Zn	-9743	77	6.422	0.073	875-1215
Th ₂ Zn-ThZn ₂	-9119	61	6.364	0.061	880-1180
ThZn ₂ -ThZn ₄	-8048	29	6.132	0.029	800-1220
ThZn ₄ -Th ₂ Zn ₁₇	-7512	41	6.117	0.042	855-1190

* a* and b* are the standard deviations for the constants a and b, respectively.

The relations in Table VI were combined with known data for the free energy of vaporization and sublimation for pure zinc to obtain the standard free energy of formation for the compounds formed. The derived expressions are summarized in Table VII. Since no data are available for the specific heats of the compounds, the derived relations were simplified to linear functions of the absolute

Table VII

Expressions for ΔF° for the Compounds in the Thorium-Zinc System

Equations	Temp. Range °K
$\Delta F^\circ(\text{Th}_2\text{Zn}) = -16,271 + 5.344T$	875-1215
$\Delta F^\circ(\text{ThZn}_2) = -28,261 + 10.290T$	880-1180
$\Delta F^\circ(\text{ThZn}_4) = -45,297 + 18.314T$	800-1220
$\Delta F^\circ(\text{Th}_2\text{Zn}_{17}) = -145,192 + 72.068T$	855-1190
$\Delta F^\circ(\text{Th}_2\text{Zn}) = -13,449 + 1.184T$	Extrapolation
$\Delta F^\circ(\text{ThZn}_2) = -22,616 + 1.970T$	692.8 to 298°K
$\Delta F^\circ(\text{ThZn}_4) = -34,010 + 1.686T$	"
$\Delta F^\circ(\text{Th}_2\text{Zn}_{17}) = -97,224 + 1.475T$	"

temperature. More precise relations can be derived from the zinc vapor pressure relations in Table VII once heat capacity data are available. Within the temperature range 773 to 1173°K the free energy given by the relations in Table VII is estimated to be within 2% of the true values, except for $\Delta F^\circ(\text{Th}_2\text{Zn}_{17})$ which is probably not better than $\pm 5\%$. The standard enthalpies of formation which may be calculated from the expressions in Table VII are estimated to be within $\pm 10\%$ of the true values within the same temperature range. The calculated room temperature ΔS° values are all small, -1 to -2 entropy units. These values were determined by extrapolation of the measured vapor pressure data and it is difficult to estimate the probable

error. However, these small negative values for ΔS° are consistent with the supposition that the standard entropies, S_{298} , for the compounds do not differ markedly from the sum of the entropies of the pure constituents and that Δ_{cp} for the respective reactions is small and negative. Some calculated values for these thermodynamic quantities are given in Table VIII.

Table VIII
Calculated Values for the Standard Free Energy,
Enthalpy, and Entropy of Formation

Compound	Temp.	$-\Delta F^\circ$ kcal/mole	$-\Delta H^\circ$ kcal/mole	$-\Delta S^\circ$ cal/mole $^\circ K$
Th_2Zn	298	13.2	13.4	1.2
	773	12.1	16.3	5.3
	973	11.1	"	"
	1173	10.0	"	"
$ThZn_2$	298	22.0	22.6	2.0
	773	20.3	28.3	10.3
	973	18.2	"	"
	1173	16.2	"	"
$ThZn_4$	298	33.5	34.0	1.7
	773	31.1	45.3	18.3
	973	27.5	"	"
	1173	23.8	"	"
Th_2Zn_{17}	298	96.8	97.2	1.5
	773	89.5	145.2	72.1
	973	75.1	"	"
	1173	60.7	"	"

A paper giving further details and summarizing this work has been submitted for publication in The Transactions of the Metallurgical Society of AIME.

2.2 Phase Diagram and Thermodynamic Properties for the Yttrium-Zinc System (P. Chiotti and K. Gill)

Fig. 2. Yttrium-zinc phase diagram.

Results of thermal analyses and metallographic data thus far obtained for the yttrium-zinc system are summarized in the phase diagram presented in Fig. 2. As in the thorium-zinc system thermal analyses were made on alloys sealed in tantalum crucibles. In addition to the seven compounds shown on the phase diagram, weak thermal arrests at 985°C and 745°C in the composition range between YZn and YZn₂ indicate the possibility of another compound in this region which is unstable outside the temperature range 985 to 745°C. This possibility is being investigated.

Zinc vapor pressure data as a function of temperature has been obtained for the two phase region Y-YZn over the temperature range 880-1110°K. The vapor pressure is represented by the relation

$$\log P = \frac{-11,351}{T} + 6.947$$

where P is in atmospheres and T is degrees Kelvin.

2.3 Zirconium-Zinc System (P. Chiotti and G. R. Kilp)

The phase diagram for the zinc-zirconium system has been published

in the Transactions of the Metallurgical Society of AIME, vol. 215, pp. 892-898, Dec. 1959.

2.4 Thermodynamic Properties for Uranium-Zinc and Zirconium-Zinc Compounds (P. Chiotti and G. R. Kilp)

The results of zinc vapor pressure measurements and calculated standard free energy, enthalpy and entropy of formation for various temperatures for the compounds in the uranium-zinc and zirconium-zinc systems have been summarized and published in the Transactions of the Metallurgical Society of AIME, vol. 218, pp. 41-44, Feb., 1960.

2.5 Thermodynamic Properties for U_2Zn_{17} and Th_2Zn_{17} from emf Measurements (P. Chiotti and M. Koizumi)

Measurements of the emf of appropriate electrolytic cells were made in an attempt to check the standard free energy, enthalpy and entropy of formation for the compounds U_2Zn_{17} and Th_2Zn_{17} as calculated from vapor pressure data. Measurements were made over the temperature range of 500 to 650°C with cells of the type

where M refers to pure uranium or thorium and (s) and (l) refer to solid and liquid states respectively. The salt phase, approximately 70 g, consisted of KCl-LiCl eutectic containing three to five w/o uranium chloride or thorium chloride. The eutectic salt containing an appropriate amount of $ZnCl_2$ was dried by passing anhydrous HCl through it for about five hours at a temperature below its melting point and an additional ten hours at 500°C. The system was then evacuated to remove dissolved HCl and thereafter maintained under

a helium atmosphere. Cleaned zinc and metal shavings (uranium or thorium) were added to the dried salt. The ZnCl_2 in the salt was displaced by the more active metal component. The pure metal anode was suspended in the salt by means of a tungsten wire. A tungsten wire was also used to make contact with the zinc-rich liquid cathode. Both silica and tantalum were tried as containers. Tantalum proved satisfactory for both the uranium and thorium cells. No visible attack of silica occurred with uranium but attack was evident in the case of thorium.

In several experiments it was observed that the anodes became contaminated with zinc after the cell had been operated for one or two weeks. Solubility of zinc in the salt phase was suspected as the source of contamination. However, qualitative tests showed no detectable zinc in salt samples withdrawn from the cells. Examination of the tungsten anode lead revealed zinc crystallites had formed on the cold part of the lead. These apparently had formed by condensation of zinc vapor. Consequently zinc may have reached the anode by surface diffusion or film flow of liquid zinc along the tungsten lead. Thereafter the anode lead was enclosed in a small quartz tube with a flared bottom which extended to within a centimeter of the fused salt surface. With this arrangement no further contamination of the anode was detected and the data discussed below were obtained.

The measured emf's for the uranium cell contained in silica can be represented by the relation

$$(1) E = 0.7903 - 5.32 \times 10^{-4} T,$$

and for the same cell contained in tantalum by the relation

$$(2) E = 0.5977 - 1.101 \times 10^{-4}T - 2.686 \times 10^{-7}T^2 .$$

In the case of the thorium cell contained in tantalum the corresponding relation is

$$(3) E = 0.6637 - 1.525 \times 10^{-4}T - 1.32 \times 10^{-7}T^2 .$$

In the uranium cell the measured emf is related to the partial molar free energy of solution of solid uranium in the saturated zinc phase by the relation

$$\overline{\Delta F}_U = -nFE = RT \ln a_U .$$

Since the zinc liquid contains very little uranium, 0.004 to 0.5 a/o in the temperature range 500 to 650°C, the deviation of zinc from unit activity may be considered negligible and

$$\Delta F^\circ(U_2Zn_{17}) = -2nFE = -6(23,060)E.$$

Similar relations may be written for the thorium cell.

Values for ΔF° , ΔH° and ΔS° for U_2Zn_{17} calculated from the emf data for 500°C and 600°C are in fair agreement with the corresponding values obtained from vapor pressure data. The corresponding values for Th_2Zn_{17} are also in fair agreement if it is assumed that the valence of thorium in the salt is four. The agreement is poor if the valence is taken to be three. Data presented in section 5.2.1 indicate that the valence of thorium as chloride in contact with liquid zinc saturated with thorium is three.

In view of these complicating factors, it must be concluded that the thermodynamic properties determined from the vapor pressure

data are more reliable than those obtained from the above emf data.

2.6 Tantalum-Zirconium System (W. L. Larsen and D. E. Williams)

The phase diagram has been established for the tantalum-zirconium alloy system and is contained in Fig. 3. The diagram in its present form was constructed from the results of metallography, X-ray diffraction,

electrical resistance and dilatometric measurements, and melting point determinations.

Tantalum and beta-zirconium exhibit complete solid solubility at temperatures just below the solidus. This solid solution decomposes monotectoidally at 800°C and 12 w/o tantalum. The solubility of tantalum in alpha-zirconium is 2 w/o at the monotectoid temperature and decreases with decreasing temperature.

Fig. 3. The phase diagram of the tantalum-zirconium alloy system.

Metallographic studies conducted during this period confirm the work done previously.

2.7 Uranium-Rhenium Alloy Investigation (W. L. Larsen, R. J.

Jackson and J. F. Smith)

The present status of the investigation is summarized in the tentative constitutional diagram presented in Fig. 4.

Fig. 4. A tentative constitutional diagram for the uranium-rhenium alloy system.

There are two eutectic reactions, one between the Re_2U intermediate phase and each of the terminal solid solutions. These reactions occur at $1104 \pm 3^\circ\text{C}$ and $2140 \pm 60^\circ\text{C}$ at compositions of approximately 12 and 65 w/o rhenium respectively.

There are two eutectoid reactions due to the solid state transformations in uranium. The alpha-beta and beta-gamma eutectoid horizontals occur at $643 \pm 3^\circ\text{C}$ and $680 \pm 3^\circ\text{C}$ respectively. The eutectoid composition for the alpha-beta transformation is estimated to be 1.5 w/o rhenium. The eutectoid

composition for the beta-gamma transformation is about 6 w/o rhenium.

An intermediate phase, Re_2U , is formed congruently on cooling at about 2200°C . This phase undergoes an allotropic transformation at $180 \pm 2^\circ\text{C}$. Hatt⁽⁵⁾, who has studied the crystal structure of this phase reports that the high temperature modification is a C14 hexagonal Laves phase, whereas the low temperature modification is orthorhombic. Experimental data indicate that the transformation temperature is

(5) B. A. Hatt, "The Crystal Structure of URe_2 ", Fulmer Research

essentially the same on either side of the stoichiometric composition. By inference, therefore, the solubility of either rhenium or uranium in the compound must be small.

An unidentified phase has been found by X-ray diffraction to exist on the uranium side of the Re_2U intermediate phase. Extensive X-ray diffraction studies have been made to determine its composition and the manner in which it forms, however, neither of these investigations is complete. It seems possible that this phase may well be metastable.

2.8 Thorium-Molybdenum Alloy Investigation (W. L. Larsen and P. E. Palmer)

The 1400°C eutectic horizontal determined previously from melting point data was confirmed by electrical resistance measurements. Efforts are still being made to locate accurately the solubility limits for the entire diagram. Metallography indicates the room-temperature solubility of thorium in molybdenum is less than one w/o.

2.9 Phase Relationships in the Nickel-Zirconium and Nickel-Hafnium Systems (W. L. Larsen and M. E. Kirkpatrick)

The phase diagrams of the nickel-zirconium and nickel-hafnium systems are being determined in conjunction with the crystallographic investigation of the intermetallic compounds of these systems. The proposed diagram for the nickel-zirconium system based on metallographic and melting point data is contained in Fig. 5.

Fig. 5. The phase diagram of the nickel-zirconium alloy system.

The investigation of the nickel-hafnium system has established the existence of the following intermetallic compounds: NiHf_2 , NiHf , $\text{Ni}_{11}\text{Hf}_9$ and $\text{Ni}_{10}\text{Hf}_7$. Crystallographic data show these to be isostructural with the corresponding nickel-zirconium phases.

2.10 Thorium-Tantalum System (W. L. Larsen, O. D. McMasters and D. E. Williams)

The study of the thorium-tantalum system was continued. X-ray diffraction, electrical resistance measurements, and metallography have been used to reveal the form of the diagram near the thorium alpha-beta transformation at the thorium-rich end of the diagram. The transformation is observed at $1380 \pm 10^\circ\text{C}$ in iodide thorium. The addition of tantalum lowers the transformation only slightly; the eutectoid temperature being $1360 \pm 10^\circ\text{C}$. Lattice parameter measurements show the maximum solubility of tantalum in alpha thorium to be less than 0.2 w/o. The solubility in beta thorium is undetermined but probably slight. The solubility of thorium in tantalum has not yet been determined but is believed to be <0.1 w/o at

the eutectoid temperature and <1 w/o at the eutectic temperature.

On the basis of metallographic data the eutectic composition has been found to be between 2 and 4 w/o tantalum instead of 7.5 w/o as previously deduced from liquidus measurements.

Efforts to locate the eutectic point more precisely will be continued.

The possibility of reactions occurring upon long heat treatment will be investigated.

The tentative phase diagram based upon work to date is presented in Fig. 6.

Fig. 6. A tentative phase diagram for the thorium-tantalum alloy system.

2.11 Distribution of Solutes Between Liquid Lead and Zinc (D. T. Peterson and R. Kontrimas)

The results of the study of the distribution of silver have been published in the Journal of Physical Chemistry, Vol. 64, 362 (1960). The title of the paper is "Distribution of Silver Between Liquid Lead and Zinc".

