PROGRESS RELATING TO CIVILIAN APPLICATIONS DURING JULY, 1956

by

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Clyde R. Tipton, Jr.

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D. STUDIES OF THE REACTION BETWEEN ZIRCONIUM ALLOYS AND WATER

A. W. Lemmon, Jr.

As assistance to WAPD, a study is being made of the factors which affect the amount of chemical reaction between water and Zircaloy 2 at high temperatures. Experimental programs for the measurement of radiation emissivity, chemical reaction rates, and diffusion rates have been completed. An experimental study of meltdown and an analysis of the heat transfer from molten droplets have also been concluded. The computational program for estimating the probable amount of reaction after a loss-of-coolant situation is nearing conclusion.

Although considerable effort was expended this month in completing the computational program, unexpected difficulties with programming and with input information have delayed the availability of final results. Results of other computations showing the temperature distribution in a breeder-blanket rod are summarized. Based on this information, the assumption of constant radial temperature appears justified. Work on this study is expected to be concluded in August.

Analysis of the Extent of Reaction and Efficacy of Cooling


Further progress has been made in attempting to predict the maximum amount of chemical reaction between Zircaloy 2 and steam during reactor-core meltdown. Previous summaries have described calculational methods and input information as well as partial qualitative results.

During July, additional work was performed in programming the equations for machine solution. Unexpected difficulties in both input information and the machine programming have required effort beyond that originally anticipated. However, it is now believed that the majority of the problems of this nature have been solved and the numerical solutions for a number of cases will be available in a few days.

As reported qualitatively in BMI-1104, an analytical solution of the temperature distribution in the breeder-blanket fuel rods during blow-down was accomplished. Three cases were considered with each based on the same initial temperature distribution (in a rod in a maximum-flux region), having a maximum temperature close to 3000 F. Results are summarized.
These results show that the assumption of a constant radial temperature throughout the subsequent computations is reasonable.

**Table D-1. Temperature Distribution in a Breeder-Blanket Fuel Rod at 15 Sec After System Rupture**

<table>
<thead>
<tr>
<th>Axial Distance From Center of Rod, ft</th>
<th>Radial Distance From Axis of Rod, in.</th>
<th>Case 1 (h = 500, $k_{av} = 2.0$)</th>
<th>Case 2 (h = 1000, $k_{av} = 2.0$)</th>
<th>Case 3 (h = 1000, $k_{av} = 1.0$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.413/4</td>
<td>682</td>
<td>618</td>
<td>720</td>
</tr>
<tr>
<td>(Position of maximum decay heat)</td>
<td>0.413/2</td>
<td>646</td>
<td>584</td>
<td>661</td>
</tr>
<tr>
<td>1.5</td>
<td>0.413/4</td>
<td>591</td>
<td>553</td>
<td>602</td>
</tr>
<tr>
<td>3</td>
<td>0.413/4</td>
<td>554</td>
<td>531</td>
<td>563</td>
</tr>
<tr>
<td></td>
<td>0.413/2</td>
<td>542</td>
<td>523</td>
<td>544</td>
</tr>
</tbody>
</table>

This work is expected to be completed during August.
A number of programs concerned with the development of fuel elements for general application are sponsored by the Reactor Development Division of the Atomic Energy Commission. These include studies in ceramics, metallurgy, and corrosion.

Efforts in the ceramics program are being concentrated on the development of graphite as a ceramic fuel-matrix material. Various graphite-encased samples prepared by extrusion are being evaluated. In the study of sinterable oxides, considerable variation in the sinter-ability of BeO powders has been observed.

The study of uranium alloys for use above 650 °C is continuing, as is the evaluation of castable alloys. The program this year is extended to include irradiation tests. Corrosion studies of various matrix and uranium-compound combinations produced by powder metallurgy are being made in 680 °F NaK. Fabrication studies are being continued in an attempt to improve the structure of the U₂Ti-Zircaloy 2 combination.

In the study of uranium corrosion, the uranium-water reaction in wet-argon atmospheres correlates well with the equation \( U + 2H_2O \rightarrow UO_2 + 2H_2 \). Attempts are being made to correlate these tests with tests in boiling water. Further zone melting to purify uranium for this study is being planned, using sintered uranium dioxide boats.

**CERAMICS**

**Refractory Fuel Elements**

L. D. Loch, G. B. Engle, and A. G. Allison

Fuel elements based on the refractory materials BeO and graphite are being investigated. Preparations to study the diffusion of UO₂ through dense BeO were continued. Further studies of fabrication methods for graphite fuel elements were made.

**BeO**

In an effort to obtain defect-free dense BeO suitable for uranium-diffusion studies, two 3/4-in. -diameter by 1/4-in. -thick disks were
prepared. BeO powder, made from the hydroxide by calcining at 1800 F, was mixed with 3 w/o camphor and pressed at 20,000 psi. The specimens were sintered at 2600 F in an argon-hydrogen atmosphere. They appeared to be dense and crack-free and will be ground and polished for use in diffusion experiments.

Graphite

A fuel-element design is being considered for operation in gas-cooled reactors at temperatures up to 1800 F. The gas might be nitrogen or helium. Current laboratory studies are concerned with fuel rods consisting of a fueled core and a graphite sheath. The core may be either undiluted fuel or a mixture of fuel and graphite. Both types are being studied.

Last month, unsintered UO$_2$ rods, 1/32 in. in diameter, were encased in graphite by an extrusion technique. This month, these extruded fuel rods were baked at 2300 F and examined radiographically. The UO$_2$ rods were, in most cases, well centered in the graphite sheath and there was about 1/4 in. of graphite at each end of the rod. A few small cracks were noted in the graphite sheaths at the end of some of the rods. This cracking may be caused by the large thermal-expansion differential between the UO$_2$ and the graphite. Further experiments are needed to perfect the techniques and adapt it to cores of larger diameters.

Experiments on the matrix-type core were directed toward determining the maximum fuel loading that can be used while retaining good strength. Six sets of 1/4-in.-diameter cores containing 50, 70, or 85 volume per cent of UO$_2$ were made this month. In three sets, the UO$_2$ was in the form of spherical nodules and, in the remaining three, in the form of short rods. After baking, the strength of the nodule-loaded cores will be compared with that of the rod-loaded cores.

In future work, fabrication experiments will be continued and uranium-loss experiments will be resumed. A fuel-element design study will be concerned with a calculation of the thermal stresses in composite fuel rods under operating conditions.

Characterization of Sinterable Oxide Powders

J. F. Quirk, G. B. Engle, and J. B. Schroeder

In this investigation of the relations between sinterability and other more basic properties of refractory oxide powders, the study of BeO prepared from Be(OH)$_2$ was continued. Previous work indicated that the sinterability of such BeO powders was affected by impurity content, calcining
temperature, and, possibly, by the state of aggregation of the Be(OH)$_2$. Studies are under way to characterize the BeO powders by quantitative measurements.

Current studies are concerned with comparing the effects of purity and calcining temperature on surface areas, lattice parameters, and on calcining weight loss for sinterable and nonsinterable BeO powders. Data for four BeO powders of varying impurity contents are given in Table E-1.

The results show that the BeO made from high-purity NH$_4$-precipitated Be(OH)$_2$ was difficult to sinterable and differed markedly from the other three lots which were sinterable. The surface area of the calcined powder was much greater for the nonsintering material. Also, the change in lattice parameters with calcining temperature was different; the parameter $a$ showing greater decrease as the temperature was increased from 1470 to 1830 F, and the parameter $c$ showing the reverse trend, i.e., an increase with higher temperature in this range. In addition, the purer material had different dehydration behavior during calcining. It retained, at 750 F, about twice as much volatile material, mainly water, as the more sinterable powders.

Effort will be continued to assess the significance of the differences that have been observed in the BeO powders. Attention will be given to determining whether the very pure Be(OH)$_2$ (Lot LPA) can be converted to a sinterable BeO powder through highly controlled calcining treatment or controlled impurity additions. These experiments will aid in assessing the effect of contaminations on sinterability. A new lot of the hydroxide will have to be prepared for this work.

