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PROGRESS RELATING TO CIVILIAN APPLICATIONS
DURING OCTOBER, 1956

by

Russell W. Dayton
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For The Atomic Energy Commission

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November 1, 1956

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REPORTS RELATED TO CIVILIAN APPLICATIONS
ISSUED DURING OCTOBER, 1956

- BMI-1130 "Effects of Impurities on the Corrosion Behavior of Zirconium-Uranium Alloys", by Warren E. Berry, James E. Reynolds, Horace R. Ogden, Robert S. Peoples, and Robert I. Jaffee.
- BMI-1134 "The Constitution of Delta Phase Alloys of the System Uranium-Molybdenum-Titanium", by Henry A. Saller, Frank A. Rough, Arthur A. Bauer, and J. Robert Doig.
- BMI-1135 "The Electrical Properties of Uranium Oxides", by Robert K. Willardson, Jerry W. Moody, and Harvey J. Goering.
- BMI-1136 "Progress Relating to Civilian Applications During September, 1956", by Russell W. Dayton and Clyde R. Tipton, Jr.

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A. DEVELOPMENT OF MATERIALS FOR HANFORD REACTORS

F. R. Shober

The use of clad specimens to successfully measure the thermal conductivity of irradiated uranium is being investigated. Thermal-conductivity measurements on solid rods of the core and the cladding material are continuing.

An investigation to determine the solubility of uranium in thorium by electrical-resistivity studies was continued. The limits of uranium solubility in thorium have been tentatively determined as 0.75 and 1.75 w/o at 800 and 1000 C, respectively.

The long-time creep properties of Zircaloy 2 are being determined at elevated temperatures. The tests have been in progress for 2830 and 2700 hr. The test at 9,000 psi and 343 C has shown no creep in the last 900 hr, and the test at 21,000 psi and 232 C has had a steady creep rate of 0.000002 per cent per hr for the last 1000 hr.

Thermal Conductivity of Uranium

H. W. Deem and C. F. Lucks

The effect of irradiation on the thermal conductivity of uranium up to 800 C is to be determined in cooperation with the Physical Metallurgy Subsection at Hanford. Exploratory measurements by the steady-heat-flow method will be made to determine the feasibility of making thermal-conductivity measurements on uranium rods clad with Zircaloy 2 with NaK as the heat-transfer media.

Hanford and Battelle have agreed on a design for the test-clad specimens, which are being made by Hanford. A uranium-1.5 w/o zirconium alloy will serve as a substitute for irradiated uranium in the exploratory work; this alloy having been shown to have a thermal conductivity of approximately 5 per cent less than that of uranium.

Battelle is starting thermal-conductivity and electrical-resistivity measurements on solid rods of the materials involved, pending receipt of the clad specimens.

Work is being done on the design of apparatus for thermal-conductivity measurements on irradiated specimens.

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The Constitution of Thorium-Uranium Alloys

R. F. Dickerson and A. A. Bauer

A project to determine the solubility of thorium in uranium has been under way for Hanford.

Electrical-resistivity measurements have been obtained on a series of specimens with varying uranium contents. While the values obtained show some variability, tentative indications of uranium solubility have been obtained at 800 and 1000 C. The limits are approximately 0.75 and 1.75 w/o uranium, respectively, upon the basis of these measurements. Resistivity measurements of specimens heat treated at 600 C showed too great a fluctuation to permit any conclusions.

Additional specimens are to be prepared for measurement in an attempt to strengthen the validity of these values.

Mechanical Properties of Zirconium and Zircaloy 2

F. R. Shober, L. L. Marsh, and J. A. VanEcho

The long-time creep strength of Zircaloy 2 is being determined at 232 and 343 C. These long-time tests are being used to obtain creep rates to be compared with those obtained from 1000-hr tests.

There are two tests in progress, one at 9,000 psi and 343 C and another at 21,000 psi at 232 C. These tests have been in progress 2830 and 2700 hr, respectively. The specimen on test at 343 C has a stepwise time-deformation curve, that is, the curve shows short periods of creep and long periods of no creep. The other specimen on test at 232 C has deformed continuously during its 2700 hr on test, exhibiting a creep rate which has generally decreased with time. Table A-1 shows the variance of creep rate with time of these tests. The tests will continue until a definite secondary creep has been established.

Creep tests at elevated temperature will be started on Zircaloy 3 and on a different lot of Zircaloy 2 when materials arrive from HAPO. Specimens of annealed and cold-worked Zircaloy 2 tubes of several diameters and wall thicknesses have been prepared for tube-burst tests. Testing at room and elevated temperatures will be started next month.

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TABLE A-1. CREEP RESULTS FROM ANNEALED ZIRCALOY 2

Time Period of Test, hr	Elongation, per cent		Creep Rate for Time Period, per cent per hr
	At Start of Time Period	At Finish of Time Period	
<u>Tested at 232 C and 21,000 PSI</u>			
15-150	0.905	0.945	0.000296
150-400	0.945	0.962	0.000068
400-750	0.962	0.967	0.000014
750-1650	0.967	0.980	0.0000145
1650-1700	0.980	0.990	0.00020
1700-2700	0.990	0.992	0.000002
<u>Tested at 343 C and 9000 PSI</u>			
100-400	0.064	0.071	0.000022
400-800	0.071	0.071	Nil
800-1350	0.071	0.089	0.000033
1350-1565	0.089	0.089	Nil
1565-1605	0.089	0.090	0.000025
1605-1925	0.090	0.090	Nil
1925-1950	0.090	0.091	0.00004
1950-2830	0.091	0.091	Nil

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Zirconium Cladding

R. F. Dickerson and F. R. Shober

Pressure bonding of zirconium cladding to uranium cores by hydrostatic pressures is being investigated as a method of cladding round HAPO-type slugs. Experimental work has been delayed by a failure in the temperature-control circuit of the furnace in the pressurizing autoclave. Several nickel-plated uranium slugs, canned in zirconium, will be pressurized for various times at 1160-1200 F upon completion of repairs.

Construction of equipment to weld the zirconium caps to the cans is nearly completed. Final adjustments will be made and equipment will be tested.

Miscellaneous Metallurgical Services

R. F. Dickerson and F. R. Shober

The stresses to produce 1 per cent total creep deformation in 100 hr at 400, 600, 730, and 800 C in beta-quenched uranium are being determined as part of a program of assistance to HAPO. Several specimens have been tested at 730 C, the remaining temperature to be investigated. Results from these tests are inconclusive and additional tests will be carried out at this temperature.

