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Metallurgy and Ceramics (UC-25)

ISC-1050

UNITED STATES ATOMIC ENERGY COMMISSION
RESEARCH AND DEVELOPMENT REPORT

SEMI-ANNUAL SUMMARY
RESEARCH REPORT IN METALLURGY

for

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Ames Laboratory Staff

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SEMI-ANNUAL SUMMARY RESEARCH REPORT IN METALLURGY

For the period January - June 1958

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

Previous research reports in this series are:

ISC-35
ISC-41
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ISC-69
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ISC-130
ISC-133
ISC-137
ISC-171
ISC-193
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ISC-248
ISC-290
ISC-300
ISC-323
ISC-339
ISC-396
ISC-423
ISC-453
ISC-485
ISC-506
ISC-531
ISC-575
ISC-607
ISC-644
ISC-708
ISC-759
ISC-835
ISC-903
ISC-977
1. Separation Studies

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

Exploratory work has continued on this method of separation of inorganic materials. The purification of compounds from which high purity metal may be prepared is one of the objectives of this effort.

Also an object of this work is to obtain information in the investigations that will aid in a better formulation of the principles on which such separations depend.

The separation tests have recently been concerned with the use of thiocyanate as an agent that promotes the separation of some metals by differential distribution of their salts between two immiscible phases. Tests on zirconium-hafnium separation have continued with the thiocyanate in the presence of sulfuric acid. One of the interfering factors in this system is the tendency for a sulfate to precipitate in the extraction.
Barium and strontium salts generally are contaminants for one another and their separation may be effected by crystallization. Exploratory tests on the separation of these two elements by thiocyanate extraction have given indications that a purification might readily be made by liquid-liquid extraction. An aqueous test feed solution, containing barium and strontium chlorides and ammonium thiocyanate, was tested for transfer and separation with a number of organic-aqueous systems. Fair transfer from the aqueous feed to the organic phase was observed with tributyl phosphate, isophorone, cyclohexanol, tertiary amyl alcohol, n-amyl alcohol, hexone and isoamyl alcohol (listing in order of decreasing transfer). All these systems also gave some separation of the strontium and barium except the isophorone. In all cases tending toward separation, the strontium distributed more to the organic than did the barium.

1.2 Separation of Particulate Impurities During Sublimation

(D. T. Peterson and R. L. Skaggs)

A report (ISC-1059) entitled "Entrainment of Non-volatile Solids in Sublimation at Reduced Pressure" by R. L. Skaggs and D. Peterson was distributed.
A fundamental analysis of some of the factors affecting entrainment in sublimation was proposed and the predictions were verified experimentally by investigation of the separation of particulate silicon carbide from ammonium chloride. It was found that for the impurity particle size distribution studied, increased system pressure was effective in reducing entrainment at a given mass rate of sublimation. The separation was also improved at a given pressure by sublimation at lower rate. The sublimation rate was found to be a function of temperature and pressure. The temperature necessary to initiate sublimation was approximately the temperature at which the vapor pressure of ammonium chloride equaled the system pressure. Above this initiation temperature, the sublimation rate increased linearly with temperature.

Thorium tetrachloride of 200 ppm oxygen content was prepared by double sublimation at controlled pressure. In the second sublimation, the vapor was passed through turnings of thorium metal to remove volatile metal chloride impurities. The purity of the thorium tetrachloride sublimed by this procedure was found to be much superior to that sublimed at low pressure under a dynamic vacuum.
1.3  Pyrometallurgical Separation of Uranium-233 from Thorium

(P. Chiotti)

It has been shown that uranium can be separated from thorium by extracting the thorium with magnesium. At temperatures below the melting point of uranium (1132°C) the uranium settles out as a finely divided solid. The uranium can be concentrated into a relatively small volume, as previously described, and then consolidated by heating to above the melting point of uranium to form a separate liquid phase of 99+ w/o uranium, or it can be consolidated by the addition of an appropriate amount of chromium and heated to just above 860°C to form a separate liquid layer of essentially eutectic composition, U-5.2 w/o Cr, (mp 860°C).

If such a process is to be applied to the separation of U-233 from thorium blanket or fuel material, the distribution of protactinium, Pa233, 27.4 day half life, and fission products between the phases involved is of considerable importance.

1.3.1  Distribution of Pa233 Between Mg-38 w/o Th and Uranium-Rich Solutions (P. Chiotti and P. F. Woerner)

In order to determine the behavior of protactinium in the above separation process, Mg-38 w/o Th alloy which had been irradiated at the
Argonne National Laboratory to an exposure of $10^{12}$ n/cm$^2$/sec for one hour was equilibrated with either uranium of U-5.2 w/o Cr eutectic. The components were sealed under an argon atmosphere inside a welded tantalum crucible. The tantalum crucible was then enclosed in a graphite crucible fitted with a screw cap top and this assembly was in turn sealed inside of a welded low-carbon steel bomb. The charge was heated to the desired temperature in a rotating resistance furnace. The furnace was mechanically rotated back and forth through an arc of approximately 180 degrees in order to break up interphase films and bring the phases into intimate contact. Thorough agitation of the charge was found to be very important in attaining equilibrium in a reasonable period of time.

After equilibration the charge was permitted to settle at temperature and cooled according to a predetermined schedule. The resulting cylindrical ingot was cut into horizontal sections and the magnesium-rich and uranium-rich phases analysed for protactinium. Analyses were made by dissolving the sections and taking aliquots for counting. The 90 kev gamma-ray transition of Pa$^{233}$ was counted with a scintillation counter and spectrometer.
Results obtained on equilibration of irradiated Mg-38 w/o Th with U-5.2 w/o Cr are given in Tables I and II. Sample numbers indicate suc-

Table I

Distribution of Pa between Mg-Th and U-Cr Phases

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight (gm)</th>
<th>Specific $10^4$ cts Activity min x gm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original Mg-Th</td>
<td>62</td>
<td>470</td>
</tr>
<tr>
<td>Mg-Th Phase -1</td>
<td>3.7</td>
<td>3.9</td>
</tr>
<tr>
<td>-2</td>
<td>7.7</td>
<td>2.4</td>
</tr>
<tr>
<td>-3</td>
<td>5.7</td>
<td>3.9</td>
</tr>
<tr>
<td>-4</td>
<td>6.0</td>
<td>3.2</td>
</tr>
<tr>
<td>-5</td>
<td>2.2</td>
<td>5.5</td>
</tr>
<tr>
<td>Interface -6</td>
<td>18.8</td>
<td>14.4</td>
</tr>
<tr>
<td>Original U-Cr</td>
<td>101.5</td>
<td></td>
</tr>
<tr>
<td>U-Cr Phase -7</td>
<td>20.7</td>
<td>272.</td>
</tr>
<tr>
<td>-8</td>
<td>11.9</td>
<td>257.</td>
</tr>
<tr>
<td>-9</td>
<td>16.9</td>
<td>250.</td>
</tr>
<tr>
<td>-10</td>
<td>21.3</td>
<td>245.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>256 ± 6 Ave.</td>
</tr>
</tbody>
</table>
**Table II**

Distribution of Pa between Mg-Th and U-Cr Phases

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight (gm)</th>
<th>Specific Activity $\times 10^4$ cts/min x gm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original Mg-Th</td>
<td>66.6</td>
<td></td>
</tr>
<tr>
<td>Mg-Th Phase -1</td>
<td>4.4</td>
<td>5.24</td>
</tr>
<tr>
<td></td>
<td>-2</td>
<td>3.22</td>
</tr>
<tr>
<td></td>
<td>-3</td>
<td>3.16</td>
</tr>
<tr>
<td></td>
<td>-4</td>
<td>3.31</td>
</tr>
<tr>
<td></td>
<td>-5</td>
<td>3.03</td>
</tr>
<tr>
<td></td>
<td>-6</td>
<td>3.10</td>
</tr>
<tr>
<td></td>
<td>-7</td>
<td>3.32</td>
</tr>
<tr>
<td></td>
<td>-8</td>
<td>3.58</td>
</tr>
<tr>
<td></td>
<td>-9</td>
<td>4.15</td>
</tr>
<tr>
<td></td>
<td>-10</td>
<td>5.40</td>
</tr>
<tr>
<td></td>
<td>-11</td>
<td>5.33</td>
</tr>
<tr>
<td>Interface</td>
<td>-12</td>
<td>3.2</td>
</tr>
<tr>
<td></td>
<td>-13</td>
<td>2.7</td>
</tr>
<tr>
<td>Original U-Cr</td>
<td>96.5</td>
<td></td>
</tr>
<tr>
<td>U-Cr Phase -14</td>
<td>21.8</td>
<td>598</td>
</tr>
<tr>
<td></td>
<td>-15</td>
<td>575</td>
</tr>
<tr>
<td></td>
<td>-16</td>
<td>589</td>
</tr>
<tr>
<td></td>
<td>-17</td>
<td>583</td>
</tr>
<tr>
<td></td>
<td></td>
<td>586 Ave</td>
</tr>
<tr>
<td>Mg-Th Phase</td>
<td>3.9</td>
<td>49.8</td>
</tr>
<tr>
<td>Turnings</td>
<td></td>
<td></td>
</tr>
<tr>
<td>U-Cr Phase</td>
<td>9.6</td>
<td>642</td>
</tr>
<tr>
<td>Turnings</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
cessive horizontal sections taken from top to bottom of the ingots. The data in Table I represent the analyses of a charge consisting of 62 grams of Mg-Th and 101.5 grams of U-5.2 w/o Cr which was mixed at 980°C for 1 1/2 hours, then permitted to settle for 1 1/2 hours in the temperature range of 950 to 870°C and finally furnace-cooled to room temperature. During mixing the charge rotated back and forth through an arc of 180 degrees at the rate of once a minute. In this case the outer surface of the ingot was not machined off prior to sectioning. It was observed that some of the protactinium concentrated on the surface of the Mg-Th phase and particularly on the Mg-Th/U-Cr interface. In subsequent experiments the procedure was changed in two respects: the charge was more vigorously agitated at temperature, approximately 50 oscillations per minute, in order to assure attainment of equilibrium and the outer surfaces of the solidified ingots were machined off and analysed separately. The data presented in Table II were obtained from a charge processed in this manner. In this case the charge was mixed at 980 ± 15°C for 1 1/4 hours, permitted to settle for 1 hour at 980°C, 1 hour at 870°C, 1 hour at 660°C and finally furnace-cooled to room temperature. By employing a longer settling period at temperatures above the freezing point of the U-Cr phase (860°C) and again just above the freezing point of the
Mg-Th phase (585°C), it is felt that a more complete precipitation of uranium and chromium with accompanying protactinium is achieved. The considerably higher activity of samples 12 and 13 in Table II indicates that an appreciable amount of precipitation takes place on cooling from the solidification temperature of the U-Cr phase to the freezing point of the Mg-Th eutectic. However, the particularly high activity of sample 13 and the concentration of activity at other interfaces, as indicated by the analyses of the turnings and sample 1, is probably due, in part at least, to segregation of impurities such as oxides, carbides or intermetallic compounds.

Excluding the interface sample 6, the data in Table I shows that 99.1% of the protactinium in the Mg-Th phase has been removed for a decontamination factor of 123. The distribution coefficient, c/m/g in the uranium-rich phase divided by the c/m/g in the magnesium-rich phase, is 68. The percent of the total initial activity accounted for by the analyses of the two phases is 90.5. The tantalum crucible walls showed a rather high activity after removal of the ingot and presumably the 9.5% not recovered remained with the crucible.