**METALLURGY**

*Uranium Alloys for High-Temperature Application*

R. F. Dickerson, F. A. Rough, A. A. Bauer, and W. E. Murr

This program is aimed at the development and evaluation of certain binary uranium alloys for use as high-temperature reactor fuels. The three alloy systems being studied include compositions of uranium-3 through 20 w/o zirconium, 3.5 through 12 w/o molybdenum, and 7 through 20 w/o niobium.

As part of the evaluation program, elevated-temperature mechanical properties are being obtained upon compositions of selectively heat-treated uranium-molybdenum and uranium-zirconium alloys. Results obtained to date are listed in Table E-2. The data were obtained on plate-type
<table>
<thead>
<tr>
<th>Lot</th>
<th>Estimated Total Impurities of Starting Hydroxide, w/o</th>
<th>Total Weight Replaced at 760 P., v/o of BeO</th>
<th>Volatile Material Retained at 760 F., v/o of BeO</th>
<th>Calculation Temperature, F</th>
<th>Compressed (d) per cent of theoretical</th>
<th>Surface Area, m(^2) per g</th>
<th>Lattice Parameters, A</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS650(n)</td>
<td>0.79</td>
<td>1800</td>
<td>5.7</td>
<td>750</td>
<td>97.6</td>
<td>100</td>
<td>2.5885, 4.377</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1470</td>
<td>97.6</td>
<td>34</td>
<td>2.6000, 4.376</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1800</td>
<td>97.6</td>
<td>34</td>
<td>2.6000, 4.376</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2100</td>
<td>97.6</td>
<td>34</td>
<td>2.6000, 4.376</td>
</tr>
<tr>
<td>LPS2(n)</td>
<td>0.25</td>
<td>1300</td>
<td>5.3</td>
<td>750</td>
<td>97.6</td>
<td>100</td>
<td>2.5885, 4.377</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1470</td>
<td>97.6</td>
<td>34</td>
<td>2.6000, 4.376</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1800</td>
<td>97.6</td>
<td>34</td>
<td>2.6000, 4.376</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2100</td>
<td>97.6</td>
<td>34</td>
<td>2.6000, 4.376</td>
</tr>
<tr>
<td>LPS4(n)</td>
<td>0.15</td>
<td>1300</td>
<td>6.1</td>
<td>750</td>
<td>97.6</td>
<td>100</td>
<td>2.5885, 4.377</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1470</td>
<td>97.6</td>
<td>34</td>
<td>2.6000, 4.376</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1800</td>
<td>97.6</td>
<td>34</td>
<td>2.6000, 4.376</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2100</td>
<td>97.6</td>
<td>34</td>
<td>2.6000, 4.376</td>
</tr>
<tr>
<td>LPS(n)</td>
<td>0.03</td>
<td>1500</td>
<td>11.2</td>
<td>750</td>
<td>97.6</td>
<td>100</td>
<td>2.5885, 4.377</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1470</td>
<td>97.6</td>
<td>34</td>
<td>2.6000, 4.376</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1800</td>
<td>97.6</td>
<td>34</td>
<td>2.6000, 4.376</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2100</td>
<td>97.6</td>
<td>34</td>
<td>2.6000, 4.376</td>
</tr>
</tbody>
</table>

(a) Compacts hydrostatically pressed at 100,000 psi and sintered 1 hr in hydrogen.
(b) From Be(OH)\(_2\) supplied by Bruh Beryllium Company.
(c) Prepared in the laboratory from H\(_2\)O-precipitated Be(OH)\(_2\).
(d) Prepared in the laboratory from NH\(_3\)-precipitated Be(ON)\(_2\).
TABLE E-2. ELEVATED-TEMPERATURE TENSILE PROPERTIES OF URANIUM-MOLYBDENUM ALLOYS, HEAT TREATED 1 HR AT 800 C AND WATER QUENCHED

<table>
<thead>
<tr>
<th>Nominal Composition (Balance Uranium), w/o</th>
<th>Temperature, F</th>
<th>Tensile Strength, psi</th>
<th>Elongation, per cent</th>
<th>Reduction In Area, per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5Mo</td>
<td>550</td>
<td>28,400</td>
<td>60.5</td>
<td>93.9</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>1,920</td>
<td>Specimen being rerun</td>
<td>Specimen did not fracture</td>
</tr>
<tr>
<td></td>
<td>1275</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5Mo</td>
<td>550</td>
<td>61,200</td>
<td>2.9</td>
<td>10.8</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>31,850</td>
<td>1.9</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1275</td>
<td>4,960</td>
<td>78</td>
<td>76.0</td>
</tr>
<tr>
<td>7Mo</td>
<td>550</td>
<td>67,400</td>
<td>4.0</td>
<td>31.8</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>36,750</td>
<td>13.8</td>
<td>27.4</td>
</tr>
<tr>
<td></td>
<td>1275</td>
<td>7,780</td>
<td>71.2</td>
<td>81.9</td>
</tr>
<tr>
<td>9Mo</td>
<td>550</td>
<td>71,870</td>
<td>13.3</td>
<td>36.4</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>47,130</td>
<td>3.4(4)</td>
<td>23.6</td>
</tr>
<tr>
<td>12Mo</td>
<td>550</td>
<td>93,570</td>
<td>11.9</td>
<td>22.6</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td></td>
<td>Specimen being rerun</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1275</td>
<td>5,470</td>
<td>(4)</td>
<td>(4)</td>
</tr>
</tbody>
</table>

(4) Specimens ruptured at grips.
uranium-molybdenum specimens, gamma quenched from 800 C, and tested at temperatures of 550, 1000, and 1275 F. From information listed in the table, it is evident that increasing the molybdenum content of the alloys greatly increases their elevated-temperature mechanical strengths. This is in agreement with previously obtained hot-hardness data.

Additional tensile data are being obtained for comparative purposes, upon uranium-molybdenum alloys with transformed-gamma structures, and these data will be reported soon.

An additional portion of the evaluation program is concerned with actual irradiation testing of selected alloys. Specimens of uranium-15 w/o zirconium alloy and uranium-10 and 20 w/o niobium alloys will be irradiated in temperature-controlled capsules (725 C) to approximately 1 a/o burnup. Providing the specimens are in suitable condition after irradiation, they will then receive a thorough postirradiation study.

Preparation and Properties of Low-Melting Alloys

F. A. Rough, R. F. Dickerson, A. A. Bauer, and W. E. Murr

The objective of this program is to screen a group of low-melting uranium alloys prior to selection of one or more of these alloys for irradiation testing. The alloys are of interest as possible power-reactor fuels. The screening is based upon results of thermal cycling, metallography, and elevated-temperature mechanical properties.

As a result of the investigation, a ternary alloy (uranium-5 w/o chromium-1 w/o molybdenum) has been selected to receive radiation tests. Triplicate specimens of the alloy will be irradiated at 280 and 600 C for a minimum total burnup of 1 a/o.

In order to round out the knowledge of the alloy selected for irradiation, a program of backup work has been undertaken. Linear-thermal-expansion and thermal-conductivity measurements at temperatures to 1600 F are to be made.

Compartmentalized Fuel Elements

S. J. Paprocki, D. L. Keller, and G. W. Cunningham

In the program concerned with the development of cermet-type fuel elements, fabrication studies as well as corrosion tests are being continued.
To determine the corrosion resistance of the six combinations being studied (U$_3$Si, U$_6$Ni, U$_2$Ti or UC in Zircaloy 2 and UC or UN in stainless) in NaK, a 500-hr test at 680 F is in progress at this time. Preliminary tests of the corrosion resistance of these combinations in 680 F degassed water was reported last month. Additional specimens are now being prepared for supplementary tests.

Fabrication studies have continued in an effort to improve the structure of the U$_2$Ti-Zircaloy 2 element. Although an ideal dispersion has not yet been obtained, an element containing a fairly uniform dispersion and good core-to-cladding bond was obtained by roll cladding at 1400 F and using U$_2$Ti which had been previously heat treated at 1470 F to form a homogeneous structure.