Abstract—The distribution coefficient of silver between liquid zinc and lead was determined over a wide concentration range at three temperatures. The coefficient did not change with concentration. The enthalpy of transfer of silver from lead to zinc was -10.9 kcal. This agrees with the value calculated from the partial molar enthalpy of silver in liquid zinc and lead.

The distribution coefficients for copper between liquid lead and zinc have been determined over a considerable range of temperature and composition. No variation of the distribution coefficient with composition was observed. The variation with temperature is given by the expression $\log K_d = 4,308/T - 2.320$. From this temperature dependence, the enthalpy of transfer was calculated and found to be -19.7 kcal. The distribution of a selected number of solute metals will be measured and the results analysed to determine what factors control the distribution coefficients.

2.12 Yttrium-Oxygen System (O. N. Carlson and W. D. McMullen)

A series of arc-melted alloys containing 0.015, 0.05, 0.1, 0.2, 0.3.....2.0 w/o oxygen was studied by microscopic and X-ray examination and by electrical resistivity measurements. The limit of solid solubility lies somewhere between 150 and 500 ppm O_2 as determined from a plot of lattice parameter versus oxygen concentration. There is evidence from resistivity and microscopic data that a eutectoid occurs at approximately 1225°C and at a composition of 0.8 w/o oxygen.

As part of this investigation some of the properties of yttrium metal of 99.9+ purity containing 200 ppm oxygen as the principal impurity were determined. The lattice constants for this metal were: $a = 3.662\text{\AA}$ and $c = 5.752\text{\AA}$ and the melting point was determined as $1495 \pm 5^\circ\text{C}$.

2.13 Ternary Metal-Carbon-Hydrogen Phase Systems (D. T. Peterson and J. Rexer)

The variation of the composition of thorium dihydride at several temperatures as a function of the hydrogen pressure was established. This information will be used to calculate the diffusivity of hydrogen in thorium dihydride from the known parabolic reaction rates.

An investigation to determine whether metals other than thorium form compounds of the type $\text{MC}_x \cdot \text{MH}_y$ has been started. Preliminary results indicate that titanium forms a compound with the formula $\text{TiC} \cdot \text{TiH}_2$.

2.14 Aluminum-Niobium Alloys (H. A. Wilhelm and T. G. Ellis)

The investigation of the niobium-aluminum binary alloy system was continued with emphasis on alloys containing less than 25 a/o niobium in aluminum. The alloys were examined and analysed using metallographic, thermal and X-ray techniques.

Alloys of niobium and aluminum having compositions from 0.01 to 10 w/o niobium were prepared by dissolving appropriate quantities of Al_3Nb in aluminum. The dissolution was carried out at 1500°C in alumina (Al_2O_3) crucibles under one atmosphere of helium

using induction heating. After dissolution the alloys were furnace cooled to room temperature. A portion of each alloy was subsequently annealed in vacuo for 18 hours at 400°C and furnace cooled. All samples were prepared for microscopic examination by mechanical polishing and by etching with a solution containing 50 parts H₂O, 10 parts 48% HF, 5 parts HNO₃ and 5 parts H₂SO₄ by volume.

Macroscopic and microscopic examination showed a "fern like" dendritic structure surrounded by a different phase in all alloys, both "as cast" and annealed. Those alloys which contained greater than 0.03 w/o niobium also contained Al₃Nb. The boundary between the "fern like" phase and the matrix was sharp and continuous. Also, the "fern like" phase was continuous across major grain boundaries in some cases.

A 5 w/o niobium alloy previously used in thermal analysis was also examined. During thermal analysis much of the undissolved Al₃Nb settled to the bottom of the melt creating a niobium rich layer at the bottom with respect to the top. Examination of the junction between the two layers showed the "fern like" dendritic structure in the top layer similar to that discussed above. The "fern-like" phase of the top layer became the matrix phase in the region of high Al₃Nb concentration.

An X-ray analysis of several alloys by the Debye-Scherrer powder method gave no indication of any phase other than aluminum solid solution and Al₃Nb. Also no change was noted in the lattice constant for aluminum solid solution from that of pure aluminum.

A five w/o niobium in aluminum alloy was thermally analysed between 500° and 700°C. Immediately after each alloy analysis, the apparatus was calibrated using 99.99+ aluminum as a standard. Niobium was found to raise the melting point of aluminum by 3°C. It appears that Al_3Nb reacts peritectically with aluminum rich liquid at 663°C to give an aluminum niobium solid solution containing approximately 0.03 w/o niobium. The effort on the investigation of the niobium aluminum phase diagram has recently been curtailed in view of published results of similar work.⁽⁶⁾

2.15 The Solubility of Thorium in Vanadium (W. L. Larsen and P. E. Palmer)

Melting point data and electrical resistance measurements have confirmed metallographic evidence of limited solid solubility of thorium in vanadium. The solid solubility limit at the eutectic temperature, 1415°C, is less than one w/o.

The results from high-temperature X-ray diffraction studies of the solubility limits have so far been inconclusive due to specimen oxidation.

2.16 Zirconium-Cobalt Alloy Investigation

2.16.1 Phase Relationships (W. L. Larsen, W. H. Pechin, and D. E. Williams)

Based upon the data obtained during this reporting period a more nearly complete phase diagram, as shown in Fig. 7 is presented.

(6) V. M. Glazov, V. N. Vigdorovich, and G. A. Korol'kov; Ahur.

Inorg. Khim., 4, 730 (1959).

Fig. 7. A tentative constitutional diagram for the zirconium-cobalt alloy system.

The 1225°C eutectic has been established at 86 w/o cobalt. It appears that there are two peritectic reactions yielding the phases Co_4Zr and $\text{Co}_{11}\text{Zr}_2$. The upper reaction isotherm occurs at 1350°C and extends to approximately 76 w/o cobalt. The lower isotherm occurs at 1270°C and extends to approximately 81 w/o cobalt.

The phase previously reported as the line compound ZrCo_2 has been found to ex-

hibit appreciable solid solubility. In the vicinity of 1300°C this solubility range extends at least from 56 to 60 w/o cobalt. There is some evidence for decreasing solubility with decreasing temperature.

During this period considerable effort was spent in developing ways of preparing alloys by powder metallurgical means in the compositional region containing the two peritectic reactions. Arc cast alloys of this general composition usually fractured upon cooling and were difficult to equilibrate. With improved methods of sample preparation the more rapid completion of the phase diagram is expected.

2.16.2 Crystallography (J. F. Smith and D. M. Bailey)

Single crystals of CoZr_2 were obtained by heating an alloy of zirconium-rich composition, with respect to stoichiometry, to just above the eutectic isotherm and allowing gravitational separation of the liquid from the network of primary crystals. One of these crystals was aligned on the Weissenberg camera for X-ray examination. The diffraction symmetry and characteristic extinction conditions were obtained from $hk0$ data taken with $\text{Cu K}\alpha$ radiation and from $hk0$, $hk1$, $hk2$, and $hk3$ $\text{Mo K}\alpha$ data. These data are compatible with the tetragonal space groups D_{4h}^{18} -- $I4/mcm$, C_{2v}^{10} -- $I4cm$, and D_{2d}^{10} -- $I\bar{4}c2$. Lattice parameters were measured from Weissenberg and rotation photographs taken with $\text{Cu K}\alpha$ radiation: $a_0 = 6.31\text{\AA}$ and $c_0 = 5.44\text{\AA}$. Qualitative agreement in both the relative intensities and positions of the diffraction peaks was found when $hk0$ $\text{Cu K}\alpha$ photographs of CoZr_2 and NiZr_2 were compared. It is now open to question whether the hexagonal crystals, previously examined and thought to be CoZr_2 (IS-17), represent a polymorphic form, a binary phase of different composition, or a phase stabilized by contamination.

For the tetragonal CoZr_2 diffraction intensities were visually estimated from timed exposures of $hk0$ Weissenberg and $h0l$ precession patterns taken with $\text{Mo K}\alpha$ radiation. These data were corrected for Lorentz and polarization effects but have not as yet been corrected for absorption or dispersion effects. The structure of NiZr_2 was chosen as a trial structure for CoZr_2 . This trial structure was refined by a

least squares method with the IBM-650 computer. The refinement with $h0l$ data produced a discrepancy index, $R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$, of 0.089 for the following structure:

Space Group D_{4h}^{18} --I4/mcm

with 4 Co at $(0, 0, 0; 1/2, 1/2, 1/2) \pm (0, 0, 1/4)$

and 8Zr at $(0, 0, 0; 1/2, 1/2, 1/2) \pm (x, 1/2+x, 0; 1/2+x, \bar{x}, 0)$

with $x = 0.1679 \pm 0.0019$.

This structure is the C16 structure typified by CuAl_2 . Further refinement with $hk0$ data is in progress.

2.17 Barium-Barium Hydride System (D. T. Peterson and M. Indig)

The results of this investigation have been published in the Journal of the American Chemical Society, Vol. 82, 5645 (1960). The title of the article is "The Ba-BaH₂ Phase System".

Abstract—The Ba-BaH₂ phase diagram was established by thermal analysis and chemical analysis of equilibrated phases.

The m.p. of barium is raised to a peritectic at 950° and 66 mole % BaH₂. A phase transformation in BaH₂ was found at 550°. The m.p. of BaH₂ obtained by extrapolation of the liquidus curve was 1200°. The solubility of BaH₂ in solid barium at 370° was 9.8 mole %.

2.18 Aluminum-Yttrium Alloy Studies (H. A. Wilhelm and R. L. Snyder)

X-ray diffraction and other studies indicate that at room temperature possibly five intermetallic compounds exist between yttrium and aluminum. These compounds are YAl₃, YAl₂, YAl, Y₃Al₂ and Y₂Al.

Eutectics exist between Al and YAl_3 , between Y_2Al and yttrium and possibly between YAl and Y_3Al_2 . Evidence points to YAl_3 existing in two closely related crystalline modifications; however, no evidence of a transition from one form to the other in the pure compound has been found. More detailed information on YAl_3 structures is reported in section 4.8 of this report.

Heat of formation data indicate that YAl_2 with a value of 58.2 Kcal/mole is the most stable of the above intermetallic compounds. This compound is highly corrosion resistant to high temperature water and high temperature air; however, it is quite brittle. Addition of a few per cent of aluminum to yttrium gave increased resistance to air corrosion.

The addition of small percentages of yttrium to aluminum increases the strength above that of pure aluminum.

The hydrogen absorbing capacity of yttrium and various yttrium-aluminum alloys was determined at several temperatures. The hydriding was performed in a quartz tube which was enclosed in an electric resistance furnace. All samples were equilibrated with hydrogen at approximately one atmosphere pressure and temperatures of about 700, 600, 500 and 400°C. In all cases the quantity of hydrogen absorbed increased linearly as temperature decreased. In view of this linear relationship, the data are completely represented by Table IX below.

Table IX

Hydrogen Capacity of Yttrium and Yttrium-Aluminum Alloys

Sample	Temperature °C	N_H/NY
99.6% Y	700	2.00
	400	2.12
Y_3Al_2	700	1.28
	400	1.37
YAl	700	0.92
	400	0.98
YAl_2	700	0.72
	400	0.76
YAl_3	700	0
	400	0

2.19 Aluminum-Tantalum Alloy Studies (H. A. Wilhelm and
D. S. Cowgill)

The work on alloys of tantalum and aluminum has as a major obstacle the preparation of some compositions. Co-melting gives very erratic results and inhomogeneous samples due to the fact that aluminum metal not only melts but boils at a temperature far below that required to melt tantalum. Co-reduction or reduction of tantalum compound in the presence of aluminum serves for alloy preparation to a fair degree for some compositions.

X-ray studies indicate that another intermetallic compound besides Al_3Ta may be formed in this alloy series. Diffusion couple studies on tantalum and aluminum in the solid state (640°C) indicate that a new intermetallic phase forms in one region of the

diffusion band. This phase could not be identified with those previously observed in the microstructure of bomb produced alloys.

A sample prepared by heating aluminum (liquid) at 700°C in contact with tantalum for 200 hours showed only one compound, Al_3Ta .

2.20 Ternary Uranium-Thorium-Vanadium Alloys (H. A. Wilhelm and K. M. Wolf)

Work on these alloys continued into this period. Due to an apparently broad valley in the ternary system in the neighborhood of the uranium rich ternary eutectic, cooling and heating curve data are not adequate for the location of the exact temperature and composition of this eutectic. Microstructures have been of some assistance; however, means of identification of ternary eutectic structure in the presence of any of the assumed three binary eutectic structures has not yet been satisfactorily developed. The liquid immiscibility gap of thorium-rich and uranium-rich phases also appears to carry into the ternary system and complicate the interpretation of the behavior of some of the alloys. The ternary eutectic is close to the uranium corner of the diagram and contains about 90 w/o uranium.

2.21 Stability of Hf_5Sn_3 in the D8_8 Structure (J. F. Smith and D. M. Bailey)

Compounds with the formula M_5N_3 often occur between transition elements, M, and Group IV B elements, N. An appreciable number of these compounds crystallize in the D8_8 structure if interstitial

impurities, particularly carbon, are present.⁽⁷⁾ In the case of silicides and germanides, reduction in content or absence of interstitial impurities results in instability of the $D8_8$ structure.⁽⁸⁾ The availability of relatively pure hafnium and tin prompted an investigation to determine whether Hf_5Sn_3 would remain stable in the $D8_8$ structure (ISC-835) with a low impurity content.

The hafnium metal which was used to prepare the samples had been purified by the iodide process. The tin metal was 'Baker Analyzed' reagent grade which had been further purified by a dressing process. Analytical data for the interstitial impurity content of the hafnium and tin are shown in Table X.