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B. DEVELOPMENTS FOR ALUMINUM-CLAD FUEL ELEMENTS

R. J. Carlson

Attempts to determine the effect of increasing extrusion speeds during the cladding of cores with mechanically attached end plugs have resulted in successful extrusion cladding at speeds up to about 60 in. per min. Failures of the cores during several tests at extrusion speeds in excess of 30 in. per min suggest that core alignment or mandrel-tip deflection may be a problem at the higher speeds.

The initial design of the extensometer for measuring circumferential strains in conjunction with the "ring-test" method for determining the transverse mechanical properties of uranium tubes has proven insensitive to small elastic strains. A new design has been built and initial tests indicate that it is sufficiently sensitive.

Diffusion couples of the aluminum-uranium alloys and 2S aluminum have been tested for 5, 10, 20, and 30 days at 400 C. There is no evidence of uranium diffusion in any of the couples.

Extrusion Cladding of Flat Plates

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

Efforts have continued toward determining the effect of increasing extrusion speeds on the cladding of cores with mechanically attached end plugs. Steel cores have been used since only the plug materials are being tested at this time.

An end plug of M276 (aluminum-12 w/o Al_2O_3), attached to a steel core, has been clad at an extrusion speed of about 60 in. per min without rupture. The plug deformed slightly, however, at the trailing end. Liner and die temperatures of 1075 F and 1100 F, respectively, were used.

In several tests at speeds above 30 in. per min, the steel cores were ruptured at a point located between the mandrel tip and die. The appearance of the failures suggests that the cores may have cocked edgewise, causing them to bind within the mandrel slot. Also, the failures may have been associated with the collapsing of the slot to such an extent that the cores were completely restrained. In this connection, tests were made with undersize steel cores. This would permit greater deflection of the mandrel slot without restraining the core, provided that back extrusion

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does not occur. Thus far, a 0.130-in.-thick core, providing a 0.036-in. clearance, was clad satisfactorily.

Future work will be concerned with a more detailed investigation of the effects of extrusion variables.

Characterization of Inclusions and Metallographic
Evaluation of DIngot-Uranium Tubes

R. F. Dickerson and C. M. Cheney

This work has been concluded and a topical report is being prepared.

Mechanical Properties of Uranium Tubes

R. F. Dickerson and F. R. Shober

The "ring-test" (in which a ring of material is subjected to a high internal pressure) method for determining the transverse mechanical properties of uranium tubes is being evaluated. Transverse properties of beta-quenched ingot uranium, as determined by the ring test, are to be compared with longitudinal properties obtained by the standard sheet-tensile tests. These properties are to be compared at -75, +75, and 300 F.

A mechanical extensometer designed to measure circumferential strains by a spring-loaded wire wrapped around the uranium tube has proven to be insensitive to small elastic strains. A new extensometer has been designed to measure changes in tube diameter during test. These changes will be measured with electric strain gages mounted on slotted cantilever beams and beryllium-copper loops. Testing of the extensometer is in progress. Results indicate that the combination of gages will be sufficiently sensitive to measure the elastic strains and have the range to measure the necessary plastic strains.

The extensometer will be calibrated and testing of beta-quenched ingot uranium will continue.

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Preparation of Aluminum-Uranium Alloys

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

A research program for the development of melting and casting techniques for aluminum-uranium alloys containing 30 w/o and more of uranium is now in progress at Battelle. The techniques developed must be capable of producing sound homogeneous ingots and must also be amenable to production techniques. Also of interest are the corrosion rates of the alloys, their relative fabricability, and the diffusion rate of the uranium from the alloys into 2S aluminum.

Diffusion couples of the aluminum-uranium alloys and 2S aluminum have been tested at 400 C for periods of 5, 10, 20, and 30 days. None of these couples show any evidence of diffusion between the alloy and the aluminum.

A study of the effect of silicon on the liquidus line of the aluminum-uranium phase diagram is being conducted in conjunction with the melting program. Aluminum-16 w/o uranium alloy castings containing 0.1, 0.2, 0.3, 0.5, and 1.0 w/o silicon have been cast and fabricated to the desired sizes for the experimental work. Tests are now being conducted on these alloys.

The casting studies on the high-uranium-content alloys are still in progress. Two biscuits of uranium have been received for use in this program and these biscuits are being cut to sizes suitable for vacuum melting prior to alloying. Work is and will continue to be concentrated on the casting of the 40 and 45 w/o uranium alloys. These alloys seem to be the most difficult to cast.

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C. PLANT ASSISTANCE TO MCW

A. A. Bauer

The study of uranyl nitrate hexahydrate decomposition has continued. X-ray and electrical-property data related to the system UO_2 -oxygen were also obtained.

Comparison of "active" and "inactive" oxide electrical-conductivity curves plotted as a function of reciprocal temperature indicates a higher activation energy for the active oxide. In other respects the curves are very similar.

Corrosion tests are being conducted on Type 304 stainless steel in boiling chloride-contaminated 18 per cent nitric acid. A break in corrosion resistance occurs at a chloride-contamination level of between 0.5 and 1.0 per cent, specimens tested in acid containing 1.0 per cent chloride or more showing significant corrosion rates.

Measurements of hydrogen solubility in dingot liner slag and analyses of hydrogen levels in feed materials have been obtained. Calculations of hydrogen-diffusion gradients produced in uranium metal under varying conditions were also made.

Investigation of Uranium Oxides

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

The study of the decomposition of uranyl nitrate hexahydrate is being continued, and a method of making Type II UO_3 has been found to be reproducible. The residual nitrogen contents of various UO_3 preparations were compared for different methods of decomposition of the nitrate. The use of acetic acid as an additive appears to give UO_3 of low nitrogen content. Further progress was made this month on the system active UO_2 -oxygen.

Previous experiments have indicated that acetic acid addition aids in the formation of Type II UO_3 . Decomposition of uranyl nitrate hexahydrate with the addition of 1 per cent acetic acid at 450 C for 4 hr was found to yield Type II UO_3 reproducibly. The Type II UO_3 thus formed has a low tap density (1.94), but it also has the lowest residual nitrogen content (0.17 w/o) of all UO_3 preparations analyzed. Type II UO_3 is being prepared in quantity to be sent to Mallinckrodt for reduction and hydrofluorination tests. The

C-2

UO₃ formed by the decomposition at 325 C of UNH containing acetic acid is Type III, of high tap density (3.60), and low nitrogen content.

