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PROGRESS RELATING TO CIVILIAN APPLICATIONS DURING JANUARY 1958

By
Russell W. Dayton
Clyde R. Tipton, Jr.

February 1, 1958

Battelle Memorial Institute
Columbus, Ohio

Technical Information Service Extension, Oak Ridge, Tenn.

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BMI-1241	"Comparison of Active and Inactive Uranium Dioxide-Oxygen Systems", by Dale A. Vaughan, J. Robert Bridge, and Charles M. Schwartz.
BMI-1242	"Evaluation of Container Materials for Zircex and Darex Nuclear-Fuel-Recovery Processes", by Paul D. Miller, Charles L. Peterson, Earl L. White, and Frederick W. Fink.
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BMI-1247	"Progress Relating to Civilian Applications During December, 1957", by Russell W. Dayton and Clyde R. Tipton, Jr.

A. DEVELOPMENTS FOR ZIRCONIUM-CLAD FUEL ELEMENTS

F. R. Shober

Test equipment has been designed and constructed to measure the thermal conductivity and electrical resistivity of uranium in zirconium capsules. Calibration of the unit has been completed. An investigation of the effect of irradiation on the thermal conductivity of UO_2 is in progress. The creep and stress-rupture properties of 15 per cent cold-worked Zircaloy 2 are being evaluated at elevated temperatures. Time at test has been extended, greater than 2000 hr, in an effort to evaluate the effect of stress on the total creep deformation at the initiation of third-stage creep.

A sound metallurgical bond has been obtained between 2S aluminum clad and nickel-plated uranium by hot-hydrostatic-pressing techniques. Bonds formed in 5 min at 950 F and 10,000 psi were as strong as those formed under the same temperature and pressure conditions in 1 hr.

An alloy-development program has been initiated in an effort to develop additional high-strength corrosion-resistant zirconium alloys. It is expected that these alloys will have greater strength than Zircaloy 2 and good corrosion life in 570 F water. The initial portion of the program will consist of screening selected alloys by hardness testing and corrosion testing.

Thermal Conductivity of Uranium and UO_2

H. W. Deem and C. F. Lucks

Programs are in progress to investigate the feasibility of making thermal-conductivity and electrical-resistivity measurements on encapsulated uranium and to evaluate the effect of irradiation on these specimens. The effect of irradiation on the thermal conductivity of UO_2 is also being investigated.

Uranium

The apparatus to be used in measuring the thermal conductivity and electrical resistivity of irradiated uranium has been completed and calibrated, and is ready to be moved to the hot cells. Specimens of unirradiated uranium in Zircaloy 2 with NaK as the heat-transfer medium are being prepared at another laboratory, and measurements of thermal conductivity and electrical resistivity will be made on these canned specimens when they are received. Meanwhile additional measurements are being made on bars of Zircaloy 2 and uranium in order to have good values for the component parts of the canned specimen assemblies.

UO_2

An apparatus for making thermal-conductivity measurements on UO_2, both before and after irradiation, has been completed. A steady-state, absolute method is being used. Some reassembly of the apparatus has been necessary and certain heaters have been changed. This has delayed calibration of the apparatus. The modified guard assembly has been completed, and further calibration runs will be made in February.

Mechanical Properties of Zirconium Alloys

F. R. Shober and J. A. VanEcho

An investigation of the creep properties of 15 per cent cold-worked Zircaloy 2 at elevated temperatures is being conducted. The stresses have been selected for determination of long-time creep properties. Two per cent total deformation was the limiting deformation, this being designated as the allowable deformation in the pressure tube under consideration. Modification of the design has caused the limiting deformation to be changed to that deformation associated with the beginning of third-stage creep. Hence the test period has been changed to include determination of that deformation. The effect of stress on the amount of total deformation at third-stage creep will be investigated.

The tests in progress are on 15 per cent cold-worked Zircaloy 2 in the 450 to 650 F temperature range and at stress levels ranging from 15,000 to 40,000 psi. The results of these tests are given in Table A-1. Those specimens on test at 550 and 650 F will be continued in an attempt to establish the time necessary to initiate third-stage creep at these stress levels. Specimen 7-1-1, which was removed from test after 2015 hr, will be brought to temperature again and reloaded at the same stress, for the same purpose. The two tests at 450 F in air will be discontinued and replaced by tests at 750 F and 15,000 psi and 550 F and 40,000 psi in vacuum. Metallographic examination will be made of all test specimens upon completion of the tests.

Zirconium Cladding

F. R. Shober and R. F. Dickerson

Nickel-plated uranium cores, both solid and internally and externally cooled core types sealed in 2S aluminum cans, are being bonded by a hot-hydrostatic-pressing technique. Results from initial tests on solid-core specimens indicate that 5 min at 950 F and 10,000 psi is sufficient to produce sound metallurgical bonds between the aluminum and the nickel-plated uranium.

The solid-core specimens were prepared by fitting the nickel-plated uranium cores in aluminum cans and closing the ends by cold press forging. The internally and externally cooled cores were prepared by sizing the cans to the nickel-plated cores and welding the ends in place. Metallographic examination of specimens cut near the ends and the center of the solid-core specimen pressurized for 5 min and 1 hr at 950 F and

TABLE A-1. CREEP PROPERTIES OF 15 PER CENT COLD-WORKED ZIRCALOY 2

Specimen	Temperature, F	Stress, psi	Time at Test[(a)], hr	Deformation at Time Indicated								Creep Rate[(b)], per cent per hr
				Load On	50 Hr	100 Hr	500 Hr	1000 Hr	1500 Hr	2000 Hr	Load Off	
7-1-2	450	40,000	2500	0.400	0.503	0.512	0.545	0.560	0.567	0.580	--	0.000026
7-1-3	450	30,000	2400	0.280	0.333	0.337	0.350	0.355	0.355	0.355	--	<0.00001
7-2-2	550	35,000	2200	0.353	0.495	0.520	0.595	0.625	0.675	0.692	--	0.000034
7-2-3	550	30,000	2100	0.275	0.375	0.385	0.415	0.440	0.455	0.47	--	0.00003
7-3-1	550	25,000	2275	0.205	0.267	0.282	0.305	0.323	0.33	0.335	--	0.00001
7-3-2	550	20,000	2250	0.178	0.223	0.227	0.245	0.250	0.265	0.265	--	<0.00001
7-1-1	650	30,000	2015.6(c)	0.315	0.537	0.592	0.745	0.875	1.025	1.183	0.882	0.00028
7-2-1	650	25,000	1975	0.230	0.385	0.420	0.510	0.548	0.580	0.612	--	0.000064
7-3-3	650	20,000	2000	0.180	0.300	0.325	0.380	0.397	0.415	0.427	--	0.000024
7-4-1	650	15,000	1100	0.110	0.185	0.205	0.245	0.265	--	--	--	--

(a) Test in progress.

(b) Based on creep deformation between 1500 and 2000 hr.

(c) Test discontinued.

10,000 psi showed a sound metallurgical bond. Slightly greater diffusion of the nickel into the uranium was evident in the specimen held at temperature for 1 hr. The strengths of the bonds produced were evaluated by welding aluminum studs to the cladding and loading in tension until the cladding separated from the core. The stress at which separation occurred was approximately 20,000 psi.

Two internally and externally cooled type specimens will be pressurized at 950 F for 5 min and 1 hr, respectively, at 10,000 psi. The bonds obtained will be evaluated.

Preparation of Aluminum, Molybdenum, and Zirconium Single Crystals

J. A. De Mastry, F. R. Shober, and R. F. Dickerson

This research has been recessed pending receipt of suitable materials.

Development of High-Strength Corrosion-Resistant Zirconium Alloys

J. A. De Mastry, F. R. Shober, and R. F. Dickerson

Considerable study has been made of zirconium and its alloys in connection with its use as a cladding material for fuel elements. A further investigation is being made to develop additional high-strength corrosion-resistant zirconium alloys. The purpose is to develop zirconium-base alloys which will have at least twice the strength of Zircaloy 2 and have good corrosion life in 570 F water. The nuclear properties, thermal conductivity, and thermal expansion coefficient should be similar to those of Zircaloy 2.

From past experience with zirconium alloys, it appears that large additions of any element (except hafnium) to zirconium will destroy its corrosion resistance. It has been found that small additions (less than 5 w/o) of some elements (such as tin, molybdenum, and niobium) decrease the corrosion resistance of high-purity zirconium only slightly. It has been further observed that very small additions (less than 1/2 w/o) of a few elements (iron and nickel) seem to give additional corrosion resistance to zirconium in water. Previous work has shown that the elements tin, molybdenum, and niobium are effective strengtheners of zirconium and that the combination of tin with either molybdenum or niobium produces high-strength heat-treatable alloys. Tin, molybdenum, and niobium have been selected for the development of high-strength corrosion-resistant zirconium alloys not only for their strengthening effect, but also for their low thermal-neutron-capture properties andfor their minimum effect upon the corrosion resistance of zirconium.

The initial portion of the program will consist of screening selected alloys. Alloys containing up to 4 w/o tin, 3 w/o niobium, and 2 w/o molybdenum will be prepared by arc melting using sponge zirconium. This' screening will consist of hardness testing in the annealed condition and of corrosion testing for 1000 hr in 570 F high-purity water. In order to select alloys falling within the strength requirements, the hardness-strength relationship will be used. Alloys which meet the requirements of these screening operations will be subjected to hot-hardness tests to obtain data on their relative fabricability. If time permits, work on the mechanical and physical properties will be initiated.

A list of alloys covering the compositions of interest has been prepared, and melts of small buttons in an arc furnace will begin as soon as the materials are available.

B. DEVELOPMENTS FOR ALUMINUM-CLAD FUEL ELEMENTS

R. J. Carlson

Studies of the aluminum-uranium phase diagram have been completed and a topical report is being prepared. Liquidus temperatures observed ranged from 855 C for the aluminum-20 w/o uranium composition to 1265 C for the aluminum-51.2 w/o uranium composition. Neither silicon nor magnesium in the amounts studied was found to affect the liquidus temperatures, although silicon additions of 1 w/o lowered the peritectic temperature from 734 C to 706 C.

The investigation of the feasibility of producing hollow aluminum-25 w/o uranium extrusion billets is nearly complete. The analysis of ingots produced using a redesigned distributor for depositing the metal in the mold cavity will complete the experimental portion of this program.

The mechanical extensometer which was designed to be used in determining the mechanical properties of uranium tubing has been calibrated and calibration curves have been prepared. The calibration is being evaluated by measuring the transverse properties of alumina, yellow brass, copper, and uranium rings.

Extrusion Cladding of Flat Plates

R. J. Fiorentino, D. C. Drennen, C. J. Slunder, and A. M. Hall

Work with the right-angle extrusion cladding tools has been delayed temporarily pending the arrival of a new mandrel. In the mandrel used previously, the two webs supporting the core plot cracked during the last test.

In the future work with the new mandrel, attempts will be made to extrude a 30-mil aluminum cladding onto 40-in.-long uranium plates connected together with M276 and M355 sintered aluminum-alloy end plugs. The nature of the welds in the cladding between successive billets will be examined.

Study of the Liquidus in Aluminum-Uranium Alloys

V. W. Storhok, A. A. Bauer, and R. F. Dickerson

The study of the aluminum-uranium system has been completed and a topical report is being prepared.

Previously reported liquidus temperatures for the 40 and 50 w/o uranium alloys were found to be in error. A reaction between the liquid metal and the platinum-

platinum 10 w/o rhodium thermocouple resulted in false breaks of the thermal-analysis curve. This was alleviated by protecting the thermocouple with a ceramic coating which separated the alloy specimen from the thermocouple.

The following is a tabulation of liquidus temperatures observed.