Similarly, the data in Table II shows that 99.6% of the protactinium in the Mg-Th phase has been removed for a decontamination factor of 255. In this case the distribution coefficient is calculated to be 149 and the percent recovery of the protactinium is 93 percent.
A sample of irradiated Mg-38 w/o Th was similarly equilibrated with pure uranium. A charge consisting of 26.5 grams of Mg-Th alloy and 95.4 grams of uranium were mixed at 1160-1180°C for 30 minutes, permitted to settle at 1180-1132°C for 30 minutes, at 660°C for 45 minutes and finally furnace cooled to room temperature. Analyses of the resulting ingot are given in Table III. The distribution of Pa$^{233}$ activity in this sample

Table III
Distribution of Pa between Mg-Th and Uranium Phases

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight (gm)</th>
<th>Specific Activity $10^4$ cts/min x gm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original Mg-Th</td>
<td>26.5</td>
<td>100.0</td>
</tr>
<tr>
<td>Mg-Th Phase -1</td>
<td>2.0</td>
<td>0.24</td>
</tr>
<tr>
<td>Mg-Th Phase -2</td>
<td>1.7</td>
<td>0.29</td>
</tr>
<tr>
<td>Mg-Th Phase -3</td>
<td>2.5</td>
<td>0.30</td>
</tr>
<tr>
<td>Interface -4</td>
<td>0.83</td>
<td>30.3</td>
</tr>
<tr>
<td>Original Uranium</td>
<td>95.4</td>
<td>---</td>
</tr>
<tr>
<td>Uranium -5</td>
<td>6.8</td>
<td>26.5</td>
</tr>
<tr>
<td>Uranium -6</td>
<td>7.9</td>
<td>25.1</td>
</tr>
<tr>
<td>Uranium -7</td>
<td>5.8</td>
<td>24.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25.4 Ave.</td>
</tr>
<tr>
<td>Mg-Th Phase Turnings</td>
<td>1.1</td>
<td>9.7</td>
</tr>
<tr>
<td>Uranium Phase Turnings</td>
<td>0.18</td>
<td>24.4</td>
</tr>
</tbody>
</table>
is similar to that obtained in the above two samples. Neglecting the interface sample, the decontamination factor for the Mg-Th phase is 357 for a removal of 99.7% of the initial protactinium. The distribution coefficient is 90.7 and the percent recovery of the protactinium is 93%.

The percent removal of the protactinium from the Mg-Th alloy, the distribution coefficients, and decontamination factors for the above three experiments are summarized in Table IV. It is evident from these

Table IV
Extraction of Pa from Mg-38 w/o Th Alloy

<table>
<thead>
<tr>
<th>Irradiated Mg-38 w/o Th gm</th>
<th>Extractant</th>
<th>% Removal of Pa from Mg-Th Phase</th>
<th>Decontamination Factor</th>
<th>Distribution Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>62</td>
<td>U-5.2 Cr - 101.5</td>
<td>99.1</td>
<td>123</td>
<td>68</td>
</tr>
<tr>
<td>66.6</td>
<td>&quot;</td>
<td>96.5</td>
<td>255</td>
<td>149</td>
</tr>
<tr>
<td>26.5</td>
<td>U</td>
<td>95.4</td>
<td>357</td>
<td>90.7</td>
</tr>
</tbody>
</table>

data that in each case over 99% of the protactinium was removed from the Mg-Th phase. The values obtained for the last two experiments are believed to be representative of the true equilibrium values. Equilibrium was probably not attained in the first experiment because of the method
employed to mix or agitate the charge. Further experiments have been conducted to check these results but radio-chemical analyses have not yet been completed.

1.3.2 Distribution of Protactinium Between Mg-Th Solutions and Fused Salts Containing MgCl₂ (P. Chiotti and H. E. Shoemaker)

In the separation of uranium from thorium by the dissolution of the thorium in magnesium, it is expected that impurities such as the alkali, alkaline earth and rare earth metals will concentrate in the Mg-Th phase. Slagging with MgCl₂ or a fused salt containing MgCl₂ should effectively remove these impurities since their free energies of formation, with the exception of the heavier rare earths, are appreciably greater than that of MgCl₂. Similarly, on the basis of free energy data the thorium and small amounts of uranium accompanying the magnesium-rich phase will not be appreciably affected. The behavior of protactinium in such a process is uncertain and its distribution is being investigated.

Mg-38 w/o Th solutions were equilibrated with two different fused salt mixtures; NaCl-48 mole % MgCl₂, m.p. 450°C and 34 w/o LiCl-46 w/o KCl-20 w/o MgCl₂. The salt mixtures were initially dried by heating them in an atmosphere of anhydrous HCl and finally by bubbling HCl through the melt. Processing of alloy-salt mixtures was carried out
in tantalum crucibles. The samples were heated in a rotating furnace and mixing was accomplished by mechanical rotation of the furnace back and forth through an arc of 180° once a minute, as described above. Consequently, in view of the results obtained in processing Mg-Th/U phases, there is some doubt whether equilibrium was attained. This possibility will be checked.

The Mg-Th alloy in these experiments did not wet the tantalum crucibles, but was apparently separated from the tantalum by a thin salt film. A thin black film was observed on the surface of the salt and at the salt-metal interface. This film contained a relatively high Pa activity.

The results obtained are given in Table V. These data indicate

Table V

Distribution of Pa$^{233}$ Activity Between Mg-39 w/o Th Solutions and Fused Salts

<table>
<thead>
<tr>
<th>Charge-grams</th>
<th>Processing</th>
<th>Initial Activity c/m/g</th>
<th>Activity after Processing c/m/g</th>
<th>Distr. Coeff.</th>
</tr>
</thead>
<tbody>
<tr>
<td>30-(Mg-Th)</td>
<td>650°C</td>
<td>4.0 x 10$^5$</td>
<td>1.2 x 10$^4$</td>
<td>38.6</td>
</tr>
<tr>
<td>30-(NaCl-MgCl$_2$)</td>
<td>Mix 30 min.</td>
<td>3.0</td>
<td>3.1 x 10$^2$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Settled 30 min.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19.7-(Mg-Th)</td>
<td>650°C</td>
<td>1.3 x 10$^5$</td>
<td>1.7 x 10$^5$</td>
<td>131</td>
</tr>
<tr>
<td>24.8-(KCl-LiCl-MgCl$_2$)</td>
<td>Mix 60 min.</td>
<td>0.0</td>
<td>1.3 x 10$^2$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Settled 45 min.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21.1-(Mg-Th)</td>
<td>650°C</td>
<td>1.4 x 10$^5$</td>
<td>1.13 x 10$^5$</td>
<td>297</td>
</tr>
<tr>
<td>26.2-(NaCl-MgCl$_2$)</td>
<td>Mix 60 min.</td>
<td>0.0</td>
<td>3.8 x 10$^2$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Settled 45 min.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
that most of the protactinium remains in the Mg-Th alloy and very little is lost to the salt phase. Chemical analyses also show no detectable amount of thorium in the salt phase.

1.3.3 Pyrometallurgical Purification of Uranium (P. Chiotti and S. J. S. Parry)

The uranium-233 separated from neutron irradiated thorium by the magnesium extraction procedure will contain some fission products such as zirconium, niobium, molybdenum, ruthenium, etc. Since the amount of U$^{233}$ to be processed would be relatively small, it may be economically feasible to put the uranium in solution in a fused salt and then selectively reduce the impurities. The uranium can finally be recovered by the use of an appropriate reducing agent such as magnesium or a magnesium alloy. The possibility of dissolving uranium in fused KCl-LiCl-ZnCl$_2$ and selectively reducing the impurities is being investigated.

It has been found that when massive uranium is brought into contact with KCl-LiCl eutectic containing 10 to 20 wt % ZnCl$_2$ at 450°C that the initial reaction rate is fairly high but the reaction soon subsides and then proceeds very slowly. The zinc displaced by the uranium forms an adherent reaction layer on the surface of the uranium consisting of a
band of $\text{U}_2\text{Zn}_{17}$ covered with a film of liquid zinc. Once the surface is coated with reaction products further reaction is diffusion controlled and is relatively slow at 450°C. The introduction of gaseous HCl into the fused salt and around the uranium has little effect. It was also observed that HCl can be bubbled through molten zinc without appreciable reaction. In this case the reaction is presumably limited by the diffusion of HCl through a $\text{ZnCl}_2$ film formed at the metal/gas interface. At 600°C and 650°C a readily measurable dissolution rate occurs. The reaction rates during the first 10 to 20 minutes were observed to be roughly 7.0 gms/cm$^2$/hr at 600°C and 14 gms/cm$^2$/hr at 650°C. The surface gradually becomes rough and sponge-like in appearance and after 10 to 20 minutes the rate drops to about half the above values and remains relatively constant. These observations show that for the practical dissolution of uranium by this procedure the uranium should be in the form of shavings or chips with a large surface to mass ratio.

The equilibration of fused KCl-LiCl-UCl$_3$ mixtures with liquid zinc at 450°C should result in practically complete removal from the fused salt of such impurities as ruthenium, molybdenum, niobium and in general any component whose chloride has an appreciably lower free energy of formation than that of $\text{ZnCl}_2$. Whether components such as uranium, zirconium, chromium and protactinium which form chlorides
with a free energy of formation of about the same or greater magnitude than that of ZnCl₂ will also depend on possible intermetallic compound formation with zinc or the activity of these components in the salt and zinc phases. Advantage can also be taken of the fact that the reduction potential of the zinc solution in equilibrium with the fused salt can be increased gradually by the addition of a stronger reducing agent such as magnesium to the zinc.

Exploratory experiments with KCl-LiCl eutectic containing 3.5 wt % uranium as UCl₃ equilibrated with zinc at 450°C show that the amount of uranium in the zinc phase is less than 100 ppm. The equilibration at 500°C of the same salt mixture with zinc containing from a 5 to 7 wt % magnesium reduced the uranium content of the fused salt to 0.05 wt %. During this equilibration the color of the salt changed from a dark purple to colorless, indicating that the uranium was essentially completely removed from the salt phase. Metallographic examination of the zinc phase showed compound crystallites, presumably U₂Zn₁₇.

Exposure of the fused salt containing UCl₃ to atmospheric oxygen also results in the formation of a colorless salt and a brown to black precipitate, indicating that the uranium has been essentially quantitatively precipitated as oxide. This is not unexpected from a
consideration of the relative free energy of formation of \( \text{UO}_2 \) and \( \text{UCl}_3 \).

The course of protactinium, zirconium and chromium in the above process will also be investigated.

2. Preparation of Pure Compounds

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

Work was continued on the preparation of high purity vanadium pentoxide in pound lots by the chlorination method. For the chlorination reaction an all-glass, rotating tube reactor was designed which allowed high conversion efficiencies of both chlorine and vanadium. The method consisted of thoroughly mixing technical \( \text{V}_2\text{O}_5 \) with carbon in a molar ratio of 2:3. The charge was then dried at 200-300°C and placed in the pyrex reaction tube. Air was passed over the charge during the interval necessary to bring the system to the desired operating temperature of between 350 to 450°C. The air flow at this time served to remove the last traces of moisture, which was objectionable because of hydrolysis of the product \( \text{VOCl}_3 \). When the operating temperature was reached, the reaction tube was rotated at a rate of 14 revolutions per minute and chlorine gas was admitted to the charge at various flow rates.

Chlorine efficiencies were determined for various flow rates in the following manner. The chlorine flow rate was obtained from a
calibrated rotameter and the percent conversion was determined from the rate of production of VOCl$_3$, which was condensed and measured volumetrically. These experiments were performed at furnace temperatures of 350 and 450°C. Since the reaction was exothermic, the actual reaction temperature was probably 50 to 100°C higher than that measured. Each charge in these experiments consisted of 1100 g. of technical V$_2$O$_5$ (%V$_2$O$_5$=89) and 110 g. of carbon.

At a temperature of 350°C the over-all chlorine efficiencies were: 58% at a flow rate of 2.0 liters/min., 62% at 2.45 liters/min. and 63% at 2.46 liters/min. At 450°C a value of 90% at 1.90 liters/min. was obtained, while the conversion of vanadium to VOCl$_3$ was ca 75% of the total vanadium content. In general, the chlorination efficiency remained above 90% at the higher temperature until the reaction was practically complete, whereupon the efficiency dropped rapidly and the run was discontinued.