**CORROSION**

**Mechanism of Uranium Corrosion**

J. B. Schroeder, C. M. Schwartz, H. D. Hannan, P. D. Miller, R. S. Peoples, J. W. Moody, R. K. Willardson, and H. Goering

As part of a long range program to develop improved reactor fuel elements, the mechanism of aqueous-uranium corrosion is being studied.

To determine whether or not sample preparation is responsible for the wide variations in the corrosion rate of uranium below 100 C, a series of samples is being run in boiling deionized water. The parameters under investigation are (1) the amount of electropolishing, (2) the length of time the sample is exposed to air between electropolishing and testing, and (3) the temperature at which the sample was exposed to air. To prevent excessive air oxidation, the pressure was reduced before the samples were heated. All of the samples were abraded through 600-grit papers. The samples were from center-cut ingot material which was alpha rolled approximately 75 per cent. The time in test was 20 hr. The results obtained to date are listed in Table E-3. No noticeable difference appears among samples given three different treatments, while the samples heated to 500 C in vacuo show slightly lower rates.

Prolonged anneals are in progress to produce very coarse-grained uranium samples for study of the epitaxy relations of the corrosion film.
Samples of UO₂, which would undergo spontaneous air oxidation to UO₂₄, are being tested in 85°C water. The object of these tests is to determine whether or not water will oxidize UO₂. The first oxide sample has been in test 40 days.

### TABLE E-3. CORROSION RATES OF URANIUM IN BOILING WATER

<table>
<thead>
<tr>
<th>Sample</th>
<th>Treatment</th>
<th>Corrosion Rate, mg/(cm²-h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>76</td>
<td>None</td>
<td>3.04</td>
</tr>
<tr>
<td>77</td>
<td>None</td>
<td>3.05</td>
</tr>
<tr>
<td>78</td>
<td>Electropolished 5 min</td>
<td>3.48</td>
</tr>
<tr>
<td></td>
<td>(current density, 1.6 amp per cm²)</td>
<td></td>
</tr>
<tr>
<td>79</td>
<td>Ditto</td>
<td>3.22</td>
</tr>
<tr>
<td>80</td>
<td>Electropolished 3 min</td>
<td>3.02</td>
</tr>
<tr>
<td>81</td>
<td>Ditto</td>
<td>3.02</td>
</tr>
<tr>
<td>82</td>
<td>Heated for 2 hr at 500°C in vacuum (5 × 10⁻⁵ mm)</td>
<td>2.50</td>
</tr>
<tr>
<td>83</td>
<td>Ditto</td>
<td>2.11</td>
</tr>
</tbody>
</table>

Studies of the uranium-water reactions in wet-argon atmospheres are being continued. The chemical reactions are followed by measurements of the amount of hydrogen evolved and the amount of uranium consumed. The initial tests have been directed toward finding the relationship between the corrosion rate and the composition of the uranium sample. Tests have been made with Du Pont Slugs, dingot grade, and zone-melted dingot-grade materials. Table E-4 summarizes the corrosion rates measured. Most tests were run for 4 hr and approximately linear rate curves were obtained. The good agreement between the values based on the hydrogen evolved, compared with those for the weight loss, indicates that the equation U + 2H₂O → UO₂ + 2H₂ may be valid at this temperature. The results also show that the corrosion rate for the dingot material is less than for the slug material which was less pure.

In order to correlate the results obtained by this technique with those for liquid-water tests, a series of experiments is being run in boiling water.
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E-9

TABLE E-4. URANIUM-WATER CORROSION RATES AT 200 C

<table>
<thead>
<tr>
<th>Test</th>
<th>Material</th>
<th>Corrosion Rate, mg/cm² (hr) Based on Hydrogen</th>
<th>Based on Weight Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>Slug</td>
<td>70.9</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>Slug</td>
<td>76.7</td>
<td>74.3</td>
</tr>
<tr>
<td>10</td>
<td>Dingot</td>
<td>62.8</td>
<td>47.5</td>
</tr>
<tr>
<td>12</td>
<td>Dingot</td>
<td>58.5</td>
<td>54.4</td>
</tr>
<tr>
<td>14</td>
<td>Zone melted</td>
<td>48.3</td>
<td>46.0</td>
</tr>
<tr>
<td>16</td>
<td>Zone melted</td>
<td>50.7</td>
<td>49.4</td>
</tr>
</tbody>
</table>

Spectrographic and metallographic analyses have been obtained on the ingot of uranium zone melted during the month of June. It will be recalled that the ingot was contained in a high-purity alumina boat and was zone melted under argon at a high ambient temperature.

Metallographic examination of several specimens from the zone-melted ingot indicated a slight, if any, segregation of nitrogen to the rear of the ingot. A slight reduction of the hydrogen content was also indicated. However, the carbon content of the ingot was higher after zone melting than before. This is surprising, since care was taken to exclude carbon from the system during the purification process. Evidently, the ingot was contaminated during handling, perhaps from the silicon carbide paper used to clean the surface of the ingot before zone melting. In general, the zone-melted ingot was somewhat cleaner than originally and a very slight difference in inclusions was noticed for specimens cut from various portions of the ingot.

The results of the spectrographic analysis for metallic impurities in the original and zone-melted ingots are listed in Table E-5.

It appears that there is a movement to the rear of the ingot for most metallic impurities. Silicon, iron, and manganese segregate most rapidly under the conditions (2-in. zone at 2 in. per hr) of the experiment. Of particular significance are the results for aluminum. Since the original ingot contained about 10 ppm of aluminum, it is obvious that uranium dissolved aluminum from the alumina boat. The spectrographic analysis indicates that the segregation coefficient of aluminum in uranium is relatively high (but less than 1). Thus, it must be concluded that alumina is not a satisfactory boat material for the zone refining of uranium.

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An investigation of crucible materials for molten uranium carried out at the Argonne National Laboratories (ANL-5149) indicated that sintered uranium dioxide might prove satisfactory for zone refining of uranium. Accordingly, a supply of MCW UO₂ powder has been ordered from which sintered boats will be fabricated.
The Reactor Development Division of the Atomic Energy Commission sponsors a series of closely integrated programs involving zirconium-uranium alloys. Studies are being made on alloys up to 70 w/o uranium.

No new conclusions have been reached on the effects of oxygen and nitrogen on the alpha-plus-beta region of the zirconium-uranium alloys.

The effects of oxygen on the kinetics of transformation of zirconium-rich alloys are to be studied.

Dynamic-modulus measurements indicate that a single mechanism of transformation is operative in the beta-to-epsilon decomposition at 100 to 550 C. These and other experiments are continuing.

The corrosion of zirconium-uranium alloys of various oxygen contents is being continued to longer times.

A new program has begun to develop a corrosion-resistant alloy containing 70 w/o uranium. As a basis for this alloy development, the effects of heat treatment are being re-evaluated, and preliminary phase studies have been made.

Specimens of the zirconium-22 w/o uranium alloy having various heat treatments are at the MTR for irradiation. Plans are also being made for the study of zirconium-50 and 70 w/o uranium alloys.

**Constitution of Zirconium-Uranium Alloys**

R. F. Dickerson and A. A. Bauer

An investigation to determine the limits of the alpha-plus-beta region of the zirconium-uranium system is being made by quantitatively studying alloys containing oxygen and nitrogen with the aim of extrapolating these ternary data back to the binary system.

Quantitative measurements have been made of the phases present in a series of alloy specimens containing various amounts of oxygen and nitrogen. X-ray and chemical composition data are also being obtained for use in the final mathematical analysis of the system.
A number of the alloys containing fairly large amounts of nitrogen were found to be segregated, the segregation probably taking place during casting. Succeeding fabrication and heat treatment was insufficient to produce homogeneous alloys. As a result, additional alloys are being prepared with more limited nitrogen contents.

Transformation Kinetics and Hardening Reaction of Zirconium Alloys Containing up to 20 w/o Uranium
D. L. Douglass, L. L. Marsh, and G. K. Manning

The transformation kinetics of zirconium–uranium alloys appear to be sensitive to the oxygen content of the base metal. Oxygen levels of 0.1 and 0.3 w/o are to be investigated so that heat treatments of sponge-base metal and slightly contaminated alloys will be better understood.