Active UO₂ samples, as described last month, were annealed at 450 C for 100 hr. X-ray diffraction patterns and ignition analyses were made after annealing. The results indicate that UO₂ compositions with oxygen/uranium ratios greater than 2.34 contain two phases, orthorhombic U₃O₈ plus a UO₂-type cubic phase at 450 C, while those with oxygen/uranium ratios less than 2.30 are single-phase-cubic. No other phases were observed in these experiments. It appears that an irreversible phase transition occurs at approximately UO₂.32 at 450 C. Further high-temperature diffraction experiments are in progress to follow the transition at other temperatures.

Work next month will be devoted to the preparation of Type II UO₃, the study of the reduction of Types II and III UO₃ in cracked ammonia, reduction of amorphous UO₃ to active UO₂, and further investigation of the properties of active UO₂.

The Electrical Properties of Uranium Dioxide

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

The temperature dependence of the electrical properties of several uranium oxides (prepared from "active" uranium dioxide) has been measured. These measurements were made on specimens which had been stabilized by annealing at 400 C. They were made to further characterize the structure of the oxides and, in particular, to determine the effects of nitrogen on the electrical properties of uranium dioxide.

In general, the curves obtained were similar to those obtained previously for inactive uranium oxides. The curves of conductivity as a function of reciprocal temperature (from room temperature to 400 C) consisted of two straight lines. In each case the change of slope occurred at about 180 C. Such behavior is strongly reminiscent of the behavior of inactive oxides. However, the activation energies measured from the slopes of the conductivity curves of active specimens were somewhat higher than those measured for inactive specimens. The activation energy, along with some other pertinent properties of these specimens, is listed in Table C-1. In Table C-1, ΔE_1 refers to the activation energy below 200 C and ΔE_2 refers to the activation energy above 200 C. (Letters in parentheses indicate the type of conductivity prevalent in that range of activation energy.) These values are to be compared with the values of 0.3 to 0.5 obtained for inactive specimens.

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TABLE C-1. SOME PROPERTIES OF URANIUM OXIDES OBTAINED FROM ACTIVE URANIUM DIOXIDE

Specimen	Conditions of Preparation		Oxygen/Uranium Ratio	Activation Energies	
	Reduced	Oxidized		ΔE_1 , ev	ΔE_2 , ev
225	Dry hydrogen	Nitrogen	2.390	0.59 (N)	0.80 (N)
227	Wet hydrogen	Air	2.392	0.50 (N)	0.69 (N)
231	Wet hydrogen	Nitrogen	2.137	0.53 (N)	0.61 (N)
237	Dry hydrogen	Oxygen	2.172	0.50 (N)	0.62 (N)

It should be noted that no real significant differences exist between the properties of those specimens exposed to oxygen (or air) and those exposed to nitrogen. Either nitrogen behaves like oxygen in the uranium dioxide lattice or, more likely, these specimens absorbed oxygen sometime after preparation, and little nitrogen had been incorporated in the lattice. That active uranium oxides of relatively low oxygen contents continue to absorb oxygen was indicated by an ignition analysis of two specimens after annealing at 400 C. The oxygen/uranium ratios of these specimens increased from 2.289 and 2.172 to 2.438 and 2.450, respectively.

X-ray analysis of the specimens under present study reveals cubic structures in each case. Electrical measurements, however, indicate the presence of a metal excess phase, possibly U_3O_{8-x} or UO_{3-x} . Since no cubic structures have been reported in the region U_4O_9 - UO_3 , the nature of the specimens under study has not been described exactly. It is obvious that such a description is fundamental to the objective of this work; that is, the characterization of active uranium oxides. Therefore, the work on active oxides will be continued.

The Corrosion Resistance of Selected Stainless Alloys

C. L. Peterson, F. W. Fink,
and R. S. Peoples

During October, the investigation of the corrosion of Type 304 stainless steel in boiling, chloride-contaminated nitric acid has been continued as part of a program of assistance to the Mallinckrodt Uranium Refining Center.

A series of tests in boiling 65 per cent nitric acid has been completed according to ASTM Recommended Practice A 262. Type 304 ELC stainless

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steel specimens from material being used in the fabrication of the Weldon Springs reconcentrator were compared with Battelle's plate stock of Type 304 ELC. The results are summarized in Table C-2.

TABLE C-2. TESTS IN BOILING 65 PER CENT NITRIC ACID

Liquid-Phase Specimens Only

Specimen	Avg Corrosion Rate ^(a) , mils/month
Weldon Springs	0.81 0.74
Plate stock	0.67 0.64 0.71 0.64

(a) Corrosion rates are the average of seven 48-hr exposure periods.

When tested by this procedure, the excessive corrosion rates did not occur for the Weldon Springs material as had occurred in similar tests which were reported in September. The only difference in testing procedures was that the tests reported in September had specimens exposed to the vapor phase in the same container as the liquid-phase specimens. The explanation for the great difference in results between the two testing procedures is not known at present.

Seven 48-hr exposure periods were completed in the series of tests involving exposure of Type 304 ELC specimens to 18 per cent nitric acid (boiling under 200 mm mercury absolute pressure) containing the various chloride contaminations described in the September report. The only specimens which showed any significant corrosion during these exposure periods were those exposed at the interface positions in acids containing 1.00 and 1.50 per cent chloride. These specimens corroded excessively during some periods and remained passive during others. One specimen, which fell from its hanger in the vapor phase of the 1.50 per cent chloride test, corroded severely after it was submerged in the liquid. Apparently, the vapor above these acid solutions activates the specimens in some manner so that, upon further exposure to the liquid, excessive corrosion can occur. In the case of the interface specimens only that portion beneath the meniscus has shown excessive corrosion.

A new series of tests in 18 per cent nitric acid boiling at 200 mm mercury has been started. The chloride concentrations are 0.50, 0.60, 0.70, 0.80, 0.90, and 1.00 per cent. Six 48-hr exposure periods have been

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completed and severe corrosion has been observed in the case of the interface specimens in the acids containing 0.80 and 1.00 per cent chloride. No appreciable corrosion has occurred on any of the other specimens.

A survey of the corrosion occurring in 30 per cent nitric acid, boiling at 275 mm mercury and containing chloride contaminations similar to those in the above tests, is planned as the next step in the investigation. Concurrently, duplicate tests for protracted exposure periods are planned. In these tests, Type 304 ELC specimens will be exposed to 18 per cent nitric acid containing 0.00, 0.05, and 0.10 per cent chloride.

Gas-Metal Studies

M. J. Trzeciak and M. W. Mallett

A study is being made of factors related to hydrogen in uranium. The purpose is to devise feasible methods for reducing hydrogen levels in ingot metal. The study includes an investigation of solubility and diffusion of hydrogen in ingot liner slag, of hydrogen levels in feed materials, and of diffusion of hydrogen in uranium metal.