The VOCl$_3$ produced in these runs was hydrolyzed with aqueous ammonia to form ammonium metavanadate which was subsequently ignited at ca 600°C to recover the high purity V$_2$O$_5$. Typical yields of V$_2$O$_5$ were about two pounds per run. Complete analytical data has not yet been assembled for this material but qualitative spectroscopic analysis indicated the presence of traces only of Cr, Si, Cu, Ca and Mg.
Nitrogen analysis on three samples from separate runs gave the following results: 16, 32 and 13 ppm.

Work has been initiated on the preparation of some anhydrous chlorides of vanadium from the high purity VOC1\(_3\) obtained in the chlorination reaction. Preliminary results indicate the reduction of VOC1\(_3\) with hydrogen leads to a mixture which may contain V\(_2\)O\(_3\), VOC1, VOC1\(_2\) and VCl\(_2\) in various proportions. Further work will be done on this and other reactions leading to the formation of vanadium chlorides.

2.2 Preparation of Pure Metal Carbonyl Compounds (R. E. McCarley and B. W. Farnum)

High pressure equipment has been obtained and installed, and several compounds have been prepared for the synthesis of vanadium and niobium carbonyl compounds. The equipment consists of an Autoclave Engineers autoclave which is equipped with a strip-heater and temperature controller, safety rupture disk, solenoid-actuated agitator, gas inlet and outlet and a sampling tube. A hand-operated gas booster pump has been connected in series with the autoclave. With the use of this apparatus, reactions may be carried out at 1 to 350 atm. of pressure and temperatures of 25 to 350°C.

Compounds which have been prepared as starting materials for the
initial exploratory reactions are $\text{VI}_2$, $\text{VI}_3$, $\text{V(AA)}_3$ (where AA = acetyl-acetonate ion), $\text{Cr(AA)}_3$ and $\text{NbI}_5$. However, no carbonyl compounds have been prepared during this period.

2.3 **Preparation of Yttrium Fluoride** (O. N. Carlson, F. A. Schmidt and F. H. Spedding)

Studies have continued on the preparation of yttrium fluoride by heating of the oxide in an anhydrous hydrogen fluoride stream at elevated temperatures. A hydrofluorination schedule of slowly increasing the temperature to $750^\circ \text{C}$ with intermittent rotation of the tube was used for all batch preparations. It was found that careful regulation of the exhaust draft on the tube increased the number of batches of fluoride having satisfactory oxygen intensity ratios (OIR). This ratio was determined spectrographically and is a relative measure of the oxygen content of the fluoride. If the oxygen intensity ratio of a batch of yttrium fluoride was greater than 0.45, the fluoride was recycled through the hydrofluorination step. In most cases one recycling was sufficient to increase the conversion so that the material would fall into the acceptable quality range of 0.25 - 0.45 OIR.

The fluoride production program was accelerated during this period in order to meet the increased demands for $\text{YF}_3$ which were imposed by the yttrium metal development and production effort.
Figure 1 graphically illustrates the production of yttrium fluoride per month for the first half of 1958. One ton of this material was sent to Corwith Corp. in Chicago for use in their metal production process.

3. Metal Preparation and Purification Studies

3.1 Vanadium Metal

3.1.1 Purification by the Iodide Process (O. N. Carlson and C. V. Owen)

A small vycor bulb was used in studies on the growth rate and efficiency of the process for purifying vanadium metal by the thermal decomposition of vanadium iodide. As much as 70 percent of the impure vanadium feed material was converted to crystal bar in a single run with this unit. This is much higher than the 25 percent yields normally obtained in the inconel apparatus used in regular operations.

Work by Morette¹ in 1938 on the reaction of vanadium with iodine, and observations made during the course of the present studies indicate that VI₂ is the species of iodide primarily responsible for the transfer of vanadium within the apparatus. VI₂ is volatile between 750-850°C, and decomposes above 850°C. A feed material of 800-825°C temperature has been found to give maximum deposition rates. Filament temperature versus

¹. A. Morette, Compt. Rend. 207, 1218 (1938).
Fig. 1 - YF$_3$ Produced During First Half of 1958.
growth rate studies have been carried out up to 1400°C with the maximum growth rate occurring at a wire temperature of about 1300°C.

Most of this work has been done using chips or shavings of bomb-reduced vanadium as feed material. However, this involves a machining operation to produce these chips, requiring considerable time and effort. In an attempt to obtain a feed material which could be prepared readily, two other forms of vanadium metal have been tried. One form was a vanadium-aluminum alloy which was produced by a bomb process using calcium and an excess of aluminum as co-reductants. The resulting alloy contained 10% aluminum by weight and was very brittle. It was crushed in a jaw crusher and the pieces were used directly as feed material for iodide refining. The crystal bar vanadium which was prepared from this feed material contained 0.16 w/o aluminum.

Since the Al-V alloy appeared to be unsatisfactory as the feed material, another form of crude vanadium was investigated. A sponge product was produced by reducing C. P. grade V₂O₅ with carbon at 1600°C. This material was crushed easily into pieces of sizes suitable for use as feed material. Crystal bar vanadium produced from the sponge contained 190 ppm carbon and 25 ppm nitrogen but was unexpectedly hard, 85 Rockwell E. The usual hardness of crystal bar vanadium is \( R_E \) 50. More work is planned with this type of feed material in an effort to improve the quality of the vanadium.
3.1.2 The Carbon Reduction of $V_2O_5$ (H. A. Wilhelm and K. M. Wolf)

Some tests of addition agents in the charge of $V_2O_5$ and carbon were made with no definite evidence of improved results. The main problem appears to be that of obtaining an inert crucible for molten vanadium metal in order to permit higher temperatures for completion of the reaction between carbon and the oxide. Crucibles made of $ZrO_2$, $CaO$, $Y_2O_3$ or $ThO_2$ were tested. The $ZrO_2$, the $Y_2O_3$ and the $ThO_2$ crucibles contained the molten vanadium metal quite well, but the $CaO$ crucible broke down at the temperature required for liquid vanadium. Spectrographic tests made on samples of vanadium melted in those crucibles that contained the liquid metal, showed that the amounts of thorium and yttrium picked up were very small, with the zirconium pick up being perhaps a bit more.

3.2 Niobium (Columbium) Metal

3.2.1 By Carbon Reductions of $Nb_2O_5$ (H. A. Wilhelm and E. R. Stevens)

Further tests were made on the effects of various addition agents on the reaction and the quality of the metal obtained by the reduction of $Nb_2O_5$ with carbon. $SiC$, $SiO_2$ and $TiO_2$ were tested as addition agents
and the quality of the metal so far obtained with the SiC and SiO₂ additions does not appear to be comparable to that obtained with the proper amount of TiO₂ addition in the charge. A number of earlier tests on the reduction of Nb₂O₅ by carbon with and without addition agents have been repeated, and the results agreed quite well with the earlier data.

3.2.2 By the Aluminum Reduction of Nb₂O₅ (H. A. Wilhelm and T. G. Ellis)

The aluminum reduction of the oxide of columbium is considered as a means of preparing alloys of these two metals and is being continued in connection with a study of these alloys. Attempts to form pure columbium metal by the aluminum reduction of the oxide have not yet been successful.

3.2.3 Purification of Niobium Metal by the Iodide Process (R. E. McCarley and W. Tadlock)

Niobium feed metal, for use in the iodide process, has been prepared by the reduction of Nb₂O₅ with carbon under vacuum as described in a previous report (ISC-835). In this reaction a 3 percent excess of carbon was used in an effort to obtain a low oxygen concentration in the metal. Apparently, however, the reaction did not go to completion and a considerable oxygen content was left in the metal as indicated in Table VI.
Table VI

Analyses of Niobium Produced by the Iodide Process

<table>
<thead>
<tr>
<th>Impurity</th>
<th>PPM in Feed Metal</th>
<th>PPM in Iodide Metal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>250-350°</td>
<td>350°</td>
</tr>
<tr>
<td>O</td>
<td>&gt;5000</td>
<td>4300</td>
</tr>
<tr>
<td>C</td>
<td>30,000</td>
<td>62</td>
</tr>
<tr>
<td>N</td>
<td>---</td>
<td>769</td>
</tr>
</tbody>
</table>

The apparatus used for the iodide reaction consisted of an 80 mm O.D. pyrex tube which was about 11 in. long and sealed at both ends. A pair of tungsten electrodes, either 1/4 or 1/8 in. diameter, was sealed in the top in addition to the leads to the high vacuum system and iodine reservoir. The feed metal was packed into an annular space bounded by the glass walls of the reactor on the outside and a molybdenum screen on the inside. This provided a cylindrical cavity about 2.5 in. diameter for suspension of the filament. The system was outgassed at 550°C and a final pressure of ca $10^{-5}$ mm. Hg before sealing off the reactor and starting the reaction. In the initial runs the filament temperature was maintained constant at about 1300°C and the feed metal temperature was varied between 250 and 500°C. Maximum growth rate of the filament occurred at a feed temperature of 450° and decreased markedly at either
higher or lower temperatures. The first noticeable growth began at the lowest temperature, i.e., 250°C. Analytical data for some non-metallic impurities are summarized in Table VI for these experiments.

Further work will be directed primarily towards elimination of the high oxygen content in both the feed metal and the iodide metal. It is obvious from the data that there must be a volatile oxyiodide formed at the temperatures investigated in order to account for the extremely high oxygen values in the iodide metal. This is not unreasonable since niobium is known to form the volatile niobium oxytriiodide, NbOI₃. A vycor vessel is being constructed in order to carry out the reactions at feed metal temperatures from 550 to 800°C. It is possible that these temperatures are above the decomposition temperature of the NbOI₃ and, hence, a better purification with respect to oxygen may be attained.

3.3 Thorium Metal

3.3.1 Purification of Thorium by the Iodide Process

(D. E. Williams, O. D. McMasters and P. E. Palmer)

The pyrex-glass apparatus for purifying thorium has been yielding approximately 250 g. per run. The needs of this group are being supplied and a small stock pile of the metal is being accumulated.
An Inconel reaction vessel for iodide-thorium production has been unsuccessful due to vacuum leaks. Efforts to perfect this equipment will be continued since it is felt that larger yields can be obtained with it.

3.3.2 Preparation by the Ca-Mg Reduction of ThF₄

(H. A. Wilhelm and R. L. Snyder)

Work has continued on the reduction of thorium tetrafluoride with calcium and magnesium to give a low melting Th-Mg alloy and a low-melting slag. In some of these reductions the calcium and magnesium were alloyed while in others the metals were used in the form of a mixture of particles of the pure metals. The process depends on a past-heating to effect separation of the fused metal and slag phases.

Considerable difficulty was encountered in this work in finding a metal crucible that would satisfactorily contain the reaction. Reductions were attempted in niobium, Carpenter 20 stainless steel, molybdenum, tantalum, graphite, 18-8 stainless steel, 430 stainless steel and titanium. As a result of this work it was found that titanium serves quite well as a crucible material.

Attempts to produce a ThMg₂ alloy as the product of reduction were not highly successful. In some reductions sodium was used in place of magnesium, but this also failed to give good results. The
use of calcium chloride as a fluxing agent for the CaF$_2$-MgF$_2$ slag was not satisfactory. Some attempts were made to produce low-melting thorium-magnesium-zinc alloy, but results were not satisfactory.

The reduction of thorium tetrafluoride according to the equation

$$\text{ThF}_4 + 0.9\text{Ca} + 1.1\text{Mg} + 1.5\text{Mg} \rightarrow \text{ThMg}_{1.5} + 0.9\text{CaF}_2 + 1.1\text{MgF}_2$$

gave a fairly good product.

Work will be continued on calcium-magnesium reduction of thorium tetrafluoride to produce thorium-magnesium alloys.

3.4 Preparation of Yttrium Metal (O. N. Carlson, J. Haefling, F. A. Schmidt and F. H. Spedding)

The production of yttrium metal on a pilot plant scale was continued during the first half of 1958. The major change that was introduced in the process during this period was the use of redistilled calcium and magnesium in massive form rather than in granular form as was used previously. This resulted in a significant decrease in oxygen content of the yttrium metal from an average of 0.30 w/o O$_2$ for the granular calcium product to 0.17 w/o O$_2$ for metal obtained with the massive materials.