Aluminum-20 w/o uranium	855 C
Aluminum-30.9 w/o uranium	1068 C
Aluminum-41.6 w/o uranium	1190 C
Aluminum-51.2 w/o uranium	1265 C

Neither silicon nor magnesium in the amounts studied were found to affect the liquidus temperatures, although silicon additions of 1 w/o lowered the peritectic temperature from 734 C to 706 C.

Preparation of Aluminum-Uranium Alloys

N. E. Daniel, E. L. Foster, and R. F. Dickerson

Melting and casting techniques capable of yielding sound, homogeneous extrusion blanks of aluminum-uranium alloys containing high concentrations of uranium are the primary concern of a research program now in progress. These alloys are desired in the form of heavy-walled cylinders suitable for extrusion to fuel elements for low-temperature water-cooled water-moderated reactors. Any casting techniques developed must yield reproducible results and the ingots produced must require a minimum of cleanup.

The investigations concerned with the production of aluminum-25 w/o uranium ingots by centrifugal casting techniques have continued. As reported previously, the ingots analyzed to date have exhibited variations in the uranium content on the order of 3 to 5 w/o.

Additional castings have been produced using a redesigned distributor for depositing the metal in the mold cavity. Distributing the molten metal evenly in the mold cavity should improve the homogeneity, and samples taken from these castings are being analyzed to determine the efficiency of this technique.

Evaluation of the above ingots will complete the experimental portion of this program.

B-3 and B-4

Development of a Mechanical Extensometer

J. A. DeMastry, F. R. Shober, and R. F. Dickerson

A mechanical extensometer has been designed and constructed with sufficient sensitivity to determine the transverse mechanical properties of uranium tubing. To evaluate the mechanical properties of irradiated uranium tubing, it was necessary to develop an extensometer that can be adapted to remote application and operation. Evaluation of the extensometer under less restricted conditions is being made. The transverse mechanical properties of several materials are being compared using both a Type A-9 SR-4 strain gage and the mechanical extensometer.

The extensometer is a split ring onto which three equally spaced knife edges have been placed. Changes in the diameter of the uranium tubing actuate push rods connected to each half of the split ring. Movement of the push rods is transmitted to two cantilever-type strain gages and two loop-type strain gages. Deflections of the strain gages are registered on SR-4 strain-gage indicators.

The extensometer has been calibrated and calibration curves have been prepared. Further evaluation of the calibration is being made by measuring the transverse properties of aluminum, yellow brass, copper, and uranium rings at room temperatures. Additional tests are to be run at 350 F in order to completely evaluate the extensometer.

C-1

C. PLANT ASSISTANCE TO MCW

D. A. Vaughan

Studies on the residual nitrogen content in UO_2 have not been conclusive, and they are being discontinued. To aid in understanding the structural changes that were previously described for the uranium dioxide-oxygen system, the density is being measured for several compositions over the range $UO_{2.00}$ to $UO_{2.25}$.

The corrosion resistance of construction materials for nitric acid reconcentrator and for a new solvent-extraction process under development at Weldon Springs is being evaluated. Prolonged-exposure tests indicate that Type 304 ELC stainless steel would offer sufficient resistance to attack, in the nitric acid reconcentrator, by solutions containing up to 30 w/o nitric acid with chloride ion concentrations as high as 0.3 w/o. However, as the nitric acid concentration increases, the chloride concentration must be decreased for safe operation. A first appraisal has been made on materials for the new solvent-extraction process that is designed to provide essentially chloride-free feed to the reconcentrator. Although lead and rigid polyvinyl chloride were not resistant to attack by the synthetic raffinate, several steels and Ti-75A titanium exhibited extremely low corrosion rates.

Fundamental studies on the kinetics of various reactions which may influence the purity and yield in the production of dingot uranium are being continued. The reaction tube used for measuring hydrogen permeation through molten magnesium fluoride slag was modified to prevent leaking at the bottom diaphragm. A run should be completed during the next period. The viscosity of magnesium fluoride was measured and found not to be significantly different from that of slag, which contains several per cent magnesium oxide or uranium dioxide. The techniques for surface-tension measurements on molten magnesium fluoride by the bubble-pressure method are described.

Investigation of Uranium Oxides

D. A. Vaughan, J. R. Bridge, and C. M. Schwartz

The study of the determination of nitrogen in uranium dioxide has been continued. Previous experiments on the colorimetric determination of nitrogen in UO_2 have not proved successful. The colors developed after the use of hydrogen peroxide, which was necessary to put the UO_2 in solution, have not been reproducible.

During January the results of previous attempts to determine the nitrogen content in UO_2 by a colorimetric method were evaluated and confirmed by additional tests. Other solution agents were considered, but none was found to be beneficial. The following conclusions are made from this work: (1) the colors developed after the use of hydrogen peroxide are not reproducible, and (2) on the basis of tests made on known nitrogen-bearing samples, with and without hydrogen peroxide, when compared with tests made on UO_2 samples, the nitrogen content of UO_2 is estimated to be less than 0.01 w/o.

A study of the relation between density and oxygen content of UO_2 is being made to aid in determining whether UO_{2+x} is an oxygen-excess or metal-deficient structure. The results of previous work, using pycnometric densities, were questionable. New samples of UO_{2+x}, with oxygen-to-uranium ratios from 2.03 to 2.23 have been made and annealed at 450 C for 100 hr. Helium density measurements are being made, and the results will be reported next month.

The Electrical Properties of Uranium Dioxide

J. W. Moody, R. K. Willardson, and H. L. Goering

The electrical properties are being determined on sintered bodies of UO_2 which were doped with other metals. No data are available to report as yet.

The Corrosion Resistance of Selected Stainless Steels

C. L. Peterson, W. C. Baytos, and F. W. Fink

Nitric Acid Reconcentrator

Investigations are in progress on the corrosion of Type 304 ELC stainless steel by chloride- and fluoride-contaminated nitric acid solutions such as might be expected to occur in the nitric acid reconcentrator at the Weldon Springs uranium refinery.

Prolonged-exposure tests in 5, 30, 38, and 45 w/o nitric acid solutions are continuing. The trends in the corrosion rates have not changed. Chloride levels as high as 0.3 w/o continue to appear safe in 5 and 30 w/o nitric acid solutions, while 0.25 w/o chloride appears to be near the upper limit in 38 w/o solutions and severe corrosion occurs with only 0.2 w/o chloride in 45 w/o acid solutions.

Studies are being readied in which the effect of sulfate additions, ranging from 5 to 5000 ppm, on the corrosion of Type 304 ELC stainless steel will be evaluated in 38 w/o nitric acid solutions boiling at 250 mm of mercury absolute pressure.

Container Materials for Proposed Solvent-Extraction Process

A new process for the recovery of nitric acid is under development at Weldon Springs. This process involves the handling of aqueous solutions containing both nitric and sulfuric acids, as well as their salts, in some type of solvent-extraction equipment at room temperature. The end result will be an essentially chloride-free feed to the reconcentrator.

Carpenter 20, Carpenter 20 stabilized, and Types 304, 304 ELC, 316, and 347 stainless steels, Ti-75A titanium, lead, and rigid polyvinyl chloride were all suggested as possible container materials for the solvent-extraction process. Specimens of these materials have been exposed for 2 weeks in the usual vapor, interface, and liquid positions in three different solutions representing extremes which may occur in this new process:

Solution	Composition
A	3 M HNO_3, 1 M $NaNO_3$
B	3 M HNO_3, 1 M $NaNO_3$, 1 M H_2SO_4
C	0.05 M $NaNO_3$, 1 M $NaHSO_4$.

The flasks containing the solutions are maintained at 75 F. Air, presaturated with similar solutions, is bubbled vigorously through, affording both agitation and aeration to the solutions.

Inspection of the specimens following 1 week of exposure showed that lead was attacked excessively when submerged in Solutions A and B. The rigid PVC showed a slight weight gain. Corrosion rates for the other materials were extremely low, being of the order of 0.01 mil per month, or less. During the second week most of the corrosion rates were even lower.

These tests will be continued. Meanwhile, most of the materials will be evaluated in actual raffinate from the Weldon Springs refinery to determine the effects of the trace elements normally present in the raffinate stream. Probably these tests will be followed by investigations of possible complications which may arise from the presence of the organic phase of the solvent-extraction process.

Gas-Metal Studies

W. R. Hansen, M. J. Trzeciak, and M. W. Mallett

A kinetic study is being made of some phases of the thermite reaction for producing dingot uranium from uranium tetrafluoride and magnesium metal. The objective is to gain an understanding of the fundamental principles governing the purity and yield of the dingot uranium product.

Presently, the permeation rate of hydrogen through molten magnesium fluoride slag is being studied. A knowledge of the permeation rate will help in determining the path followed by hydrogen just following the thermite reaction. This knowledge will aid in designing methods for lowering the hydrogen contamination of the dingot uranium product.

In addition, a study is being made of the effect of impurities on the viscosity and surface tension of molten magnesium fluoride slag. These two properties might affect the settling rate of uranium droplets formed in the thermite reaction. That is, more rapid settling of uranium particles would leave fewer particles entrapped in the slag as it solidifies, and a greater yield would result.

Permeation of Hydrogen Through Molten Magnesium Fluoride Slag

Work to obtain a gastight seal between the diffusion diaphragm and the molybdenum reaction tube proper is continuing. It was reasoned that molybdenum in the diaphragm was not sufficiently ductile, when fitted at room temperature, to "flow" and give a seal tight enough to prevent seepage of molten slag. Hence, a 1-mil-thick nickel washer was inserted between the diaphragm and the reaction tube. Nickel has the advantage at room temperature that it will "flow" under pressure and fill irregularities in the mating surfaces. Nickel also has a much greater coefficient of thermal expansion than molybdenum. Thus, when the system is heated, a tighter seal will be effected.

Experiments with this modification are scheduled for an early trial.

Viscosity Determinations

Measurements previously reported indicated that the viscosity of molten magnesium fluoride slag was less than 3 and probably greater than 1.5 centipoises. These values were based on calibration data obtained with s-tetrabromoethane over a viscosity range of about 4 to 12 centipoises. Subsequently, calibration points below 4 centipoises were obtained using water at three temperatures. These data did not agree with the extrapolated curve of the s-tetrabromoethane data. Therefore, more calibration points were obtained using acetone, carbon tetrachloride, n-butyl alcohol, and amyl alcohol. All these points supported the water data within the limits of experimental error. Apparently the literature values for s-tetrabromoethane were in error.

Viscosities of the following systems were measured: Mallinckrodt magnesium fluoride slag, and cp magnesium fluoride alone and with additions of magnesium oxide and uranium dioxide. The data based on the new calibration are tabulated as follows:

System	Temperature, C	Viscosity, centipoises
MgF_2	1370	7.6
MgF_2 + 2.5 w/o MgO	1370	8.5
MgF_2 + 4.7 w/o MgO	1370	6.5
MgF_2 + 6.4 w/o MgO	1370	6.5
MgF_2 + 6.4 w/o MgO	1415	4.5
MgF_2 + 1.2 w/o UO_2	1370	6.5
MgF_2 + 4.6 w/o UO_2	1370	6.3
MgF_2 + 11.3 w/o UO_2	1370	5.0
Mallinckrodt MgF_2 slag	1360	6.5

In each case, six to ten viscometer readings were taken. Based on the standard deviation, the sensitivity of measurements is estimated to be ±1 centipoise with a probable error of about ±0.6 centipoise.

As shown in the tabulation, the additions of magnesium oxide and uranium dioxide to cp magnesium fluoride have little, if any, effect on the viscosity at 1370 C. If the sensitivity of measurement (±1 centipoise) is considered, the variations in viscosity measurements are not significant. Also, the change in viscosity in going from 1370 to 1415 C in the MgF_2-6.4 w/o MgO system is small. As would be expected, however, the viscosity is less at 1415 than at 1370 C. The viscosity of the Mallinckrodt slag at 1360 C is about the same as that of the other systems.