Attempts are under way to find suitable heat-treating liquid media that neither dissolve, react with, or contaminate the specimen. Preliminary work indicated that silver will be satisfactory for solution treating at 1000 C for times up to 1 hr. The most promising isothermal bath at 550 C appeared to be a lead–12 w/o antimony eutectic. Other metals tested were lead, lead–62 w/o tin, lead–65 w/o bismuth, antimony–9 w/o zinc, and tin–40 w/o antimony.

The quenching dilatometer will be used in conjunction with metallography to determine the TTT curves.

Transformation Kinetics of Zirconium Alloys Containing 20 to 70 w/o Uranium
R. R. Dickerson, F. A. Rough, and A. A. Bauer

A study of the kinetics of the beta-to-epsilon transformation in alloys containing 20 to 70 w/o uranium is being conducted. Emphasis in this study is being placed on the zirconium–50 w/o uranium alloy.

Electrical-resistivity measurements made on a specimen aged at room temperature show that transformation occurs at room temperature at a slow but measurable rate. The resistivity was found to have increased by 1.08 per cent over a 24-day period.

Meanwhile, X-ray examination of a 50 w/o uranium specimen during transformation in a high-temperature X-ray camera has been completed.
The films obtained are being analyzed. Additional specimens have been heat treated for study in the X-ray spectrometer.

Dynamic-modulus measurements have been completed on a series of heat-treated samples of the 50 w/o uranium alloy. From these measurements, a transformation-rate curve has been established showing the percentage of transformation produced by a heat treatment of 1 hr at temperatures ranging from 100 to 350 C. When plotted versus the reciprocal of absolute temperature, the percentage of transformation appears as a straight line on probability paper. These data indicate a single mechanism is operative in the beta-to-epsilon decomposition over the complete range of temperatures investigated. Additional modulus measurements are planned in order to complete the rate studies.

Resistivity measurements during transformation are also planned.

Corrosion of Zirconium-Uranium Alloys

W. E. Berry and R. S. Peoples

A part of the AEC Reactor Development Division program is a study of the corrosion behavior of potential fuel alloys of uranium-zirconium. Corrosion tests are being conducted in static degassed high-purity water at 500, 600, and 680 F. The alloys being studied contain 7 through 70 w/o uranium additions to crystal bar, sponge, and high-oxygen (0.3 w/o) sponge zirconium.

Studies designed to determine the effect of water temperature and zirconium melting stock on corrosion behavior of bare alloy samples are now under way. Before corrosion testing, all samples were heat treated 1 hr at 800 C and slowly cooled. After 8 weeks of (1344 hr) exposure, alloys containing 50 plus w/o uranium are corroding at linear rates at all test temperatures. A comparison of corrosion rates for these alloys at the three test temperatures is presented in Table F-1. In general, increasing corrosion rates can be correlated with an increase in test temperature, increasing uranium content, or increasing oxygen content (from the several zirconium melting stocks). Alloys containing 70 w/o uranium were completely oxidized after 7 days of exposure in 600 and 680 F water. Alloys containing less than 50 w/o uranium, particularly those exposed to 500 F water, do not yet exhibit steady corrosion rates after 1344 hr of exposure.

The above tests are being continued.
**TABLE F-1. EFFECT OF TEMPERATURE AND VARIOUS ZIRCONIUM MELTING STOCKS ON THE CORROSION BEHAVIOR OF ZIRCONIUM-URANIUM ALLOYS IN HIGH-TEMPERATURE WATER**

<table>
<thead>
<tr>
<th>Nominal Uranium Content, w/o</th>
<th>Zirconium Melting Stock</th>
<th>Weight Change Rate(^{(a)}), mg/(cm(^2))(hr), After a 1344-Hr Exposure at Temperature Indicated</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>Crystal bar</td>
<td>500 F: -0.002</td>
</tr>
<tr>
<td></td>
<td>Sponge</td>
<td>600 F: -0.004</td>
</tr>
<tr>
<td></td>
<td>Sponge + 0.3 w/o O</td>
<td>680 F: -0.004</td>
</tr>
<tr>
<td>55</td>
<td>Crystal bar</td>
<td>500 F: -0.002</td>
</tr>
<tr>
<td></td>
<td>Sponge</td>
<td>600 F: -0.002</td>
</tr>
<tr>
<td></td>
<td>Sponge + 0.3 w/o O</td>
<td>680 F: -0.004</td>
</tr>
<tr>
<td>60</td>
<td>Crystal bar</td>
<td>500 F: -0.004</td>
</tr>
<tr>
<td></td>
<td>Sponge</td>
<td>600 F: -0.005</td>
</tr>
<tr>
<td></td>
<td>Sponge + 0.3 w/o O</td>
<td>680 F: -0.005</td>
</tr>
<tr>
<td>70</td>
<td>Crystal bar</td>
<td>500 F: -0.004</td>
</tr>
<tr>
<td></td>
<td>Sponge</td>
<td>600 F: -0.005</td>
</tr>
<tr>
<td></td>
<td>Sponge + 0.3 w/o O</td>
<td>680 F: -0.013</td>
</tr>
</tbody>
</table>

\(^{(a)}\) Calculated when rate change became linear with time.
\(^{(b)}\) Gained weight; little weight change over last 1008-hr exposure.
\(^{(c)}\) Completely oxidized within a 168-hr exposure.

**Development of Corrosion-Resistant 70 w/o Uranium Alloys**

F. A. Rough, A. A. Bauer, W. E. Berry, and R. S. Peoples

As part of the zirconium-uranium alloy program, a study aimed at improving the corrosion resistance of the zirconium-70 w/o uranium alloy has been undertaken. Possible approaches to such improvement which are being considered are: (1) heat treatment to produce the most corrosion-resistant stage in the beta-zirconium or gamma-uranium decomposition, (2) ternary alloying to tie up the excess alpha uranium (above that of intermediate-epsilon composition) in the form of a compound or intermediate phase, and (3) ternary alloying to increase the stability and corrosion resistance of the beta-zirconium phase.

The first two approaches have been under active investigation.
In order to tie up the excess alpha uranium in a 70 w/o uranium alloy, it is necessary that the ternary addition form a uranium-rich compound or intermediate phase and that the epsilon phase exist in equilibrium with it. Elements that have been considered for this purpose are iron, molybdenum, nickel, silicon, and titanium.

The phase relationships in the zirconium-uranium-titanium system are known to meet the necessary requirements, and a brief study of the zirconium-uranium-silicon system indicates the necessary phase relations are present in this system, also. However, these conditions are not met in the zirconium-uranium-iron and zirconium-uranium-nickel systems, where alpha uranium apparently exists in equilibrium with one of the zirconium-iron or zirconium-nickel compounds. The phase relationships in the zirconium-uranium-molybdenum system were not apparent, an unidentified phase being observed along with the beta-zirconium and epsilon phases.

On the basis of these data, some small experimental melts of the zirconium-70 w/o uranium alloy with molybdenum, silicon, or titanium additions have been prepared and heat treated for a preliminary look at the effectiveness of these additions in improving corrosion resistance.

Meanwhile, a study of the effect of various heat treatments on the corrosion resistance of the binary zirconium-70 w/o uranium alloy has been under way. Corrosion tests are being conducted in 680 F degassed high-purity water. Specimens tested have received the following heat treatments:

(1) 1 hr at 800 C, water quench
(2) 1 hr at 800 C, furnace cool; anneal 96 hr at 650 C, furnace cool to 625 C, hold 25 hr, furnace cool
(3) 1 hr at 800 C, water quench; 10, 1,000, 100,000 sec at 400 C, water quench
(4) 1 hr at 800 C, water quench; 10, 1,000, 100,000 sec at 500 C, water quench
(5) 1 hr at 800 C, isothermally transform 10, 1,000, 100,000 sec at 400 C, water quench
(6) 1 hr at 800 C, isothermally transform 10, 100, 1,000 100,000 sec at 500 C, water quench.