This change in the process resulted in an alteration of the apparatus employed in the reduction step. The massive chunks of calcium and magnesium were melted in a titanium or zirconium
reaction pot under a helium atmosphere. The YF$_3$ and CaCl$_2$ were then added to the reaction pot from a hopper which could be attached to the head of the reaction retort. This insured complete reaction between the calcium and the YF$_3$ and good slag-metal separation and made it possible to carry out the complete reduction step in a single heating. The titanium content of the yttrium metal prepared in a titanium reaction vessel was 0.15 w/o.

A graph of the yttrium metal produced per month is shown in Fig. 2. A typical analysis of the yttrium produced during this period is given in Table VII.

Table VII

Typical Analysis of Vacuum Arc-Melted Yttrium Ingots Produced During 1958

<table>
<thead>
<tr>
<th>Element</th>
<th>Ave. Content (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>250 ppm</td>
</tr>
<tr>
<td>N</td>
<td>175</td>
</tr>
<tr>
<td>Fe</td>
<td>150</td>
</tr>
<tr>
<td>Ti*</td>
<td>100</td>
</tr>
<tr>
<td>Ti**</td>
<td>1500</td>
</tr>
<tr>
<td>Zr*</td>
<td>7000</td>
</tr>
<tr>
<td>Ca</td>
<td>10</td>
</tr>
<tr>
<td>Mg</td>
<td>30</td>
</tr>
<tr>
<td>Si</td>
<td>150</td>
</tr>
<tr>
<td>Cu</td>
<td>50</td>
</tr>
<tr>
<td>Ni</td>
<td>350</td>
</tr>
<tr>
<td>B</td>
<td>10</td>
</tr>
<tr>
<td>O$_2$</td>
<td>1700</td>
</tr>
</tbody>
</table>

* Y-Mg alloy prepared in Zr pot.
** Y-Mg alloy prepared in Ti pot.
Fig. 2 - Yttrium Metal Produced as Arc-melted Ingots During First Half of 1958.
Meanwhile, experiments have been carried out designed to determine the sources of oxygen and to eliminate them if possible. A large reduction was divided into several alloy portions. These portions were exposed to varying humidity conditions for periods of from one to five days to determine the reactivity of the alloy toward atmospheric moisture. Similar tests were made on sponge from the same reduction. The exposed alloy or sponge was then processed into yttrium ingots and analytical samples taken from each ingot. The results are given in Table VIII.

Table VIII

Effect of Humidity on Reactivity of Y-Mg Alloy and on Y Sponge

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Form of Metal Exposed</th>
<th>$O_2$ in Resulting Arc-melted Y (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal crushing &amp; handling procedure</td>
<td>Alloy &amp; sponge</td>
<td>2700</td>
</tr>
<tr>
<td>Exposure of air in laboratory for 1 day</td>
<td>alloy</td>
<td>3470</td>
</tr>
<tr>
<td></td>
<td>sponge</td>
<td>3200</td>
</tr>
<tr>
<td>Exposure to air in laboratory for 5 days</td>
<td>alloy</td>
<td>2550</td>
</tr>
<tr>
<td></td>
<td>sponge</td>
<td>2500</td>
</tr>
<tr>
<td>Exposure to 100% humidity for 1 day</td>
<td>alloy</td>
<td>5700</td>
</tr>
<tr>
<td></td>
<td>sponge</td>
<td>2800</td>
</tr>
<tr>
<td>Exposure to 100% humidity for 5 days</td>
<td>alloy</td>
<td>6300</td>
</tr>
<tr>
<td></td>
<td>sponge</td>
<td>1950</td>
</tr>
<tr>
<td>Alloy crushed in dry box instead of jaw crusher</td>
<td>alloy</td>
<td>2205</td>
</tr>
</tbody>
</table>
The results of these tests show rather conclusively that the alloy is quite reactive toward atmospheric moisture, particularly under conditions of high humidity. They suggest that handling and crushing of the alloy must be done under low humidity conditions. The sponge does not appear to be nearly as reactive as the alloy and was inert under the test conditions.

A study was made of the effect of the condition of drying the \( \text{CaCl}_2 \) upon the quality of the yttrium metal obtained. The method employed in this process has been to vacuum dry the chloride at 400°C for 8 hours. Drying the \( \text{CaCl}_2 \) in a stream of HCl effects the quality of the \( \text{CaCl}_2 \), and subsequently the yttrium metal, as shown in Table IX.

**Table IX**

| Effect of Conditions of Drying \( \text{CaCl}_2 \) on Quality of Yttrium Metal |
|---------------------------------|-----------------|
| **Treatment of \( \text{CaCl}_2 \)** | \( \text{O}_2 \) in Arc-melted Y (ppm) |
| Dried in stream of HCl at 450°C | 1430 |
| Repeat of above | 1667 |
| Vacuum dried at 400°C | 1920 |
| Vacuum dried at 400°C followed by HCl treatment at 450°C | 1300 |
| Repeat of above | 1375 |
Drying of large batches of CaCl$_2$ in an HCl stream was attempted for use in large scale reductions but it was found that no significant reduction of oxygen content was obtained on this scale.

Two experiments were run using lithium as the reductant in place of calcium. The oxygen content of the yttrium thus prepared was 1350 and 1650 ppm.

A series of small reductions was made using various mixtures of calcium and lithium as the reductant with magnesium as alloying addition. This reaction was carried out satisfactorily employing a 82 w/o Ca - 18 w/o lithium reductant. This gives a low melting slag of CaF$_2$·LiF requiring no CaCl$_2$ flux. The fluidity of the slag depends upon a eutectic in the CaF$_2$·LiF system at about 60 w/o CaF$_2$ and melting at 700°C. Excellent slag-metal separations were observed and high metal recoveries were obtained. Several large scale (100 pound) reductions were made using the Ca-Li reductant. The oxygen content of the yttrium prepared in this manner varied from 1000 ppm to 2120 ppm with an average of 1400 ppm O$_2$ on 14 ingots. The intermediate alloy obtained from this process is somewhat pyrophoric and more reactive than the Y-Mg alloy from the standard reduction.
3. 5 Uranium Metal by the Carbon Reduction of Uranium Oxide

(H. A. Wilhelm and E. P. Neubauer)

The continued work on the carbon reduction of uranium oxide was directed toward three objectives. These were (a) to find some means or material which would contain the molten charge at the elevated temperatures required for the completion of the reaction; (b) to lower the carbon content of the product metal; and (c) to increase the metal yields.

The use of a ZrO₂ coating between a graphite crucible and a jolt-packed UO₂ liner was abandoned when the protective action of the ZrO₂ broke down at the high temperatures required to complete the reaction of the charge. One way to protect the UO₂ container was to eliminate the graphite crucible from the system. A 20 mil tantalum cylinder was used as the susceptor in the induction furnace, and UO₂ was used for insulation. A pressed and sintered UO₂ crucible was used to contain the charge. The crucible life was still just one reduction because of wetting action of the liquid product, but the crucibles remained intact and there was no metal loss due to crucible failure.

With the container problem temporarily solved, some attempts were made to get a density separation of the residual carbon and the uranium. Efforts were made to control the cooling rate of the molten
metal product of the reduction so that the uranium carbide might have time to float to the top. Because induction stirring occurred whenever the induction current was turned on to retard the cooling, this approach met with only limited success, especially with the small size charges employed.

The yields of uranium metal ranged from 70% - 80%. This is very low and it is attributed to the volatility of UO₂ at temperatures required to get appreciable reduction. Uranium metal is of about the same volatility as UO₂ at the temperatures reached, but the metal is not formed until the end of the reaction and there isn't much time for an appreciable loss to take place. One reduction was made under a partial pressure of flowing argon in hopes that this would suppress the volatilization of the oxide, but it also slowed down the reaction and apparently nothing was gained with this approach.

While searching for a refractory in which the UO₂ reduction could be carried out, a slug of uranium metal was heated to 1800°C in an yttrium oxide crucible. Upon cooling, the metal fell free of the crucible, and no reaction with or attack on the crucible was evident. The crucible was found to have good thermal shock resistance. It is also a good container for melting thorium. An yttrium oxide crucible was badly corroded by the molten metal from a carbon reduction of UO₂, however.
3.6 Preparation of Tantalum Metal (H. A. Wilhelm and C. B. Hamilton)

Some of the methods for producing high purity tantalum are being investigated. Three methods that appeared worth consideration here were the sodium reduction of the fluoro tantalate, the aluminum or aluminum-calcium reduction of tantalum oxide and the carbon reduction of the pentoxide. Preliminary experiments have indicated that the carbon reduction may have advantages over other present methods of producing metallic tantalum.

If a less than stoichiometric amount of carbon is used to reduce the tantalum oxide, the excess oxygen is boiled off at around 2200°C in a vacuum, possibly as TaO₂. The remaining metal sponge gives a ductile metal when arc-melted, but it is still much harder than Fansteel tantalum similarly melted here.

3.7 Purification of Barium Metal (D. T. Peterson)

Barium metal of higher purity than was available was needed for the investigation of the reaction of barium with calcium chloride and the study of the barium-barium hydride system. As barium is rapidly contaminated by exposure to the atmosphere, the purified barium had to be handled under argon in a tight glove box to preserve the benefit of
the purification process. A bath still capable of distilling 1000 grams of barium was designed and constructed. The still was designed so that it would be loaded and unloaded in a glove box.

A number of distillations, starting with cast barium sticks, were made at 800°C and 8 mm argon pressure. The distilled barium was obtained in the form of a bright dense mass of crystals. The residue which was left contained a small amount of metal but was principally a crust of barium oxide. The barium oxide crust was in the form of large crystals which had a dark blue to red color due to a small amount of dissolved barium. The results of an analysis of the crude barium and the purified barium are given in Table X. Distillation of barium

<table>
<thead>
<tr>
<th>Element</th>
<th>Crude Barium</th>
<th>Distilled Barium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>790</td>
<td>73</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>440</td>
<td>40</td>
</tr>
<tr>
<td>Iron</td>
<td>50</td>
<td>23</td>
</tr>
<tr>
<td>Manganese</td>
<td>47</td>
<td>77</td>
</tr>
<tr>
<td>Silicon</td>
<td>M</td>
<td>W</td>
</tr>
<tr>
<td>Magnesium</td>
<td>W</td>
<td>VW</td>
</tr>
<tr>
<td>Nickel</td>
<td>VW</td>
<td>ND</td>
</tr>
<tr>
<td>Aluminum</td>
<td>W</td>
<td>Trace</td>
</tr>
</tbody>
</table>
resulted in a considerable decrease in the carbon and nitrogen content and a moderate decrease in the metallic impurities with the exception of manganese. The oxygen content could not be determined by the amount of barium oxide in the residue, indicating a considerable decrease in the oxygen content. The melting point of the crude barium was 717°C and the melting point of the distilled barium was 729°C. This increase in the melting point indicates that a significant improvement in the purity was obtained by distillation.

4. Alloy Investigations

4.1 Phase Relations and Thermodynamic Properties of the Th-Zn System. (P. Chiotti and K. Gill)

A study of the thorium-zinc system with the objective of establishing the equilibrium diagram and some of the thermodynamic properties of the compounds formed has been initiated. This system is of particular importance in the production of thorium metal and in the pyrometallurgical processing of thorium fuel or blanket material.

A review of the literature indicates at least two compounds in the system. The compound Th$_2$Zn$_{17}$ has been reported by Makarov.
and Vinogradov. A second compound Th$_2$Zn was reported by Wilhelm. A eutectic was also reported between Th$_2$Zn and pure thorium. Two more compounds and three more eutectics have been found in this investigation. Thermal analysis and metallographic data were used to determine the phase boundaries.

The metals employed in this investigation were Ames Laboratory thorium containing less than 1800 ppm impurities and Bunker Hill slab zinc with a purity of 99.99+ percent.