It is concluded that the presence of several weight per cent MgO or UO_2 in MgF_2 does not change viscosity sufficiently to affect the yield of the uranium product. This concludes the presently scheduled work on viscosity.

Surface Tension

Further consideration was given to applying the bubble-pressure method to surface tension measurements on molten magnesium fluoride. It was concluded that the method appears quite practical.

The technique involves measuring the maximum pressure required to force a gas bubble from a capillary tube immersed in molten magnesium fluoride. The equation for calculating surface tension is,

$$\gamma = \frac{r}{2} (p_{max} - h\,d\,g),$$

where

γ = surface tension

r = radius of the capillary

p_{max} = maximum pressure required to force the gas bubble through the capillary tube

h = the depth to which the capillary is immersed in the molten MgF_2

d = density of the molten MgF_2

g = acceleration of gravity.

The pressure, p_{max}, is expressed in terms of h′ and d′ for the manometric fluid, and of g. The term h d g of molten MgF_2 represents the hydrostatic head that needs to be overcome by the gas pressure. The pressure over and above this head is the force required to overcome the surface tension of the molten MgF_2 around the bubble.

Some of the physical dimensions of the proposed experimental system using a butyl phthalate manometer are as follows:

r = 0.03 cm

h = 3 cm

$$d = 2 \text{ g per cm}^3$$

$$d' = 1 \text{ g per cm}^3.$$

The surface tension of MgF_2 may be about 100 dynes per cm, the same order of magnitude as that for similar molten salts. If so, a value of about 13 cm will be observed for the difference in height between the two arms of the manometer. This value can easily be measured to within 2 per cent.

D-1

D. PROCESSING OF FEED MATERIALS

E. L. Foster

Two studies are in progress that are concerned with the operation of the Feed Material Production Center by National Lead of Ohio. These are the examination of factors affecting the quality of vacuum-induction-melted uranium and the theoretical study of the solidification of pure uranium ingots. Both of the studies have the same ultimate objective, the improvement of uranium-fuel-slug quality. In addition, the solidification study should provide a method of evaluation for melting and casting variables for future casting needs.

Solidification of Uranium

E. L. Foster, C. K. Franklin, B. Schwartz,
and R. F. Dickerson

A basic study of the solidification of uranium castings is in progress. Investigations of pouring temperature, mold design, cooling rates, and other casting variables are being made to determine their effect on the quality of production-type uranium ingots. As a method of analysis, mathematical models have been constructed which consist of a set of simultaneous equations. The equations, expressed in terms of small finite increments of time, make possible the calculation of the transient heat flow through the casting and its mold. Using these equations, the influence of a variable or variables on the melt during its solidification can be evaluated. In addition to the theoretical studies, further examination of the metallurgical variables is commencing. A portion of this will involve small-scale foundry experiments wherein some of the factors will be studied under controlled conditions.

The preparation of a program for the computers wherein the heat flow is calculated for a mathematical model with 48 ingot cells and 28 mold cells in a pie slice of a casting has been made. (The model used previously contained 20 cells.) This increase will permit a more detailed examination of the time-temperature field, and the accuracy of the analysis should be improved. As before, this model includes considerations of superheat, pouring time, variations in mold preheating, the release of heat of fusion, and environmental temperatures, i.e., those of the cooling jacket and the bottom of the crucible. One additional consideration in this model, not used in the previous analysis, is the variation of the thermal conductivity of the casting and mold materials with temperature. At this time, the coefficients for this variation are not known, so constant thermal conductivities will be used until the required data become available. Another new feature included in this model is consideration of the change from conductive to radiative heat transfer between the casting and mold wall as the outer skin of the casting solidifies and contracts away from the mold.

Experimental determination of the physical properties of uranium and graphite materials will be made. These properties include the thermal conductivity, total normal emissivity, and the linear thermal expansion of the materials. In addition, thermal resistance measurements of the mold-wash material will be obtained. These properties, obtained at the desired temperature range, will be utilized in the refined mathematical analysis. It is expected that these experiments will start during the coming month.

Examination of Factors Affecting the Quality of Induction-Melted Uranium

R. W. Endebrock, E. L. Foster, and R. F. Dickerson

Various data reported in the literature have indicated that uranium-fuel-slug quality and the quantity of certain nonmetallic impurities found in the metal may have a direct relationship. Consequently, a research program is now in progress to study possible reactions of various process-related impurities that may occur during the vacuum melting of uranium. The program is comprised of two complementary phases. One phase is experimental, centering about a 10-lb-capacity vacuum-melting furnace; the other is a survey of the literature.

Evaluations have been completed on an initial test series which was conducted by obtaining the rate, quantity, and analysis of gas evolved at various temperature levels from 2000 to 2500 F during the melting of dingot uranium. As reported previously, the gas evolved at any of the test-temperature levels was found to be predominantly hydrogen. In a blank test in which no uranium was present, however, a typical water-gas reaction evidently occurred at the 2500 F temperature level. Since only small quantities of carbon monoxide were found in gas samples taken over uranium melts, it is suspected that a water-gas reaction may provide carbon monoxide for a secondary reaction with the uranium melt. Moreover, the analyses showed that each gas sample contained approximately 2 volume per cent of water, indicating a continuous source of water. If these reactions occur, then a gaseous-phase mechanism for introducing carbon is implied.

As a consequence, a second series of tests is under way in an attempt to resolve the implied role of moisture and to indicate what precautions should be taken in all succeeding tests. In this series, blank tests (no uranium present) are to be run on uncoated and MgO-coated graphite crucibles and on a zirconia crucible under controlled-moisture conditions. Melting tests, using dingot stock, will then be run under conditions similar to those of the blank tests. Water sources which were particularly troublesome during past experiments in contributing to system variations include (1) slow drying of the crucible cement (sillimanite), (2) condensation of moisture on the water-cooled walls of the furnace (especially manifested in varying weather conditions), and (3) water that is bound in the MgO coating even at relatively high temperatures (2000 F). Steps are being taken to reduce all factors causing system variation to a low level.

E. GENERAL FUEL-ELEMENT DEVELOPMENT

F. A. Rough and D. C. Carmichael

Fuel-element development programs supported by the AEC Division of Reactor Development are reported in this section.

No new data are available from the study of stainless steel-clad specimens containing enriched UC or UN.

Methods of fabricating cermet fuel elements with high loadings of fuel compound in a metal matrix are being studied. The strength of UO_2-stainless steel cermets has been improved by techniques giving better density and distribution of the matrix. Results indicate that a UO_2-stainless steel cermet has good thermal conductivity.

A study is being made of the feasibility of using the hydride of a zirconium-uranium alloy as a fueled moderator. Specimens have been prepared for irradiation testing, and phase boundaries have been determined for the zirconium-1 w/o uranium alloy hydride system at temperatures of about 600, 650, and 700 C, and for the zirconium-50 w/o uranium alloy hydride system at about 650 C.

Development of Dispersed UC and UN Fuel Elements

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

Irradiation specimens containing 24 w/o fully enriched UN and UC dispersed in stainless steel and clad with Type 318 stainless steel have been given preirradiation leak checks by exposure to boiling nitric acid. As soon as the analyses are completed, encapsulation will be initiated. Tensile tests are being run on dispersions of UN and UC in Type 347 stainless steel; however, no additional data are available at this time.

Fabrication of Cermet Fuel Elements

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

Techniques are being developed for the fabrication of fuel elements which contain 60 to 90 volume per cent of fuel dispersed in a metal matrix. Specimens containing UO_2 dispersed in Type 302B stainless steel have been prepared by hot-pressing techniques, and the specimens have been tested for tensile strength, electrical resistivity, and shock resistance. In addition, pressure bonding is being investigated as a method of cladding these cermets.

Calculations of the ultimate tensile strength at room temperature have been made from bend-test data on hot-pressed compacts. The values range from 15,200 psi at 80 volume per cent UO_2 to 76,600 psi at 40 volume per cent UO_2 dispersed in stainless steel. These values are somewhat higher than previously reported, and it is believed that these higher values are a result of having a better distribution of the metal matrix and a slightly increased compact density.

The thermal conductivity has been calculated on the basis of electrical-resistivity measurements, and the results indicate that a cermet of 60 volume per cent UO_2 in Type 302B stainless steel has twice the thermal conductivity of UO_2 at a temperature of 460 C. At higher temperatures, an even higher ratio could be expected.

Fueled Zirconium Hydride Moderator

H. E. Bigony and J. B. Vetrano

Studies are continuing to evaluate zirconium hydride-2 w/o uranium as a fueled moderator for potential use in gas-cooled reactors. Structural evaluation and pressure-composition-temperature determinations are in progress, as well as encapsulation of specimens for irradiation.

Structure and Pressure-Composition-Temperature Studies

Investigation of the pressure-composition-temperature relationships in the zirconium-uranium-hydrogen ternary system is continuing. Absorption isotherms have been run for a zirconium-1 w/o uranium alloy at 601, 651, and 703 C, and a zirconium-50 w/o uranium at 652 C. The results for the 1 w/o alloy are given in Table E-1.

TABLE E-1. PHASE BOUNDARIES IN THE ZIRCONIUM-1 w/o URANIUM ALLOY HYDRIDE SYSTEM

	601 C		651 C		703 C	
Phase-Boundary Designation	Hydrogen Sorption, cm^3 per g	Pressure, cm of mercury	Hydrogen Sorption, cm^3 per g	Pressure, cm of mercury	Hydrogen Sorption, cm^3 per g	Pressure, cm of mercury
$\alpha(\alpha+\beta)$	6.6	0.254	7.0	0.053	5.9	0.06
$(\alpha+\beta)\beta$	--	--	25.5	0.086	18.5	0.09
$\beta(\beta+\delta)$	--	--	95.6	0.278	103.4	1.12
$(\beta+\delta)\delta$	--	--	161.1	0.285	168.5	1.19

Equilibrium in the 601 C run was extremely slow of attainment. The run was discontinued after 85 cm^3 of hydrogen had been absorbed without the appearance of a new phase boundary. For the 50 w/o alloy, which was hydrided at 652 C, the results were in substantial agreement with those which Gulbransen* determined at 649 C. The limits of the lower multiphase region were 9.1 and 35.1 cm^3 of hydrogen per g of alloy at 0.15 and 0.19 cm of mercury pressure, respectively. The limits of the upper multiphase region were 48.5 and 79.6 cm^3 of hydrogen per g of alloy at 0.29 and 0.30 cm of mercury pressure, respectively.

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*Gulbransen, E. A., et al., Research Report 100FF1010-R1, Westinghouse Research Laboratories.

Encapsulation and Irradiation

The radiation-effects study of the fueled moderator material, zirconium hydride-2 w/o uranium, is continuing. Two irradiation capsules, BMI-20-1 and -2, will each contain four fueled and four nonfueled control specimens under 1 atmosphere of hydrogen at room temperature. The design operating temperatures are 1500 F for Capsule BMI-20-1 and 1200 F for Capsule BMI-20-2. The operating temperature of the specimens in Capsule BMI-20-1 will be monitored by six thermocouples. Capsule BMI-20-2 will not be instrumented, but the operating temperature of the specimens in the capsule will be calculated from the ratio of the thermal-neutron fluxes during operation.

Specimen fabrication for the irradiation program is complete. All specimens, both fueled and unfueled, are hollow cylinders which are 1/2 to 1 in. long, 3/16 in. in OD, and 1/16 in. in ID. The composition of the fueled specimens is $ZrU_{0.008}H_{1.7}$ and that of the unfueled specimens is $ZrH_{1.7}$. Identification marks have been engraved on the specimens and the preirradiation inspection, including measurements of physical dimensions and density, is in progress.