The solubility of hydrogen in liner slag was measured at 1050 C and 1 atm hydrogen pressure and found to be 72 ppm. The rate of hydrogen absorption was rapid initially for about 20 min; 42 ppm was absorbed. The remaining 30 ppm was absorbed slowly over a period of 45 min.

The times required to produce or alter hydrogen gradients from core to surface in uranium cylinders were calculated for various conditions of temperature and hydrogen pressure. The treatments correspond to those found in uranium production. Calculations were made for a 1.44-in.-diameter uranium rod with an initial hydrogen content of 5 ppm. It was desired to determine the time required to give a gradient with a hydrogen level of 2 ppm at a diameter of 1.36 in. It was found that at 650 C, in vacuum, 6 min is required to produce this gradient. Repeating the calculations with the same objective and under the same conditions but with a hydrogen pressure of 258 mm mercury instead of vacuum, a treatment time of 24 min was found. The hydrogen pressure of 258 mm mercury is the equilibrium pressure equivalent to a solubility of 1.2 ppm at 650 C. The dimensions 1.44 and 1.36 in. are rod diameter and finished slug diameter, respectively.

Vacuum-fusion analyses were made of three magnesium fluoride slag samples. Hydrogen levels ranged from 15 to 40 ppm.

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In an experiment designed to lower the hydrogen content of magnesium metal, dry helium was bubbled through molten magnesium. Samples were taken at regular intervals and analyzed. Results of analyses show that this technique is capable of lowering the hydrogen content to about 4 ppm.

The water content of several lots of magnesium chips is being measured to determine the degree of variation. Preliminary results show water contents ranging from 23 to 115 ppm. The hydrogen levels corresponding to these amounts of water are 3 and 13 ppm, respectively.

Work is continuing on solubility measurements of hydrogen in both molten and solid slag. In addition, it is planned to undertake a study of the diffusion of hydrogen in slag when solubility values are established.

Experiments are being conducted to determine the effect of certain treatments on an imposed hydrogen gradient within a uranium slug. The treatments consist of storage in moist atmospheres followed by heating in a salt bath.

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D. STUDIES OF THE REACTION BETWEEN ZIRCONIUM
ALLOYS AND WATER

A. W. Lemmon, Jr.

A study is being made of the probable extent of chemical reaction at high temperatures between Zircaloy 2 and water. Experimental programs for providing basic data for the mathematical analysis have been completed. During October, additional effort was expended in attempting to predict the probable maximum extent of chemical reaction which might occur in the PWR after loss of coolant.

The extent of reaction in the PWR core after loss of coolant has been computed for additional sets of conditions. Computations directed toward predicting the extent of oxidation of a molten Zircaloy 2 droplet as it falls through steam and water have been completed and a topical report prepared.

Analysis of the Extent of Reaction
and Efficacy of CoolingL. E. Hulbert, A. W. Lemmon, Jr.,
and R. B. Filbert, Jr.

Additional cases have been computed in the program directed at the prediction of the probable maximum extent of chemical reaction which might occur in a loss-of-coolant situation in the PWR. Conditions for other cases yet to be computed are being planned.

Of the cases computed during October, the most significant results were obtained for the so called "stoichiometric steam" condition. For this condition, only enough steam was fed at each time interval to react completely by the time it reached the end of the passage. Results are not completely analyzed, but some indication can be obtained by comparison of the time required to reach the melting temperature. As reported in BMI-1128, under adiabatic conditions the maximum-flux blanket rod will reach the melting temperature of 3320 F in 1111 seconds. For the stoichiometric steam condition, the same blanket rod reached a maximum temperature of 3230 F in 455 seconds. Subsequent behavior is still being investigated. The maximum-flux seed plate would reach the melting temperature in 205 seconds for the adiabatic case and in 103 seconds for the stoichiometric-steam case.

Effort is being made to complete these computations during November.

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Cooling of Molten Zircaloy 2 Droplets in Water

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

The object of this phase of the program was to determine analytically the extent of oxidation of a molten Zircaloy droplet as it falls through steam and water.

Work has been concluded on this phase of the program and a topical report has been prepared during the month.

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E. GENERAL FUEL-ELEMENT DEVELOPMENT

F. A. Rough

Various Reactor Development Division programs in the fields of metallurgy and ceramics are included in this section.

In the research on refractory fuel elements, experiments to measure the diffusion of UO_2 through dense BeO were continued. Further fabrication studies and uranium-loss measurements were made on UO_2 -graphite fuel elements.

The relation between sinterability and more basic properties of oxide powders was continued with the study of BeO prepared from $\text{Be}(\text{OH})_2$.

In the study of uranium alloys for high-temperature applications, numerous tensile data have been obtained on various binary zirconium alloys. Binary alloys with molybdenum and niobium are also a part of this program.

Specimens of the uranium-5 w/o chromium-1 w/o molybdenum alloy are being prepared for irradiation as part of the study of low-melting alloys.

In the development of dispersion-type or compartmentalized fuel elements, the fabrication of various structures is being studied to develop better corrosion behavior.

Various experiments designed to understand the mechanism of uranium corrosion are in progress. These experiments include studies of the oxidation of UO_2 , the study of UO_2 films, and tests correlating hydrogen evaluation with the corrosion rate.

CERAMICSRefractory Fuel Elements

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

BeO

A dense BeO disk with a coating of UO_2 , produced by decomposing uranyl oxalate on one face, was exposed to an alpha-sensitive photographic

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plate to determine the initial UO_2 concentration prior to making a diffusion heat at 2350 F. A 6-day exposure did not produce any alpha tracks so the specimen now is being exposed for 20 days.

Graphite

UO_2 -graphite fuel elements are being developed for potential use in a gas-cooled reactor. Fabrication studies are concerned with both rod- and sphere-shaped elements, as the conceptual design of the proposed reactor is not far enough along to decide which shape is preferable from the reactor-physics and heat-transfer standpoints.

A major objective of the fabrication work to date has been to obtain relatively high uranium loadings, which would be required if natural or slightly enriched fuel were to be used. Criticality calculations made last month showed that a graphite-moderated power reactor would be attractive only if enriched fuel were used, in which case the required fuel loadings would be very low. No new work on high fuel loadings was started this month but experiments already in progress were completed.

Rod- and sphere-shaped elements with high fuel loadings (18 and 25 volume per cent, respectively) were baked at 2300 F during the month. The rods, which consisted of 3/16-in.-diameter UO_2 cores clad with 1/8 in. of unfueled graphite, were straight and showed no signs of cracks after baking. The baked spheres, consisting of UO_2 cores, 0.4 in. in diameter, covered with 1/8 in. of unfueled graphite, had severe cracks in the graphite clads.