All of the alloys were prepared in the same manner. The thorium was cleaned in a solution of HNO$_3$, Na$_2$SiF$_6$ and H$_2$O, rinsed in water and acetone, then dried and weighed. The zinc was cleaned in dilute HCl, washed in water and acetone, then dried and weighed. The charge was enclosed in a tantalum crucible by welding on a preformed tantalum cap. The cap also had a thermocouple well welded in it which was used in measuring the temperature of the alloy during thermal analyses. The tantalum crucible was then enclosed in a stainless steel bomb. The bomb was made by welding a stainless steel cap on each end of a stainless steel

2. E. S. Makarov and S. I. Vinogradov, Kristallografiia 1, part 6 (1956).
pipe. All welding operations were carried out in an argon atmosphere. The assembly was then heated in a rotating resistance furnace at temperatures up to 1200°C. At temperatures above 1150°C equilibrium could be obtained in less than 30 minutes. Below 1150°C the samples were rotated at temperature up to four hours. After the initial equilibration the outer stainless steel bomb was removed, the tantalum crucible containing the alloy placed in the thermal analysis apparatus, and a differential heating and cooling run made. The construction of this apparatus was such that the tantalum crucible could be heated under an inert atmosphere.

The phase diagram based on thermal and metallographic data is shown in Fig. 3. Since thermal analyses were made under constrained vapor conditions this diagram may not represent the true equilibrium diagram at one atmosphere pressure. The zinc vapor pressure as a function of temperature will be measured by a dew point method. Further work will also be done to establish the zinc-rich liquidus curve at lower temperatures.

4.2 Study of Allotropic Transitions in Thorium-Yttrium Alloys

(O. N. Carlson and D. T. Eash)

Investigation of the thorium-yttrium system was undertaken for the principal purpose of studying the solid state phase interactions at
Fig. 3 - Phase Diagram Based on Thermal and Metallographic Data.
high temperatures. Since the atomic diameters of yttrium and thorium are nearly identical, if yttrium exhibits a high temperature BCC form as is suggested from other observations, a complete series of solid solutions at elevated temperatures would be expected. The solidus of the Th-Y system has been determined by a melting bar technique to be a continuous curve extending from the melting point of yttrium (1510°C) to the melting point of thorium (1755°C). This evidence strongly suggests a continuous solid solution region immediately below the solidus.

Cooling curves of arc-melted alloys showed a thermal arrest at 1460°C in alloys over a composition range of 60 to 90 w/o Y. A 30 w/o Y alloy exhibits a strong cooling curve break at 1385°C and a 10 w/o Y alloy at 1445°C.

Preliminary results of resistivity versus temperature curves on these alloys verify the above transitions. Microscopic examination of thorium-yttrium alloys reveals a eutectic or eutectoid in the region of 30 w/o Y.

The polishing and etching of alloys in this system is difficult to do with reproducible results. Vibratory polishing equipment has been installed in an attempt to improve the quality of the microstructures.
4.3 Tantalum-Zirconium System (D. E. Williams and R. J. Jackson)

On the basis of an extensive metallographic study conducted during this period as well as previous electrical resistance and dilatometric tests, the monotectoid composition and temperature have been established as 12% tantalum and 800°C. The maximum solubility of tantalum in alpha-zirconium was found to be $1.5 \pm 0.5\%$ at 800°C, decreasing rapidly with decreasing temperature. This information completed the investigation of the tantalum-zirconium alloy system. A brief summary of the results of this investigation follows.

The solidus curve of the diagram contains a minimum near 25% tantalum and 1820°C. At about 50% tantalum, the solidus starts to rise more rapidly to reach the observed melting point of tantalum, 2940°C. Below the solidus there exists a continuous solid solution which decomposes on cooling except on the extreme tantalum rich side. The intermediate alloys form two solid solutions, while the zirconium-rich alloys transform as a result of the beta to alpha transformation in zirconium. The result of these two factors is a monotectoid at 12% tantalum and 800°C. The monotectoid horizontal extends to 96% tantalum where it is terminated by the boundary of the tantalum-rich solid solution. The solubility limit of zirconium in tantalum is about 2% at room temperature.
4.4 Additions of Magnesium to Thorium (J. F. Smith, D. E. Williams and W. H. Pechin)

Work on this system has consisted mainly of attempts to produce homogeneous alloys in the composition range of 70 to 100% thorium. These alloys, due to the high vapor pressure of magnesium, could not be prepared by arc-melting. It was also attempted to prepare these alloys in an open crucible with a flux and a helium atmosphere. The resulting melts were of poor quality and contained a large number of inclusions.

The most successful method to date has been to seal the alloying constituents in a tantalum tube and heat them with a muffle or an induction furnace. The tantalum crucible is protected from oxidation by either a silica capsule or a helium atmosphere. The closed tantalum crucibles have been heated to 1450°C with only slight end-bulging due to the pressure of the magnesium. Heavy wall tantalum crucibles are used in the high temperature experiments.

Magnesium turnings and small pieces of thorium sheet were used as starting materials in an effort to keep the reaction time as short as possible. The melts prepared to date have all separated into at least two layers. The upper layer has been found to consist of a eutectic structure with primary crystals of a compound presumed to be ThMg₅.
The bottom layer is similar but contains particles of a darker, less regular phase, which may be the compound ThMg₂. X-ray diffraction studies have identified one of the phases in the upper layer as ThMg₅. X-ray work also indicates that the bottom layer contains a thorium phase. No other phase has been identified.

4.5 Tantalum-Vanadium System (O. N. Carlson and D. T. Eash)

The investigation of the tantalum-vanadium system was completed during this period and the results presented at the Reactive Metals Conference at Buffalo, New York in May, 1958. These will be published in the proceedings of that conference. The salient features of the Ta-V system are as follows:

1. The system consists of a complete series of solid solutions, above 1320°C. There is a minimum in the solidus at 1820°C and approximately 30 w/o Ta.

2. An intermediate phase, identified as β or TaV₂, is rejected from solid solution at 1320°C at a composition of approximately 64 w/o Ta.

3. The structure of the intermediate phase, β, is isomorphous with the FCC Laves phase, MgCu₂, and has a lattice parameter of

\[ a = 7.163 \text{ Å}. \]

4. The boundaries of a two phase region extend from 27.5 w/o Ta to 87.5 w/o Ta at 900°C.
4.6 Yttrium-Niobium Alloy Investigation (O. N. Carlson, V. C. Marcotte, D. E. Williams)

An investigation of the properties and phase relationships of the yttrium-niobium system was initiated during this period.

A complete series of alloys was prepared by arc-melting in a tungsten-electrode furnace. Only the 2%, 5%, and 95% yttrium alloys were homogeneous after the first melting. Through the use of smaller charges and with thorough remelting, the 70%, 80% and 90% yttrium alloys were homogenized. The rest of the alloys have not been improved by this procedure.

Melting points have been determined for those alloys which have been made homogeneous. These are listed below.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Melting Point (Solidus)</th>
</tr>
</thead>
<tbody>
<tr>
<td>95Y</td>
<td>1410°C</td>
</tr>
<tr>
<td>90Y</td>
<td>1395°C</td>
</tr>
<tr>
<td>80Y</td>
<td>1445°C</td>
</tr>
<tr>
<td>70Y</td>
<td>1460°C</td>
</tr>
</tbody>
</table>

Temperature resistance measurements on the 90% yttrium alloy show an inflection at 1400°C which corresponds to the eutectic temperature. The eutectic composition is believed to be near 95% yttrium. This information results from metallographic study.
In an effort to establish the liquidus of this system, niobium crucibles have been loaded with one of the lower melting alloys and then welded closed. The crucible is heated by induction to a temperature above the liquidus of the alloy it contains. This temperature is maintained for several hours to establish equilibrium, then the crucible is quenched with helium. Analysis of the equilibrium mixture will give the composition coordinate of the liquidus at the quenching temperature. Test runs have been made and the method appears feasible for alloys which have a liquidus temperature below the melting point of niobium, 2420°C. A suitable container is being sought for the high-melting alloys.

4.7 Uranium-Rhenium Alloy Investigation (J. F. Smith, R. J. Jackson and D. E. Williams)

Work was initiated on the establishment of the uranium-rhenium phase diagram. An extensive survey of the literature revealed very little information concerning previous work on this alloy system.

Alloys covering the uranium rich end of the system were prepared by arc-melting. The as-cast alloys as a whole are not ductile and do not respond to cold working. The 10% rhenium alloy is an exception in that it could be reduced by cold rolling.

4.8 Thorium-Molybdenum Alloy Investigation (D. E. Williams and P. E. Palmer)

The shape of the phase-diagram of the thorium-molybdenum system
has been established as a simple eutectic with no detectable solubility of either constituent at room temperature. The best method of establishing the solubility limits at elevated temperatures appears to be that of high-temperature x-ray analysis. A high temperature modification of an x-ray spectrometer is being placed in operating condition for the thorium-molybdenum solubility determination.


On the basis of previous work, the compounds Ni$_3$Zr and Ni$_4$Zr were thought to exist, however, further investigation has failed to substantiate their presence. The proposed diagram contains the six intermetallic compounds listed below with their melting or decomposition temperatures.

- \( \text{NiZr}_2 \) - Congruent melting at 1100°C.
- \( \text{NiZr} \) - Congruent melting at 1280°C.
- \( \text{Ni}_{10}\text{Zr}_7 \) - Peritectic decomposition at 1200°C.
- \( \text{Ni}_5\text{Zr}_2 \) - Peritectic decomposition at 1180°C.
- \( \text{Ni}_7\text{Zr}_2 \) - Congruent melting at 1420°C.
- \( \text{Ni}_5\text{Zr} \) - Peritectic decomposition at 1300°C.
The crystallographic investigation of the intermetallic compounds has yielded the following information. The lattice of the Ni₅Zr compound is face-centered cubic with a parameter $a_0 = 6.71 \text{ Å}$. This agrees with the lattice parameter quoted by Smith and Guard who have found that Ni₅Zr is isostructural with Ni₅U and Cu₅U.

The compound, NiZr, has been found to be orthorhombic with $a_0 \approx 3.26 \text{ Å}$, $b_0 \approx 9.97 \text{ Å}$, and $c_0 \approx 4.08 \text{ Å}$. The symmetry and cell constants were determined from Okl and lkl Weissenberg data, and hkO, hkl, hOtl, and hll precession data. A set of multiple films obtained with a Weissenberg camera and CuKα radiation were judged by visual estimation to provide Okl and lkl intensity data. These intensity data were corrected for dispersion effects. A trial structure was chosen from a $P(x, y)$ Patterson projection and refined by a least squares method with an IBM-650 computer. A value

$$R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|} = 0.165$$

was obtained for the following

structure:

Space Group, $D^{17}_{2h}$ - Cmcm

with 4Ni $(0, 0, 0; 1/2, 1/2, 0) \pm 0, y, 1/4; \quad y = 0.082$

and 4Zr at $(0, 0, 0; 1/2, 1/2, 0) \pm 0, y, 1/4; \quad y = 0.361$.

The lattice of the NiZr$_2$ compound has been determined as tetragonal with $a_0 = 6.50 \text{ Å}$ and $c_0 = 5.24 \text{ Å}$. The structure was determined from hkO and higher order Weissenberg data, and hh$\ell$, Ok$\ell$ and higher order precession data. Ok$\ell$ intensity data were obtained by visual estimation of timed precession pictures taken with Mo Kα radiation. A trial structure for NiZr$_2$ was chosen from a P(x, y) Patterson projection and refined with an IBM-650 using a modified least squares treatment. A value $R = 0.076$ was obtained for the following structure:

Space Group, $D^{18}_{4h}$ - I4/mcm

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

and 8Zr at $(0, 0, 0; 1/2, 1/2, 1/2) \pm (x, 1/2+x, 0; 1/2+x, x, 0); \quad x = 0.1629$.