Fabrication of the capsule components has been completed. The capsule material is Type 348 stainless steel. Measurements of the weights and physical dimensions of the compounds are in progress. The thermocouples for Capsule BMI-20-1 are being fabricated from Chromel-Alumel thermocouple material insulated with magnesium oxide swaged in a stainless steel sheath. The tips of the thermocouples are chromium plated for resistance to the formation of the uranium-nickel and uranium-iron eutectics.

The specimens in each capsule will be separated by spacers and supported during irradiation by a single 1/16-in.-OD molybdenum tube through the center of the specimens. A nickel-cobalt dosimeter wire will be inserted in the center of each molybdenum tube, and other dosimeters will be provided outside the specimens and capsule.

Capsule BMI-20-1 will be irradiated for seven normal MTR cycles at a flux of 1×10^{14} nv to achieve a calculated burnup of 20 a/o of the total uranium. Capsule BMI-20-2 will be irradiated for a period of approximately nine cycles.

F. STUDIES OF URANIUM AND URANIUM-ALLOY FUELS

F. A. Rough and A. W. Hare

The various research programs on uranium-alloy fuels are reported in this section. These programs are sponsored by the AEC's Reactor Development Division.

Irradiation of Capsules BMI-8-5 and BMI-8-6 containing zirconium-uranium alloys is being continued at the MTR.

The results of the initial studies of transformation kinetics which were based on hardness measurements are reported in the research and development program on gamma-phase uranium alloys.

The literature survey which has been made to obtain and evaluate existing information regarding the preparation of uranium-niobium alloys is essentially complete. There is a large portion of this system for which little or no information has been published.

Further progress is reported on the research concerned with the mechanism of uranium corrosion in water with emphasis on development of techniques to determine the oxidation state of surface films.

Radiation Stability of Uranium-Zirconium Alloys

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

Capsules BMI-8-5 and BMI-8-6 are currently being irradiated at the MTR. zirconium-50 w/o uranium alloy specimens (Capsule BMI-8-5) and the three zirconium-22 w/o uranium alloy specimens (Capsule BMI-8-6) are tentatively scheduled to remain in the MTR until about March 7, at which time the specimens will have received a calculated burnup of about 2 total a/o.

The literature survey of the uranium-zirconium alloy system is being concluded. Upon completion of this survey a final report will be issued which summarizes and evaluates the present technology of this alloy system.

Development of Gamma-Phase Uranium Alloys

V. W. Storhok, A. A. Bauer, and R. F. Dickerson

The project aimed at developing a metastable gamma-phase alloy by ternary and quaternary alloying with chromium, molybdenum, niobium, ruthenium, vanadium, and zirconium is continuing. The program consists of studies of kinetics, corrosion testing, thermal analysis, metallography, and hot-hardness testing.

Initial studies of transformation kinetics based on hardness neasurements have been completed. Among the uranium-7.5 w/o molybdenum base alloys, 3 w/o additions of niobium and 2 w/o additions of ruthenium apparently increase gamma stability. Additions of 2 w/o vanadium and up to 10 w/o zirconium seem to have a deleterious effect. The gamma stability of uranium-10 and -20 w/o niobium alloys is improved by up to 10 w/o zirconium additions. With the uranium-10 w/o niobium alloy, 1 and 5 w/o additions of molybdenum appear to have equal stabilizing effects, while no improvements were noted with 0.5 w/o chromium and 2 w/o vanadium additions. Among uranium-20 w/o zirconium alloys, 3 and 5 w/o additions of niobium and molybdenum have about the same effect on gamma stability, while 5 w/o additions of either niobium or molybdenum to the uranium-40 w/o zirconium alloy result in equal improvements. These data were obtained by measuring changes in hardness as a function of increasing aging time. Uranium-zirconium and uranium-molybdenum alloys were aged at 500 C while uranium-niobium alloys were aged at 550 C.

Since gamma-phase uranium alloys generally exhibit improved corrosion resistance, all the alloys are being corrosion tested in high-temperature water in the hope that some indication of gamma stability may be obtained. On the basis of previously reported corrosion behavior in 500 F water, a number of promising alloys were selected for corrosion testing in 680 F water. These alloys were heat treated 4 hr at 900 C and water quenched and are now on test. As yet no data have been obtained.

As an indication of the effect of ternary additions on high-temperature strength, hot-hardness measurements are being made on all alloys. From data gathered to date, increasing niobium and molybdenum contents generally results in an increase in hot hardness for the uranium-20 w/o zirconium base alloy. At 900 C, the effect is approximately the same for either addition, the hardness increasing from 7.5 DPH for the base alloy to 12.8 DPH for a 5 w/o niobium addition and to 10.3 DPH for a 5 w/o molybdenum addition. Molybdenum apparently has a greater hardening effect at 500 C; an alloy with 5 w/o molybdenum had a hardness of 292 DPH compared with 249 DPH for a 5 w/o niobium alloy. Additional hardness data are being gathered.

Thermal-analysis data are being gathered on all alloys involved in this investigation. Insufficient data are currently available to draw any conclusions as to the effect of varying amounts of additions on gamma decomposition temperature.

Additional alloys are being prepared to fill gaps in present data and to investigate the effect of ruthenium and niobium combinations on the uranium-7.5 w/o molybdenum alloy.

Preparation of Uranium-Niobium Alloys

N. E. Daniel, E. L. Foster, and R. F. Dickerson

A study concerned with the applicability of uranium-niobium alloys as possible reactor fuels is in progress. The purposes of this program are twofold: (1) to obtain and evaluate the existing information regarding preparation of the alloy constitutional diagram, physical and mechanical properties, corrosion behavior, and the effects of radiation, and (2) to resolve deficiencies that are found in the literature and to broaden the scope of the existing knowledge regarding alloys in this system.

In order to accomplish the first of the aforementioned purposes a literature survey has been conducted and is essentially complete. However, there are numerous areas in which little or no information has been published and attempts are being made to gather this information by direct contact with other laboratories. In addition to the literature survey, an experimental program has been concerned with preparation of high-quality alloy material and the subsequent fabrication of this material. This effort has been concentrated on the alloys containing 20 and 80 w/o niobium and is now being expanded to include alloys in the γ_1-γ_2 region. From a cursory evaluation of the melting tests made to date, there is reason to believe that the inhomogeneities encountered in melting the uranium-10 w/o niobium alloy will also be encountered in other alloys in this system. However, these inhomogeneities may be eliminated by suitable heat treatment of the cast material or by fabrication and subsequent heat treatment.

Future studies will encompass not only melting of the alloys, but also preliminary fabrication and heat treatment in attempts to improve homogeneity of the alloys. Fabrication of the alloys will be attempted after they are clad in molybdenum and have been homogenized for periods up to 16 hr.

Mechanism of Aqueous Corrosion

E. Adelson, C. M. Schwartz, D. A. Vaughan, O. M. Stewart,
W. E. Berry, P. D. Miller, and F. W. Fink

The aqueous-corrosion products of uranium are being studied to aid in understanding the corrosion process. Owing to previous difficulties in obtaining a material balance between evolved hydrogen and weight loss, for the case of UO_2 as assumed corrosion product, other tests are being made to determine the oxidation state of the uranium in the reaction product.

During January the experimental techniques for studying the uranium L_{III} X-ray absorption edge were modified. Theoretical calculations were made on the optimum thickness of uranium for maximum edge intensity and samples of UO_2 and UO_3 with constant uranium content were prepared. In addition to a difference in the breadth of the absorption edge between UO_2 and UO_3, which was reported in BMI-1247, the edge was found to occur at a shorter wavelength for UO_3 than for UO_2. This is consistent with published data. Attempts to improve the resolution are in progress. It is planned to make similar studies of the X-ray absorption edge of samples of corrosion product.

Previous experiments in steam at 200 C have indicated that the uranium oxide corrosion product oxidizes further when exposed to air, thus preventing an accurate determination of oxygen in the corrosion product. Present equipment is being modified to permit the analysis of the uranium oxide without removing it from the corrosion test vessel.

G-1 and G-2

G. FATIGUE STUDIES OF INCONEL

W. S. Hyler and R. J. Favor

This program has the objectives of obtaining basic fatigue information on Inconel and establishing quantitative relationships among the variables of temperature, stress, strain, time, and cyclic frequency for Inconel.

The scope of the investigation includes temperatures of 1200, 1400, and 1600 F. Previously, data obtained at 1600 F were reported. At 1200 F the evaluations under completely reversed loading were also completed.

During January initial data at 1200 F and load ratio of 0.25 have been obtained. These data will be reported after the 1200 F investigation has been completed.

During February it is expected that the investigation at 1200 F will be completed. In addition, an evaluation at 1400 F, load ratio of ∞, and cyclic frequency of 1 cps will be initiated.

H. REACTOR MATERIALS AND COMPONENTS

F. A. Rough and A. W. Hare

This section reports the various research programs which are supported by the AEC Division of Reactor Development and are concerned with reactor materials and components.

The results of continuous-weighing oxidation tests in dry air at 1000 and 1200 C on niobium-tungsten alloys are discussed. Several new alloys, including ternary alloys, are being prepared to further develop the theory of oxidation.

The results of metallographic and diffraction analysis, oxidation tests, and conductivity and thermoelectric power measurements on UO_2 - La_2O_3 samples are reported on the program concerned with the valence effects of oxide solutions in uranium dioxide.

It is reported in the high-temperature high-pressure solid-state studies that the first die has been tested and has operated satisfactorily. The problems concerned with pressure calibration of the die are also discussed.

Routine progress is reported for the investigation of rubbing surfaces in sodium environments.

The studies of the fundamental principles associated with hydrostatic pressure bonding are continuing. In the analytical phase of this work, a revision of the theory in terms of pressure, geometry, and material properties is being carried out so that a more accurate estimate can be made of the material parameters involved in hydrostatic pressure bonding. Routine progress is reported on the experimental phase of this work.

Oxidation-Resistant Niobium Alloys

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

The objective of this program is to study the oxidation of pure niobium and the mechanisms by which various alloying additions affect the oxidation behavior. Previous work has shown that size and valence of the alloying element affect the oxidation behavior in the low alloying range (15 a/o maximum), while the nature of new oxide phases formed determine oxidation behavior in the high alloying range. Present work includes oxidation testing of binary alloys at 1000 and 1200 C, and preparation of new binary and ternary alloys.

Continuous-weighing oxidation tests in dry air at 1000 and 1200 C have been completed on four niobium-tungsten samples and two niobium-vanadium samples. The results are given in Table H-1. The behavior of niobium-tungsten alloys at 1200 C was significantly different from that at 1000 C. At the lower temperature, tungsten effected only a slight decrease in the linear oxidation rate, while at 1200 C, tungsten promoted

TABLE H-1. OXIDATION DATA FOR NIOBIUM ALLOYS IN DRY AIR

Sample	Composition, a/o	Test Temperature, C	Parabolic Rate Constant, (mg/cm^2)^2 per hr	Transition to Linear Rate, hr	Linear Rate Constant, mg/(cm^2)(hr)	Weight Gain, mg per cm^2					
						1 hr	2 hr	3 hr	4 hr	5 hr	6 hr
0-30(a)	100 Nb	1000	100	0.1	30.0	30.0	61.3	89.8	114.2	136.9	158.6
0-70(a)	Nb-1W	1000	-	0	(35)(c)	43	76.5	101	120	136	152
0-101	Nb-5W	1000	112	0.2	(30)	26.1	60.8	88.4	-	-	-
0-74(a)	Nb-10W	1000	108	0.1	(27)	32.4	57.5	76.5	92.0	106	115.5
0-77(a)	100 Nb	1200	-	0	(93)	107.7	-	-	-	-	-
0-105	Nb-17.5V	1200	(200)(b)	0.6	68.7	53.3	115	-	-	-	-
0-106	Nb-25V	1200	-	0	(198)	160.3	-	-	-	-	-
0-102	Nb-1W	1200	-	0	(70)	64.2	-	-	-	-	-
0-103	Nb-5W	1200	1020	1.3	13.5	29.9	45.1	-	-	-	-
0-104	Nb-10W	1200	640	3	6.3	24.2	35.0	43.6	51.4	58.3	64.8

(a) Data from previous tests included for comparison.