Table X

Analyses of Alloying Components for Interstitial Impurities

Element	Hafnium w/o	Tin w/o
Carbon	0.03 ^x	0.0027 ^x
Oxygen	0.02 [*]	0.0005 [*]
Nitrogen	0.009 [#]	n.d. [*]
Hydrogen	0.001 [*]	n.d. [*]
Boron	n.d. ⁺	n.d. ⁺

n.d. --not detected, x--combustion-conductometric analysis,

*--vacuum fusion analysis, +--spectrographic analysis, #--Kjeldahl analysis.

(7) H. Nowotny, B. Lux, and H. Kudielka, *Mh. Chem.* 87, 447 (1956).

(8) E. Parthé and J. T. Norton, *Acta Cryst.* 11, 14 (1958); H. Nowotny, A. W. Searcy, and J. E. Orr, *J. Phys. Chem.* 60, 677 (1956).

An alloy on the tin-rich side of the stoichiometric ratio was prepared by arc melting under a helium atmosphere. The excess tin was dissolved in dilute HNO_3 . Debye-Scherrer patterns taken on the residue were indexed on the basis of a hexagonal structure with $a = 8.39_1 \text{ \AA}$ and $c = 5.82_3 \text{ \AA}$. These patterns showed qualitative agreement in both line position and intensity with the D8_g structure.

Single crystals were separated from the dissolution residue and mounted so that the axis of rotation was the c-axis. The symmetry of the layer line patterns obtained with Weissenberg and precession cameras indicated space group symmetry $\text{P6}_3/\text{mcm}$, $\text{P6}_3\text{cm}$, or P6c2 . Since the D8_g structure has the symmetry $\text{P6}_3/\text{mcm}$, intensities were calculated on the basis of the D8_g structure:

6 Hf_1 in 6(g): $x, 0, 1/4$ with $x = 0.23$;

4 Hf_2 in 4(d): $1/3, 2/3, 0$ parameterless;

6 Sn in 6(g) : $x, 0, 1/4$ with $x = 0.60$.

Experimental values for the diffraction intensities were obtained by the multiple film technique with a Weissenberg camera and $\text{Cu K}\alpha$ radiation. A comparison of observed and calculated values for $(hk0)$ reflections is shown in Table XI. The discrepancy index, $R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$, for these data is 0.146 which is adequate to verify the structure. The observed intensity values include corrections for Lorentz and polarization effects plus an artificial temperature factor but no additional corrections.

Table XI
Observed Structure Factors Compared With Calculated
Structure Factors Based on the $D8_8$ Structure for Hf_5Sn_3

hk0	$ F_o $	F_c	hk0	$ F_o $	F_c	hk0	$ F_o $	F_c
120	49.5	-49.6	240	29.6	-38.4	400	25.7	23.4
130	25.5	-23.0	250	17.4	22.9	440	35.9	36.6
140	51.4	68.5	260	21.4	-22.7	450	<4	5.4
150	15.0	-19.6	270	21.2	-15.9	460	<4	- 6.2
160	38.7	-36.7	300	64.4	62.1	500	54.4	47.5
170	19.5	16.5	330	<4	4.9	550	30.4	35.2
180	<4	- 1.2	340	8.5	-11.2	600	11.9	15.8
200	21.4	-18.9	350	<4	6.4	700	<4	- 3.7
220	15.7	15.5	360	<4	5.1	800	24.4	17.9
230	<4	-10.6	370	<4	- 5.3	900	32.6	30.0

Cursory attempts to vary the parameters in either direction resulted in an increase in the discrepancy index. However, extensive effort on parameter refinement was not warranted since the primary interest was in the nature of the structure and not in a precise determination of interatomic distances.

In their study of the stabilization of Mo_5Si_3 in the $D8_8$ structure by carbon, Nowotny et al (1954) report the structure to be unstable with less than 0.9 carbon atom per unit cell. A reasonable estimate of the impurity content of the compound Hf_5Sn_3 can be made from the analyses of the hafnium and tin. On this basis Hf_5Sn_3 contains less

than one carbon atom per twenty unit cells and a total of only one impurity atom of any of the analyzed species per ten unit cells. The interstitial impurity content is thus an order of magnitude less than that necessary to stabilize Mo_5Si_3 in the D8_8 structure. The implication of these data is that tin is more tolerant of the D8_8 structure than either silicon or germanium, and it is at least possible that the presence of interstitials is not necessary for the stability of Hf_5Sn_3 in the D8_8 structure.

3. Physical and Mechanical Properties of Metals and Alloys

3.1 Tensile Properties of Yttrium-Titanium and Yttrium-Zirconium Alloys (O. N. Carlson and D. W. Bare)

The room-temperature tensile properties of yttrium-titanium alloys were investigated for the complete binary system. The yield and ultimate tensile strengths of the alloys increase with increasing titanium content, attaining maximum values at 70 w/o. This is seen

from the plot of tensile data versus composition shown in Fig. 8.

A yield point was observed in all alloys containing greater than 30 w/o Ti and in unalloyed titanium sponge. A yield point was not observed in crystal bar

Fig. 8. Tensile and yield strengths versus w/o titanium for yttrium-titanium alloys. titanium but appeared in the

1 and 3 w/o Y alloys. There is a general increase in uniform elongation and reduction in area as titanium is added to yttrium.

Yttrium-zirconium alloys exhibit a similar increase in the yield and tensile strengths with increasing zirconium content. These properties reach maximum values of 32,000 and 54,000 psi respectively at 40 w/o Zr and remain constant at these values over the composition range of 40 to 90 w/o Zr. The binary alloys exhibit a ductility minimum in the composition range of 5 to 20 w/o Zr. This lack of ductility has caused some difficulty in preparing tensile specimens of these compositions. Yield points were observed in all zirconium-rich alloys tested.

3.2 Tensile Properties of Yttrium-Magnesium Alloys (O. N.

Carlson, D. W. Bare and E. D. Gibson)

An investigation of the tensile properties of magnesium-rich alloys of yttrium and magnesium has been carried out between 70° and 600°F. The addition of less than 5 w/o yttrium decreases the strength of magnesium at room temperatures but the addition of 5 to 10 w/o Y raises the yield and tensile strengths. At temperatures of 200, 400 and 600°F the effect of alloying becomes more apparent. All alloys exhibit a higher strength at 400°F than at room temperatures suggesting the possibilities of a creep resistant magnesium alloy at elevated temperatures.

Methods for preparing yttrium-rich magnesium alloys were investigated. Alloys containing less than 5 w/o Mg are of interest because of the possibility of obtaining a high strength alloy by heat

treatment. Several techniques have been employed in an effort to prepare these alloys but none of them have been successful. Yttrium turnings and powder of the compound, YMg , were pressed into compacts and annealed at $800\text{--}900^\circ\text{C}$ for several days. An Y and Mg couple, consisting of a cylinder of Mg within a cylinder of Y, was held at 1200°C for 100 hours in an attempt to form an alloy by solid state diffusion.

3.3 Effect of Hydrogen on Tensile Properties of Yttrium (O. N. Carlson and E. D. Gibson)

The tensile properties of yttrium-hydrogen alloys are being studied as a function of temperature. Alloys containing 1000 ppm H_2 were prepared and tested at 20, -65 and -196°C . The addition of 1000 ppm hydrogen has little effect on the tensile properties of yttrium at room temperature. At liquid nitrogen temperatures (-196°C) the alloy fractures in a brittle manner.

3.4 Mechanical Properties of High Purity Yttrium (O. N. Carlson and E. D. Gibson)

Tension tests were carried out on high-purity yttrium over a wide temperature range. These tests revealed that marked changes occur in the strength and ductility of yttrium as the temperature is varied. As is seen from Fig. 9 the tensile strength decreases from 28,000 psi at -187°C to 7600 psi at 450°C and exhibits a plateau in the temperature range of 0 to 200°C . Uniform elongation over the entire temperature range increases from 12 % at -187°C to 25 % at 450°C .

Fig. 9. Tensile strength versus temperature for yttrium metal.

The change in tensile strength at 200°C is accompanied by a rapid drop in the strain hardening exponent above this temperature.

The basic deformation mechanisms operable in yttrium at room temperature are being investigated using yttrium single crystals. Determination of the slip and twinning systems at room temperature is underway using Laue X-ray patterns and microscopic examination to determine the orientation of the planes of deformation.

3.5 Plastic Properties of Vanadium

3.5.1 Effect of Hydrogen on Ductility of Vanadium and V-Nb

Alloys (O. N. Carlson and A. L. Eustice)

The tensile properties of iodide vanadium were determined as a function of hydrogen concentration. It was shown that the presence of 10 ppm hydrogen is sufficient to cause embrittlement of vanadium over a limited temperature range. The temperature of the observed ductility minimum was established as approximately -105°C for a strain rate of

0.008 in/in/min and at -80°C for a strain rate of 0.5 in/in/min. The temperature and range of this embrittlement is also dependent upon hydrogen concentration. Hydrogen was found to raise the yield stress of vanadium quite markedly in the regions of minimum ductility. The brittle behavior of vanadium at these temperatures is attributed to this delayed yielding effect. A detailed discussion of this work is presented in a paper entitled "Effect of Hydrogen on the Tensile Properties of Vanadium" to be published in the Transactions of the Metallurgical Society.

Hydrogen embrittlement in vanadium-niobium alloys was investigated as a function of alloy composition and hydrogen content. Bend and tension tests were carried out in the temperature range of -196°C to 25°C . The embrittlement temperatures were determined as a function of alloy composition. This is described more fully in a paper entitled "Hydrogen Embrittlement in Vanadium-Niobium Alloys" by A. L. Eustice and O. N. Carlson to be published in the Transactions of the ASM, Vol. 53, 1961.

3.5.2 Effect of Oxygen on Vanadium and V-Ti Alloys (O. N. Carlson and S. Bradford)

A study of the effect of oxygen on the lattice parameter, hardness, strength and ductility of vanadium and vanadium-titanium alloys was initiated during this period. A series of vanadium-oxygen alloys varying in oxygen content from 100 ppm to 3000 ppm was used in the lattice parameter measurements. Portions of the arc-melted buttons were

rolled into thin sheets and these were recrystallized by annealing in vacuo at 900°C. X-ray diffraction photographs were taken in a back-reflection camera with Mo K α radiation in order to get reflections of higher order. Approximately 15 lines could be measured and the lattice constants were determined by a least-squares method of calculation.

Fig. 10. Lattice parameter versus oxygen content of vanadium metal.

A plot of lattice parameter versus oxygen content is shown in Fig. 10. The lattice constant of vanadium is $3.026 \pm 0.001 \text{ \AA}$ for low oxygen concentrations. The hardness versus oxygen curve (see Fig. 11) varies from 70 R_E at 600 ppm oxygen to 19 R_E at 80 ppm.

It was noted that hydrogen has a significant effect on the vanadium lattice. A

high purity vanadium specimen

that had been pickled in HCl was found to have the unusually high parameter of 3.031 Å. After removal of hydrogen from the specimen by heating in vacuo, a value of 3.028 Å was obtained.

Bend tests were run on vanadium containing from 100 to 2800 ppm oxygen at temperatures between 24° and -196°C. For ductile specimens a steady increase in the maximum bending load was observed with decreasing temperature or increasing oxygen concentration. All samples

Fig. 11. Hardness versus oxygen content of crystal-bar vanadium.

were ductile at -50°C . At -85°C and below, the samples with 1500 ppm oxygen or less were ductile but those containing more than 1800 ppm oxygen were brittle. The composition region between 1500 and 1800 ppm is somewhat erratic.

A study of the deoxidation of vanadium by addition of titanium was begun. A series of vanadium alloys containing 2000 ppm oxygen and from 0 to 5 w/o titanium was prepared.

These alloys were hard and brittle and only those containing less than 0.5 w/o Ti could be cold rolled. Consequently a second alloy series was prepared containing only 350 ppm oxygen. Measurement of the lattice parameter of the alloys in this series was attempted, but the presence of titanium distorts the diffraction patterns making their measurement extremely difficult. No significant decrease in hardness or increase in ductility was produced by the addition of titanium.

3.6 Ductility of Chromium Metal and Cr-Y Alloys (O. N. Carlson and F. A. Schmidt)

A bend test apparatus was constructed for use in comparing the ductility of various grades of chromium metal and also of chromium

alloys. Specimens 1" x 3/8" x 0.040" were tested in the as-arc-melted conditions. Samples of chromium metal received from different commercial suppliers were evaluated by the bend test. Chromium containing 4000-5000 ppm oxygen and 50-250 ppm nitrogen had a brittle-ductile transition temperature between 200 and 250°C, whereas chromium with 700 ppm oxygen and 20 ppm nitrogen present exhibited a transition at 170°C-185°C. Iodide refined chromium containing 180 ppm oxygen and 3 ppm nitrogen had a brittle-ductile transition temperature of 65°C to 75°C. This metal was obtained from the Chromalloy Corporation.

Several Cr-Y alloys were tested for bend ductility at room temperature. It was found that commercially pure chromium-base alloys containing more than 5 w/o yttrium underwent a 90 degree angle bend at room temperature. However, the addition of yttrium to crystal-bar chromium did not produce the improvement in ductility that was expected, as is seen from the data presented in Table XII.

3.7 Plastic Properties of Thorium Metal (D. T. Peterson and H. Klievoneit)

The plastic properties of Ames thorium were studied by tensile tests over the temperature range from -196° to 900°C at several strain rates. The yield point phenomena which was observed at room temperature in annealed specimens was found to disappear at temperatures above and below room temperature. The yield point was also eliminated at all temperatures by charging with 30 ppm of hydrogen and quenching

Table XII
Brittle-Ductile Transition Temperature of Cr-Y Alloys

Source of Chromium	w/o Y Added	B-D Transition Temp. °C	Deflection before fracture(in mils)
Electromet	0	200°C	
"	1	> 25°	25
"	3	> 25°	69
"	5	< 25°	
"	10	< 25°	
"	20	< 25°	
"	30	< 25°	
"	40	< 25°	
Belmont	0	225-250	
"	0.5	> 25°	5
"	1	> 25°	35
"	3	> 25°	25
"	5	> 25°	112
Chromalloy	0	70°	
"	1	90°	

to room temperature. A strong dependence of the magnitude of the yield phenomena on the grain size of the specimen was found. The difference between the upper and lower yield point decreased with increasing grain size.