The lattice parameters of the orthorhombic Ni$_{10}$Zr$_7$ compound have been determined as $a_0 \approx 9.18 \text{ Å}$, $b_0 \approx 9.27 \text{ Å}$, and $c_0 \approx 12.44 \text{ Å}$. Diffraction symmetry and characteristic extinctions indicate space group symmetry, $D^{15}_{2h}$ - Pbca. No trial structure has been postulated for this compound;
however, the following sets of positions seem feasible for occupancy:

40Ni in 5 sets of the type \( \pm (x, y, z; \frac{1}{2}+x, \frac{1}{2}-y, \bar{z}; \bar{x}, \frac{1}{2}+y, \frac{1}{2}-z; \frac{1}{2}-x, \bar{y}, \frac{1}{2}+z) \)

24Zr in 3 sets of the type \( \pm (x, y, z; \frac{1}{2}+x, \frac{1}{2}-y, \bar{z}; \bar{x}, \frac{1}{2}+y, \frac{1}{2}-z; \frac{1}{2}-x, \bar{y}, \frac{1}{2}+z) \)

and 4Zr in \((0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0; 0, \frac{1}{2}, \frac{1}{2}; 0, 0, \frac{1}{2})\).

Eutectic points have been observed at the following temperatures and compositions.

- 960°C and 17% Ni
- 1010°C and 27% Ni
- 1060°C and 52% Ni
- 1170°C and 87% Ni

The eutectoid composition has been substantiated as 1.3% nickel. The temperature of the eutectoid has been established as 840°C by means of electrical resistance measurements.

The solubility limit of nickel in alpha-zirconium is approximately 0.1% at 840°C while the maximum solubility of nickel in beta-zirconium is 1.9% at 960°C. The terminal solid solution on the nickel-rich end of the diagram contains a maximum of 3.0% zirconium at 1170°C from which it decreases to less than 0.1% zirconium at room temperature.
Several hafnium-nickel alloys have been prepared by arc-melting and examined metallographically.

4.10 **Thorium-Tantalum System** (D. E. Williams, and O. D. McMasters)

The alloys of this system have been given extensive homogenization treatment by repeated arc-melting and annealing. Since the data obtained previously from the inhomogeneous alloys are somewhat questionable, a reinvestigation is being made.

High temperature-resistance measurements have been inhibited by thermocouple reaction with the specimens at about 1400°C, near the transformation temperature in thorium. The tungsten-iridium, tungsten-niobium, and tungsten-tantalum thermocouples have been tried and have proven inaccurate at high temperatures when placed in direct contact with the specimen.

Determination of the melting points of the homogenized alloys is now in progress. The results from the samples which have been run indicate the eutectic horizontal exists at $1565 \pm 20^\circ C$ rather than $1700^\circ C$ which was reported previously.

4.11 **The Uranium-Hafnium System** (D. T. Peterson and D. J. Beerntsen)

A phase transformation in high hafnium alloys was found by
electrical resistivity measurement and identified by microscopic examination of quench alloys as a monotectoid reaction. The transformation temperature was found to be about 1200°C and the monotectoid composition about 50 atom percent. Interpretation of the microstructures of these alloys was complicated by the presence of alpha hafnium which was stabilized by dissolved oxygen. The crystal bar hafnium contained sufficient oxygen to cause the appearance of alpha hafnium in alloys which in the absence of oxygen would have been one phase alloys.

Uranium hafnium alloys containing between 13 and 75 atom percent hafnium when quenched from above 1200°C were found to contain a phase which gave an X-ray diffraction pattern similar to the uranium-zirconium delta phase. This phase was never observed in alloys which were furnace cooled or quenched from below 1200°C. These alloys gave diffraction patterns of only alpha uranium and alpha hafnium in every case. Consequently, the delta phase was assumed to be a metastable phase in this alloy system. Alpha hafnium was found with the delta phase in most of the quenched samples. The appearance of this alpha hafnium had already been observed by microscopic examination and attributed to the effect of oxygen. Alloys containing more than 75 atom percent hafnium and quenched from above 1200°C transformed to alpha uranium, alpha hafnium
and a small percentage of delta. Samples containing less than 15 atom percent hafnium transformed to alpha uranium and alpha hafnium. It appears that the delta phase is formed during quenching in alloys over a considerable composition range, but outside of this range the high temperature solid solution transforms to the equilibrium phases.

4.12 Yttrium-Titanium System (O. N. Carlson, D. Bare and F. H. Spedding)

The study of the titanium-yttrium alloy system has been continued during this report period. Rockwell A hardness measurements were made on various alloy compositions to determine the effects of the addition of titanium to yttrium and of yttrium to titanium upon the hardness of the starting materials. The addition of 5 w/o Ti increases the hardness of yttrium from 14 $R_A$ to 28 $R_A$ and 10 w/o Ti to 35 $R_A$. The hardness of crystal bar titanium containing 440 ppm $O_2$ ($R_A$ 18) was increased by additions of 0.5, 2.0 and 7.5 w/o yttrium to $R_A$ 20, 28 and 34, respectively. A similar increase was noted with the addition of yttrium to high purity titanium sponge. However, the hardness of a poor quality titanium sponge containing 1500 ppm $O_2$ was lowered from $R_A$ 50 to $R_A$ 35-40 by the addition of 5 w/o Y. This latter effect is believed to be due to gettering of the oxygen from solid solution in the titanium.
Thermal analysis and electrical resistance vs temperature curves of yttrium-rich alloys show a small arrest or break around 1100°C. Since this is well below the eutectic temperature of 1350°C and no changes in microstructure are apparent in this region, there is no obvious explanation for this effect.

A series of alloys were quenched from various temperatures to determine the limits of primary solid solubility. At the maximum, the solubility of titanium in yttrium at the eutectic temperature was determined to be less than 1 wt. % and of yttrium in titanium less than 2 wt. %.


An investigation of the yttrium-magnesium system was initiated during this period. This system is of particular interest because of the importance of yttrium-magnesium intermediate alloys in the metal production process developed at the Ames Laboratory. Furthermore, because of possible application of both yttrium and magnesium to reactor use, knowledge of the interactions between these metals and the properties of their alloys would be of inestimable value.

Alloys were prepared in sealed tantalum crucibles by mixing weighed amounts of magnesium and yttrium sponge at a temperature sufficient to form a molten alloy. Adequate mixing was assured by use
of an oscillating furnace. The system exhibits a eutectic at 26 w/o Y and 570°C, and intermediate phases near the compositions of 40, 60 and 80 w/o Y. These compounds decompose peritectically at 610, 780 and 935°C, respectively. A eutectoid structure is observed in a 90 w/o Y alloy with thermal evidence for a horizontal at 780°C in that alloy.

4.14 A Study of Aluminum and Niobium Alloys (H. A. Wilhelm and T. G. Ellis)

Both aluminum and niobium have properties that favor their use in atomic reactors. Alloys of these metals might possibly prove superior to either pure metal in certain atomic energy applications. The first major problem in this study has been the preparation of the alloys. Since the melting point of niobium is far above the boiling point of aluminum, the direct co-melting of the two metals does not appear promising.

Basic information on the Al-Nb alloy phase diagram is the next major objective after working out techniques for making the alloys. Work at present is directed toward studying the aluminum-rich end of the system and the nature and properties of the alloys there before working with alloys rich in niobium.

Powder metallurgy techniques were tried in an effort to prepare the Al-Nb alloys but the results did not appear promising. A bomb process in which a master alloy of niobium in aluminum is first prepared, followed
by a solution of the master alloy in liquid aluminum, appears to offer some possibilities for preparing the aluminum-rich alloys and investigations are continuing along these lines.

No difficulty was encountered in preparing the master alloy. However, difficulty has been encountered in diluting this master alloy. Two procedures were attempted but neither has been successful yet. The master alloy with the required Al dilutent was placed in an MgO crucible within a graphite heater. This charge was then heated to and held at 1200°C ± 50°C under 1 atm He for 1/2 hour in an induction furnace. The charge was then furnace cooled to room temperature. Inspection of the charge upon removal from the crucible showed the master alloy still intact at the bottom of the charge. It was deduced from this attempt that the charge temperature during dissolution must be considerably higher, possibly near the melting point of the master alloy, for the dissolution to have a reasonable rate. The melting temperature of the alloy is estimated to be approximately 1700°C.

Since MgO reacts with graphite at high temperatures the second attempt used only a MgO crucible insulated with firebrick as a reaction vessel. The heat was supplied by an induction furnace using the Al and master alloy charge as a self-heater. An advantage of using this type of heating is the eddy currents set up within the molten metal that increases the mixing and dissolution rate.
The charge was placed in the reaction vessel and heated to 1600 ± 50°C in an induction furnace under 1 atm of He. Appreciable vaporization of the Al occurred at this temperature. The temperature of the metal charge was reduced to 1200°C ± 50°C and held for 1/2 hour. The charge was then furnace cooled to room temperature. Inspection of the charge showed some dissolution had taken place. However, a small piece of master alloy was still visible in the bottom of the charge.

Further attempts to directly dissolve this master alloy with Al, using extended times for dissolution, also proved unsuccessful. The reason for this difficulty is thought to be the extreme temperature difference between the melting points of the Al and the master alloy. At a temperature approaching the melting point of the master alloy, volatilization of the already molten Al becomes appreciable. Thus, melting the master alloy in the presence of Al is virtually impossible.

All of the dissolution attempts made previously were performed in an induction furnace using the charge as a self heater. An attempt was made to dilute the master alloy by arc-melting. The technique used was to strike the arc on the master alloy, melt it, and then melt the Al by contact with the molten master alloy. The Al, instead of dissolving the master alloy, tended to form an Al cladding around the
master alloy. A probable reason for this Al cladding is that the Al vola-
tilizes at a temperature lower than the melting point of the master alloy. Thus, the master alloy lays in the molten Al as a solid rather than a liquid.

The arc-melting method for dissolving the master alloy in Al has been abandoned. Further investigations will consist of attempts to make master alloys that are richer in aluminum and some of the aluminum-rich alloys directly by the bomb reduction method.

4.15 The Solubility of Thorium in Vanadium (D. E. Williams, and P. E. Palmer)

Melting point, temperature-resistance, metallographic and X-ray data were collected in an attempt to determine the solubility limits of thorium in vanadium.

Several melting-point determinations of the 1% and 2% thorium alloys were made. While one specimen of the 2% thorium alloy melted near the temperature of the eutectic horizontal, 1415°C, most of the other specimens of these alloys were found to melt about 300°C above the eutectic temperature. A melting point of 1830°C was obtained for the crystal-bar vanadium being used in this investigation.

The temperature-resistance data were obtained using apparatus containing purified helium to prevent excessive vaporization of vanadium
at elevated temperatures. The plot of electrical resistance vs. temperature for the 2% thorium alloy exhibited an anomaly at 1415°C, the eutectic temperature. A large number of the resistance runs were unsuccessful due to the reaction of the thermocouple or potential leads with the specimen.

Metallographic investigation of vanadium-rich alloys which had been annealed at 1015°C for 70 hours and then cooled slowly to room temperature indicated no solid solubility. All the alloys subjected to this treatment were found to have two phases.

The X-ray investigation with a precision back-reflection camera confirms other data which suggest virtually no solubility of thorium in vanadium at room temperature. A high-temperature X-ray camera was set up for use in the investigation. Most of the period was required to place the camera and associated vacuum and heating equipment in operating condition.

The results obtained from the solubility studies indicate no measurable terminal solid solution on the vanadium-rich end of the diagram at room temperature. The maximum solubility of thorium in vanadium is probably less than 2% at 1415°C, although this value is still uncertain.

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

An investigation of the Ba-BaH₂ system was started to provide
basic information on metal-metal hydride systems. As BaH$_2$ is a saline hydride, a phase system similar to those formed by barium with barium halides was expected.