(b) Parabolic rate is estimated, since parabolic rate increased gradually with time up to 0.6 hr.

(c) Linear rates in parentheses are estimated, since reaction rates of these samples decreased gradually with time.

parabolic behavior with significantly lower rates than pure niobium. At 1200 C, niobium-5 a/o tungsten formed a protective scale and oxidized parabolically for 1.3 hr, while niobium-10 a/o tungsten oxidized parabolically at a slightly lower rate for 3 hr before transition to linear behavior occurred. The important feature of these results is not so much that the weight gains were reduced (vanadium, titanium, and molybdenum effected similar reductions in weight gain at 1200 C), but that the scales were so protective. Previously, the best alloys had exhibited parabolic behavior for less than 1 hr at 1200 C.

The mechanism by which tungsten improves the oxidation behavior at 1200 C is not immediately apparent. Although its high valence (+6) should reduce diffusion rates in a compact Nb_2O_5 film, its large crystal radius (+18.6 per cent compared to niobium) indicates that tungsten should expand the Nb_2O_5 scale, promoting cracking and linear behavior.

Niobium-17.5 a/o vanadium oxidized almost parabolically for 0.6 hr at 1200 C, the rate then becoming linear. Niobium-25 a/o vanadium oxidized linearly at a high rate. This behavior is similar to that observed at 1000 C, and reflects increasing amounts of a liquid oxide (V_2O_5 or a complex niobium-vanadium oxide) which fluxes the scale and causes high oxidation rates.

Sixteen new binary and ternary alloys are now being arc melted and rolled to strip for oxidation testing. The compositions of these alloys are:

Niobium-5, -10 a/o rhenium

Niobium-5, -10, and -20 a/o iron

Niobium-12.5 a/o titanium-4 a/o molybdenum

Niobium-19 a/o titanium-6 a/o molybdenum

Niobium-25 a/o titanium-7.5 a/o molybdenum

Niobium-12.5 a/o titanium-7.5 a/o chromium

Niobium-19 a/o titanium-11 a/o chromium

Niobium-25 a/o titanium-15 a/o chromium

Niobium-12.5 a/o titanium-6 a/o vanadium

Niobium-19 a/o titanium-9 a/o vanadium

Niobium-25 a/o titanium-12.5 a/o vanadium

Niobium-11 a/o titanium-5.5 a/o molybdenum

Niobium-6 a/o molybdenum-9 a/o vanadium

Of the new binary systems planned, rhenium additions may be beneficial because its high valence (+7) should inhibit ionic diffusion in the scale. Iron has a favorable size (-14.3 per cent compared to niobium) and may promote parabolic oxidation behavior through the size-effect mechanism. The ternary alloys are combinations of beneficial binary additions as determined previously, selected so as to provide maximum information about oxidation behavior in the ternary systems.

H-4

Valence Effects of Oxide Solutions in Uranium Dioxide

W. B. Wilson, J. Moody, A. Gerds, W. M. Albrecht,
R. Bennett, and C. M. Schwartz

Modified methods for the production of solid solutions are being investigated, in continuation of the work discussed in BMI-1247. An additional revision in sample preparation was introduced when it was found that BeO and probably hydrocarbon contamination was detected in undesirable amounts in the system used for sintering the specimens. The tentative approach, presently being evaluated to eliminate this difficulty, has been to adopt a tantalum susceptor insulated with Alundum. Samples of UO_2 containing 40, 50, and 60 w/o La_2O_3 or 45 w/o Sc_2O_3 have been prepared, using this technique for the second sintering. These are presently being evaluated and appear to be suitable. At present, as a further refinement, it appears desirable to eliminate the binder being used, for maximum purity.

Metallographic and diffraction analysis of the specimens produced to date has indicated that the 50 and 60 w/o La_2O_3 contain a small amount of a grain-boundary phase. This is apparently La_2O_3 whose cell size has been reduced by UO_2 in solution. Since the amount of La_2O_3 is near the reported solubility limit (70 w/o) this may indicate either an incomplete reaction or excess solubility. The sample of 45 w/o Sc_2O_3 fired <u>in vacuo</u> did not form a solid solution with UO_2 but did form a solid solution when fired in air at 2500 F. Apparently, the U^{+4} size is too large, whereas the U^{+6} ion size is smaller and allows the solid solution to form.

Air-oxidation tests of specimens of UO_2, UO_2 - 50 w/o La_2O_3, and UO_2 - 45 w/o Sc_2O_3 were run for 3 hr at 2500 F in moving air as a test of valence state. The UO_2 pellet was completely transformed to powder and converted to U_3O_8. The 50 w/o La_2O_3 solid solution retained its shape and size and showed no signs of powdering. A slight lowering of the fluorite lattice parameter of this sample was detected and is interpreted as oxidation which occurs as follows:

$$2RO_2 + 2\overset{1}{R}_2O_3 + O_2 \rightarrow 6(R,R^1)O_2$$

The Sc_2O_3 solid solution with UO_2 remained as a fluorite-type solid solution for 3 hr at 2500 F. Analysis of weight-gain data indicates that both the UO_2-La_2O_3 solid solutions gained in accord with the expected reactions but that UO_2 had not. The apparent failure of the UO_2 to gain weight is probably due to the loss of volatile U_3O_8, since diffraction analysis indicated that the UO_2 had fully oxidized to U_3O_8.

Modification of the microbalance equipment to operate in air has been completed and work has been initiated to compare the oxidation behavior of UO_2 with the solid solutions.

Conductivity and thermoelectric power of the UO_2-La_2O_3 samples have been analyzed as a function of temperature from ambient to 800 C. The results indicate that the electrical properties of the specimens are affected by prior history. The room-temperature conductivity increases with aging at room temperature and decreases as the specimens are heated above 400 C. This makes it difficult to determine the exact effect of La_2O_3 additions on UO_2. However, it appears that the p-type conductivity of

UO_2 decreases with increasing La_2O_3 content and becomes *n*-type when the La_2O_3 content exceeds about 50 mole per cent. The activation energy necessary to free a charge carrier of specimens quenched from elevated temperature appears to be independent of La_2O_3 content.

Work will continue to confirm the nonoxidizing properties of the solid solutions and to relate their behavior to the electrical, structural, and chemical analyses.

High-Temperature High-Pressure Solid-State Studies

W. B. Wilson and C. M. Schwartz

Experimental testing and calibration of the first die unit was initiated in January. Various functions of performance of the unit were subjected to preliminary test, including cooling, thermal and electrical insulation, temperature and pressure calibration, and power requirements.

In general, the performance of the unit to date was satisfactory with the exception of the pressure calibration. This calibration was attempted by utilizing the bismuth transition and relating it to the press load. A "working" estimate of pressure may also be obtained by using the strength of the die materials as an estimate of pressure and, of course, by the direct calculation of pressure through the hydraulic system, neglecting friction. ("Friction" here refers to friction in the press at low loads and is offset by the force of gravity of the 20,000-lb ram weight.)

In the two experiments performed to date, the pressure was increased to failure. The bismuth transition was not detected, probably because of the choice of materials used as an insulator. It is believed that this material, Lavite, loaded up as a column in the die. Thus, such severe departure from "hydrostatic" conditions occurred internally that the transition was not detected, due to poor transmission of pressure to the specimen.

In the second experiment, immediately before failure of the carbide piston, a transition was possibly detected but occurred at a pressure estimated to be much too high to be bismuth.

Direct calculation of the pressure indicated that in excess of 600,000 psi was achieved before failure. This is close to the 700,000 to 900,000-psi level predicted for the unit, based on the crushing strength of the carbide.

These preliminary experiments suggest a special technique, which appears entirely feasible for synthesis of materials. In this technique, the limitations of the unsupported right-circular-cylinder design may be overcome by pushing the top of the piston flush with the die with a massive block of carbide. This in effect would produce a "bomb" which has been "sealed" at 600,000 psi or just below the limit of strength of the carbide piston. Additional pressure may then be generated by raising the temperature internally. In theory, at least, such technique should be capable of the most extreme pressure and temperature even though these cannot be controlled independently.

Work will continue to detect the bismuth transition for final calibration. Modifications are being made to achieve higher pressures including use of the "bomb" technique.

Rubbing Surfaces in Sodium Environments

J. W. Kissel and J. H. Stang

An inert-atmosphere test apparatus has been constructed to study the friction behavior of sodium-immersed sliding surfaces. During January, a few exploratory experiments were carried out, using unlubricated and mineral-oil-lubricated surfaces (in air at room temperature). The chief objective of these tests has been to examine the operating characteristics of the apparatus and of the friction-sensing and -recording devices.

The conditions for these preliminary experiments have been as follows:

Specimen combination	1/2-in.-diameter hardened (to Rockwell 62 C) steel ball sliding against a flat surface of unhardened tool steel
Linear speed of flat specimen	about 1/4 ipm (about 1/10 mm per sec)
Net contact loads applied normally to fixed sphere	75, 93, and 143 g
Corresponding Hertzian loads (maximum stress at center of contact area)	80,000, 85,000, and 100,000 psi

When an unlapped poorly cleaned flat specimen was used, the average coefficient of kinetic friction was of the order of 0.02 to 0.05; in such cases, the presence or absence of mineral oil made little difference. This lack of sensitivity to apparent lubrication is not particularly surprising, since the initial contamination of the ground surface probably provided a lubricating film; it is likely that the contact loads used were too light to break through this film and establish metal-to-metal contact. In subsequent experiments, a lapped specimen, carefully cleaned by acetone and ether washes, was used. Average coefficients of kinetic friction obtained immediately after the surface was dried were in the 0.19 to 0.21 range; after 4 days in air, with no further treatment to the flat, the corresponding range was 0.15 to 0.17. Breakaway friction values with the carefully prepared flat were quite distinct, ranging from 0.24 to 0.32.

The kinetic friction forces during the runs made thus far have not been constant but have varied with some periodicity, suggesting "slip-stick" behavior. In fact, the sharpness of the fluctuations increased with applied load and, at the 143-g load level, slip-stick behavior was quite pronounced.

As a whole, the data obtained with the apparatus under the test conditions thus far employed are quite reasonable. However, prior to runs with sodium, a few additional check-out experiments are contemplated at higher-than-room temperatures, perhaps with an inert atmosphere.

Basic Studies of Pressure Bonding

S. J. Paprocki, E. S. Hodge, S. D. Beck, D. C. Carmichael,
and P. J. Gripshover

An investigation is in progress to study the fundamental principles associated with hydrostatic pressure bonding. The principal emphasis is placed on a study of the deformation of bodies under hydrostatic pressure in order to determine the conditions required to insure that surfaces placed together will attain the sufficiently close contact needed to bond.

Analytical Studies of Pressure Bonding

In an effort to obtain an understanding of the behavior of bodies under hydrostatic pressure, a study is being made of the compression of a thick-walled circular cylinder under external hydrostatic pressure. The theoretical approach first used for this problem attempted to predict deformations in terms of pressure, geometry, and material properties which were expected to vary with temperature. Allowance for variations with time was made possible by regarding the material properties as varying with time also. However, it is thought now that the theory would be improved if variations with time were shown explicitly, so that the material parameters would be independent of time as well as independent of the pressure and geometry. An effort is being made presently to produce a revised theory in terms of these more uniform material parameters. This involves obtaining a strain-hardening function which describes the creep behavior of the material. If this revision can be effected, a more accurate estimate can be made of the material parameters involved in hydrostatic pressure bonding.