The temperature dependence of the flow stress at constant strain and strain rate can be divided into three temperature intervals. From -196° to 100°C , the flow stress decreased linearly with temperature and the flow stress decreased with decreasing strain rate. From 200° to 400°C , the flow stress was nearly constant and did not vary with the strain rate. Above 400°C , the flow stress again decreased with increasing temperature and with decreasing strain rate. At all temperatures, thorium showed extremely high ductility even when charged with hydrogen. The uniform elongation was always more than 40% and the reduction in area at fracture was usually about 60 %. Strain hardening was more rapid at -196° than at higher temperatures and deformation to a given extent produced greater hardening at low temperatures than at higher temperatures. The results of this investigation are being compiled for publication.

3.8 Work Hardening of Thorium (W. L. Larsen and D. E. Williams)

Conflicting data exist in the literature concerning the work hardening of thorium. Davenport⁽⁹⁾ and Lowenstein⁽¹⁰⁾ reported that beyond 50% reduction further working softens thorium. Hamby⁽¹¹⁾ reported a

(9) E. S. Davenport, "Metallography of Commercial Thorium", AIME Tech. Publication No. 226 (1929).

(10) P. Lowenstein, "Technical Progress Report for the period April, 1952 through September, 1952", MIT-1102 (1952).

(11) D. E. Hamby, "Interim Report on Metallurgy of Thorium and Thorium Alloys", ORNL-1090 (1951).

sharp increase in hardness with reductions up to 10 %, relatively little change upon further reduction to 70 %, and thereafter a further increase in hardness. Work was undertaken in an attempt to discover the relation of hardness to cold work and the reasons for the discrepancy in the reported data.

Working was done by cold rolling, using reductions of 0.002 inch per pass. Two kinds of rolling were done; unidirectional rolling, in which rolling direction was held constant during successive passes, and compression rolling, in which the sample was rotated slightly between passes.

The arc-melted thorium buttons used in the initial stages of the compression rolling tests had a maximum thickness of about 1/4 inch. Thus, beyond 80 % reduction the warping of the thin samples as it passed through the rolls was too great to permit reliable hardness measurements. For greater reduction by compression rolling and for unidirectional rolling, samples were prepared from thick slices of a 4 inch diameter arc-cast billet. These were given to a 30 % reduction and a recrystallization anneal at 825°C before testing.

Typical Vickers hardness values, obtained using a 10 kg. load, are plotted in Fig. 12. These curves agree closely in both form and magnitude with those of Hamby.

The softening reported by other investigators may arise from the different methods of cold reduction employed or may be unreal and dependent upon the methods of hardness measurement used. This point will be investigated further.

Fig. 12. Work hardening of Ames thorium.

<u>Phase</u>	<u>$\chi \times 10^6$ e.m.u. per g.</u>
Al (pure)	+0.62
β (Al_{23}V_4)	+0.65
γ (Al_3V)	-0.12
δ (Al_8V_5)	+2.6
V (pure)	+6.0

The results indicate pairing in the aluminum-rich alloys of the electrons which are responsible for the strong paramagnetism of pure vanadium.

4. Solid State Investigations

4.1 Magnetic Susceptibility of Aluminum-Vanadium Alloys

(J. F. Smith and
J. D. Greiner)

Measurements of the magnetic susceptibility of the phases in the aluminum-vanadium alloy system are in progress. Preliminary values at room temperature for some of the phases are available:

4.2 Anisotropic Thermal Expansion of Indium (J. F. Smith and R. W. Meyerhoff)

Initial measurements of the coefficients of thermal expansion of indium both parallel and perpendicular to the c-axis have been made by X-ray diffraction. The values between $\mu 3^\circ$ and 60°C are:

parallel to the c-axis	-12.2×10^{-6} per $^\circ\text{C}$
perpendicular to the c-axis	55.9×10^{-6} per $^\circ\text{C}$

The spread in values previously reported in the literature quite probably indicates that the anisotropy in thermal expansion is sensitive to the degree of purity of the sample though the volume coefficient of expansion is relatively insensitive. Additional measurements on macrocrystals will be made with a dilatometer.

4.3 Measurement of the Elastic Constants of Single Crystals of Thallium Metal (J. F. Smith and M. L. Shepard)

Measurements of the five independent elastic constants of hexagonal single crystals of thallium are in progress. Preliminary values in units of 10^{11} dyne/cm² at liquid helium and liquid nitrogen temperatures are:

	<u>4.2°K</u>	<u>77.8°K</u>
C_{11}	4.404	4.340
C_{12}	2.148	2.141
C_{13}	3.044	2.951
C_{33}	5.999	5.831
C_{44}	0.876	0.830

These values are uncorrected for dimensional changes resulting from the cooling of the samples to the temperature of measurement from

room temperature. Measurements of the anisotropic thermal expansion of single crystals are in progress. These latter measurements will provide data for making the dimensional corrections.

4.4 Crystallographic Studies on the Nickel-Zirconium and Nickel-Hafnium Systems (W. L. Larsen and M. E. Kirkpatrick)

The precision lattice dimensions for the tetragonal NiZr_2 phase as determined from single crystal data are; $a_0 = 6.477\text{\AA}$ and $c_0 = 5.241\text{\AA}$. The compound has the C_{16} structure typified by CuAl_2 and the space group symmetry, $D_{4h}^{18}-14/\text{mcm}$. A qualitative comparison of diffraction intensities and extinction conditions from NiZr_2 and NiHf_2 data indicates the two compounds are isostructural. The lattice dimensions of the NiHf_2 compound, $a_0 = 6.743\text{\AA}$ and $c_0 = 5.584\text{\AA}$, are somewhat larger than expected on the basis of the elemental atomic diameters of hafnium and zirconium and the cell dimensions of NiZr_2 .

The structure and lattice constants of the NiZr phase were determined and the compound was shown to be isostructural with the NiHf phase. The orthorhombic structure is similar to the B_f structure type typified by zeta- CrB . The lattice constants of the NiZr compound are; $a_0 = 3.268\text{\AA}$, $b_0 = 9.937\text{\AA}$, and $c_0 = 4.101\text{\AA}$. The approximate lattice dimensions of the NiHf compound are; $a_0 = 3.22\text{\AA}$, $b_0 = 9.82\text{\AA}$ and $c_0 = 4.12\text{\AA}$.

Further study of the $\text{Ni}_{10}\text{Zr}_7$ intermediate phase has revealed the existence of limited solid solubility which produced a change in symmetry for compositions rich in zirconium with respect to stoichiometry. All data previously reported concerning this compound were obtained from a crystal having the composition of the zirconium-rich boundary of the

phase. The stoichiometric phase has the space group symmetry D_{2h}^{15} -Cmca or C_{2v}^{17} -C2ca. The lattice dimensions for the stoichiometric compound are: $a_0 = 12.386\text{\AA}$, $b_0 = 9.156\text{\AA}$ and $c_0 = 9.211\text{\AA}$. Intensity data for the 0kl and h0l zones of reflections were obtained by visual judging of precession and Weissenberg photographs. Structure factors calculated on the basis of the centric space group D_{2h}^{18} do not agree with the observed structure factors. Therefore, the structure refinement was carried out for a trial structure based on the noncentric space group, C_{2v}^{17} . A least-squares refinement was applied and a reliability factor, $R_1(h0l) = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} = 0.186$, was obtained

for the following structure: Space Group C_{2v}^{17} Czca

12 Zr atoms in 3 sets, $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0) + (x, 0, 0; x, \frac{1}{2}, \frac{1}{2})$

16 Zr atoms in 2 sets, $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0) + (x, y, z; x, \bar{y}, \bar{z}; x, \frac{1}{2}+y, \frac{1}{2}-z; x, \frac{1}{2}-y, \frac{1}{2}+z)$

40 Ni atoms in 5 sets, $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0) + (x, y, z; x, \bar{y}, \bar{z}; x, \frac{1}{2}+y, \frac{1}{2}-z; x, \frac{1}{2}-y, \frac{1}{2}+z)$.

The positional parameters are listed in Table XIII. The y-parameters are approximations based on the zirconium-rich structure. The structure determination of the zirconium-rich $Ni_{10}Zr_7$ phase has been completed and the optimum parameters for this structure are listed in Table XIV.

X-ray data obtained from a single crystal of $Ni_{10}Hf_7$ indicate the hafnium phase is isostructural with the stoichiometric $Ni_{10}Zr_7$ phase. The lattice dimensions of the orthorhombic $Ni_{10}Hf_7$ compound are: $a_0 = 12.275\text{\AA}$, $b_0 = 9.078\text{\AA}$ and $c_0 = 9.126\text{\AA}$.

Table XIII

Atomic Parameters for the Stoichiometric $\text{Ni}_{10}\text{Zr}_7$ Structure

Parameter	Atom	No. of Positions	x/a	y/b	z/c
P_0	Zr	4	0.046	0	0
P_1	Zr	4	0.358	0	0
P_2	Zr	4	0.743	0	0
P_3	Zr	8	0.299	0.259	0.248
P_4	Zr	8	0.546	0.316	0.313
P_5	Ni	8	0.241	0.006	0.200
P_6	Ni	8	0.404	0.020	0.291
P_7	Ni	8	0.403	0.294	0.009
P_8	Ni	8	0.691	0.292	0.011
P_9	Ni	8	0.548	0.108	0.106

Table XIV

Optimum Parameters for the Zirconium-rich Structure of the Phase $\text{Ni}_{10}\text{Zr}_7$

Parameter	Atom	No. of Positions	x/a	y/b	z/c	B/λ^2
P_0	Zr	4	0	0	0	1.14
P_1	Zr	8	0.336	0.998	0.990	2.44
P_2	Zr	8	0.238	0.259	0.244	3.17
P_3	Zr	8	0.496	0.316	0.318	2.54
P_4	Ni	8	0.195	0.006	0.208	1.72
P_5	Ni	8	0.358	0.020	0.296	0.94
P_6	Ni	8	0.356	0.294	0.004	1.39
P_7	Ni	8	0.641	0.292	0.015	1.03
P_8	Ni	8	0.508	0.108	0.102	2.06

4.5 Vibrational Amplitudes of Atoms in Crystals (P. Chiotti and E. R. Ryba)

The change in X-ray reflection intensity as a function of temperature for various reflections from single crystals, 10 mm x 25 mm x 1.5 mm, of copper and zinc has been measured over the temperature range from 13°C to near the melting temperature of each metal. The thermal expansion over the same temperature range was also determined from the change in "d" spacing for the reflections.

The integrated intensities for the 400 reflection of copper may be represented by the relation

$$\ln R_{400} = 7.5347 - 5.8266 \times 10^{-4} T - 9.7993 \times 10^{-7} T^2 + 3.4911 \times 10^{-10} T^3,$$

and the mean square vibrational amplitude normal to these planes by the relation

$$\mu_{400}^2 = 6.9644 \times 10^{-19} + 12.049 \times 10^{-22} T + 2.0223 \times 10^{-24} T^2 - 0.7219 \times 10^{-10} T^3.$$

In these relations R is the integrated intensity in arbitrary units, μ^2 the mean square vibrational amplitude in cm^2 and T is the temperature in °C. The measured change in interplanar spacing may be represented by the relation

$$d_{400} = (0.903396 \pm 0.000053) + (1.231 \pm 0.026) \times 10^{-5} T + (3.56 \pm 0.26) \times 10^{-9} T^2$$

where d_{400} is in Angstrom units and T in °C. The integrated intensities were scaled to the base temperature of 13°C by calculating the mean square vibrational amplitude at this temperature from the Debye-Waller theory. The Debye temperature employed was 315°K.

Similarly for the zinc single crystal the integrated intensities were scaled by employing a Debye temperature of 200°C for vibrations in the direction parallel to the hexagonal c axis and 320°K for vibrations perpendicular to the c-axis. The experimental data are represented by the relations

$$\ln R_{0006} = 5.5584 - 3.7238 \times 10^{-3} T - 8.90406 \times 10^{-7} T^2 - 1.0249 \times 10^{-8} T^3$$

$$\ln R_{2110} = 6.9496 - 7.1009 \times 10^{-4} T + 2.3858 \times 10^{-6} T^2 - 7.8106 \times 10^{-9} T^3.$$

The relations for the mean square vibrational amplitude along the c and a-axes were calculated to be

$$\mu_{0006}^2 = 15.1085 \times 10^{-19} + 6.4091 \times 10^{-21} T + 1.5388 \times 10^{-24} T^2 + 1.7639 \times 10^{-26} T^3,$$

and

$$\mu_{2110}^2 = 5.7295 \times 10^{-19} + 3.1579 \times 10^{-21} T - 1.0610 \times 10^{-23} T^2 + 3.4736 \times 10^{-26} T^3,$$

respectively. The units in these relations and the similar relations for copper are the same. The change in d spacings with temperature were fitted by the relations

$$d_{0006} = (0.823251 \pm 0.000059) + (5.134 \pm 0.074) \times 10^{-5} T - (6.22 \pm 1.8) \times 10^{-9} T^2$$

and

$$d_{2110} = (1.324878 \pm 0.000089) + (1.20 \pm 0.11) \times 10^{-5} T + (2.47 \pm 0.28) \times 10^{-8} T^2.$$

Each of the above relations, except for the $2\bar{1}\bar{1}0$ data, represents the combined data for three or more heating and cooling cycles. The standard deviations for the constants in the relations for the d spacings are included in parenthesis with the constants. Most of the measured and scaled intensities for copper lie within $\pm 6.0\%$ of the values given by the least squares curve for $\ln R_{400}$. The measured integrated intensities for the 0006 reflection for zinc showed much less scatter than the copper data. A greater degree of scatter was observed for the integrated intensities for the $2\bar{1}\bar{1}0$ reflections. In this case only one run, involving 42 measurements, was made and the data lie within $\pm 10\%$ of the least squares curve for $\ln R$ given above.