Thermal analysis was used to obtain data on melting temperatures and other transformations. A thermal analysis capsule made of type 304 stainless steel was developed with which thermal analyses could be made up to 1050°C without loss of barium or contamination of the sample. Barium-barium hydride samples were prepared by placing a weighed amount of barium in a capsule, reacting the barium with the necessary quantity of hydrogen at 250-300°C and sealing the capsule by welding. The thermal analysis capsule was placed in a quartz tube during the thermal analysis run to reduce the loss of hydrogen from the sample. The results of the thermal analyses are given in Table XI. The melting temperature of the

<table>
<thead>
<tr>
<th>Composition Atomic Percent Hydrogen</th>
<th>Thermal Arrests Melting</th>
<th>Solid Transformations</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>729°C</td>
<td></td>
</tr>
<tr>
<td>13.4</td>
<td>732-738°C</td>
<td></td>
</tr>
<tr>
<td>21.6</td>
<td>735-746°C</td>
<td>485°C</td>
</tr>
<tr>
<td>34.1</td>
<td>763-788°C</td>
<td>586°C</td>
</tr>
<tr>
<td>47.2</td>
<td>891°C</td>
<td>602°C</td>
</tr>
<tr>
<td>63.5</td>
<td>&lt;980°C</td>
<td></td>
</tr>
</tbody>
</table>
samples increased continuously from the melting point of pure Ba. This indicates that BaH₂ is in solid solution in barium over a wide composition range. The transformation which gives the lower thermal arrest has not been identified. Specimens containing barium cannot be examined by conventional metallographic methods because barium is too reactive. Even in a glove box, a free barium surface becomes tarnished in a few minutes. However, examination of the surface of the 13.4% and 47.2% hydrogen samples, prepared by polishing with fine abrasive paper in a glove box, indicated that the former was one phase while the latter contained two phases.

5. Solid State Investigations

5.1 Magnetic Susceptibility of Thorium Metal (J. F. Smith and J. D. Greiner)

The magnetic susceptibility of crystal bar thorium has been measured in the temperature range 130-300°K. The measured values are shown in the accompanying table. No field dependence, and hence no indication of ferromagnetic impurity, was observed. Measurements on samples at room temperature cut from a rod in the 'as prepared' condition agree with measurements on arc melted material within the precision of measurement.
Table XII

Magnetic Susceptibility of Thorium Metal

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>Mass Susceptibility (e. m. u./gm.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>136</td>
<td>0.411 ± 0.009</td>
</tr>
<tr>
<td>151</td>
<td>0.401 ± 0.006</td>
</tr>
<tr>
<td>209</td>
<td>0.407 ± 0.001</td>
</tr>
<tr>
<td>256</td>
<td>0.409 ± 0.002</td>
</tr>
<tr>
<td>257</td>
<td>0.418 ± 0.006</td>
</tr>
<tr>
<td>276</td>
<td>0.411 ± 0.001</td>
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<tr>
<td>279</td>
<td>0.412 ± 0.002</td>
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<tr>
<td>291</td>
<td>0.410 ± 0.003</td>
</tr>
<tr>
<td>300</td>
<td>0.411 ± 0.001</td>
</tr>
<tr>
<td>Average</td>
<td>0.410 ± 0.002</td>
</tr>
</tbody>
</table>

5.2 Thermal Expansion of Calcium Metal (J. F. Smith and B. T. Bernstein)

The linear coefficients of thermal expansion of calcium metal have been measured for f. c. c. calcium and b. c. c. calcium. The determination was accomplished by comparing measured values of the d-spacings from individual X-ray reflections at different temperatures. The diffraction data were taken on a geiger-counter diffractometer modified for high temperature work. The apparatus allows the use of bar specimens which can be maintained under an inert atmosphere of purified helium. Values of 2θ were measured with a precision of
± 0.025 degrees. Values of the d-spacings computed from the 2θ measurements were fit to the equation

\[ d_{hk\ell} = d_{O, hk\ell} (1 + \alpha T) \]

by the method of least squares. Values for the linear coefficient of thermal expansion of the f.c.c. phase are shown in Table XIII. Each value is based upon five to nine experimental points. The greater thermal attenuation of intensity for higher angle reflections accounts for the trend toward narrowing temperature range and reduced precision with increasing Bragg angle.
In the case of the b.c.c. phase, the effect of thermal attenuation was so severe that only the (211) reflection persisted at elevated temperatures with sufficient intensity and with a significantly large shift in position to be usable to calculate a meaningful coefficient of thermal expansion. The value obtained from the (211) reflection in the range 467-603°C was $(33.6 \pm 1.6) \times 10^{-6}$ per °C. A very rough check of this value was obtained from the only two reliable $d_{310}$ values which were obtained at 467°C and 523°C. Calculation of the expansion coefficient from these two points gave a value of $33 \times 10^{-6}$ per °C.

The measured values for the linear coefficient of expansion for the f.c.c. phase are in good agreement with the values of $22.5_2 \times 10^{-6}$ per °C reported by Erfling\textsuperscript{5} for the range 20-40°C and of $22.0 \times 10^{-6}$ per °C reported by Cath and Steenis\textsuperscript{6} for the range 0-300°C but is somewhat lower than the value of $25 \times 10^{-6}$ per °C obtained by Bridgman.\textsuperscript{7} All three of these latter values were obtained.

\textsuperscript{5} H. Erfling, Ann. Physik 41, 467 (1942).
by dilatometric measurements. No expansion data were available for comparison with the present value for the b.c.c. phase.

Reference values for the lattice parameters were obtained by extrapolation. A value, $a_0 (26^\circ C) = 5.5884 \pm 0.0002 \, \text{Å}$, was obtained for the f.c.c. phase and a value, $a_0 (467^\circ C) = 4.480 \pm 0.005 \, \text{Å}$, was obtained for the b.c.c. phase.

5.3 Measurements of Elastic Constants of Metal Single Crystals (J. F. Smith and C. L. Arbogast)

5.3.1 Beryllium

Measurements of the five independent elastic constants of single crystalline beryllium as a function of temperature are in progress. These measurements are being made by the pulse-echo technique, and the apparatus has recently been modified to use an unrectified pulse in order to obviate the necessity of using a transit time correction. In Fig. 4 are shown the three transit times which have so far been measured as a function of temperature. The precision of each measured value is of the order of 0.2%. Elastic constants calculated from the values indicated by the smoothed transit time curves are tabulated in Table XIV. In agreement with what might be expected because of the very high Debye temperature of beryllium, the elastic constants are observed to approach constant values below about 200°K.
Fig. 4 - Measured Transit Times for Ultrasonic Pulses in Single Crystalline Beryllium.
Table XIV

Three Elastic Constants for Beryllium Single Crystals
(all in units of $10^{11}$ dynes/cm²)

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>$\frac{1}{2}(c_{11} - c_{12})$</th>
<th>$c_{33}$</th>
<th>$c_{11}$</th>
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<tr>
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<td>28.69</td>
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<tr>
<td>280</td>
<td>13.27</td>
<td>32.08</td>
<td>29.00</td>
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<tr>
<td>260</td>
<td>13.35</td>
<td>32.25</td>
<td>29.21</td>
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<tr>
<td>240</td>
<td>13.40</td>
<td>32.38</td>
<td>29.38</td>
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<tr>
<td>220</td>
<td>13.42</td>
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<tr>
<td>140</td>
<td>13.45</td>
<td>32.44</td>
<td>29.56</td>
</tr>
<tr>
<td>100</td>
<td>13.45</td>
<td>32.44</td>
<td>29.56</td>
</tr>
<tr>
<td>77</td>
<td>13.45</td>
<td>32.44</td>
<td>29.56</td>
</tr>
<tr>
<td>4.2</td>
<td></td>
<td></td>
<td>29.56</td>
</tr>
</tbody>
</table>

5.3.2 Yttrium (O. N. Carlson and E. D. Gibson)

Attempts to grow large single crystals of yttrium for use in the measurement of elastic constants by ultrasonic methods and to study the deformation modes in the metal were made during this period. Solid state annealing methods were used because of the crucible contamination of yttrium during melting. Both strain annealing and annealing of arc cast material were tried. Annealing times varied from five to forty-eight hours and various size specimens ranging from one inch in diameter
to one-quarter inch in diameter were used in the experiments. No consistent results were obtained in these tests even in successive runs under identical conditions. The one successful growth of a large single crystal was an anneal at 1275°C for twenty-four hours of a one-half inch diameter rod which had been given no previous strain treatment. It appears that large grain growth is limited to certain specific crystallographic directions in yttrium and that successful growth of single crystals depends on this orientation.

5.4 Structure of U₂Zn₁₇ (D. Peterson and C. L. Vold)

The structure of U₂Zn₁₇ is being investigated as this compound has been found to have at least two crystalline modifications and the compound is important in some pyrometallurgical separation processes. A number of single crystals of this compound have been examined by X-ray diffraction. All of the patterns could be indexed on the basis of hexagonal unit cells with \( a_0 = 8.96 \text{ Å} \) and \( c_0 = 9.0 \text{ Å}, 13.5 \text{ Å}, 18.0 \text{ Å} \) or \( 27.0 \text{ Å} \). The variable periodicity of the lattice in the \( c \) direction can be explained by assuming different stacking sequences of a basic 4.5 Å layer. Diffraction intensities from these crystals are being measured so that the structure of this phase can be determined.
5.5 Low Temperature Mechanical Properties of Vanadium

(O. N. Carlson, G. Smith, S. Bradford and A. Eustice)

As was reported previously, crystal bar vanadium metal undergoes a change from ductile to brittle fracture at about -100°C. At still lower temperatures, -140° to -190°C, the metal exhibits some ductility. Previous data indicate that the addition of hydrogen to vanadium raises the brittle-ductile transition temperature sharply. The role of hydrogen in the brittle-ductile transition of vanadium is being investigated in detail. This is presently being carried out by internal friction measurements on vanadium as a function of hydrogen content and temperature. The apparatus for these studies is now being tested.

The effect of varying the strain rate upon the brittle-ductile transition was studied over the range of 0.005 to 40 in/in/minute. The transition temperature was not found to vary significantly with strain rate, at least in the range investigated. It was observed, however, that vanadium exhibits ductility at the high strain rates (4 to 40 in/in/min) at temperatures below -100°C whereas brittle fracture occurs at this temperature and below at the slower strain rates. At all strain rates there is a sharp decrease in the degree of ductility at the transition temperature.

The investigation of the brittle-ductile transition in vanadium-
niobium alloys was initiated during this period. Since both metals have been reported to exhibit brittle-ductile transitions, and since they form a continuous series of body centered cubic solid solutions, this system was chosen for a study of the behaviour of the brittle-ductile transition across a binary substitutional solid solution region.

A bend test was selected to determine the transition temperature of the various V-Nb alloy compositions. Since it is known that degree of cold work, grain size and other variables may affect the results of a bend test, all specimens were cold rolled and annealed to produce a uniform grain size and to remove residual stresses. The following experiments were performed to determine the recrystallization temperature of niobium and vanadium. Sections of arc-melted buttons of vanadium and niobium were cold rolled into 40 mil plates. This represented a reduction in cross-sectional area of greater than 90 percent. The recrystallization temperature was determined by heating these bars under vacuum for 4 hours with a temperature gradient along the specimen. The results of these experiments indicate that both niobium and vanadium require annealing at temperatures of approximately 1300°C to bring about complete recrystallization.
6. Other Investigations

6.1 Vacuum Fusion Analysis of Metals (D. T. Peterson and M. Indig)

The samples of yttrium metal to which known amounts of nitrogen had been added were analysed by vacuum fusion. The results are shown in Table XV. The base metal from which the samples were prepared contained 2.21 x 10^-4 moles of oxygen and nitrogen per gram. As the weight of the samples was about 2 grams, the amount of gas evolved from the base metal was much greater than the amount of nitrogen which was added. Consequently, a variation of one percent in the total percentage

<table>
<thead>
<tr>
<th>Moles of N₂ Added</th>
<th>Moles of N₂ Recovered</th>
<th>Percent Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.95 x 10^-5</td>
<td>5.94 x 10^-5</td>
<td>150%</td>
</tr>
<tr>
<td>4.43 x 10^-5</td>
<td>6.23 x 10^-5</td>
<td>141%</td>
</tr>
<tr>
<td>5.84 x 10^-5</td>
<td>8.48 x 10^-5</td>
<td>145%</td>
</tr>
<tr>
<td>6.81 x 10^-5</td>
<td>6.46 x 10^-5</td>
<td>95%</td>
</tr>
</tbody>
</table>
of gas recovered would make a 10 percent variation in the nitrogen recovery percentage. A variation of five percent in vacuum fusion results is usual and explains the large variation in the nitrogen recovery. In order to determine this recovery accurately, it would be necessary to use yttrium metal containing less oxygen because the amount of nitrogen which can be added is limited by difficulties in charging.