Experimental Studies of Pressure Bonding

No specimens were required by the anlytical studies until the end of the present reporting period; therefore, no results are available.

Specimens are now being prepared to be pressurized at 6000 psi and 500 F for periods of 2, 4, and 6 hr. These specimens are thick-walled aluminum tubes with both ends sealed. Duplicate specimens will be run at each of the three conditions to insure reliability of the results obtained. The amount of deformation produced in these specimens will be used to test the validity of proposed mathematical models for predicting the flow characteristics of metals during pressure bonding. The values obtained for these specimens will be compared with previous results obtained at a lower pressure using the same temperature and times.

I. PHYSICAL RESEARCH

F. A. Rough and B. W. Dunnington

Programs of physical research supported by the AEC Division of Research are reported in this section.

Last month in BMI-1247 reports of results were included for programs of research on properties of uranium compounds, constitution of uranium alloys, and solid-state studies of UNC and of UC_2. Research is continuing on these programs, but results are not included in this report.

In the study of bonding fundamentals, the role of diffusion is being evaluated. Calculated and experimental results correspond over a limited time range for almost every experimental case. Evaluation of data is continuing in order to understand the cause of deviations occurring at the longer times.

In the study of niobium-hydrogen reaction kinetics, surface reaction appears to be affecting sorption rates, giving inexplicable results. Experiments are planned to study desorption rates, which should be diffusion dependent. Additional equilibrium data at 300 to 600 C and hydrogen pressures of 0.6 to 10 mm of mercury confirm earlier results. These studies are continuing.

The phenomenon of hydrogen migration on zirconium hydride under a thermal gradient is being studied. A theoretical examination of the various factors affecting the migration is in progress. Results of experiments to determine diffusion coefficients of hydrogen in the delta hydride are reported.

Study of Bonding Fundamentals

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

Studies have been continued on the solid-state bonding process for the purpose of relating the adhesion behavior of metals to material properties and experimental conditions. In a typical experiment, the normal force of adhesion is measured at the contact region between a hemispherical needle point and a plane surface. The contacting surfaces are exposed to various conditions of time and temperature to stimulate an increase in the bonded area and therefore increase the adhesive strength of the contact. Several theories have been advanced to explain the material transport which takes place to increase the bonded area. Kuczynski* has proposed a theory based on volume diffusion as the mechanism for material transport in sintering of metal powders. On the basis of this theory, coefficients of volume self-diffusion have been predicted which show reasonable agreement with results of radioactive-tracer determinations. Kuczynski studied the rate of sintering between spherical metal powders and flat plates, measuring optically the change in contact radius with changing time. In the present

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*Kuczynski, G. C., "Self Diffusion in Sintering of Metallic Particles", Trans. AIME, Journal of Metals, 185, 169-178 (1949).

work, the relation derived by Kuczynski has been modified by making allowance for the finite initial contact area established by application of a preload. The preload was immediately removed in order to allow bond growth to occur under negligible external pressure. The equation expressing bond growth between a spherical particle and plate with zero initial contact area is:

$$\text{Area} = \pi x^2 = \left[\frac{40 \sigma \delta^3 a^2 D_V t}{kT} \right]^{2/5} . \qquad \text{(I-1)}$$

With allowance for an initial contact area the equation becomes:

$$\pi x^2 = \pi x_o^2 \left[1 + \left(\frac{81 \sigma \delta^3 a^2 D_V t}{4k \, x_o^5 \, T} \right)^{1/3} \right]^2 , \qquad \text{(I-2)}$$

where

x = contact radius at time, t

x_o = initial contact radius formed by preloading

σ = surface tension

δ = interatomic spacing

a = radius of curvature of needle or powder particle

D_V = coefficient of volume self-diffusion

t = time

k = Boltzmann's constant

T = temperature.

Both equations are subject to certain geometrical restrictions and are valid only when the ratio of contact radius to radius of curvature is much less than unity. The logarithmic form of Equation (I-2) can be differentiated giving:

$$\frac{d \ln \left(\sqrt{\frac{A}{A_o}} - 1 \right)}{d \ln t} = 1/3 \quad .$$

Thus, a logarithmic plot of $\left(\sqrt{\frac{A}{A_o}} - 1\right)$ versus time would be linear with a slope of 1/3. The same relation should hold when $\sqrt{\frac{F}{F_o}}$ replaces $\sqrt{\frac{A}{A_o}}$. Experimental values of adhesion forces and contact areas calculated from electrical-resistance measurements have been compared with values obtained from this equation. In the temperature range from 600 to 800 C, the experimental results do not show the predicted linear correspondence, but have a varying slope which decreases with increasing time. In almost every instance, there is a time range over which the calculated and experimental curves correspond. It is evident, however, that the theoretical model is not adequate over the entire range of bonding times. The range of slopes determined experimentally for time up to 60 min are tabulated below:

Temperature, C	$\frac{d \ln \left(\sqrt{\frac{F}{F_o}} - 1\right)}{d \ln t}$	$\frac{d \ln \left(\sqrt{\frac{A}{A_o}} - 1\right)}{d \ln t}$
600	0.50-0.40	--
650	0.54-0.26	0.7 -0.34
700	0.55-0.26	0.67-0.34
800	0.59-0.18	0.47-0.20

The calculated slope of 1/3 is based on the volume diffusion-transport mechanism. It also depends on the assumption that the geometry is that of a spherical surface touching a plane surface.

An eventual decrease in the rate of bond growth by this mechanism must be anticipated, since the amount of material transport required for a given increment of area will increase rapidly with an increase in contact radius. The high initial growth rate suggests that, in the initial stages of bond growth, mechanisms other than volume diffusion are effective. The possibilities include surface and grain-boundary diffusion (which proceed more rapidly than volume diffusion), an increased rate of volume diffusion due to deformation at contact, and transport of metal by evaporation and condensation.

In bonding experiments between gold needles and silver flats, silver was observed to deposit on the gold needle. The deposits occur both when contact is made, and when the specimens are placed in close proximity without contact. The observed deposition of silver on gold shows that evaporation and condensation can occur under the conditions used in these tests. It is not established whether condensation of metal at the surface of minimum radius (i.e., the bond junction) can be related to equilibrium pressures by the Kelvin equation. If this is the case, then the bond growth should proceed at a rate proportional to $t^{2/3}$.* A study of this process is being made.

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*Kuczynski, G. C., loc. cit.

The decrease of the experimental slope at longer bonding times has not yet been resolved quantitatively. Metallographic sections of bond junction are being studied to determine the geometrical factors that influence the rate of bond growth. Measurements are also being made of needles exposed to varying experimental conditions to determine the extent of deformation occurring at the contact, and to establish whether the geometrical limits on the theory have been exceeded.

Niobium-Gas Reactions

W. M. Albrecht and W. D. Goode

A study of the kinetics and mechanisms of the reaction of hydrogen with niobium is being made. Data for the rates of formation of several solid solutions using 1/4-in.-diameter cylindrical specimens were reported previously. These early experiments gave erratic results and slow reaction rates when the system pressure was greater than 10^{-5} mm of mercury during the initial heating period. Further experiments have been made at 500 C to determine whether there is any contamination of the specimen while it is being heated in vacuum to the reaction temperature. Niobium specimens were heated for various lengths of time before obtaining rate data with hydrogen. It was found that heating the specimens in system pressures of the order of 10^{-6} mm of mercury for times up to 1 hr did not affect the reaction of hydrogen with the metal.

From diffusion theory, the initial rate of sorption should be parabolic. However, if the rate of diffusion is quite rapid the initial parabolic behavior may not be discernible from the experimental data. Once the concentration of hydrogen in the core starts to increase, the rate appears to be linear until the equilibrium hydrogen composition is approached. Therefore, where diffusion is quite rapid, the initial rate of sorption could appear linear even if the reaction were diffusion controlled.

Another aspect of diffusion-controlled rates is that they should vary inversely as the square of the diameter. Therefore, several experiments were made at 450 to 500 C to determine the effect of specimen diameter on sorption rate. The results are shown in Table I-1. It is seen that the initial rate of sorption varies little with specimen diameters ranging from 0.29 to 0.97 cm. This indicates that a surface reaction is probably controlling the sorption rate and not diffusion of hydrogen within the metal.

The surface reaction for desorption probably does not interfere with the diffusion process, so determination of the diffusion rates during desorption of hydrogen from niobium may be feasible. Experiments of this type are being planned.

In order to extend the equilibrium diagram of the niobium-hydrogen system, the low-pressure equilibrium study is being continued. Equilibrium data obtained at 300 to 600 C at hydrogen pressures from about 0.5 to 10 mm of mercury agree with the results of the previous study. Also, preliminary results of the elevated temperature X-ray study at 300 to 400 C of specimens with hydrogen-niobium ratios of 0, 0.097, 0.24, and 0.54 show lattice expansions of the body-centered-cubic phase of the metal as the hydrogen concentration increases. The low-pressure equilibrium and X-ray studies are continuing.

TABLE I-1. EFFECT OF SPECIMEN DIAMETER ON THE RATE OF SORPTION OF HYDROGEN BY NIOBIUM

Temperature, C	Product Composition, H/Nb	Diameter, cm	Initial Linear Rate Constant, 10^{-2} ml/(cm^2)(sec)
500	0.1	0.29	1.07
500	0.1	0.60	0.97
450	0.5	0.56	1.40
450	0.5	0.97	1.35

Migration of Hydrogen in Zirconium Hydride

J. B. Vetrano, W. M. Albrecht, and R. J. Harrison

The object of this investigation is to study the phenomenon of the migration of hydrogen in zirconium hydride. From a knowledge of the isothermal diffusion coefficients of hydrogen in zirconium and zirconium hydride as a function of temperature and hydrogen concentration, and from a knowledge of the thermodynamic properties of the hydrogen-zirconium system, an attempt will be made to derive an expression to describe hydrogen migration under a thermal gradient.

A theoretical examination of the various factors affecting migration of hydrogen in zirconium hydride under a thermal gradient and the probable relative magnitude of these factors is continuing. The extent to which the standard phenomenological equations expressing the flow of matter as a linear function of the gradients of temperature and concentration may be expected to be valid under the conditions planned for experimentation is being studied. The contribution of purely thermodynamic parameters to the coefficients in these equations is being evaluated by comparing these equations to the more fundamental ones in which the gradient of chemical potential rather than the concentration gradient is considered as the driving force for matter flow. For example, it is expected that thermodynamic data based on knowledge of the equilibrium pressure of hydrogen over the hydride as a function of temperature and composition may be used to deduce a time dependency of the measured thermal-diffusion coefficient. It is well known that thermodynamic data relating to the nonideality of a linear system may be used to account for the difference between ordinary diffusion coefficients and self-diffusion coefficients. It is possible that experiments using isotopic hydrogen as a tracer would be valuable in the study of thermal-diffusion mechanisms in zirconium hydride.

Since the last report of this work, in BMI-1232, the diffusion coefficients of hydrogen in delta zirconium hydride have been measured at 200 to 600 C by the moving-boundary technique. In this technique the rate of movement of the hydride-metal (delta-alpha) boundary into a hydrogen-saturated core is measured. The diffusion coefficients are listed in Table I-2. These values are slightly lower than those obtained by extrapolations of the low-temperature data presented by Gulbransen and Andrew* who used a weight-gain technique to measure diffusion coefficients.