With two exceptions, all the above samples were completely oxidized or cracked within a 4-day exposure in 680 F water. The samples which
were isothermally transformed 100 and 1000 sec at 500 C corroded at a uniform linear rate of minus 0.70 mg/(cm²)(hr) and exhibited corrosion life of 33 to 37 and 22 to 26 days, respectively. These are the first zirconium-70 w/o uranium alloys in the Battelle program to withstand more than 7 days of exposure in 680 F water. The above results indicate: (1) that at this composition level retained beta is not corrosion resistant, (2) that essentially complete transformation of beta results in the formation of sufficient alpha uranium to destroy corrosion resistance, and (3) that in a partially transformed condition, probably representing epsilon supersaturated with uranium, the alloy exhibits its best corrosion resistance. The reasons for the apparent dependence of corrosion resistance on the temperature and mode of transformation are unknown at present.

Radiation Stability of Zirconium-Uranium Alloys

A. W. Hare, A. E. Austin, A. A. Bauer, and R. F. Dickerson

Work is progressing on the radiation-effects program for 22, 50, and 70 w/o uranium-zirconium alloys. Specimens of each alloy will be irradiated to total burnups of 2 a/o and at temperatures of approximately 450 C and 650 C.

Nine specimens of 22 w/o uranium-zirconium alloy representing three different heat treatments have been shipped to the MTR and are being irradiated in NaK-filled capsules. Three specimens of the same alloy, representing the three different heat treatments, will be encapsulated in a temperature-controlled capsule and shipped to the MTR during August, 1956.

The melting and fabrication of zirconium-50 and 70 w/o uranium alloy specimens for the irradiation tests has been initiated. It is planned to study the effect of beta grain size on the radiation stability of the zirconium-50 w/o uranium alloy. A limited heat-treating and fabrication study is being made for the purpose of achieving maximum grain refinement of the beta grain size. The effects of heat treatment on the 70 w/o uranium alloy are also being studied.

The fission-gas-analysis apparatus has been designed and assembly and testing of the equipment will begin as soon as all of the component parts have been delivered. The capsule-opening device which has been designed to contain fission gases and products is currently being constructed and will be completed by September, 1956.
G. CORROSION STUDIES OF ZIRCONIUM

R. S. Peoples

The AEC Reactor Development Division program concerned with the corrosion behavior in high-temperature water and steam of zirconium and zirconium alloys is described in this section.

Long-time corrosion tests are being continued on zirconium, Zircaloy 2, and modified Zircaloy 2 compositions in 600 and 680 F degassed water and 750 F steam. Data based on up to 46 months of exposure indicate that Zircaloy 2 is an excellent cladding material. Considerable amounts of hydrogen, nitrogen, and oxygen can be tolerated before corrosion properties are seriously impaired. Modified Zircaloy 2 compositions (lower tin, 0.25 to 0.5 w/o) continue to exhibit good resistance to high-temperature water and steam.

Studies concerned with the reaction kinetics of zirconium with water vapor at atmospheric pressures and with determining the rate of hydrogen in the corrosion of zirconium in high-temperature water have been completed.

Corrosion of Zirconium and Zirconium Alloys

W. K. Boyd and R. S. Peoples

Long-term corrosion studies to determine composition variables which affect the corrosion behavior of zirconium-base alloys are being continued. Samples of binary zirconium-tin, zirconium-iron, and zirconium-nickel alloys, and Zircaloy 2 and modified Zircaloy 2 compositions are being studied in 600 and 680 F degassed water and superheated steam (750 F, 1500 psi).

Specimens representing seven different melts of Zircaloy 2 continue to exhibit a dark tarnish film and corrosion rates of about 5 mg/(dm^2)(month). There has been no indication of transition or breakaway after 46 months of exposure to 600 F degassed water.

Data based on approximately 13 months of exposure show that the corrosion resistance of Zircaloy 2 is not affected by hydrogen additions in the range 500 to 1500 ppm. Similar results have been observed for Zircaloy 2 containing up to 6000 ppm oxygen. However, with oxygen contents in excess of 6000 ppm, corrosion resistance is impaired. Nitrogen additions of
less than 200 ppm do not significantly affect corrosion rates, whereas levels above 200 ppm destroy resistance to high-temperature water and steam.

Zirconium Corrosion Committee
Program

Studies guided by the Zirconium Corrosion Committee program to develop new zirconium alloys with properties superior to Zircaloy 2 have been continued. Sponge-base ternary and higher order alloys containing combinations of iron, nickel, and tin in the range of from 0.04 to 0.50 w/o (total alloy content 1 w/o or less) are being evaluated in 680 F water and 750 F steam. After an additional 1 month of exposure (total, 13 months), weight-gain data are similar to those reported in Tables G-1 through G-3 of BMI-1104. The following trends have been observed:

(1) In general, tin-nickel alloy combinations exhibit somewhat better corrosion resistance to 750 F steam than do alloys containing equivalent additions of tin and iron. The reverse, however, is true for 680 F degassed water.

(2) Vacuum heat treatments based on a slow cool from 775 C or a water quench from 900 C have little or no significant effect on the corrosion behavior of the tin-iron or tin-nickel alloys under investigation.

(3) A progressive decrease in corrosion resistance has been observed for zirconium-0.25-0.5 w/o tin-0.25-0.5 w/o iron alloys with increasing nitrogen content in the range from 70 to 300 ppm.

(4) Ternary and quaternary tin-iron-nickel alloys containing 200 ppm aluminum are not so resistant as those containing lesser amounts.

Effect of Heat Treatment

Binary zirconium-iron and zirconium-nickel alloys exhibit best corrosion behavior to 750 F steam if their microstructures are composed of a fine dispersion of compound particles in an alpha matrix. Structures containing large colonies of compound particles separated by alpha platelets are noticeably less resistant. Observations are based on 11 months of exposure.

Corrosion studies are being continued on all phases of the program.
H. REACTOR MATERIALS DEVELOPMENT

H. A. Sailer

A number of programs on the development of materials for general reactor application are sponsored by the Reactor Development Division of the Atomic Energy Commission and Argonne National Laboratory.

In the development of aluminum phosphate enamels for uranium, emphasis is being placed on the reduction of crazing and improvement of the thermal-shock resistance of these coatings.

A number of experiments are being continued to study the zirconium-UO$_2$ reaction at temperatures of 950 to 1600 F.

A higher rate of vapor deposition of molybdenum on stainless steel tubing has been obtained by hydrogen reduction of molybdenum pentachloride. Purified molybdenum pentachloride is being prepared for additional experiments intended to improve the quality of the molybdenum coatings.

The development of oxidation-resistant niobium alloys is also continuing. Research is now directed toward further understanding of the oxide scale. Binary alloys which have shown promise are being evaluated further, and a program of ternary alloying is planned.

The constitution of uranium-titanium alloys with up to 6 w/o titanium is being re-evaluated.

Enameling of Special Metals

B. W. King, M. C. Brockway, and E. D. Dietz

Coatings of porcelain enamels are being investigated for application to uranium. Such coatings might serve both as thermal and diffusion barriers, and for protection against corrosion.

The phosphate coatings developed in past work often crazed when applied at thicknesses of from 5 to 10 mils. To reduce crazing and improve thermal-shock resistance, primary interest this month was directed to the application of thin, partially devitrified coatings. If such coatings could be developed, they would be expected to provide good resistance to thermal cycling and, despite relative thinness, to function effectively as thermal and diffusion barriers.
Initial efforts to produce partial devitrification were made by attempting to exceed the solubility of uranium oxide in the enamel during the firing cycle. Soda-lead-silicate enamels containing calculated UO$_2$ contents ranging from 5 to 20 w/o were used. Attempts to devitrify these coatings by increasing the firing time and/or reducing the coating thickness were not successful.

Next month, other approaches will be tried to produce a thin, partially devitrified coating on uranium. Also, specimens of zirconium coated with enamels developed in prior work on this program will be evaluated in thermal-cycling tests.

**Kinetics of the Zirconium-Uranium Dioxide Reaction**

M. W. Mallett, J. W. Droge, A. F. Gerds, and A. W. Lemmon

Fuel elements composed of UO$_2$ clad with zirconium are being considered for reactor use. The compatibility of zirconium and UO$_2$ is being studied in the temperature range of 950 to 1600 F by means of sandwich-type elements in which a plane face of zirconium is in intimate contact with a plane face of UO$_2$.