An attempt is being made to correlate these data with other properties, such as the electrical resistivity, and a final report is being prepared.

4.6 Characteristics of the Uranium Transformations (P. Chiotti and J. Mason)

Previous work on the isothermal transformation characteristics for uranium was summarized in ISC-893, June, 1957. Some questions have been raised relative to the temperature range for the $\alpha \rightleftharpoons \beta$ and $\beta \rightleftharpoons \gamma$ transformations. A number of experiments were repeated with wire specimens of comparable purity in a different furnace in which the constant temperature zone was several times the length of the constant temperature zone in the furnace previously used. The results obtained were similar to those previously reported. An appreciable scatter in the temperature at which the transformations start, either on heating

or cooling was observed. Whether this was in part due to variations in carbon content with time as a result of contamination or decarbonization by residual gases in the furnace is not known. Donze and Faivre, *Comptes Rendus*, 246, 3619 (1958) have shown that carbon content and the degree of super heat into the beta region affect the velocity of the $\beta \rightarrow \alpha$ transformation on cooling as well as the temperature at which the transformation starts. However, their experiments were carried out with constant cooling rates of 4°C per hour. Once the transformation started it proceeded to completion over a temperature span of only a few degrees; the greater the degree of supercooling the narrower the temperature span. In the present work samples were held for one half hour at some temperature in the beta range and then rapidly cooled to within the transformation range. The samples were then held at constant temperature for five minutes. If no transformation was apparent in this period of time the temperature was lowered two to three degrees and again held at constant temperature for five minutes. This process was repeated until a temperature was reached at which transformation occurred. Samples which required a high degree of supercooling to initiate the transformation proceeded to near completion within two or three degrees, however, if once started the transformation was arrested by reheating, usually about 10°C, the transformation thereafter proceeded in a stepwise manner on further cooling as previously observed, (See ISC-893).

Some further data have also been obtained with a 3/16 inch square cross-section by five inches long bar. In this case the bar was mounted

between water-cooled copper electrodes and heated by passing an electric current through it. The resistance across approximately one centimeter length near the middle of the bar was measured. The thermal history and resistance as a function of temperature are shown in Fig. 13. It is evident that heating in the beta range for 8 to 10 minutes results in suppression of the resistivity break for the $\beta \rightarrow \alpha$ transformation. The transformation still occurs, as evident from thermal arrests, but the change in resistance characteristic of randomly oriented

Fig. 13. Electrical resistivity of uranium as a function of temperature and thermal history.

polycrystalline uranium is absent, indicating a high degree of preferred orientation and anisotropy in the electrical resistivity of one of the phases, probably alpha, or both of the phases. This preferred orientation is retained after several cycles through both transformations. However, more rapid cycling through one or both of the transformations restores the alpha-beta resistivity break and presumably randomized the crystal structure. Repeated cycling sometimes results in anomalous resistivity breaks in the beta range, that is, an increase in resistivity occurs on cooling at a temperature between the normal transformation temperatures.

polycrystalline uranium is absent, indicating a high degree of preferred orientation and anisotropy in the electrical resistivity of one of the phases, probably alpha, or both of the phases. This preferred orientation is retained after several cycles through both transformations. However, more rapid cycling through one or both of the transformations restores the alpha-beta resistivity break and presumably randomized the

The fact that the preferred orientation is regenerated on heating indicates that the nucleation of the beta phase is coherent with the alpha phase. Retention of a given orientation on cooling could be explained on the basis of the movement of phase interfaces present in the colder parts of the sample. In this case no new nuclei would have to form.

The continued decrease in the resistance above 780°C indicated by curve C is most probably caused by changes in dimensions of the bar in the region of the resistance probes due to yielding of the relatively soft gamma uranium under thermal or transformation stress or due to slight shifts in the probe positions. Since these probes are only one centimeter apart slight changes in their position can produce a pronounced change in the measured resistance. However, these effects cannot explain the disappearance of the $\alpha \rightarrow \beta$ break since it reappears on rapid thermal cycling of the bar.

4.7 Magnetic Susceptibility of Sodium Tungsten Bronze (J. F. Smith and J. D. Greiner)

Sodium tungsten bronze is nonstoichiometric sodium metatungstate, Na_xWO_3 . Samples of various sodium concentrations were prepared by electrolysis. A plot of susceptibility versus sodium concentration is shown in Fig. 14 and it may be noted there that the data are fit reasonably well by a straight line relationship.

4.8 Crystal Structures of YAl_3 (J. F. Smith, D. Bailey, H. A. Wilhelm and R. L. Snyder)

Crystals etched from an alloy of 30 w/o yttrium in aluminum were found to exhibit two distinct growth habits, needles and platelets.

Fig. 14. Magnetic susceptibility of sodium tungsten bronze at 25°C.

The 30 w/o alloy contained a preponderance of the platelet form with only a few rather large needles present. Other alloys of 20 w/o and 15 w/o yttrium in aluminum were similarly etched with NaOH. It was observed that as the yttrium content decreased, with the attendant lowering of the temperature of crystallization, the percentage of needles increased and the needles became smaller in

size. From an alloy of 6 w/o yttrium, a composition on the aluminum side of the eutectic, only very fine needles and no platelets were obtained. An alloy of 30 w/o yttrium quenched from 680°C produced only crystals of the platelet form. The implication is that YAl_3 undergoes an allotropic transformation at a temperature near the eutectic temperature, 640°C.

A crystal of the needle form of YAl_3 was isolated from a 30 w/o yttrium alloy and was mounted and aligned on the Weissenberg camera for X-ray investigation. This crystal exhibited the diffraction symmetry and systematic extinctions of space groups $P6_3/\text{mmc}$, $P\bar{6}2c$,

and $P6_3mc$. The following lattice parameters were measured from rotation and Weissenberg X-ray pictures: $a_0 = 6.28\text{\AA}$ and $c_0 = 4.58\text{\AA}$. The intensities of the $hk0$ reflections were measured with the proportional counter attachment for the Weissenberg camera employing $Cu K\alpha$ radiation. These data were corrected for Lorentz and polarization effects but no corrections were made for absorption or dispersion effects. The structure of $ThAl_3$ was chosen as a trial structure for YAl_3 and was refined by a least squares method with the I. B. M. 650 computer. The atomic form factors employed in the computations were those of Thomas and Umeda⁽¹²⁾. The refinement produced a value for the "discrepancy index"

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} = 0.034$$

for the following structure for the needle form of YAl_3 :

Space Group $P6_3/mmc$

with 2 Y at $\pm (2/3, 1/3, 1/4)$

and 6 Al at $\pm (x, 2x, 1/4; 2\bar{x}, \bar{x}, 1/4; x, \bar{x}, 1/4)$

with $x = 0.146$.

A crystal of the platelet form of YAl_3 was isolated from the 30 w/o yttrium alloy and aligned on the Weissenberg camera. Initial examination of the diffraction patterns from this crystal indicated apparent 6-fold diffraction symmetry with $a_0 = 6.19\text{\AA}$ and $c_0 = 21.3\text{\AA}$. Ten layers of Weissenberg data were taken. Layers $hk0$ through $hk8$ were found to satisfy the extinction conditions for space groups $P6_3/mmc$, $P\bar{6}2c$, and $P6_3mc$. Additional extinctions of the form $h-k = 3n$ occur in $hk0$,

(12) L. H. Thomas and K. Umeda, (1957). J. Chem. Phys. 26, 293.

hk3, and hk6 data. These additional extinctions are characteristic of a rhombohedral unit cell indexed on a hexagonal basis. In addition, hk9 data have the same symmetry and extinctions as hk0 data. This violates the extinction conditions for the hexagonal space groups listed above. These observations, plus the ratio of the c_0 lattice parameters of the two crystalline form, ($c_{\text{platelet}} = 4.5 c_{\text{needle}}$), indicate that the structure of the platelet form of YAl_3 may be based on a rhombohedral unit cell with a stacking disorder such that the basic repeat unit in the c-direction is nine atom layers thick. This could be accomplished with a stacking of the type

ABCBCACAB ABCBCACAB ABCB-----.

As yet intensity data have not been taken in order to check this postulated structure, but work is in progress.

5. Separation Studies

5.1 Liquid-Liquid Extraction (H. A. Wilhelm and M. L. Andrews)

Work on the separation of barium and strontium was continued. A feed solution 0.67M in barium and 0.67M in strontium as chlorides entered a 20 stage laboratory extractor at stage 11. With certain flow ratios of the liquids including aqueous scrub entering at stage 1 and organic solvent entering at stage 20, the aqueous phase delivered from the extractor at stage 20 carried the major part of the barium with a purity of less than 50 ppm strontium. The strontium product delivered in the organic phase from stage 1 analyzed 1.8% barium; however, an extraction employing different flow ratios gave with the 20 stage extractor a strontium product containing only parts per million of barium.

In this investigation the organic phase is tributyl phosphate and NaSCN is used to effect adequate distribution of the metals between the liquid phases. Analyses are being performed to determine the stagewise distribution data on the chloride, sodium and thiocyanate ions as well as that of the barium and strontium during an extraction.

5.2 Pyrometallurgical Separations

5.2.1 Selective Oxidation-Reduction Reactions (P. Chiotti and S. J. S. Parry)

Some details on the separation of various components by selective oxidation-reduction reactions in a two phase system consisting of KCl-LiCl eutectic and zinc were presented in the Annual Summary Research Report, IS-17, Nov. 1959. Work has continued with this system and a number of reactions involving chromium, zirconium, cerium, uranium, thorium, protactinium and yttrium have been investigated.

In all of these experiments tantalum was used as the container. Zinc chloride was employed as an oxidizing agent and magnesium as a reducing agent. In one series of experiments the dried salts and metallic components (total mass of charge was about 50g) were sealed in tantalum crucibles. Each tantalum crucible was sealed in a graphite crucible with a screw cap top which in turn was sealed inside a welded steel container. The charge was equilibrated at temperature in a rocking furnace for periods ranging from one to four hours. It was then permitted to settle for 15 minutes and cooled with an air blast. In another series of experiments charges consisting of approximately 800 grams of KCl-LiCl eutectic and 800 grams of zinc in which the

various components had been dissolved were equilibrated in tantalum containers under an inert atmosphere. Anhydrous ZnCl_2 was added step wise; each addition was followed by an equilibration period of one half hour or longer with vigorous stirring of the charge, and after a settling period of 15 minutes a sample of the salt was taken for analysis. This procedure was continued until the zinc in the salt phase reached a concentration of 1.0 to 2.0 w/o. The concentration of other components in the salt phase usually did not exceed 2.0 w/o. Thereafter magnesium was added in steps and samples similarly taken. Periodic samples of the metal phase were also taken, but in most cases the concentration of the component in the zinc phase was determined from a material balance based on the amount initially added and the amount found in the salt.

The equilibrium constant K_N is a more useful index than the usual distribution coefficient for evaluating the distribution of a particular component between the two phases. However, in order to obtain a value for K_N the valence states for the components in the salt phase must be known. Furthermore, K_N will be constant only if K_r , the ratio of activity coefficients of products and reactants, is constant. This condition is reasonably well satisfied in dilute solutions.

Analyses of the data thus far obtained for equilibrations carried out at 700°C as well as 500°C indicate that the average valence for thorium and zirconium is both three so long as the equilibrium concentration of zinc chloride in the salt phase is 1.0 w/o or less. At higher zinc chloride concentrations displacement toward higher valence states may occur to an extent which is uncertain. It was

observed in the second series of experiments that some zirconium was lost from the salt phase, presumably due to volatilization of ZrCl_4 resulting from the reaction

Experiments have shown that the zirconium can be effectively removed by volatilization by operating under reduced pressure. Zirconium losses by volatilization have made it difficult to establish the true valence of zirconium. Further work is being done to check the valence states of both zirconium and thorium in this system.

Fig. 15. Log-log plot of oxidation-reduction data for zirconium and chromium in a KCl-LiCl/zinc system at 700°C; open points obtained on oxidation with ZnCl_2 , and $\bullet$ points obtained on reduction with magnesium. (S) and (M) refer to salt and metal phase respectively.

The data in Fig. 15 were obtained by the second procedure described above from a system containing zirconium and chromium as components. The equilibration temperature was 700°C. If a valence of two is accepted for zinc it is apparent that the data are consistent with the following reactions:

1. $\text{Cr} + \text{ZnCl}_2 \rightarrow \text{CrCl}_2 + \text{Zn}$
2. $\text{Zr} + 3/2\text{ZnCl}_2 \rightarrow \text{ZrCl}_3 + 3/2\text{Zn}$
3. $\text{Zr} + 3/2\text{CrCl}_2 \rightarrow \text{ZrCl}_3 + 3/2\text{Zn}.$

For reaction 1,

$$K_N = \left(\frac{N_{\text{CrCl}_2}}{N_{\text{ZnCl}_2}} \right)_{\text{salt}} \left(\frac{1}{N_{\text{Cr}}} \right)_{\text{zinc}} = \left(\frac{n_{\text{Cr}}}{n_{\text{Zn}}} \right)_{\text{salt}} \left(\frac{n_M}{n_{\text{Cr}}} \right)_{\text{zinc}}$$

where N represents mole fraction and n represents actual number of moles, and n_M is the total number of moles of zinc-rich liquid. The number of moles of zinc-rich liquid varied by less than 3% throughout the course of the experiment and was treated as a constant. The maximum concentration of chromium and zirconium in the zinc phase was 1.4 w/o ($N = 0.0176$) and 1.6 w/o ($N = 0.0115$) respectively. The maximum concentrations in the salt phase were 1.02 w/o zirconium, 0.18 w/o chromium and 2.3 w/o zinc. If K_r is constant then

$$\log n_{\text{Cr}}(\text{salt})/n_{\text{Cr}}(\text{zinc}) = \log n_{\text{Zn}}(\text{salt}) + C$$

and the slope of the log-log plot of the corresponding data should reveal the relative valence of chromium and zinc. A straight line with a slope of one represents the data quite well and it may be concluded that the valence of chromium and zinc is the same, namely plus two. Corresponding plots for reactions 2 and 3, Fig. 15, show a slope of 3/2 indicating a valence of three for zirconium. However, as the concentration of zinc and zirconium attained their maximum value in the salt, some zirconium was lost by volatilization. Chemical analyses of the zinc phase at the end of the oxidation cycle made an appropriate correction possible. The two oxidation points corrected are indicated by arrows in Fig. 15.