Fabrication of elements with low fuel loadings was confined to rod-shaped elements containing 0.030-in.-diameter cores of dense UO_2 (made from active powder) or nondense UO_2 (made from Mallinckrodt powder). These specimens contain approximately 1 volume per cent of UO_2 . They will be baked at 2300 F and examined. Spherical elements containing 1 volume per cent also will be made.

Measurements of uranium losses from UO_2 -graphite, rod-shaped elements in flowing nitrogen have been hampered by oxidation of the graphite. In experiments made this month, using nitrogen with a dew point of minus 95 F and a fused-quartz furnace tube, some oxidation still occurred. Tests indicated that the fused-quartz tube initially was more nearly gastight than the porcelain tube used previously, but that air leakage through the tube occurred after about 15 hr of heating at 2300 F, the desired test temperature. As it is necessary to run tests continuously for periods of at least 100 hr, efforts to find a furnace tube that will not leak excessively will be continued. A glazed aluminum oxide tube will be tried.

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To obtain approximate uranium-loss rates, experiments in which the UO_2 -graphite rods are heated in evacuated fused-quartz capsules also are being made. This month, a specimen was heated at 2300 F for a total time of 89 hr. The fused-quartz capsules were replaced every 15 to 25 hr during the test. After removal from the furnace, the fused-quartz capsules were washed in nitric acid and the wash solutions analyzed for uranium. Under these conditions, the rate of uranium loss was constant at $0.011 \mu\text{g}/(\text{cm}^2)(\text{hr})$ throughout the 89-hr test period.

In future work, fabrication of rod- and sphere-type UO_2 -graphite fuel elements will be continued and representative specimens will be selected for fission product retention studies. Further uranium loss experiments will be run at 2300 F and reactor design studies will be continued.

Characterization of Sinterable Oxide Powders

J. F. Quirk and N. Mosley

Research to investigate the relations between sinterability and other more basic properties of oxide powders was continued with the study of BeO prepared from $\text{Be}(\text{OH})_2$. Previous work showed the sinterability of BeO is critically affected by its calcination temperature, and indicated that the relation between calcination temperature and sinterability may be influenced by the impurities in the starting hydroxide.

In an effort to determine the effect of impurities, four lots of $\text{Be}(\text{OH})_2$ of varying purity have been prepared by precipitation from BeSO_4 solutions with NaOH or NH_3 . Preparation of these four hydroxides was completed this month; two of the lots were analyzed spectrographically and examined microscopically. The results are summarized in Table E-1.

Except for the expected large difference in sodium content and a small difference in magnesium, the two analyzed hydroxides appeared to be quite similar chemically. However, their microstructures were quite different.

Sintering trials will be made on BeO prepared from these hydroxides and from two additional hydroxides that were precipitated from a solution of recrystallized BeSO_4 . Analytical work will be continued in an effort to determine the effect of impurities on the calcination temperature-sinterability relation.

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TABLE E-1. CHARACTERISTICS OF $\text{Be}(\text{OH})_2$ PRECIPITATED FROM BeSO_4 SOLUTION

	<u>$\text{Be}(\text{OH})_2$, Lot 29</u> <u>(NaOH Precipitant)</u>	<u>$\text{Be}(\text{OH})_2$, Lot 29A</u> <u>(NH_3 Precipitant)</u>
Spectrographic Analysis, ppm BeO		
Sodium	2000	100
Lithium	25	<5
Magnesium	300	10
Calcium	50	30
Strontium	<20	<20
Barium	<5	<5
Zinc	<30	30
Boron	15	30
Aluminum	300	400
Silicon	400	400
Chromium	40	30
Manganese	15	<1
Iron	100	200
Nickel	15	5
Lead	<20	20
Apparent Refractive Index	1.54	1.53
Microscopic Examination		
Optical Characteristics	Isotropic, crystallite grain	Isotropic, nodular aggregates
Dye-Absorbent Particles	<10%	>80%

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METALLURGYUranium Alloys for High-Temperature Application

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

Work is continuing on binary uranium alloy systems containing molybdenum, zirconium, and niobium additions, respectively. The alloys are being investigated for application as high-temperature reactor fuels.

Table E-2 lists tensile data obtained from variously heat-treated specimens of uranium-3 through uranium-20 w/o zirconium alloys. The heat treatments used in the tensile study were selected on the basis of microstructure and hot-hardness data from a total of seven exploratory treatments given each alloy composition.

The effects of the different heat treatments upon elevated temperature tensile properties are given in Table E-2. Specimens that were isothermally transformed at 550 C or were cooled by controlling furnace rates between 750 and 570 C generally possess greater tensile strengths than those that were furnace cooled to 670 C and annealed at that temperature for 24 hr.

The uranium-15 w/o niobium alloy (chemical analyses: top of ingot 14.2 w/o niobium; bottom of ingot 14.4 w/o niobium) has been successfully fabricated into flat strip. The material was forged from salt bath at 1175 C into 1-in. -square stock and then rolled into 0.100-in. -thick strip from a helium atmosphere furnace at 900 C. Tensile specimens are being machined from the strip for elevated temperature evaluation.

In addition, fabrication studies are being made on the uranium-20 w/o niobium alloy. A number of finger bars have been prepared for the purpose of investigating the effect of different heat treatments and rolling temperatures on fabricability.

Preparation and Properties of Low-Melting Alloys

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

Irradiation testing of the cast uranium-5 w/o chromium-1 w/o molybdenum alloy is planned in order to evaluate this alloy for use as a low-melting power-reactor fuel. Small diameter castings of this alloy have been made with uranium of 20 per cent enrichment, and the castings are being machined to produce 0.100-in. -diameter by 1.000-in.-long pins for irradiation testing.