TABLE I-2. DIFFUSION COEFFICIENTS FOR HYDROGEN IN DELTA ZIRCONIUM HYDRIDE

Temperature, C	Diffusion Coefficient, cm^2 per sec
200	1.5×10^{-10}
300	3.1×10^{-9}
400	1.1×10^{-7}
500	3.4×10^{-7}
600	3.1×10^{-6}

As reported in BMI-1232, the diffusion rate of hydrogen in beta zirconium is too rapid to permit use of the concentration-gradient technique to obtain diffusion coefficients. Therefore, experiments were made with a technique based on measuring the rate of absorption of hydrogen by a cylindrical specimen at 700, 750, and 800 C. It was found that the data obtained did not follow diffusion theory. Apparently a surface reaction is controlling the sorption rate. Presently, other experimental techniques are being considered.

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*Gulbransen, E. A., and Andrew, K. F., J. Electrochemical Society, 101, 560-566 (November, 1954).

J. CORROSION PROBLEMS ASSOCIATED WITH THE RECOVERY OF SPENT REACTOR FUEL ELEMENTS

C. L. Peterson, P. D. Miller, E. F. Stephan, J. D. Jackson,
T. E. Snoddy, and F. W. Fink

The evaluation of materials of construction for use in the various proposed processes for the recovery of spent reactor fuel elements has been continued.

The Darex Process

Uranium can be recovered from fuel elements containing stainless steel by the Darex process in which the elements are first dissolved in dilute aqua regia. The chlorides are stripped from the solution with concentrated nitric acid, and, after suitable adjustment, the dissolved uranium is recovered by solvent extraction.

Dissolver Studies on Titanium

As was described in BMI-1247, Ti-75A and Ti-55A titanium are being studied under conditions simulating those present at certain stages in the dissolution process. The results of this work will be reported at the conclusion of the study. To date, results with titanium are encouraging.

FAT Studies on Titanium

Various types of titanium specimens are being evaluated in boiling-refluxing conditions in simulated feed-adjustment-tank (FAT) solutions. No deleterious effects have been noted after inspections following 1 and 4 weeks of exposure in the solution simulating the beginning condition.

Titanium is also being evaluated in a solution simulating the final boil-down concentration. The specimen consists of a 1/2-in. titanium (Ti-55A) tube through which steam at 140 C is passed to maintain the solution at the boiling point (approximately 125 C). A preliminary examination after a few days did not disclose any corrosion.

The Thorex Process

In the Thorex process, fuel elements containing thorium metal or ThO_2 are declad by suitable means and then dissolved in a nitric-hydrofluoric acid solution. The projected treatment of stainless steel-clad elements will probably involve decladding in a sulfuric acid solution.

The study of several stages of this thorium-fuel-recovery process has been initiated. A solution of 13.0 M HNO_3 and 0.05 M NaF is being investigated as a starting composition. Specimens were evaluated in refluxing solutions of the above composition contained in Teflon retorts fitted with Karbate condensers. Carpenter 20 stabilized showed a corrosion rate of about 50 mils per month and Type 17-7PH steel showed a rate of about 100 mils per month after exposures of 38 and 61 hr, respectively.

The Fluoride-Volatility Process

Fuel elements containing zirconium as a diluent or cladding can be reclaimed by a fluoride-volatility process. The first step consists of hydrofluorinating the elements in a molten bath of ZrF_4-NaF with a stream of HF. A material of construction for this hydrofluorinator is being sought.

Monel was exposed in the melt for 1000 hr at 650 C at an HF flow rate of 10 g per hr. A penetration rate of about 25 mils per month, or greater, was experienced at areas of highest gas velocity.

A specimen of INOR-1 was exposed under the same conditions for about 430 hr. No intergranular attack or penetration was indicated by metallographic examination. Weight-change measurements were of no value because of the large buildup of metallic nickel crystals on the specimen walls. The explanation for this mass transfer is not known at present. A similar deposition of crystals was observed on a specimen of INOR-8 which was exposed for about 60 hr.

K-1 and K-2

K. EVALUATION OF A REFLECTOR-CONTROLLED HETEROGENEOUS BOILING REACTOR

R. G. Wilson, D. A. Dingee, and J. W. Chastain

A basic study of the effects caused by voided regions which pass completely through a reactor core is being made. This kind of void situation occurs frequently in reactor work, as it did in the earlier reflector-control experiments. It is believed that more information regarding the effects of voids is desirable.

A plastic-moderated unreflected 24-in. cube is being used for the study. Parallel voids of different cross-sectional areas which pass completely through the core are being introduced and the effects on various reactor parameters are being observed. The amount of moderator is being held constant in the various void conditions for the purpose of eliminating one effect and thus simplifying the calculations.

Data taken during December were analyzed and plans for future experiments with this reactor system were established. The analysis showed that, for the condition of thirty-two 1-1/2 by 1-1/2 by 24-in. uniformly distributed parallel voids, the critical mass is 8930 ± 45 g. This is an increase of about 610 g over the condition of no through voids. The change in reactivity between these two conditions was calculated to be $-0.0249 \pm 0.0013 \frac{\Delta k}{k}$. The worth of one control element was found to be the same in both these cases within the accuracy of the experiment.

The neutron leakage from the core was measured with bare indium foils. The ratio of the neutron leakage integrated over one face of the reactor perpendicular to the voids to the neutron leakage integrated over one face of the reactor parallel to the voids was found to be 2.72.

Future experiments with this system will be carried out to obtain corresponding data for several other void conditions.

L. STUDIES OF SODIUM-TANTALUM COMPATIBILITY AT ELEVATED TEMPERATURES

J. H. Stang

Research is being conducted for Los Alamos Scientific Laboratory to obtain information concerning the creep behavior of commercial types of tantalum in environments of high-temperature sodium and inert gas and concerning the weldability of tantalum. The reactor application involved is LAMPRE, which will feature an all-tantalum core, cooled by flowing sodium, to contain the molten plutonium-alloy fuel mixture.

Creep tests in progress during January have indicated (1) that creep of tantalum during 1200 F sodium exposures may be similar to that during comparable inert-gas exposures (this is based on initial data from two corrosion-creep experiments just under way), and (2) that inert-atmosphere creep of tantalum welds (at 1200 F) may not be greatly different than that of the original material. Resistance-welding studies have continued, but a significant problem still not overcome is that of electrode sticking when melting is produced in weld nuggets. Four different tube-to-header joint designs for resistance welding appear to hold promise on the basis of metallographic examinations.

Tantalum-Sodium Compatibility Studies

G. E. Raines, C. V. Weaver, and J. H. Stang

The creep and corrosion behavior of stressed tantalum specimens exposed to 1200 F flowing sodium is being investigated. The exposures are being made in small forced-convection polythermal loop systems fabricated of Type 316 stainless steel; these loops are equipped with appropriate facilities for stressing the specimens and monitoring creep.

During January, the first two experiments in this research were started. The first of these is being run with a specimen of annealed sintered tantalum, while the second is with a specimen of annealed arc-cast tantalum; the nominal stress level being employed in each case is 15,000 psi. At the end of 257 hr, the annealed sintered material has deformed 2.9 per cent and has exhibited a minimum creep rate of about 0.0046 per cent per hr. These values agree fairly well with corresponding inert-atmosphere creep values for sintered tantalum which was exposed to sodium prior to creep testing (see BMI-1232). This particular comparison, which, of course, is based on very limited data, would indicate that stress-corrosion effects with the tantalum-sodium combination are not especially significant.

The experiment with arc-cast tantalum has been in progress only 120 hr. While the minimum creep rate has not yet been established, it would appear that it will be low and in fair agreement with the corresponding rate during inert-atmosphere loading.

Two more experiments are planned to begin during February; in these, the two materials now being tested will be subjected to loads different from those now maintained (probably lower in the case of the sintered material and higher in the case of the arc-cast material). At the conclusion of these experiments, a fair appraisal of the factors being investigated should be possible.

High-Temperature Mechanical Properties of Tantalum

G. F. Huber, C. J. Slunder, J. G. Dunleavy, and
A. M. Hall

Currently, the main effort in this research is being placed on obtaining fine-grained degassed tantalum for 1200 F inert-atmosphere creep testing; the process being investigated involves a high-temperature thermal-degassing step followed by cold-working and annealing steps. During January, attempts were made to degas specimen stock at a temperature somewhat above 4800 F (this temperature hitherto has been in the 4500 to 4800 F range) to obtain an ultrapure material for subsequent treatment. However, at this higher temperature, several difficulties were encountered with the degassing apparatus. Consequently, modifications to the apparatus have been necessary and have delayed investigation of the effect of various factors involved in the grain-refining steps. The apparatus modifications have now been nearly completed and it is anticipated that degassing runs can resume in February.

Specimens having a bead weld normal to the direction of load are being evaluated in creep tests (at 1200 F in helium) now in progress. These specimens were prepared from a sheet of as-rolled arc-cast tantalum on which a bead-on-plate weld had been drawn. Nominal stress levels being employed are 15,000 and 17,500 psi. At the end of 400 hr, the total deformations are 0.34 per cent and 0.57 per cent, respectively; minimum creep rates at 400 hr are 0.00006 and 0.00035 per cent per hr. Thus far, the weld-containing specimens have exhibited greater initial deformation than the original sheet, but their creep rates are only slightly higher. As a comparison, a control specimen of as-rolled arc-cast material subjected to 15,000 psi has deformed about 0.1 per cent in 400 hr, and its minimum creep rate is about 0.00004 per cent per hr.

Weldability of Tantalum for High-Temperature Systems

R. L. Koppenhofer, S. M. Silverstein, and R. P. Sopher

During January, a phase of this research directed toward determining factors which contribute to porosity in arc-welded tantalum joints was renewed. Preliminary arc-welding and metallographic studies using a new lot of material showed that the weld beads contained porosity in the weld region. Attempts are now being made to control and concentrate this porosity by various welding techniques. If this plan proves successful, the material adjacent to the porous area will be analyzed, and a comparison will be made between the constituents present and those present in unwelded tantalum. In this way, elements which are causing porosity in welds of some lots of tantalum should be distinguishable.

L-3 and L-4

Results of recent exploratory resistance-welding tests with tantalum indicate that four of eight tube-to-header joint designs being investigated may be successful. Studies are being continued on the promising ones to develop welding conditions and techniques for making satisfactory joints.

Metallographic examinations of spot welds made in tantalum sheet have indicated that solid-phase-type bonding can be obtained. Although melting can be produced in the weld nugget by increasing the welding heat, electrode sticking becomes a problem. It has been found that RWMA Class 2 copper-alloy electrodes give the best results for welding sheet material. These electrodes have been internally and externally water cooled during welding.

Hardness surveys made on spot welds in tantalum sheet have indicated that hardness differences do not exist in similar areas of solid-phase bonds and bonds in which melting occurred. There is, however, a gradual decrease in hardness from approximately 370 VHN for the base metal to approximately 170 VHN at the center of the weld interface in each type of bond.

M. DEVELOPMENTAL STUDIES FOR THE PWR

R. W. Dayton

Preparations are being made for a continuation of the work on PWR flow studies.

Preliminary tests were made of the X-ray photometer. A low counting rate and a high background activity were found; attempts to correct these difficulties are being made.

Methods of preparing Zircaloy 2 surfaces for pressure bonding fuel plates are being investigated, with results similar to those previously reported. Chromium has been found to be the most suitable barrier layer, for preventing reaction between Zircaloy 2 and UO_2. An irradiation-test sample which appears to be satisfactory has been prepared.

Reactor Flow Studies

L. J. Flanigan and H. R. Hazard

Flow studies using air in a quarter-scale model of the PWR reactor are being conducted to determine the effects of lower-plenum geometry on mixing and flow distribution in Core 2. Previously reported work includes completion of flow studies to determine core-flow distribution, shield velocities and directions, flow-baffle pressure loss, and mixing for two-, three-, and four-loop operation with the basic 9-ft core design and with the basic 9-ft core with flow deflectors.

Additional studies are being initiated with two additional core lengths. Drawings of the flow baffle for the quarter-scale model to simulate a 7-1/2-ft basic core design have been received and are being revised to include instrumentation for pressure measurement and a layout of the hole pattern for the bottom of the baffle.