Figures 16 and 17 show data obtained for the transfer of cerium, uranium and zirconium at 700°C by oxidation with ZnCl_2 and by reduction with magnesium respectively. Similar data obtained at 500°C

show a more effective separation of cerium from uranium. In either case the separation was not as effective as initially expected on the basis of available free energy data. The experimental data imply a very strong negative deviation from Raoult's law for cerium in zinc. Work at ANL by Johnson and Yonco, Chemical Engineering Summary Report ANL-5959, March, 1959, p 124, shows that this is indeed the case. They find that the activity coefficient of cerium in zinc at 508°C is of the order of 3.4×10^{-10} .

Fig. 16. Transfer of solutes, cerium, uranium and zirconium at 700°C from a zinc-rich phase to KCl-LiCl eutectic by oxidation with ZnCl₂; moles M(Ce, U, Zr) in salt versus moles ZnCl₂ added.

Fig. 17. Transfer of solutes, cerium, uranium and zirconium at 700°C from KCl-LiCl eutectic to a zinc-rich phase by reduction with magnesium; moles M in salt versus moles magnesium added.

Although the data show appreciable scatter, approximate values for the equilibrium constant, K_N , the ratio of the mole fraction of

products to mole fraction of reactants, for several reactions have been determined and are summarized in Table XV.

The values of K_N listed under 6, 7, 8 and the third value under 1 were calculated from data obtained from equilibrations carried out in sealed tantalum containers. The relative amounts of oxidizing or reducing agent and components were varied in the individual equilibrations.

For equilibrations in which the amount of component in the zinc phase exceeded the solubility limit in zinc, the solubility limit as determined for the binary zinc system was used in the calculations. These are listed in Table XVI. No attempt was made to determine the effect of the presence of a second component on the solubility of a particular component in zinc.

The values for K_N given in Table XV can also be expressed as w/o ratios. If both components have the same valence in the salt, as for reaction 1,

$$\left(\frac{\%U}{\%Th} \right)_{\text{salt}} \left(\frac{\%Th}{\%U} \right)_{\text{zinc}} = K_N \cong 9.0$$

If the valence states are not the same, as in reaction 3, an appropriate expression can be obtained, in this case:

$$\log K_N = \log \left(\frac{\%Zr}{(\%Zn)^{3/2}} \right)_{\text{salt}} \left(\frac{1}{\%Zr} \right)_{\text{zinc}} + \frac{3}{2} \log(100 \times 65.38) - \frac{1}{2} \log 55.9.$$

The numbers in the last two terms represent the average molecular weight of the zinc phase (usually 99+% zinc) and the salt phase (KCl-LiCl eutectic containing small amounts of $ZrCl_3$, $ThCl_3$ etc.) respectively.

Table XV

Equilibrium Constants, K_N , for Oxidation-Reduction Reactions
in a KCl-LiCl/Zinc System

Reaction	Components in System	Temp. °C	$K_N (N \leq 0.015)$
1. $U + ThCl_3 \rightarrow UCl_3 + Th$	U, Th, Zr	700	9.0 ± 1.3
	Th, U	700	8.8 ± 0.6
	U, Th, Pa*	500	2.0 ± 0.5
	U, Th, Zr	500	2.3 ± 1.3
2. $Ce + UCl_3 \rightarrow CeCl_3 + U$	Ce, U, Zr	700	10.8 ± 2.0
	Ce*, U	500	9.1
	Ce, U	500	18
3. $Zr + 3/2 ZnCl_2 \rightarrow ZrCl_3 + 3/2 Zn$	U, Th, Zr	700	2.04×10^3
	U, Th, Zr	700	3.22×10^3
	Zr, Cr	700	1.5×10^3
	Ce, U, Zr	700	1.7×10^3
	Zr, U	650	1.8×10^3
	Zr, Cr	500	1.5×10^3
	U, Th, Zr	500	$(4.0 \pm 2.0) \times 10^3$
4. $Zr + 3/2 CrCl_2 \rightarrow ZrCl_3 + 3/2 Cr$	Zr, Cr	700	68
	Zr, Cr	500	280
5. $Cr + ZnCl_2 \rightarrow CrCl_2 + 3/2 Zn$	Zr, Cr	700	7.6
	Cr, U	650	4.5
	Cr, U	625	5.1
	Zr, Cr	500	3.0
6. $Th + PaCl_3 \rightarrow ThCl_3 + Pa$	Th, U, Pa*	500	10.0 ± 6.0
7. $U + PaCl_3 \rightarrow UCl_3 + Pa$	Th, U, Pa*	500	20.0 ± 1.3
8. $Y + UCl_3 \rightarrow YCl_3 + U$	U, Y*	500	1.0 ± 0.5

* Radioactive tracer added, concentrations in the zinc and salt phases determined radiochemically.

Table XVI
Solubility Limits of Metals in Zinc

	500°C		700°C	
	w/o	Mole Fraction	w/o	Mole Fraction
U	0.033	9.0×10^{-5}	1.48	4.1×10^{-3}
Th	0.022	6.1×10^{-5}	0.99	2.8×10^{-3}
Zr	0.24	1.72×10^{-3}	Not exceeded	
Cr	1.2	1.5×10^{-2}	"	"
Ce	0.012	5.6×10^{-5}	"	"
Y	0.014	1.03×10^{-4}	"	"

The values for the equilibrium constants obtained in the various experiments are fairly consistent. In experiments involving different components some variation in K_N for a particular reaction may result due to interaction between the solute components. The mutual effects of the solute components on their activity coefficients are not known. Scatter in the experimental data was too large to permit any such significance to be associated with the variations of the K_N values listed in Table XVI.

5.2.2 Distribution of Cerium, Yttrium and Protactinium Between Mg-38 w/o Th and KCl-LiCl Eutectic Containing $MgCl_2$ (P. Chiotti and S. J. S. Parry)

The distribution of cerium, yttrium and protactinium between Mg-38 w/o Th and KCl-LiCl eutectic containing $MgCl_2$ has been measured in an

attempt to determine the extent to which such components may be separated from Mg-Th eutectic. These equilibrations were carried out in sealed tantalum cans in the same manner as the small scale equilibrations described in section 5.2.1. The results obtained are summarized in Table XVII. The amount of yttrium and cerium present in each case was in the range of 1.2 to 0.8 w/o based on the total weight of charge. In the case of protactinium neutron irradiated Mg-38 w/o Th was used and the distribution of protactinium-233 between the two phases was determined radiochemically.

5.2.3 Distribution of Cerium Between Mg-38 w/o Th and U-5.2 w/o Cr (P. Chiotti and S. J. S. Parry)

Three experiments were performed to determine the extent to which a Mg-38 w/o Th phase extracts cerium from U-5.2 w/o Cr. These equilibrations were carried out at 1000°C in tantalum crucibles. The amount of cerium present was roughly 0.2 w/o based on the total weight of the two phases. Cerium-144 was added as a tracer and the cerium concentration was determined radiochemically. The results summarized in Table XVIII show that the cerium is very effectively extracted by the Mg-Th phase.

5.2.4 Precipitation of Solutes as Hydrides from Liquid Metal Solvents (P. Chiotti and P. F. Woerner)

Work on the precipitation of solutes from liquid metals with hydrogen at one atmosphere pressure has been completed and the results have been summarized by Paul F. Woerner, Ph.D. Thesis,

Table XVII

Distribution of Cerium, Yttrium, and Protactinium Between Mg-38 w/o
Th and KCl-LiCl Eutectic Containing MgCl_2

Temp. °C	Salt w/o MgCl_2	Component	K_d w/o in salt w/o in metal	R wt. salt wt. metal
700	15	Ce	2.6	2.8
			2.5	2.5
800	"	"	1.2	4.5
"	"	"	2.0	3.3
"	"	"	2.1	1.5
"	"	"	2.3	0.75
"	"	"	1.7	0.65
800	"	"	2.3*	0.67
"	"	"	3.0*	0.59
"	"	"	2.6*	0.38
"	"	"	3.0*	0.37
600	"	Y	7.1	1.4
"	"	"	6.8	1.1
"	"	"	8.7	1.0
700	"	Pa	0.0020**	1.3
650	20	"	0.0076**	1.3

* Metal phase contained 10 w/o zinc

** K_d - distribution coefficient counts/min/g in salt divided by
counts/min/g in metal

Table XVIII

Distribution of Cerium Between Mg-38 w/o Th and
U-5.2 w/o Cr at 1000°C

$\frac{\text{Wt. Mg-38 Th}}{\text{Wt. U-5.2 Cr}}$	$K_d \frac{\text{w/o Ce in Mg-Th}}{\text{w/o Ce in U-Cr}}$
0.64	0.58×10^3
0.47	3.7×10^3
0.46	3.0×10^3

Iowa State University, Ames, Iowa, 1960. Some details relative to this investigation have been presented in an earlier report of this series, IS-17. The results obtained for the solubility of yttrium, zirconium and thorium in some liquid metals are summarized in Table XIX. The residual concentration data of these solutes in the same solvents, after equilibration with hydrogen at one atmosphere pressure, as well as other data, are presented in Table XX. In the case of aluminum saturated with zirconium no significant change in the amount of zirconium in solution was observed upon equilibration with hydrogen at one atmosphere pressure. This was also observed to be the case for yttrium in zinc. The solubility of yttrium in zinc as a function of temperature shows a discontinuity in slope at 685°C, the peritectic decomposition temperature for YZn_{11} . See section 2.2.

The mole fractions of solutes in the solvents equilibrated with hydrogen were calculated on the assumption that the concentration of hydrogen in the solvent was negligible. Experiments are being conducted to check the validity of this assumption.

Table XIX

Solubility of Various Solutes in Liquid Metal Solvents as
a Function of Temperature

$$\log_{10} N = -\frac{A}{T} + B$$

Solvent	Solute	A	Probable error in A	B	Probable error in B	Temp range °C
Zn	Y	4769	348	2.946	0.332	685-850
Zn	Y	7663	169	5.902	0.195	495-685
Al	Zr	4089	316	0.896	0.305	650-850
Al-70 w/o Mg	Th	3267	121	-0.056	0.134	500-815
Mg-55 w/o Zn	Th	2067	156	1.144	0.187	500-815

Table XX

Residual Solute Concentration in Various Liquid Metal Solvents Equi-
libriated With Hydrogen at a Pressure of One Atmosphere

$$\log N = -\frac{A}{T} + B$$

Solvent	Solute	A	Probable error in A	B	Probable error in B	Temp range °C
Mg	Ca	2343	137	1.285	0.137	625-900
Mg	Y	8458	624	5.703	0.605	650-913
Mg-55 w/o Zn	Y	4857	134	3.199	0.140	485-850
Mg	La	3625	107	2.395	0.107	655-850
Mg	Ce	1376	137	0.0028	0.137	597-850
Mg	Th	4603	215	2.810	0.214	650-850
Mg-55 w/o Zn	Th	1880	30	0.558	0.0326	500-815
Mg-70 w/o Al	Th	3441	91	-0.152	0.098	500-815

The reaction of hydrogen with solutes which form stable hydrides is also being investigated as a method for determining the thermodynamic properties of intermetallic phases or compounds. Measurements of the equilibrium hydrogen pressure over a system consisting of CaH_2 , CaMg_2 and a magnesium-rich solid solution are being made in an attempt to determine the thermodynamic properties for the compound CaMg_2 . The data thus far obtained yield a value for the standard free energy of formation for CaMg_2 which is in agreement with the free energy of formation obtained by other methods. However, the temperature dependence of the free energy, or the enthalpy of formation has not been satisfactorily determined. Such reactions will be extended to other systems of interest if the present investigation proves successful.

6. Other Investigations

6.1 Diffusion of Hydrogen in Thorium (D. T. Peterson and D. G. Westlake)

The results of this investigation have been published in the Journal of Physical Chemistry, Vol. 64, 649 (1960). The title of the article is "Diffusion of Hydrogen in Thorium" by D. T. Peterson and D. G. Westlake.

Abstract—The diffusivity of hydrogen in thorium was measured from 300 to 900°C. Over this temperature range, $D = 2.92 \times 10^{-3} \exp (-9750/RT)$. The diffusivity increased with concentration above 600° but did not vary significantly with purity, grain size or cold working. Two different methods of determining diffusion constants were used and gave similar values.

6.2 Diffusion of Carbon in Thorium (D. T. Peterson)

The diffusion of carbon in thorium was studied at 1000, 1100 and 1200°C. Cylinders of thorium were carburized by packing in powdered graphite and heating at temperature for a measured length of time. The carbon concentration gradient along the radius of the cylinder was measured by sampling and analysing for carbon by the combustion method. The diffusion coefficients were calculated from the rate of saturation of the specimen and also by a differential method. The results of the two methods of calculation were in very good agreement. The diffusion coefficients decreased with increasing carbon content at each temperature. The diffusion coefficients from the rate of saturation method are given in Table XXI and the solubility of carbon in thorium in Table XXII. The activation energy for diffusion of carbon in thorium was 38 kcal.

6.3 Vapor Pressure of Calcium over Solutions of Calcium in Molten Calcium Chloride (D. T. Peterson and E. Johnson)

The vapor pressure of calcium over solutions of calcium in calcium chloride was measured by a carrier gas method at two temperatures and a range of calcium concentrations. The vapor pressure varied with the square of the calcium concentration up to the solubility limit. This concentration dependence indicates that calcium forms two solute particles on dissolving in molten calcium chloride. There was considerable scatter and lack of reproducibility in the experimental data which must have been due to an undetected experimental error. The procedure will be examined to find the source of the erratic results and modified to improve the accuracy and precision.