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TABLE E-2. TENSILE DATA ON ZIRCONIUM-URANIUM ALLOYS WITH VARIOUS HEAT TREATMENTS

Zr Content, w/o	Temperature, F	Modulus, psi x 10 ⁶	0.2 Per Cent Yield Strength, psi	Ultimate Tensile Strength, psi	Elongation in 2 In., per cent	Reduction in Area, per cent
<u>1 Hour at 800 C, Furnace Cooled to 670 C, Held 24 Hr, Furnace Cooled</u>						
3	550	13.5	45,000	67,050	22.1	60.9
3	1000	5.3	22,600	24,910	29.1	(a)
3	1275			8,500	19.0	(a, b)
5	550	18.6	45,300	72,250	21.9	57.8
5	1000	3.8	22,700	27,490	35.3	(a)
5	1275			5,900	67.0	(a, b)
7	550	16.0	52,800	81,050	19.5	51.8
7	1000	4.3	24,800	32,500	35.1	(a)
7	1275			2,500	61.0	(a, b)
10	550	16.8	56,600	88,100	21.6	51.0
10	1000	4.1	27,300	33,780	35.5	77.0
10	1275			12,440		(b, c)
15	550	14.7	60,400	91,600	19.8	36.8
15	1000	6.2	29,600	35,840	37.5	76.0
15	1275			1,750		(b, c)
<u>1 Hour at 800 C, Furnace Cooled to 750 C, Furnace Cooled From 750 to 570 C at 1/2 Deg Per Min, Furnace Cooled</u>						
10	550	16.3	75,300	103,900	15.8	49.6
10	1000	5.6	24,800	40,000	61.8	(a)
10	1275			1,750		(b, c)
15	550	16.6	75,900	107,400	17.3	38.2
15	1000	6.1	28,000	45,200	39.6	77.8
15	1275			2,360		(b, c)
20	550	16.2	87,600	118,500	16.0	36.4
20	1000	2.8	32,000	47,500	44.5	(a)
20	1275			4,020		(b, c)

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TABLE E-2. (Continued)

Zr Content, w/o	Temperature, F	Modulus, psi x 10 ⁶	0.2 Per Cent Yield Strength, psi	Ultimate Tensile Strength, psi	Elongation in 2 In., per cent	Reduction in Area, per cent
<u>1 Hour at 800 C, Isothermally Transformed for 2 Hr at 550 C, 10 Min at 780 C, 2 Hr at 550 C, 10 Min at 780 C, 2 Hr at 550 C, Water Quenched</u>						
5	550	17.2	65,300	95,830	17.4	53.8
5	1000	6.8	17,700	31,500	56.0	(a)
5	1275			7,600	25.5	(a, c)
7	550	18.9	71,800	107,510	12.5	37.4
7	1000	4.0	21,200	33,580	55.0	(a)
7	1275			3,780	46.0	(a)
<u>1 Hour at 800 C, Isothermally Transformed, 2 Hr at 550 C, Water Quenched</u>						
20	550	20.0	129,300	159,500		(d)
20	1000	6.4	31,500	56,600	37.5	(a)

(a) Fracture reduced to knife edge. Per cent reduction in area impossible to obtain.

(b) Modulus unobtainable.

(c) Did not fracture specimen. Specimen elongation more than extension of bellows on vacuum tank.

(d) Sheared pins in grips. Ultimate tensile strength higher than indicated.

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The specimens will be irradiated in triplicate at two different temperatures to approximately 1 a/o burnup. Preirradiation measurements, to be duplicated after irradiation testing, are now being obtained.

Compartmentalized Fuel Elements

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

Fabrication studies are being conducted on several promising cermet-type fuel elements. The six combinations currently under investigation are U_2Ti , U_6Ni , U_3Si , or UC dispersed in a Zircaloy 2 matrix and clad with Zircaloy 2, and UC or UN dispersed in a stainless matrix and clad with stainless.

Although all of the elements listed above may be fabricated by methods described in previous reports, fuel elements are now being fabricated by the following method in an effort to obtain a more corrosion-resistant core. The fuel-matrix powder mixture is cold pressed at 50 tsi; the green powder core is then assembled with the frame and clad and the entire assembly is hot pressed; and the hot-pressed pack is then hot rolled to final thickness.

All six combinations have been fabricated by this procedure, but only the U_2Ti -Zircaloy element which was pressed and rolled at 1300 F has been examined metallographically and submitted for corrosion in 680 F water. Microscopic examination indicates that there is a good core-to-clad bond and no reaction between the U_2Ti and the Zircaloy 2.

Metallographic and corrosion specimens of the other five combinations are being prepared at the present time.

CORROSION

Mechanism of Uranium Corrosion

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

The mechanism of aqueous uranium corrosion is being studied as part of the program to develop corrosion-resistant fuel elements for atomic reactors.

Samples heated to 650 C in very low oxygen atmospheres (see BMI-1129) have been tested in boiling deionized water for varying lengths

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of time. The results in Table E-3 show that the initial corrosion rate is greatly reduced compared to untreated samples. The scatter in the data is probably due to minor variations in the oxide film, thickness, microstrain, etc. These films apparently fail at the site of a defect in the film and then are destroyed by undercutting. Analyses of diffraction line shape show that these films contain microstrain. Attempts are being made to produce and study strain-free oxide films.

Uranium dioxide made by the thermal decomposition of uranyl oxalate was tested for 1 week in boiling deionized water. At the end of the test, it was found the oxide had been oxidized from $\text{UO}_2.04$ to $\text{UO}_2.31$. After the sample was dried, it underwent air oxidation to $\text{UO}_2.41$. Oxide made by corroding a sample of metal was found to be $\text{UO}_2.43$. This oxide would air oxidize to $\text{UO}_2.69$. This study is continuing.

During the next month, attempts will be made to detect hydrogen evolution during the corrosion testing of oxides and to examine the adherent films with the ellipsometer.

Corrosion rate studies of uranium at elevated temperatures are being made in argon-water atmospheres. The experiments are designed to permit measurements of the weight loss of the uranium as well as measurements of the evolved hydrogen. Two values for corrosion rates can then be calculated. Table E-4 includes the values obtained to date. The first tests at 100 C were made to establish the validity of the procedure by comparing results in argon-water with those obtained in liquid water at the same temperature. Each procedure gave a corrosion rate of approximately $2.9 \text{ mg}/(\text{cm}^2)(\text{hr})$ which agrees fairly well with other results reported in the literature. The rates obtained in the next three tests, Numbers 10, 12, and 24, made on the dingot material at 200 C were slightly higher than those rates found for the zone-melted dingot uranium in Tests 14 and 16. Spectrographic analysis made on the dingot and the zone-melted dingot showed little difference except in aluminum content. The zone-melted uranium contained more aluminum (obviously a "pickup" from the Alundum crucible) than the original dingot material. The difference in corrosion rates may have been due to this aluminum. The Du Pont slug uranium, which was less pure than either of the above materials, gave the highest corrosion rate in the 200 C tests (Numbers 4 and 8), although all of the values at 200 C were somewhat lower than those reported by Howe and Jones for tests in steam. It is believed that the purity of the starting material may account for these small differences.