The test facility is being moved into a new laboratory building. It is estimated that the move will be completed early in March.

X-Ray Photometric Examination of Fuel Elements

J. B. Schroeder and C. M. Schwartz

An X-ray photometer is being developed for examination of microsegregation in fuel elements. Preliminary tests were made of the beam attenuation in a test filler plate 0.139 in. thick; the transmitted intensity appears lower than estimated on the basis of extrapolation from the experimental conditions of the initial feasibility studies. Furthermore, a high background count rate was found. This appears attributable to Bremsstrahlung from the beta activity of the filler plate.

X-ray pinhole photographs were obtained to check the beam geometry. The focal spot appears displaced from the axis of the radiation cone; this may be the cause of the low intensity.

The possible error in beam alignment is being tested further, and will be corrected. Attempts are being made to reduce the background rate by means of additional shielding around the detector tube.

Pressure Bonding of Zircaloy 2-Clad Fuel Elements Containing Compartmented Oxide Fuel Plates

S. J. Paprocki, E. S. Hodge, D. C. Carmichael,
P. J. Gripshover, and H. D. Hanes

A Zircaloy 2-clad fuel element containing compartmented uranium dioxide fuel is being considered for PWR Core 2. An investigation is being conducted to study the preparation of these elements by pressure bonding. This process utilizes hydrostatic pressure at elevated temperatures to achieve bonding. Studies are being continued to determine suitable conditions for obtaining good Zircaloy 2-to-Zircaloy 2 bonding and to determine a feasible barrier layer to prevent fuel-cladding reaction. Specimens are also being prepared for irradiation testing.

Specimens are being pressure bonded to investigate the effect of surface preparation on bonding. The ultimate objective of this study is to obtain a perfect bond. Such a bond is one in which there is no trace of contamination and in which there is complete grain growth across the original interface so that, after bonding, the interface cannot be identified by examination and testing. Previous results of this study have indicated that hot-rolled or annealed Zircaloy 2 that has been machined or belt abraded can be successfully bonded. Additional specimens have shown that belt-abraded surfaces bond more consistently than machined surfaces, and that cold-rolled material can also be satisfactorily bonded if it has been belt abraded according to developed techniques. Variables in the belt-abrading process which have been investigated to determine their effect on the bonds obtained between abraded Zircaloy 2 surfaces are belt speed, coolant, abrasive material, and amount of metal removal. Results indicate that cold-rolled material requires a slower belt speed than hot-rolled material to obtain good bonding surfaces. Sulfonated oil is preferable to water for a coolant; a suitable abrasive material is 60-grit silicon carbide. The amount of metal removal does not appear to be critical except that sufficient material must be removed to produce a clean surface.

In an attempt to activate the surfaces of Zircaloy 2 and thereby promote bonding, a specimen was prepared with bonding surfaces that had been cathodically charged with hydrogen. The thin surface layer of zirconium hydride did not improve bonding significantly; an additional specimen is being prepared with a thicker hydride layer. A hot-rolled and metallographically polished specimen was bonded to determine the effect of surface smoothness on bonding. This specimen yielded only 75 per cent grain growth across the bond interface, indicating that surface smoothness may influence the extent of bonding. However, the possible effects of other variables, such as surface contamination and surface work, could not be determined for this specimen. A similar specimen which had been prepared from cold-rolled and metallographically polished components exhibited only 45 per cent grain growth across the bond interface, which suggests that hot-rolled material may bond more readily than cold-rolled material. A specimen with components which were beta annealed in a good vacuum previous to bonding was not satisfactorily bonded, apparently due to slight oxidation of the surfaces during annealing. The annealing of Zircaloy 2 will have to be followed by a surface treatment to remove contamination before bonding.

A study is also being conducted to determine a suitable barrier layer to prevent reaction between the uranium dioxide cores and the Zircaloy 2 cladding during pressure bonding. The results of specimens containing no barrier layer have demonstrated that the temperature of bonding is critical in determining the amount of reaction. Thus the necessity for a barrier layer cannot be finally evaluated until the bonding study is completed and the minimum satisfactory temperature for bonding is known.

If a barrier layer is necessary, chromium appears to be very suitable for this purpose. Specimens intentionally made defective and containing cores electroplated with a 0.0005-in. coating of chromium have exhibited no growth or apparent attack after 4 weeks in 750 F steam and 3 weeks in 680 F water. The chromium apparently does not have a deleterious effect on the corrosion resistance of the Zircaloy 2 and also has good corrosion resistance itself. Metallographic examination of these specimens after bonding revealed no reaction between the chromium barrier layer and the Al_2O_3-21 w/o UO_2 fuel and no detectable diffusion of chromium into the Zircaloy 2. Chromium appears to be an effective barrier even if an as-bonded sample is heat treated at 1650 F for 4 hr or at 1850 F for 15 min. A method of electroplating oxide cores with a thin coating of chromium has been developed.

Iron and nickel also appear to be satisfactory barrier layers but are not as desirable as chromium. Intentionally defected samples having 0.0005-in. and 0.001-in. iron barriers have been on test for 8 weeks in 750 F steam and 3 weeks in 680 F water with no visible growth or attack, except for a slight rusting of the iron layer. Specimens rendered defective and containing barriers of nickel foil and nickel coatings deposited by electroplating and chemical displacement, have shown only slight growth after 8 weeks in 750 F steam and 8 weeks in 680 F water.

Postbonding heat treatments in the high-alpha-phase or low-beta-phase regions for Zircaloy 2 have been found to improve the bonding obtained between surfaces which bond poorly, such as pickled surfaces. Bonded specimens have been heat treated to study the effect of these treatments on fuel-cladding reaction. The alpha-phase annealing was performed at 1650 F for 4 hr and the beta annealing was done at 1850 F for 15 min. The specimens were enclosed in a quartz tube with an argon atmosphere during heat treatment. Specimens with no barrier between 100 w/o UO_2 and Al_2O_3-21 w/o UO_2 cores and the Zircaloy 2 cladding were given the heat treatments and examined metallographically. The uranium reaction zone for the cores diluted with Al_2O_3 was increased from 0.0002 to 0.0003 in. by the alpha anneal and to 0.0006 in. by the beta anneal. Specimens containing the undiluted UO_2 cores showed a 0.0003-in. zone of uranium reaction after bonding and exhibited a 0.001-in. zone after alpha annealing and a 0.002-in. zone after beta annealing. Zircaloy 2-clad cores which had barriers showed that nickel and iron barriers diffused into the Zircaloy 2 during a beta anneal, but chromium barriers appeared to remain unchanged. Specimens from this study which have been defected by drilling a 0.040-in. hole through the cladding are being corrosion tested in 680 F water.

X-ray examination of one group of corrosion specimens indicated that some of the UO_2 in the cores had been oxidized to U_3O_8. However, bare cores have exhibited no appreciable attack or weight change after 6 weeks in 680 F water or 750 F steam. Since the observed core oxidation occurred in only one group of specimens, it appears that the attack was due to insufficient deoxidation of the steam during one of the corrosion tests.

Two irradiation specimens were prepared using hot-rolled and machined components. The cores were coated with 0.0003 in. of chromium to prevent fuel-cladding reaction. There was a failure of one can during pressure bonding, so both specimens were heat treated at 1850 F for 15 min, since this treatment has been found to disclose helium entrapped in core compartments during a can failure. The core compartments of the specimen from the defective can swelled during heat treatment, indicating that some helium had entered the specimen before sealing was complete. No swelling was observed in the other specimen, assuring that there had not been a can failure and helium had not been entrapped. Metallographic examination of the edges of this specimen showed grain growth across the bond interface.

N-1

N. EVALUATION OF URANIUM MONOCARBIDE AS A REACTOR FUEL

F. A. Rough

Because of its high uranium density, reported high thermal conductivity, and refractory nature, uranium carbide appears attractive as a reactor fuel. This is the first report of a program to evaluate the monocarbide. It is expected that satisfactory techniques will be developed for the casting of small slugs of carbide having near theoretical density for use in irradiation tests up to burnups of several thousand megawatt days per ton.

Casting Techniques for the Preparation of Uranium Monocarbide

A. C. Secrest, E. L. Foster, and R. F. Dickerson

The first objective of the research program is to produce cast specimens suitable for irradiation. Initially, uranium carbide will be prepared by procedures that will yield material whose carbon content is as close as possible to its stoichiometric composition. Emphasis will then shift to finding better fabrication techniques associated with arc melting and casting. Also, carbides with carbon contents both above and below the stoichiometric amount will be prepared to study the effects on the properties and irradiation performance.

Experience indicates that uranium monocarbide specimens may be castable, and available arc-melting furnaces are currently being used in the preparation of materials. However, an arc-melting unit intended to produce larger shapes is being constructed. Small buttons weighing approximately 100 g have been prepared by melting stoichiometric amounts of biscuit uranium and spectrographic carbon rod. The buttons, prepared under a helium atmosphere, were sound and did not fracture upon cooling. However, it should be noted that these specimens were cooled at a slower than normal rate from 1000 F to room temperature. Approximately 1 hr was required to cool from 1000 F to room temperature. This procedure is believed to have prevented fracturing, since buttons which were cooled at the normal rate shattered. Preliminary tests on the buttons indicate that they can be machine ground without fracturing and have a hardness of the order of 725 VHN. Techniques are being studied for coating this material with a metal, since coated specimens will be required for thermal-conductivity determinations.

The uranium carbide specimen size for the irradiation program has been established. On the basis of thermocouple size, capsule size, center-line temperature, and flux requirements, a 3/8-in.-OD by 2-in.-long specimen was selected.

Immediate plans are to produce cast material of suitable size and shape for thermal-conductivity determinations and for compatibility studies of UC with NaK at 600 C. Concurrent with the above plans will be a study of properties of uranium monocarbide, such as hardness, density, and microstructure.

N-2

Irradiation Capsule Design for Uranium Monocarbide

R. H. Barnes, E. M. Chandler, and G. D. Calkins

It is tentatively planned to irradiate uranium-carbide specimens in stainless steel capsules containing NaK as the heat-transfer medium. The MTR will be utilized for the irradiations. Each capsule will contain two specimens and will be instrumented to monitor temperature. One thermocouple will be inserted into a hole in one of the specimens to obtain the central core temperature and another at the surface of the specimen. Changes in the temperature drop between the thermocouples will serve roughly as an indication of a change in the thermal conductivity of the specimens.

Some of the preliminary phases of the irradiation capsule design are completed. Plans for NaK-uranium carbide compatibility tests have been formulated and preliminary capsule-design calculations have been completed on a uranium 4.8 w/o carbon fuel material.

Tests to check the compatibility of uranium carbide with NaK in stainless steel capsules at 1200 F are planned early in the program. These tests will show whether it is feasible to use stainless steel capsules with a NaK heat-transfer medium for the irradiation phase of the study. Two specimens of uranium-4.8 w/o carbon will be encapsulated in each of three NaK-filled stainless steel capsules and held at a temperature of 1200 F for three different periods of time. Tentative plans are for periods of 2, 4, and 8 weeks. Two additional capsules, one containing two specimens of material having a lower carbon content and the other containing two specimens having a higher carbon content, will be encapsulated and operated at the same temperature to check the effects of variations in composition. The tentative period for the variable-composition tests is 4 weeks. The specimens in all tests will be held in baskets fabricated from a material which does not react with uranium or carbon at the test temperature.

Preliminary calculations on fission rate indicate that an enrichment in uranium-235 of 8.3 per cent is optimum for 0.375-in.-diameter specimens. Irradiation specimens of smaller diameter than this are not desirable for the program because of the necessity for inserting thermocouples in one of the specimens in each capsule, and also because smaller sizes may not be representative of the conditions of potential use.