Table XXI
Diffusion Coefficients for Carbon in Thorium

Temperature	Diffusion Coefficient	Time, sec.
1000°C	7.9×10^{-9}	2.6×10^5
	10.5×10^{-9}	5.2×10^5
	11.4×10^{-9}	8.6×10^5
	7.9×10^{-9}	1.7×10^6
	7.4×10^{-9}	2.6×10^6
1100°C	3.9×10^{-8}	8.6×10^4
	3.6×10^{-8}	4.3×10^5
	2.8×10^{-8}	7.8×10^5
1200°C	11.1×10^{-8}	9.4×10^4
	5.6×10^{-8}	3.4×10^5
	5.9×10^{-8}	4.1×10^5
	3.6×10^{-8}	7.8×10^5
	4.1×10^{-8}	11.2×10^5

Table XXII
Solubility Limits of Carbon in Thorium

Temperature	This Investigation	Peterson & Mickelson
1000°C	0.63 w/o	0.56 w/o
1100°C	0.80 w/o	
1200°C	1.06 w/o	0.90 w/o

6.4 Thorium Metallography (D. T. Peterson)

An investigation of new electrolytes for the preparation of thorium specimens for metallographic examination was made. The results of this study have been summarized and issued as IS-155, "Some Metallographic Observations on Thorium Metal".

6.5 Transport Reactions of Some Vanadium Halides (R. E. McCarley and J. W. Roddy)

One of the most difficult vanadium halides to prepare in a high state of purity is vanadium(III) chloride. The difficulty arises from the relative thermodynamic stabilities of the compounds VCl_4 , VCl_3 and VCl_2 . At the temperatures required for chlorination of either vanadium metal or vanadium oxides, e.g. V_2O_3 or V_2O_4 , the equilibrium constant for the reaction

is sufficiently large that VCl_4 is the chief product obtained from the chlorination reactions. A subsequent step is then required for formation of VCl_3 , whereby the inverse of reaction (1) is utilized.

Under the conditions usually employed for the decomposition of VCl_4 , many of the impurities which may be present remain with the VCl_3 . Further purification of VCl_3 by sublimation is rendered impractical owing to the decomposition

which becomes important at the temperatures required for vaporization.

A possible solution to the purification problem may be found in the utilization of chemical transport reactions, i. e., reactions where the

compound is transported through a temperature gradient T_1 to T_2 by formation of a gaseous species stable at T_1 , but unstable at T_2 . Such a reaction may be represented, in the case of vanadium(III) chloride, by the equation

With this in mind, an investigation of some possible reactions has been initiated. During this period attention was centered on the reactions of VCl_3 and VCl_2 with bromine, as well as solid solubility and compound formation in the system $\text{VCl}_3\text{-VBr}_3$.

The VCl_3 used in this work was prepared by decomposition of VCl_4 at 154°C under reflux and inert atmosphere. The purity of this material was found to depend greatly on the source of the VCl_4 . When VCl_4 produced by chlorination of crystal bar vanadium was employed, a satisfactory product resulted. However, several attempts to prepare the VCl_4 from V_2O_3 by chlorination with carbon tetrachloride led to products of unacceptable purity. The first step in this reaction must involve conversion of V_2O_3 to VOCl since the latter compound was always obtained in those reactions stopped short of completion. In subsequent steps the VOCl was converted to VCl_4 , with some conversion of carbon tetrachloride to hexachloroethane, and possibly other long chain chlorocarbons. Hexachloroethane has been identified as one product of the reaction. On subsequent decomposition of the VCl_4 , the chlorocarbons were difficult to remove from the VCl_3 and a product of a low degree of purity was obtained.

Several reactions of bromine and VCl_3 were performed in the following manner. A sample of VCl_3 at elevated temperature was contacted with bromine vapor in a sealed, evacuated Pyrex tube. The bromine was contained in a special arm of the tube so that the vapor pressure could be regulated by use of constant temperature baths. During the course of the reactions little of the bromine was actually consumed, but the VCl_3 was transported from the hot reaction zone to cooler regions of the tube. Some difficulty has been encountered in the analysis of the products, which contain both chlorine and bromine. Analytical data for the products of two such reactions, along with reaction conditions are given below:

P_{Br_2} (mm. Hg)	Reaction Temp. °C	%V	%Cl	%Br	Total %	Atom Ratio Cl/V	Br/V
220	400	31.8	65.5	2.5	99.8	2.96	0.05
67	400	32.1	66.2	1.6	99.9	2.97	0.03

It is evident that some bromine has entered into solid solution in the deposited VCl_3 . Work is now in progress to determine the dependence of the solid solution formation on the bromine pressure. Transpiration experiments designed to determine equilibrium constants and nature of the vapor species are also in progress.

Preliminary results of an X-ray diffraction study of solids in the system VCl_3 - VBr_3 indicate solid solution formation over the complete range of compositions. Samples very low in bromine content were prepared by the transport reaction; those with Br/V ratio greater than

0.1 were prepared by heating mixtures of VCl_3 and VBr_3 at 600-650°C in sealed evacuated tubes. The sample of the composition VCl_2Br was obtained by direct reaction of VCl_2 and bromine at 400°C. X-ray powder patterns for all samples were successfully indexed on the basis of a hexagonal unit cell. The derived lattice constants are given in Table XXIII.

Table XXIII

Lattice Constants for Solid Solutions in the System

 $\text{VCl}_3\text{-VBr}_3$

Sample No.	Nominal Composition*			Formula	Lattice Constants		
	%V	%Cl	%Br		a(Å)	c(Å)	c/a
1	32.4	67.6	--	VCl_3	6.01	17.34	2.88 ₅
2	32.1 [†]	66.2	1.6 [†]	$\text{VCl}_{2.97}\text{Br}_{0.03}$	6.18	17.87	2.89 ₂
3	31.8 [†]	65.5	2.5 [†]	$\text{VCl}_{2.96}\text{Br}_{0.05}$	6.06	17.46	2.88 ₁
4	29.8	56.0	14.2	$\text{VCl}_{2.70}\text{Br}_{0.30}$	6.08	17.56	2.88 ₈
5	25.3	35.1	39.6	VCl_2Br	6.16	17.98	2.91 ₉
6	23.0	23.0	54.0	$\text{VCl}_{1.44}\text{Br}_{1.50}$	6.24	18.09	2.89 ₉
7	19.2	7.6	73.2	$\text{VCl}_{0.57}\text{Br}_{2.43}$	6.33	18.28	2.88 ₈
8	17.5	--	82.5	VBr_3	6.38	18.48	2.89 ₇

* Determined from the weights of VCl_3 and VBr_3 used for preparation of the solid solution

[†] Determined by direct analysis

When the lattice constants are plotted vs composition of the solid in the system $\text{VCl}_3\text{-VBr}_3$, a linear relationship is obtained for a_0 over

the range of compositions examined. The c_o values show considerable scatter but also appear to be linearly dependent on the composition. These results indicate that VCl_3 and VBr_3 are completely miscible in the solid state and also that the solid solutions exhibit almost ideal behavior. Further work to confirm these observations with the bromine-rich solutions is in progress.

6.6 Reduction of Vanadium Oxytrichloride with Hydrogen (R. E. McCarley and J. W. Roddy)

The results of this investigation have been accepted for publication in the Journal of Inorganic and Nuclear Chemistry. An abstract of the paper, "The Hydrogen-Vanadium(V) Oxytrichloride Reaction", is given here.

Abstract—The reaction of hydrogen and $VOCl_3$ has been investigated over the temperature range 500 to 850°C. Pure $VOCl$ was obtained as the reaction product at 600-635°C; but at higher temperatures mixtures of V_2O_3 , VCl_2 and $VOCl$ resulted. Thermal decomposition of $VOCl$ at 650 to 900°C proceeded with formation of V_2O_3 , VCl_2 , VCl_3 and VCl_4 ; this reaction was related in a definite way to the hydrogen reduction. X-ray powder diffraction data are given in the paper for $VOCl$ and VCl_2 .

6.7 Preparation of Pure Vanadium Pentoxide (R. E. McCarley and J. W. Roddy)

The results of this work have been published in the Journal of Less Common Metals, 2, 29 (1960). An abstract of the paper is given here.

Abstract—A method for the preparation of high purity V_2O_5 from a technical grade oxide has been developed. The method includes the reaction of the impure oxide with chlorine and carbon, hydrolysis of the resultant $VOCl_3$ in aqueous ammonia, and ignition of the precipitated NH_4VO_3 at 500-600°C. V_2O_5 containing a maximum of ca. 100 ppm impurities was produced in kilogram quantities both cheaply and efficiently by this process.

6.8 Niobium Halides

6.8.1 Reactions of Niobium(V) Halides with Pyridine (R. E.

McCarley and B. G. Hughes)

Work on the reaction of pyridine with $NbBr_5$ was continued and extended also to the reactions with other niobium(V) halides and tantalum(V) halides. These reactions are of considerable interest because of the reduction of the metal to a lower valence state. For example, in the case of the reactions of the niobium halides with pyridine, the niobium was reduced to the average oxidation state +4. While $NbCl_5$, $NbBr_5$ and NbI_5 were all reduced by pyridine under similar conditions, the only tantalum halide to show evidence for reduction was TaI_5 .

Reaction of $NbBr_5$ with a large excess of pyridine at room temperature led to formation of a green, insoluble solid. Removal of the excess pyridine on the vacuum line gave, by weight gain data, a pyridine/ $NbBr_5$ reaction ratio of 3.38-3.40. Analysis of the solid also supported this reaction ratio. It has been demonstrated that pyridinium bromide may be extracted from the reaction mixture either by washing the solids

with dry chloroform or by sublimation at 150°C . In either case the pyridinium bromide was identified by its infrared spectrum or by its X-ray diffraction powder pattern. Up to $1/5$ of the total bromide was removed by these techniques, which indicated that one mole of pyridinium bromide was formed for each mole of NbBr_5 used in the reaction. Attempts to identify the oxidation product of pyridine have not been successful.

That the preponderance of the niobium is in a lower oxidation state has been demonstrated by the behavior of the product on hydrolysis in dilute acids or by titrations with standard oxidizing agents. The results of the titrations have not been consistent and have depended greatly on the solvent system selected for the experiment. For example, titrations in 1M acetic acid with potassium dichromate indicated from 35 to 70 percent of the niobium to be in the +4 oxidation state, while titrations in 1N sulfuric acid with ceric sulfate indicated up to 90 percent of the niobium was in the reduced valence state.

Solutions of the reaction product in dilute aqueous acids exhibited a deep blue color, and were unstable to air oxidation and separation of niobium(V) oxide. When dissolved in 50 volume percent sulfuric acid the solution was pink and gave absorption bands with maxima at 502 and 697 $\text{m}\mu$ in the visible region of the spectrum. The product of the reaction of NbCl_5 and pyridine exhibited an absorption spectrum identical to that of the bromide in the 50 volume percent sulfuric acid solutions.

Reaction of NbCl_5 and pyridine under conditions similar to those used for the NbBr_5 reaction yielded a brown solid, the composition of which corresponded to $\text{NbCl}_5 \cdot 2.54\text{C}_5\text{H}_5\text{N}$. The behavior of this product towards hydrolysis and the titrations with standard oxidizing agents was entirely analogous to that of the bromide.

The reaction of NbI_5 and pyridine also resulted in reduction of the niobium, but otherwise the reaction was very much different from that of either NbBr_5 or NbCl_5 . In this case all products were completely soluble in the pyridine and the solution exhibited a green color. On removal of excess pyridine by vacuum distillation, it was found that iodine was lost from the product. Heating the solid product at 100°C and 10^{-3} mm Hg affected the complete removal of the volatile iodine species and left a residue of $\text{NbI}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$. Treatment of the volatile iodine species with aqueous acid produced elemental iodine, a reaction expected of the compound $\text{C}_5\text{H}_5\text{NI}_2$. Thus, it is thought that the reduction of NbI_5 in pyridine proceeds according to the reaction

Further information about the compound $\text{NbI}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$ is given in section 6.8.2 of this report.

The reaction of TaBr_5 and pyridine gave no evidence for reduction of the tantalum. The only product of this reaction was the simple adduct $\text{TaBr}_5 \cdot \text{C}_5\text{H}_5\text{N}$, the composition of which was established by both weight gain data for pyridine and analysis of the solid. Further work on this reaction was not considered pertinent to this investigation.

Preliminary work on the reaction of TaI_5 and pyridine has indicated that reduction of tantalum does take place by a reaction similar to

that of NbI_5 . Thus, reaction of TaI_5 in an excess of pyridine at 25°C for 48 hours, removal of excess pyridine on the vacuum line, and pumping the product at 100°C and 10^{-3} mm Hg for 22 hours, yielded a product of the composition $\text{TaI}_{4.36} \cdot 1.98\text{C}_5\text{H}_5\text{N}$. The volatile iodine compound was found in the cold trap of the vacuum line, as in the case of the NbI_5 reaction. An X-ray diffraction powder pattern of this tantalum compound also proved to be essentially identical with that of $\text{NbI}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$. Thus good evidence for the reaction

has been obtained. However, either this reaction did not go to completion under the experimental conditions, or the $\text{C}_5\text{H}_5\text{NI}_2$ was incompletely removed from the product by the vacuum treatment at 100°C . A comparison of the thermal stabilities of NbI_5 and TaI_5 would tend to support the former possibility. Additional work will be performed to support these observations.

6.8.2 Reactions and Properties of the Niobium(IV) Halides

(R. E. McCarley and B. A. Torp)

The investigation of the chemical and physical properties of the compounds NbCl_4 , NbBr_4 and NbI_4 was initiated to support the work on the reactions of the niobium(V) halides and pyridine, and to expand the available information on the chemistry of niobium in its lower valence states. Corbett has reported the preparation of NbI_4 , and Schäfer has reported a more extensive study of the synthesis and properties of NbCl_4 . No previous report of NbBr_4 has appeared in the literature.