The data obtained should aid in predicting the useful life of the elements in service.

The heating of the thin-walled zirconium-UO$_2$ elements at 950, 1100, and 1200 F in autoclaves is continuing. It is anticipated that the 1200 F tests will be terminated in August. The large element from this test then will be machined into thin layers and each layer will be analyzed for uranium and oxygen to determine the transfer of these elements to the zirconium jacket.

Oxygen analyses obtained on thin layers in the zirconium of an element heated at 1450 F for 495 hr appeared erratic and showed poor agreement with the uranium analyses. Additional samples will be machined from the other end of this element in an attempt to obtain agreement.

The heating of the 1600 F element for 500 hr has been started. The walls of the large element used in this experiment were reduced from 1/8 to 1/16 in. and the dead load on the element increased from 370 to 720 psi. This was done in an attempt to maintain the desired intimate contact and minimize the formation of the voids at the interface as the reaction proceeds.
The analytical data obtained previously from a large element heated for 95 hr at 1600 F were considered from the viewpoint of diffusion of oxygen into zirconium.

A model was assumed which approximates the actual observed conditions. Equations representing this model were found. They described the diffusion from a constant initial concentration through a first region and past a boundary into a second region of unlimited thickness. This first region corresponds roughly to the two-phase area adjacent to the UO\textsubscript{2} and the thin uranium-rich phase. The second region corresponds to the oxygen-diffusion-affected and unaffected zirconium-phase base metal. Using a portion of the experimental data, constants in the equations were evaluated. The computed numerical values for oxygen concentration versus distance of penetration approximate the curve found experimentally. Although the model is probably not sufficiently valid to permit the evaluation of reliable diffusion constants or distribution coefficients, comparison with the diffusion constant for oxygen in Zircaloy 2 indicates that the uranium-rich layer (considered as part of the first region) acts as an effective diffusion barrier.

The 500-hr 1600 F experiment now in progress should help to clarify this point. In addition, an experiment will be set up in which a 1-mil piece of uranium foil will be used to separate the zirconium from the UO\textsubscript{2}. This should aid in determining the role that uranium plays as a barrier for the diffusion of oxygen.

**Vapor Deposition of Molybdenum Coatings on Stainless Steel Tubing**

C. F. Powell and I. E. Campbell

As part of a program of assistance to Argonne National Laboratories, Battelle is developing processes for vapor depositing molybdenum coatings on small-bore Type 304 stainless steel tubing.

Previous work was concerned with the deposition of molybdenum on the outside of 0.1835-in.-diameter tubes by the pyrolysis of molybdenum hexacarbonyl at reduced pressure, and by hydrogen reduction of molybdenum pentachloride at reduced pressure. Coatings of uniform thickness were applied to 20-in. lengths of tubing by the carbonyl decomposition process, but the coatings were of nonuniform quality, tending to be brittle, and the deposition rate obtained in the apparatus available was very low, of the order of 0.01 to 0.02 mil per hr. The coatings obtained by reduction of molybdenum pentachloride in this same apparatus were brittle, nonadherent, and very nonuniform in thickness.
During the past month, specimens were coated in the new, enlarged coating unit (intended to be the prototype of a production-scale coating unit). Molybdenum pentachloride also was purified by vacuum sublimation.

The enlarged coating unit consisted of a stainless steel chamber 24 in. long by 12 in. in diameter. The specimen (or specimens) of tubing was suspended along the axis of the chamber and heated by its own resistance. The coating atmosphere was injected at the midpoint of the chamber and exhausted at either end of the chamber. The size and shape of the chamber and the method of injecting the coating atmosphere were designed to provide a flow of fresh coating atmosphere to all parts of the specimen, and thus insures coating uniformity.

Specimens of tubing, coated by hydrogen reduction of molybdenum pentachloride in this apparatus, at a temperature of 900°C and a total pressure of 4 mm mercury, received coatings varying in thickness by 25 per cent from end to midpoint of a 19-in. length. Coating uniformity probably can be further improved by a slight modification of the method of vapor injection. The coatings were brittle and nonadherent, probably because of insufficient purification of the coating atmosphere. A deposition rate of 0.2 mil per hr was obtained.

Molybdenum pentachloride was purified by fractional vacuum sublimation. However, the yield of purified material was too small for a satisfactory deposition run.

During the coming month, larger amounts of molybdenum pentachloride will be purified and molybdenum will be deposited therefrom using purified hydrogen.

Oxidation-Resistant Niobium Alloys

W. D. Klopp, C. T. Sims, and R. I. Jaffee

This project is an extension of work carried on during fiscal 1956 for the AEC Research Division. The objective is to study the oxidation and contamination of niobium by oxygen or air above 600°C, and the effects of various alloying additions on these reactions. Two topical reports are now being prepared, covering the work of the previous year. One report describes the oxidation and contamination of pure niobium; the second describes the effects of fifteen binary additions upon these reactions.

During the first year's work, niobium was found to oxidize linearly in both oxygen and air in the range 600 to 1200°C, forming Nb2O5 as the major scale. The reaction rate was less in air than in oxygen. Contamination was
found to occur by oxygen diffusion, and the "contamination rates" were similar in both oxygen and air. Four alloying additions were found to markedly improve the oxidation resistance of niobium. These were chromium, molybdenum, titanium, and vanadium. Titanium was also very effective in reducing contamination.

During the month of July, results were obtained from X-ray diffraction patterns made on the gray-white scale from a pure niobium rod oxidized in a 0.1-atm pressure of oxygen at 800°C, and also on the thin black subscale which adhered to the metal. The gray-white scale, which was protective when formed under these conditions, has been identified as the low-temperature modification of Nb₂O₅. (Brauer* reported that this form of Nb₂O₅ is stable between 500 and 900°C, while the middle- and high-temperature modifications, which differ only in cell dimensions, are stable at 1000 and 1100°C, and above 1100°C, respectively.) The diffraction patterns on this gray-white scale were difficult to interpret, and it was not possible to determine the oxide crystal structure. No conclusions as to the composition or structure of the adherent black film could be drawn from the X-ray pattern taken. An additional pattern will be obtained from a powder sample of this film.

Additional binary alloys of niobium with chromium, molybdenum, titanium, and vanadium are now being prepared by arc melting to provide further information on optimum concentrations for oxidation resistance. Ternary alloys of these four elements with niobium are also being prepared for oxidation testing at 600, 800, and 1000°C, as described in detail previously.

Tests will also be conducted on pure niobium in dry and wet air, as it appears from available data that moisture has a significant effect on the oxidation rates. In order to evaluate more fully the effects of various alloying additions on the oxidation behavior of niobium, constant weighing tests will be conducted on selected alloys, and X-ray diffraction patterns made on the alloy scales. The fabricability and mechanical properties of the more oxidation-resistant alloys will be studied at room and elevated temperatures.

**Uranium-Titanium Alloy Studies**

D. L. Douglass, L. L. Marsh, and G. K. Manning

The uranium-rich portion of the uranium-titanium system is being investigated so that the martensitic and eutectoid reactions may be understood and applied to the heat treatment of uranium-titanium alloys.

A redetermination of the phase diagram from 0 to 6 w/o titanium is being carried out by dilatometry, inverse-rate and differential thermal analysis, hot hardness, and metallography. Equipment is currently being adapted for the thermal analysis. Alloys containing 0.5, 1, 2, 3, 4, 5, and 6 w/o titanium are being melted and fabricated.

A topical report for work performed during the past fiscal year has been completed.
A number of basic programs in the broad field of materials, including ceramics, metallurgy, and gas-metal studies, are sponsored by the Research Division of the Atomic Energy Commission.

In the study of properties of uranium compounds, emphasis is currently on methods of preparation. Studies of the kinetics of reaction of various compounds with oxygen and nitrogen and of thermodynamic properties will begin at some future time.

Study of the tensile transition in uranium is being continued. This basic study is being broadened to include other materials, such as zinc.

Investigations of constitutional diagrams include the uranium-carbon and various uranium ternary alloys.