The two tests, Numbers 26 and 27, made on the dingot material in the flowing argon-water atmosphere at 400 C gave somewhat erratic results. Further tests are planned to determine if the rate of corrosion is so rapid that the availability of water could account for the variations observed.

TABLE E-3. CORROSION RESULTS OF URANIUM SAMPLES WITH AN ADHERENT OXIDE FILM

Sample	Time in Test, hr	Wt Loss, mg	Calculated ^(a) Wt Loss for Unprotected Surface	Approximate Film Thickness, A
126	10	0.59	32.8	481
127	10	1.04	32.8	706
128	20	5.82	65.6	602
129	20	8.12	65.6	796
130	30	4.69	98.4	816
131	30	3.56	98.4	817
132	32	43.7	105	764
133	32	55.7	105	891
134	42	41.1	138	630
135	42	47.9	138	832
136	52	95.3	171	666
137	52	98.2	171	786
138	53.5	130	175	868
139	53.5	138	175	802
140	65.5	174	214	468
141	65.5	160	214	572
142	66	95	216	633
143	66	101	216	760

(a) Based on a corrosion rate of $3.28 \text{ mg}/(\text{cm}^2)(\text{hr})$.

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TABLE E-4. CORROSION RATES OF URANIUM IN WATER

Material	Test	Environment	Temp, C	Time, hr	Wt Loss, mg/(cm ²)(hr)	H ₂ Evolved, mg/(cm ²)(hr)	Calculated Wt Loss ^(a) , mg/(cm ²)(hr)
Dingot	18	Liquid H ₂ O	100	4	2.5	--	--
				21	2.7	--	--
				47	3.0	--	--
				96	2.9	--	--
				120	3.0	--	--
				144	2.9	--	--
Dingot	20	Argon + water vapor ^(b)	100	6	2.9	0.04	2.2
Dingot	10	Ditto	200	4	53	0.80	48
Dingot	12	Ditto	200	4	58	0.90	55
Dingot from boiling test	24	Ditto	200	6	61	0.92	54
Zone melted	14	Ditto	200	4	48	0.78	46
Zone melted	16	Ditto	200	4	51	0.84	49
Du Pont slug	4	Ditto	200	1	--	1.20	71
Du Pont slug	8	Ditto	200	1	74	1.30	77
Dingot	27	Ditto	400	4	328	6.02	355
Dingot	26	Ditto	400	6	212	3.22	190

(a) Based on the equation: $U + 2H_2O \rightarrow UO_2 + 2H_2$.

(b) Composition: 90 w/o water, 10 w/o argon.

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Additional future work will consist of an evaluation of the effect of alloying constituents and of films on the corrosion rates at various elevated temperatures.

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F. STUDIES OF ZIRCONIUM-URANIUM ALLOYS

F. A. Rough

A number of programs of study of zirconium alloys containing up to 70 w/o uranium are in progress.

Study of the constitution of zirconium-uranium alloys containing oxygen is proceeding well, although there is a minor effect of residual nitrogen. Evaluation of alloys containing nitrogen will, it is hoped, make possible a complete evaluation.

Routine progress has been made in the studies of the kinetics of transformation of these alloys.

The corrosion of alloys containing 45 to 60 w/o uranium and up to 0.3 w/o oxygen has continued in high-temperature water for 3024 hr. Data on crystal-bar and sponge-base zirconium alloys are comparable to data of previous studies. Development of zirconium-base alloys to contain 70 w/o uranium and resist corrosion by high-temperature water is continuing.

A number of capsules containing 22 w/o uranium samples are in various states of progress in the radiation program.

Constitution of Zirconium-Uranium Alloys

R. F. Dickerson and A. A. Bauer

A study of zirconium-uranium alloys containing oxygen and nitrogen additions is being made for the purpose of determining the solubility limit of the alpha-plus-beta zirconium region in the binary system.

Quantitative lineal measurements are being made, by means of a Hurlbut counter, on specimens containing varying amounts of oxygen and nitrogen additions to determine their effect on the quantity of alpha and beta phases produced. These data are being analyzed mathematically to determine the variation in the beta versus alpha-plus-beta solubility limit with oxygen and nitrogen content.

A tentative analysis has been completed showing the effect of oxygen on this limit. However, the calculations indicate that allowance for the effect of nitrogen present in the analyzed specimens must be included, particularly in the specimens containing small amounts of oxygen.

Measurements are now being obtained on zirconium-uranium specimens containing nitrogen additions. When these measurements are completed, a thorough analysis should be possible.

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

Dilatometric analysis thus far has been fraught with experimental difficulties. The sensitivity of the Atcotran recorder appears to be too low to detect transformation, and corrosion of the samples and of the fused-quartz holding rods by the liquid-metal heat-treating media is excessive. Of the many molten alloys investigated, none seems able to remain inert for long periods of time. If the dilatometer is found unsuitable to warrant further consideration, emphasis will be placed upon metallographic and X-ray diffraction techniques for these kinetic studies.

The kinetics of the beta-to-epsilon decomposition is being studied in zirconium alloys containing 20 to 70 w/o uranium.

W. E. Berry and R. S. Peoples

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series containing 7 through 70 w/o uranium additions to crystal-bar, sponge, and high-oxygen sponge zirconium are being evaluated in 500, 600, and 680 F degassed high-purity water. All samples were annealed 1 hr at 800 C and slowly cooled prior to corrosion testing.

Alloys now on test containing 45, 50, 55, 60, and 70 w/o uranium are corroding at linear rates at all test temperatures after a 3024-hr (126 days) exposure. Corrosion results for these alloys are presented in Table F-1. Data obtained to date continue to indicate that corrosion rates increase with (1) increasing water temperature, (2) increasing uranium content, and (3) increasing oxygen content in the zirconium melting stock. A number of alloys still on test containing less than 45 w/o uranium do not exhibit steady corrosion rates after a 3024-hr exposure. Corrosion rates in 680 F water of 50 and 60 w/o alloys tested in this program are slightly lower than those obtained in previous studies with similarly treated alloys (results reported in BMI-1087 and BMI-1130). Corrosion rates for crystal-bar and sponge zirconium-50 w/o uranium alloys currently under evaluation are: -0.15 and -0.17 $\text{mg}/(\text{cm}^2)(\text{hr})$, respectively, as compared with rates of -0.17 and -0.20 $\text{mg}/(\text{cm}^2)(\text{hr})$, respectively, in previous programs.

In the present work, the corrosion rate for the sponge zirconium-60 w/o uranium alloy is -0.26 $\text{mg}/(\text{cm}^2)(\text{hr})$ as compared with corrosion rates of -0.29 to -0.34 $\text{mg}/(\text{cm}^2)(\text{hr})$ in other programs.