It has been found that NbI_4 dissolves in anhydrous pyridine with formation of an emerald green solution. The solubility in this solvent at room temperature is ca. 200 g/L. Rough magnetic susceptibility measurements on the saturated solution have shown it to be paramagnetic. Removal of excess pyridine on the vacuum line at 25-50°C and $<10^{-3}$ mm Hg gave a purple solid of the composition $\text{NbI}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$. This solid has also proven to be paramagnetic.

Dahl and Wampler have shown NbI_4 to be diamagnetic and to possess some degree of metal-metal bonding in the solid state. The paramagnetism of the solid $\text{NbI}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$ and its pyridine solution indicate that the metal-metal bond is broken in the reaction with pyridine and that the resulting compound is probably a monomeric species. A more detailed study of the magnetic properties of the pyridine adduct will be undertaken since data of this type are not readily available, nor well understood, for elements of the second and third transition series.

The synthesis of NbBr_4 has been accomplished by reaction of NbBr_5 with niobium metal at 400°C in a sealed tube. In this reaction the partial pressure of NbBr_5 was maintained at ca. 200 mm. For higher reaction temperatures and the same NbBr_5 pressure, the predominant product was NbBr_3 . Additional work to establish the optimum conditions for formation of NbBr_4 is in progress. A study of the properties and reactions of this compound will also be undertaken.

6.9 Air Oxidation of Yttrium and Yttrium Alloys (O. N. Carlson, R. L. Wells and F. A. Schmidt)

A study was made of the air oxidation properties of yttrium metal at elevated temperatures. Tests were run up to 925°C using a semi-continuous weighing apparatus. Arc-cast yttrium containing approximately 0.5 w/o titanium, 700 ppm fluorine and 700 ppm oxygen was used in this study. Negligible weight gains were observed below 450°C in a 24-hr period. The rate increases with increasing temperature, reaching a maximum at 700°C where the rate falls off somewhat and reaches a minimum at 750°C. Above this temperature the oxidation rate increases rapidly and becomes catastrophic at 900°C. As can be seen from Figs. 18 and 19 most of these curves are not linear on a log-log plot for the 24-hour period although some appear to have straight-line segments with different slopes. The hardness of the base metal was found to increase with increasing temperature due to the diffusion of oxygen into the metal lattice during oxidation. The oxide layer increased in thickness and the metal-oxide interface became more regular as the temperature of oxidation was increased. The results of this investigation are described in detail in a recent report entitled "A Study of the High-Temperature Air Oxidation of Yttrium Metal". (13)

A survey of the oxidation behavior of several yttrium-base alloys was undertaken. Binary alloys containing 5 w/o of Be, Al, Ti, V, Cr,

(13) O. N. Carlson, F. A. Schmidt and R. L. Wells, USAEC Report No. IS-115, March 1960.

Fig. 18. Plot of weight gain vs time of oxidation of yttrium metal for temperatures of 450 to 700°C.

Fig. 19. Plot of weight gain vs time of oxidation of yttrium metal for temperatures of 750 to 925°C.

Mn, Fe, Co, Ni, Zr, Nb, Mo, Ag, In, Sn, Hf, Ta, Th, and U were given a preliminary survey by heating in a muffle furnace at 900°C for 24 hours. The more corrosion-resistant alloys of this series were then tested more thoroughly.

The 5 w/o Be alloy which appeared somewhat promising was tested at 900°C, 800°C, 700°C, and 600°C. At 900°C, a sample of the annealed alloy obeyed the parabolic rate law and the weight gain was relatively low, 9 mg/cm², after 24 hours. At 700°C and 800°C, however, the oxidation rate was surprisingly high gaining 18.2 mg/cm² in a 24-hour period. At 600°C the rate was again lower gaining 1 mg/cm² in 24 hours. The anomalies

in the temperature-oxidation

rate curves are currently being investigated using higher purity metal.

6.10 Investigation of the Oxides of Niobium and Niobium Alloys

(W. L. Larsen and V. C. Marcotte)

An investigation of the oxidation of niobium and niobium alloys was commenced after the completion of an extensive survey of the published work in this field.

Niobium specimens were heated in air at 100°C intervals from 400°C to 1000°C. The specimen heated to 1000°C produced the high temperature or alpha form of Nb_2O_5 while all the other specimens formed the low temperature, or gamma modification. According to recent work the gamma-alpha transformation temperature is 830°C. However, this transformation is grossly affected by minor impurities and by heating and cooling rates. According to Goldschmidt⁽¹⁴⁾ the gamma form of Nb_2O_5 is metastable. However, oxides produced at 600°C have been held at 600°C in excess of 500 hours with no reversion to the alpha form discernable from X-ray data.

The phase diagram of the Nb_2O_5 - TiO_2 system is being investigated in an effort to expand the work done by Roth and Coughanour.⁽¹⁵⁾

A series of mixtures of the oxides was prepared by dry-pressing at 16,000 psi followed by sintering at 1400°C. X-ray diffraction patterns

(14) H. J. Goldschmidt, J. Inst. Met. 87, 235 (1959).

(15) R. S. Roth and L. W. Coughanour, "Phase Equilibrium Relations in the Systems Titania-Niobia and Zirconia-Niobia", J. Research Nat. Bur. Stand. 55, No. 4 (October, 1955).

of the compacts have established the location of two compounds, Nb_2O_5 and TiO_2 and $3\text{Nb}_2\text{O}_5 \cdot \text{TiO}_2$ at approximately the same compositions reported by Roth and Coughanour. The X-ray diffraction results indicate the compounds are located very near the stoichiometric compositions.

Apparatus is being constructed and work begun on an investigation of the mechanism of oxidation of niobium and niobium-titanium alloys. It is too early to report any results of this work.

6.11 High Pressure X-ray Diffraction Camera (J. F. Smith and R. W. Meyerhoff)

An X-ray diffraction camera for use at high pressures has been constructed and is in the process of testing and calibration. The salt KNO_3 undergoes a polymorphic transition near 3600 Kg/cm^2 . This transition was observed to occur at a calculated pressure of 5500 Kg/cm^2 in the camera and indicated an appreciable frictional loss in the process of compression. Even with the large frictional loss however, measurements of the lattice constant of tungsten show that pressures up to $18,000 \text{ Kg/cm}^2$ had been obtained in the camera.

APPENDIX I: LIST OF REPORTS FROM THE AMES LABORATORY

1. Reports for Cooperating Laboratories

- ISC-1076 H. A. Wilhelm. A History of Uranium Metal Production in America.
- ISC-1095 Lawrence Burkhart and R. W. Fahien. Pulse Column Design.
- ISC-1115 Ames Laboratory Staff. Physics. Semi-Annual Research Report. July-December, 1958.
- ISC-1116 Ames Laboratory Staff. Chemistry. Semi-Annual Research Report. July-December, 1958.
- ISC-1173 William S. Rawls and L. J. Laslett. The Determination of Photoneutron Thresholds.
- IS-1 C. V. Banks, O. N. Carlson, A. H. Daane, V. A. Fassel, R. W. Fisher, E. Olson, J. E. Powell and F. H. Spedding. Studies on the Preparation, Properties and Analysis of High Purity Yttrium Oxide and Yttrium Metal at the Ames Laboratory.
- IS-2 John Walker and Ed Olson. Preparation of Yttrium Fluoride Using Ammonium Bifluoride.
- IS-3 Edwin H. Olson, M. Smutz and Clayton W. Watson. Extraction Equipment and Sampling Technique Used in Semi-Continuous Silver-Uranium Extraction Studies.
- IS-8 G. Burnet and R. Tischer. Preparation of Yttrium Fluoride Using Fluorine.
- IS-14 Ames Laboratory Staff. Physics. Semi-Annual Summary Research Report. January-June, 1959.
- IS-15 Ames Laboratory Staff. Chemistry. Semi-Annual Summary Research Report. January-June, 1959.
- IS-16 Ames Laboratory Staff. Engineering. Semi-Annual Summary Research Report. January-June, 1959.
- IS-17 Ames Laboratory Staff. Metallurgy. Annual Summary Research Report. July, 1958-June, 1959.
- IS-26 Glenn Murphy and Robert E. Uhrig. Observations on Creep of Tantalum.
- IS-47 O. N. Carlson and A. L. Eustice. Vanadium-Chromium Alloy System.

- IS-48 J. R. Bohn, R. E. Uhrig and Glenn Murphy. A Method of Specimen Corrosion Protection for High Temperature Creep Testing.
- IS-50 R. Kniseley, V. A. Fassel and F. Lentz. Misidentifications in the Arc Spectra of the Rare Earths.
- IS-57 D. H. Dennison, F. H. Spedding and A. H. Daane. The Determination of the Melting Point, the Vapor Pressure, and the Decomposition Temperature of Yttrium Tri-iodide.
- IS-66 Robert L. Hammel and Robert E. Uhrig. An Autographic Elevated Temperature Creep Testing Facility.
- IS-67 Toshihiro Okada. Note on the Determination of the Magnetoresistance Tensor of a Crystal Having the Symmetry O_h or O .
- IS-107 C. D. Wirkus and D. R. Wilder. Uranium Glass I. Fundamental Considerations.
- IS-115 O. N. Carlson, F. A. Schmidt and R. L. Wells. A Study of the High-Temperature Air-Oxidation of Yttrium Metal.
- IS-125 R. L. Hammel. Creep of Tantalum Under Cyclic Elevated Temperatures.
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APPENDIX II: LIST OF SHIPMENTS

<u>Destination</u>	<u>Item</u>
University of Arizona General Stores Building Fifth Street and Mountain Avenue Tucson, Arizona	5 gm ytterbium oxide
Monsanto Chemical Company Mound Laboratory Miamisburg, Ohio	1 lb cerium metal
University of California Los Alamos Scientific Laboratory Los Alamos, New Mexico	2 metal cylinders lanthanum and cerium 50 gm lanthanum metal 50 gm neodymium metal
Michigan State University P. O. 39530 East Lansing, Michigan	20 gm cerium metal
H. B. Nicholas B-11 Research Building Iowa State University Ames, Iowa	10 gm yttrium oxide 10 gm lanthanum oxide 10 gm cerium oxide 10 gm neodymium oxide 10 gm dysprosium oxide 4 gm samarium oxide 2 gm gadolinium oxide 2 gm erbium oxide 2 gm ytterbium oxide 1 gm praseodymium oxide 1 gm holmium oxide 1 gm thulium oxide 1 gm terbium oxide 1 gm lutetium oxide
Mr. Sebastian Amer Box 122, Station A Ames, Iowa	20 gm Er_2O_3
Dr. Milton Burton Department of Chemistry University of Notre Dame Notre Dame, Indiana	10 gm Dy_2O_3 25 gm La_2O_3 25 gm Gd_2O_3 25 gm Y_2O_3 4 gm Lu_2O_3
Mr. Pierre Pelen French Embassy 2535 Belmont Road N. W. Washington, D. C.	samples of uranium metal (natural)

<u>Destination</u>	<u>Item</u>
University of California Receiving Department 2000 Carleton Street Berkeley 4, California	25 gm ytterbium metal 25 gm thulium metal 50 gm samarium metal
Dr. Masao Atoji Oak Ridge National Laboratory Oak Ridge, Tennessee	30 gm lutetium metal 30 gm ytterbium metal 30 gm terbium metal 2 glass vials of thorium carbide-thorium deuteride x-ray powder samples 46 gm lutetium carbide 110 gm thorium carbide 42 gm ytterbium dicarbide 30 gm Lu_2O_3 30 gm Yb_2O_3
Dr. Richard J. Weiss Materials Research Laboratory Ordnance Materials Research Office Watertown 72, Massachusetts	1 pc gadolinium metal appx. 10cm x 5cm x 0.1cm
Iowa State University Room 142 Research Building Ames, Iowa	200 ml 5% rare-earth chloride solutions: YCl_3 , NdCl_3 , GdCl_3 , DyCl_3 and YbCl_3 1500 ml 5% gadolinium chloride solution
J. C. Jamieson R. 21, 5641 S. Ingleside Avenue Chicago 37, Illinois	100 gm cylinder cerium metal
Mr. Warren DeSorbo General Electric Company Schenectady, New York	50 gm crystal bar vanadium
Dr. Glenn A. Crosby University of New Mexico Albuquerque, New Mexico	10 gm Sm_2O_3 10 gm Dy_2O_3
Mr. Dave Drennen Battelle Memorial Institute Columbus 1, Ohio	50 gm crystal bar hafnium metal
Mrs. Mary E. White Massachusetts Institute of Technology Cambridge 39, Massachusetts	1 gm yttrium metal

<u>Destination</u>	<u>Item</u>
Professor Paul A. Beck University of Illinois Urbana, Illinois	100 gm crystal bar wire appx. 1/16" diameter vanadium
Phillips Petroleum Company Atomic Energy Division Idaho Falls, Idaho	18 pc. 1" x 1/2" x 1/8" yttrium metal
Argonne National Laboratory Bailey Road Lemont, Illinois	250 gm distilled yttrium metal
Acct. Prop. Affr. Warehouse 335 Fort Belvoir, Virginia	5 gm praseodymium metal 5 gm samarium metal 5 gm neodymium metal 5 gm dysprosium metal 5 gm terbium metal 5 gm gadolinium metal 5 gm holmium metal
Veterinary Physiology & Pharmacology Room 100, Vet Physiology Ames, Iowa	1200 ml 5% dysprosium chloride solution 0.5 gm gadolinium oxide 0.5 gm dysprosium oxide 0.5 gm ytterbium oxide 0.5 gm yttrium oxide
Brookhaven National Laboratory Warehouse 100 Upton, L. I., New York	3 pc. thulium metal
Mr. W. E. Jardner Atomic Energy Research Establishment Harwell, Didcot Berks, England	5 gm crystal bar vanadium
Dr. Alvin Boltax Nuclear Metals Inc. Concord, Massachusetts	1 - 1" x 0.35" x 0.03" thorium metal