In the program on bonding fundamentals, surface condition has been found to be important. Reasonably consistent results have been obtained both by annealing and by electropolishing. Mechanically polished surfaces yielded variable results.

A study of niobium-gas reactions is being initiated. Kinetics of reaction of hydrogen and nitrogen with niobium are to be determined, as well as other physical data.

Properties of Uranium Compounds

L. D. Loch, M. J. Snyder, A. W. Lemmon, and M. W. Mallett

This research is to determine fundamental properties of refractory binary compounds of uranium. These materials have possible utility as nuclear fuels.

Preparation of sintered compacts for physical-property measurements was continued. Also, two new phases of the program were initiated: (1) a study of reactions between the uranium compounds and common gases, and (2) measurements of the thermodynamic properties of the compounds.

Because of difficulties previously encountered in preparing USi\textsubscript{2} and USi\textsubscript{3}, much of the work this month has been directed toward the improvement of the methods of preparation.
Although the literature indicates that cold, dilute H$_2$SO$_4$ is nonreactive with the uranium silicides and nickelides, tests showed that the silicides and UNi$_2$ are attacked rapidly. U$_4$Ni was attacked only very slowly. Hence, acid washing cannot be used to remove iron and, accordingly, steel balls cannot be used in milling. Tungsten carbide was selected as an alternative grinding medium. Further tests showed that finer initial crushing (through 30 mesh) permitted ball milling to a satisfactory fineness in much shorter times than used previously. Chemical analyses are being made of samples milled under these conditions.

Several sintered silicide shapes broke while being machined for thermal-conductivity and thermal-expansion tests. Some of these showed dark inclusions, possibly caused by intergranular oxidation or nitriding during sintering. Meanwhile, plans are being made to improve the sintering through use of a higher purity argon atmosphere. Additional sintered powder compacts of USi$_2$ and USi$_3$ are being machined, and compacts of U$_3$Si$_2$, USi, UNi$_2$, and UAl$_2$ are ready for sintering.

Additional attempts to form UB$_2$ and UB$_4$ by sintering stoichiometric mixtures of the elements in high vacuums are planned, since initial attempts at a pressure of 10 $\mu$ were unsuccessful. Additional experiments are also planned on the preparation of uranium carbides.

Attempts were made to purify carbon-contaminated US, prepared by carbon reduction of UO$_2$, by firing in hydrogen having a dew point of minus 30 C. Carbon contamination was markedly reduced, but some oxidation resulted. US will be prepared by another process.

A new batch of mixed uranium nitride ($UN_x$, $x>1$) powder was prepared by reacting ammonia with uranium powder from the hydride. This will be used in further attempts to sinter UN.

Studies of the reactions between the uranium silicides and oxygen or nitrogen will begin next month. This will be a qualitative study of the kinetics of the reactions. The reaction rates at different temperatures will be measured by the weight gain of the sample or by metering the amount of gas taken up as a function of time.

The thermodynamic research will begin with a measurement of the heat of formation and the heat capacity of USi$_2$. These data will permit calculation of the free energy of formation of USi$_2$ and will provide good estimates of this quantity for the other silicides and, possibly, for the borides as well.
Investigation of the Tensile Transition in Alpha Uranium

L. L. Marsh and G. K. Manning

The tensile transition in alpha uranium is being studied in an effort to determine the mechanism producing the change from a shear-type to a semicleavage-type fracture. Metallographic observation of deformation markings produced in tension at various temperatures from -75 to 200 F has shown that slip lines become finer and the amount of twinning increases as the temperature is reduced from 200 F. It has also been observed that grain size and grain orientation appear to influence both the type of deformation process within the grains and the relative abundance of slip and twinning. In general, the larger the grain size the greater is the probability for finding inhomogeneous deformation, i.e., grains deforming entirely by slip or by twinning.

During the current fiscal year, effort will be directed toward further clarification of the deformation mechanisms involved in the tensile transition in uranium. Also, parallel studies will be conducted on high-purity zinc in order to ascertain the generality of conclusions reached on uranium. Zinc has a tensile transition in the same temperature range and can thus provide data for comparison. In addition, uranium containing various quantities of carbon will be prepared to determine the effect of carbon on the tensile transition. The study of the effect of additions of oxygen and nitrogen will be started at a later date.

Constitutional Diagrams of Uranium Alloys

F. A. Rough

A concentrated effort is being made on the constitution of a limited number of uranium systems. Included in this effort are a re-evaluation of the uranium-carbon system by high-temperature X-ray diffraction and a study of a few important uranium ternary systems.

High-Temperature X-Ray Diffraction
Studies of the Uranium-Carbon System

W. B. Wilson, A. E. Austin, and C. M. Schwartz

Direct investigation of the uranium-carbon phase diagram utilizing high-temperature X-ray diffraction will be performed to evaluate the existing phase diagram.
Initially it is intended to investigate at high temperatures the region between UC and UC₂, studying phase fields and, if possible, solubilities of uranium and carbon in the stoichiometric compounds.

Preliminary work during July involved sample preparation, specifically the preparation of arc-melted buttons of nominal UC and UC₂ compositions. These will be powdered and sintered to form samples suitable for X-ray diffraction study. Intermediate compositions between UC and UC₂ will be obtained by mixing powder and sintering. It is anticipated that some difficulty may be encountered in sintering the small samples required.

Preliminary tests have been started, to evaluate the fabrication difficulties and also to determine the effect of the high-temperature diffraction-camera atmosphere on these samples, since there is present a small but finite partial pressure of hydrocarbon.

Uranium-Base Ternary Alloys

R. F. Dickerson and A. A. Bauer

An investigation to determine the phase relationships which occur between the intermediate delta phases of the uranium-zirconium and uranium-molybdenum systems has begun. It is planned to enlarge this program in the future to include a study of the phase relationships in the uranium-rich portions of the uranium-zirconium-iron, -nickel, and -silicon ternary systems.

Alloys for this study, ranging in composition from uranium-52 w/o zirconium to uranium-15 w/o molybdenum have been prepared by arc melting crystal-bar zirconium, biscuit uranium, and high-purity molybdenum sheet. Specimens are being removed for thermal analysis, and the remaining arc-melted bars are to be fabricated for metallographic and X-ray studies.

Study of Bonding Fundamentals

J. B. Melehan, F. C. Holden, H. R. Ogden, and R. I. Jaffee

Experiments have continued in the study of factors operative in the solid-state bonding of metals. In this month's work, emphasis has been placed on microscopic-scale bonding in which gold needle points are bonded to flat gold surfaces.
Of significance has been the effect of the surface condition of the flat specimen, both on experimental reproducibility and on bond strength. When gold needles were bonded to mechanically polished surfaces of annealed gold, high bond strengths were obtained, with large scatter in bond-strength values. However, when the mechanical polishing was followed by an anneal, variance in strength values was appreciably diminished. Bond strengths were also much lower. For example, when the bonding surface was mechanically polished, bond-strength values for 60-min tests at 400°C varied between 0.2 and 1.0 g. When the bonding surface was annealed, bond strengths under the same experimental conditions occurred in the range 0.1 to 0.4 g. An electropolished surface was also used, and results were comparable to those obtained by annealing, occurring in the range 0.2 to 0.5 g.

It appears that there is a distinct dependence of bonding characteristics on the condition of the bonding surfaces. It is not possible to control surface condition by mechanical polishing methods. The amorphous or smeared surface layer is probably nonuniform in structure; hence, the poor reproducibility. The cold-worked surface can be eliminated either by annealing, which recrystallizes the smeared layer, or by physical removal with electropolishing. In this condition, there has been no noticeable dependence of bond strength upon applied load and time of load application.

To this point, the effect of surface condition has been observed qualitatively. Immediate future work will continue in the systematic study of cold work on bond strengths. Plans are to cold work the flat gold specimen in measured degrees and observe the dependence of bond strengths on cold work.

Niobium-Gas Reactions

M. W. Mallett, W. M. Albrecht, and A. Levy

As part of the program for the Research Division of the AEC, a study of the kinetics and mechanism of the reactions of niobium with hydrogen and nitrogen is being initiated. Determination of the rates of diffusion of hydrogen and nitrogen in niobium is also included in the study.