6.2 Reaction of Barium with Calcium Chloride (D. T. Peterson, J. A. Hinkebein and E. W. Johnson)

A report on the results of this investigation has been written and has been accepted for publication in the Journal of Physical Chemistry. The title of the paper is "Equilibrium in the Reaction of Barium with Calcium Chloride".

The reaction of barium with calcium chloride in the liquid state was investigated by quenching and analysing equilibrated samples and by thermal analysis. The reaction appeared to obey the ideal law of mass action over a large part of the salt composition range. The equilibrium constant at 900° was 116 and at 950°, was 87. The solubility of metal in the salt phase varied with composition in a manner which indicated that this solubility was controlled by the composition of the liquid metal phase. The solubility of metal chloride in the liquid metal decreased from the solubility of calcium metal to a minimum at 0.1 mole fraction barium and then increased to the value for barium.
6.3 Distribution of Silver Between Liquid Lead and Liquid Zinc

(D. T. Peterson and R. Kontrimas)

The concentration range over which the distribution coefficient has been determined at 508°C has been extended to 8.0% silver in the zinc phase. As a result of an improvement in the design of the filter pipette used to sample the liquid lead and zinc, the experimental scatter of the values found for the distribution constant has been decreased. The apparent decrease in the distribution constant with increasing silver content has been shown to be due to the entrapment of zinc in the lead sample. The average value of 23 measurements of the distribution coefficient at 508°C was 81 ± 8. The distribution coefficient did not change with silver concentration up to 8.0% silver. The investigation cannot be extended to higher concentrations of silver as the solubility of silver in zinc is about 8% at 508°C.

6.4 Absorption of Hydrogen by Thorium (D. T. Peterson and D. G. Westlake)

The rate of absorption of hydrogen by thorium at constant pressure and temperature was measured from 450 to 700°C at pressures up to 400 mmHg. The rate of absorption followed the parabolic rate law. This indicated that the rate controlling step was the diffusion of hydrogen through a protective hydride surface layer. The reaction rate was independent of pressure at
-500°C but became somewhat pressure dependent at higher temperatures. The temperature dependence of the absorption rate at constant pressure can be expressed by an Arrhenius type equation. The diffusivity of hydrogen in thorium hydride cannot be calculated because of concentration gradient in the hydride layer is not known. The rate of absorption was the same for annealed crystal bar thorium, as-swaged crystal bar thorium and annealed Ames thorium.

6.5 Solubility of Thorium Dihydride in Thorium Metal (David T. Peterson and D. G. Westlake)

The saturation solubility of thorium dihydride in thorium was studied by saturation of samples and subsequent analysis. The solubility increased from about 1 at pct at 300°C to above 20 at pct at 800°C. Over this temperature range the log of the solubility was a linear function of the reciprocal absolute temperature for thorium of good purity. The heat of solution of thorium dihydride was found to be 7.9 kcal per atom of hydrogen in crystal bar thorium and 6.6 kcal per atom of hydrogen in Ames thorium.

6.6 The Effect of ThO₂ on Thorium-Hydrogen Equilibrium (D. T. Peterson and J. Rexer)

The effect of ThO₂ on thorium-hydrogen equilibria was investigated to determine whether ThO₂ was responsible for the variation in hydrogen
equilibrium pressure with composition in the region where thorium metal and thorium hydride coexist. This variation has been reported by two independent investigations and did not appear to be due to temperature gradients nor experimental errors. The equilibrium hydrogen pressure at 700°C over Ames thorium (1.1% ThO$_2$) and thorium containing 4.0% ThO$_2$ was determined up to the composition of the lower hydride. The variation of the equilibrium pressure with hydrogen content in the two-phase region that had been previously reported for Ames thorium was verified. The sample containing 4.0% ThO$_2$ did not show this variation. The variation seems to be due to ThO$_2$ dissolved in thorium hydride. In Ames thorium, the first hydride which is formed, is saturated with ThO$_2$ and has a lower dissociation pressure. As more hydride is formed, the concentration of ThO$_2$ in the hydride decreases and the dissociation pressure increases. The sample containing 4.0% ThO$_2$, on the other hand, has enough ThO$_2$ to keep the thorium hydride saturated and no variation of the equilibrium pressure was observed. This hypothesis was confirmed by microscopic examination of samples of thorium dihydride. These samples did not contain the globules of ThO$_2$ which were present in the metal. Decomposition of the hydride produced thorium metal in which the ThO$_2$ was present as a very fine dispersion rather than large globules or dendrites.
6.7 The Effect of Hydrogen on Tensile and Impact Properties of Thorium (D. T. Peterson)

The results of this investigation were presented at the Third Annual Reactive Metals Conference, AIME, and will be published in the proceedings of that meeting.

The effect of hydrogen on the room temperature tensile properties and impact strength of Ames thorium was determined. The samples were charged with hydrogen at 800°C and tested in the slow cooled and in the quenched condition. The ductility of thorium in these tests was not reduced by small additions of hydrogen, but large concentrations of hydrogen decreased the impact values and the reduction in area of tensile samples. The 0.2 pct offset strength of slow cooled samples was decreased by additions of hydrogen. The quenched samples increased in hardness and offset strength with hydrogen content. Quenched samples were found to have the same ductility as slow-cooled samples.

6.8 Mechanical Metallurgy of Yttrium Metal (O. N. Carlson, E. D. Gibson and F. H. Spedding)

With the acquisition of a new Tinius-Olsen Universal Tensile Testing Machine an investigation of the tensile properties of yttrium metal was initiated. The investigation includes a determination of the effects of various
alloying additions or impurities upon the ductility and strength of yttrium metal. Work has been started on the preparation of tensile specimens and on a study of a treatment to control the grain size in the various specimens.

In an effort to correlate hardness vs. oxygen content of yttrium metal, tests were run on nineteen experimental ingots differing in oxygen content from 1000 to 9600 ppm. The Brinell hardness using a 10 mm ball indenter and a 500 kg load was measured on each specimen. Graphical plots of hardness vs. oxygen content, carbon, nitrogen, titanium and total impurity contents showed only general trends but no smooth curves could be drawn from the data. Observations that hardness increases with increasing oxygen and carbon content and that hardness decreases with titanium content up to a 1 w/o Ti addition were made during the course of testing. A marked degree of anisotropy in hardness was also noted since different results were obtained with transverse sections than with longitudinal sections of the same ingot. This anisotropy was also noted in the elliptical nature of the hardness indentations. No correlation of hardness to any specific impurity could be made due primarily to the wide variation in total impurity content of the ingots tested.

6.9 Some Metallographic Observations on Yttrium Metal

(O. N. Carlson, D. T. Eash and F. H. Spedding)

A large number of etchants were tried on yttrium metal. Solutions
containing HNO₃ as the active agent were the most satisfactory. The principal impurity phase in the grade of yttrium used in the investigations was identified as Y₂O₃.
APPENDIX I: LIST OF REPORTS FROM THE Ames Laboratory

1. Reports for Cooperating Laboratories

ISC-867 Riley Schaeffer and Hampton Smith. Isotopic Equilibria of Nitrosyl Chloride.


ISC-945 William J. Lane and J. S. Fritz. Metal-Indicator Systems in (Ethylenedinitrilo)tetraacetic Acid Titrations.


ISC-1030 R. G. Barnes. Bibliography of Titles of Articles in the Field of Nuclear Quadrupole Resonance Spectroscopy of Solids.


ISC-1074 Peter H. Vossos and R. E. Bundle. Crystal Structure and Magnetic Properties of LiCuCl₃·2H₂O.
2. Publications

Amma, E. L. and R. E. Rundle

Anderson, Gerald S. and Sam Legvold

Anderson, G. S., S. Legvold and F. H. Spedding

Arajs, Sigurds and Sam Legvold

Arajs, Sigurds and Sam Legvold

Banks, Charles V., Clara I. Adams and John Richard

Banks, Charles V. and Dennis W. Barnum

Banks, Charles V., Keith E. Burke and Jerome W. O'Laughlin

Banks, Charles V., J. P. LePlante and John J. Richard

Banks, Charles V., James A. Thompson and Jerome W. O'Laughlin

Barnes, R. G. and R. D. Engardt

Barnes, R. G. and R. A. Hultsob
Barghusen, John, Jr. and Morton Smutz

Corbett, John D.

Corbett, John D.

Dahl, June L. and Frederick R. Duke

Duke, Frederick R. and James P. Cook

Duke, F. R. and R. A. Fleming

Duke, Frederick R. and Marlowe L. Iverson

Duke, F. R. and Boone Owens

Duke, Frederick R. and Boone Owens
Transport Numbers of the Pure Fused Salts, LiNO₃, NaNO₃, KNO₃, and AgNO₃. J. Electrochem. Soc. 105, 548-549 (1958).

Flesch, Gerald D. and Harry J. Svec

Fritz, James S., Marlene J. Richard and Shirley K. Karraker

Fritz, James S., Marlene Johnson Richard and William J. Lane

Fritz, James S. and Gerald R. Umbreit
Hammer, C. L. and R. H. Good, Jr.  

Herman, R. and C. A. Swenson  

Jennings, L. D. and C. A. Swenson  

Junk, Gregor and Harry J. Svec  

Kniseley, Richard N., Velmer A. Fassel, Beverly B. Quinney, Carl Tremmel, William A. Gordon and William J. Hayles  

Laslett, L. Jackson  

McCarley, Robert E., Don S. Martin, Jr. and Lee T. Cox  
Solid State and Solution Exchange of Platinum Between $\left[\text{Pt(en)}\text{Br}_7\right]$ and $\left[\text{Pt(en)}\text{Br}_7\right]^+. J$. Inorg. Nucl. Chem. 7, 113-118 (1958).

McMullan, Richard K. and John D. Corbett  

Smith, Harold G. and R. E. Rundle  

Smith, J. F. and J. R. Ogren  

Spedding, F. H., K. Gschneidner, Jr. and A. H. Daane  

Svec, H. J., A. A. Read, D. W. Hilker

Swenson, C. A.

Thoburn, W. C.

Thoburn, W. C., S. Legvold and F. H. Spedding

Worden, D. G. and G. C. Danielson
## APPENDIX II: LIST OF SHIPMENTS

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<th>Item</th>
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<tr>
<td></td>
<td>100 gm thulium oxide</td>
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<tr>
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<td>20 gm lutetium metal</td>
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<td>100 gm lutetium oxide</td>
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<td>Midwest Microlab, Inc. Indianapolis, Indiana</td>
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<tr>
<td>Brown University Providence, Rhode Island</td>
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</tr>
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</table>
Dr. Joseph Graca  
Iowa State College  
Ames, Iowa

5-200 mg pellets each of  
yttrium metal  
lanthanum metal  
cerium metal  
neodymium metal  
gadolinium metal  
ytterbium metal  
dysprosium metal

150 pellets, 100 mg each of  
yttrium metal  
cerium metal  
neodymium metal  
gadolinium metal  
dysprosium metal  
ytterbium metal  
cylinders of neodymium metal as follows:  
6 1" x 2" diam.  
6 1/2" x 2" diam.  
6 1/4" x 2" diam.  
6 1/8" x 2" diam.

Battelle Memorial Institute  
Columbus, Ohio

50 gm dysprosium metal

Carnegie Institute of Technology  
Pittsburgh, Pennsylvania

5 gm lanthanum metal

General Electric Research Laboratory  
Schenectady, New York

200 gm yttrium metal

University of Arizona  
Tucson, Arizona

20 gm neodymium oxide

Syracuse University  
Syracuse, New York

491 gm calcium