The kinetics of the niobium-nitrogen reaction will be investigated at a 1-atm pressure of nitrogen in the temperature range of about 500 to 1400°C. A microbalance (gravimetric technique) and/or Sieverts apparatus (manometric technique) will be used. From the kinetic data, an equation for the variation of rate constant with temperature will be derived and an activation energy for the reaction evaluated.
The properties of the reaction films will be studied by means of X-ray and metallographic techniques. Also, semiconductor properties will be determined: i.e., whether the protective films are either n- or p-type semiconductors and what the identity of the diffusing species is. The pressure dependency of the reaction will be investigated at nitrogen pressures of 1, 1/2, 1/4, and 1/8 atm at two temperatures.

The diffusion coefficients for nitrogen in niobium will be determined in the temperature range of about 800 to 1400 C by the use of the concentration-gradient technique. From the data obtained in the diffusion study, terminal solubilities of nitrogen in niobium will be calculated.

The techniques for the study of the niobium-hydrogen reaction will be similar to those for the niobium-nitrogen reaction. Reaction rates will be determined in the range of about 100 to 1000 C, using the microbalance and/or Sieverts apparatus.

In order to initiate this study, 3 kg of niobium metal is being ordered from Fansteel Metallurgical Corporation. An investigation of reports of high-purity niobium being produced in Germany shows that it is produced only in very small quantities and that the Fansteel material is probably equal or superior to any mass-produced Continental niobium. Also, an effort is being made to obtain a reputedly excellent grade of niobium produced in Great Britain.
Studies of flow in models of the thermal-shield region and of the upper-plenum region of the PWR are being continued. It has been found that flow distribution changes in the thermal-shield region as flow is varied. Instrumentation of the upper-plenum region is being completed in preparation for flow studies.

The work on modified uranium dioxide materials has been completed, and is summarized in this report.

Air-Flow Studies on PWR Pressure Vessel

H. R. Hazard and L. J. Flanigan

To provide design data for the Westinghouse PWR reactor, Battelle is conducting flow studies in a quarter-scale model using air flow to simulate coolant flow in the prototype. Work previously reported includes installation of the model with its auxiliary equipment and instrumentation, completion of the study of flow distribution in the core, and work on a study of flow in the thermal-shield region. Studies in a flat-plate model of a section of the thermal shield were started. In July, shield flow studies were nearly completed, work on the flat-plate model of the shield region was nearly completed, and studies in the upper-plenum region were begun.

The study of the flow in the outer passage between the thermal shields, where a flow reversal occurs above the middle operating loop with three loops operating, was completed. Additional yaw tubes were installed through the model flange to obtain data just above the entrance to the shield passage. From complete data analysis, it was concluded that adequate flow velocities for heat transfer occurred throughout the outer-shield passage, including the zone of reverse flow.

Instrumentation was begun on the quarter-scale model in preparation for studies of flow in the upper-plenum region. A preliminary traverse using a hot-wire anemometer to study the flow through the control-rod guides showed that most of the flow passes through the lower third of the control-rod guide length. During this study, it was found that many of the rod guides were loose at the bottom and inaccurately spaced, so the model was disassembled and the guide assembly was repaired. While the model is open, the instrumentation for upper-plenum studies is being completed.

Studies of shield flow in the 1-1/2-scale flat-plate model of a portion of the thermal-shield region have been continued. With the diameter of the
transfer hole from Channel 1 to Channel 2 fixed at 5.25 in., the diameter of the transfer hole from Channel 1 to Channel 3 has been varied from 4 to 6 in. For each configuration test runs were made at four flow rates. Test results show that, as flow through the model was increased by a factor of three, the percentage of total flow passing through Channel 3 increased by about 3 per cent. This occurred with each transfer-hole size. Further analysis of the test data may show the factors involved.

During August, it is expected that two studies will be completed and a third nearly completed. An undrilled baffle plate is to be installed under the core of the quarter-scale model to force all flow through the shield region, permitting shield flow data to be taken at higher Reynolds numbers. This work will be done immediately when the special baffle plate is received. Work on the flat-plate model of the shield region is nearly finished and should be completed early in August. It is also anticipated that studies of flow in the upper-plenum region with the first hold-down barrel will be nearly completed in August.

Modified UO₂ Fuel-Element Cores

D. J. Bowers, W. A. Hedden, and M. J. Snyder

Work on modified UO₂ bodies for the WAPD-PWR program was completed this month. The following summarizes this research.

Improvements in corrosion and thermal-fracture resistance of a UO₂ ceramic were sought through the use of selected additions of beryllia, beryllium, ceria, silica, silicon, silicon nitride, or zirconia. Nuclear considerations dictated that the modified bodies contain at least 80 volume per cent of UO₂ after sintering.

Sound specimens meeting this UO₂-content requirement were made with the beryllia, ceria, silica, or zirconia. These ceramics, with the exception of UO₂-silica, had as good resistance to 650 °F water and 750 °F steam as the unadulterated UO₂ ceramic.

Adding refractory-grade beryllia to the UO₂ powder compacts improved, by a factor of about 1.7, the thermal-fracture resistance of sintered specimens. Readily sinterable beryllia powder did not give this benefit. Variations in sintering treatment appreciably affected the thermal-fracture characteristics of the UO₂-BeO specimens. Minor additions of ceria or titania to UO₂-beryllia powder compacts resulted in increased densities at lower sintering temperatures, but thermal-fracture resistance was not improved through their use.
Dense, strong specimens were made using ceria as the additive to UO$_2$. Ceria was the most effective density promoter during sintering of the major additives studied. UO$_2$-ceria specimens, however, were only slightly better in thermal-fracture resistance than those of UO$_2$ alone.

Zirconia-UO$_2$ combinations had adequate density and strength, but the zirconia had a deleterious effect on the thermal-fracture resistance of UO$_2$.

UO$_2$-silicon cermet specimens had low density and strength, presumably because of the formation of a reaction product. The reaction occurred on sintering in hydrogen, argon, or in a vacuum, and, to a lesser degree, on hot pressing. The reaction product was isolated, but not identified. It was unstable when resintered by itself and with UO$_2$.

Satisfactorily dense and sound sintered compacts were not produced with either beryllium or silicon nitride as the additive.

A topical report covering the work in detail has been prepared and will be issued soon.
K. EVALUATION OF A REFLECTOR-CONTROLLED HETEROGENEOUS BOILING REACTOR

J. W. Chastain

A control system which makes possible long-time unmanned operation of a reactor is being investigated. This system of control makes use of the height of the water reflector surrounding the core. The annular reflector tank is connected to a pressurized surge tank and water is exchanged, depending on which has the higher pressure. Specifically, a drop in the power level reduces the pressure in the reactor which permits water to flow into the reflector tank. This increased reflector height cuts down neutron leakage, tending to drive the power back to its initial value.

With the original analysis completed, two separate experiments are being set up. One of these is a full scale mock-up of the hydraulic system, driven by an electronic reactor simulator. The second is a critical experiment to provide input data for the simulator.

Presently, equipment is being constructed for the hydraulic system. The critical-assembly support table and the core structure are designed and are being constructed.

Critical Experiment

W. S. Hogan, R. F. Redmond, J. W. Chastain, and S. L. Fawcett

The critical experiments are being conducted to determine the range of control and the effectiveness of a movable lateral reflector. In addition, information will be obtained which will permit an evaluation of the transient behavior of the reactor system.

The core will be made up of aluminum boxes 1-1/2 by 1-1/2 by 43 in. long. These boxes will contain aluminum drawers which hold the various strips of material simulating the reactor core. The core boxes are being assembled and the core table will be completed during the coming month. The two source drive units are complete.

The Hazards Summary Report has been completed.
During July efforts on this study have been directed toward completing the pressure-vessel racks. All components required for the mock-up of the control system, except for stock items such as pipe, are on order or have been received.

Delivery schedules on all items except the pressure vessels have not been changed. Because of a breakdown in the manufacturer's equipment, the pressure vessels will not be delivered until the second week in August. This will not appreciably affect the over-all project schedule.

Assembly of the hydraulic system will continue in August.