The above studies are being continued.

Development of Corrosion-Resistant 70 w/o Uranium Alloys

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

An investigation aimed at the development of a corrosion-resistant 70 w/o uranium alloy is being made. The zirconium-70 w/o uranium alloy is serving as the base alloy for this study.

Two approaches are being studied as possible means of improving the corrosion resistance of the base alloy, heat treatment and ternary alloying. The primary purpose of ternary additions is to tie up the alpha-uranium phase which precipitates from the zirconium-70 w/o uranium alloy in the form of a compound or intermediate phase. Upon the basis of previous experimental work, molybdenum, silicon, and titanium have been selected for this purpose.

Heat treatment of the zirconium-70 w/o uranium alloy has been found effective in improving corrosion resistance, isothermal transformation of the beta-zirconium phase at 500 C for about 100 sec markedly increasing

TABLE F-1. EFFECT OF TEMPERATURE AND VARIOUS ZIRCONIUM MELTING STOCKS ON THE CORROSION BEHAVIOR OF ZIRCONIUM-URANIUM ALLOYS IN HIGH-TEMPERATURE WATER

Nominal Uranium Content (Balance Zirconium), w/o	Zirconium Melting Stock	Weight Change Rate ^(a) , mg/(cm ²)(hr) After 3024 Hr of Exposure at Temperature Indicated		
		500 F	600 F	680 F
45	Crystal bar	(b)	-0.043	-0.11
	Sponge	-0.003	-0.051	-0.14
	Sponge + 0.3 w/o O	-0.004	-0.057	-0.15
50	Crystal bar	-0.001	-0.062	-0.15
	Sponge	-0.003	-0.069	-0.17
	Sponge + 0.3 w/o O	-0.005	-0.084	-0.21
55	Crystal bar	-0.003	-0.069	-0.15
	Sponge	-0.003	-0.080	-0.18
	Sponge + 0.3 w/o O	-0.006	-0.096	-0.25
60	Crystal bar	-0.003	-0.066	-0.19 ^(a)
	Sponge	-0.005	-0.093	-0.26 ^(c)
	Sponge + 0.3 w/o O	-0.015	-0.19	-0.64 ^(c)
70	Crystal bar	-0.36 ^(c)	(d)	(d)
	Sponge	-0.71 ^(c)	(d)	(d)
	Sponge + 0.3 w/o O	-1.23 ^(c)	(d)	(d)

(a) Calculated when rate change became linear with time.

(b) Gained weight; little weight change over last 1512 hr of exposure.

(c) Samples cracked or completely oxidized prior to 2520 hr of exposure.

(d) Completely oxidized within a 168-hr exposure.

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corrosion life in 680 F water. Additional specimens are being heat treated for verification of these results and for corrosion tests in other heat-treated conditions. Similarly, ternary alloys have been prepared for corrosion test in a variety of heat-treated conditions. Included are quench, quench-and-temper, isothermal-transformation, and furnace-cooling treatments.

Radiation Stability of Zirconium-Uranium Alloys

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

The radiation-effects program for the zirconium-uranium alloys is being continued. Specimens of zirconium-22, 50, and 70 w/o uranium will be irradiated in both temperature-controlled capsules and noncontrolled capsules to a burnup of about 2 a/o.

Irradiation Capsules BMI 8-2 and BMI 8-3 have been irradiated and returned to Battelle's hot-cell facility. The irradiation of Capsule BMI 8-1 has been completed, but the capsule has not been shipped to Battelle as yet. These three were noncontrolled capsules. Each capsule contained three zirconium-22 w/o uranium specimens representing three representative microstructures.

The temperature-controlled capsule, BMI 8-4, has been delivered to the MTR and has been successfully operating for 1 week at the required temperature of 650 C. This capsule contains one specimen of each microstructure of the zirconium-22 w/o uranium alloy.

A fission-gas-analysis apparatus which will be used to measure the amount of fission gas which is released from the specimens during irradiation has not been completed. The irradiation capsules will be opened when this equipment has been completed and tested.

G-1

G. CORROSION STUDIES OF ZIRCONIUM

R. S. Peoples

This section describes results of research for the AEC Reactor Development Division pertaining to the study of the corrosion behavior of zirconium and zirconium alloys in high-temperature water and steam.

Long-term corrosion tests have been continued for samples of Zircaloy 2 with and without additions of hydrogen, oxygen, or nitrogen. Modified Zircaloy 2 compositions also are being studied in 600 and 680 F degassed water and 750 F steam.

Corrosion of Zirconium and Zirconium Alloys

W. K. Boyd and R. S. Peoples

Specimens representing seven different melts of Zircaloy 2 have been exposed to 600 F degassed water. After more than 3 years of exposure, the samples show a black tarnish film and an average total weight gain of 50 mg per dm². To date, there has been no indication of transition or breakaway.

Data based on 16 months of exposure in 680 F degassed water continue to indicate that the corrosion behavior of Zircaloy 2 is not affected by (1) hydrogen additions in the range of 500 to 1500 ppm, (2) nitrogen contents up to 200 ppm, and (3) oxygen contents of 6000 ppm. Oxygen and nitrogen contents above 6000 and 200 ppm, respectively, destroy resistance.

Zirconium Corrosion Committee Program

In support of the Zirconium Corrosion Committee's program to develop new corrosion-resistant zirconium-base alloys, sponge-base alloys containing combinations of tin and iron, tin and nickel, or tin, iron, and nickel in the range of 0.05 to 0.5 w/o (total alloy content) are being evaluated in 680 F water and 750 F steam. Weight-gain data based on a total exposure time of 478 days are similar to those reported in Tables G-1 through G-3 in BMI-1136. The following trends have been observed:

- (1) Slow cooling from 775 C or water quenching from 900 C does not affect the corrosion behavior of the tin-iron and tin-nickel alloys.

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- (2) Tin-iron alloys (0.2 to 0.5 w/o tin-0.03 to 0.5 w/o iron) are more resistant to 680 F water than are tin-nickel alloys of similar composition; however, the tin-nickel alloys have superior resistance to 750 F steam.
- (3) Increasing nitrogen content from 70 to 300 ppm results in a progressive decrease in the corrosion resistance of 0.25 to 0.5 w/o tin-0.25 to 0.5 w/o iron alloys. A similar effect is noted for alloys containing 200 ppm aluminum.

Effect of Heat Treatment

Data based on over 1 year of exposure to 750 F steam indicate that, for binary zirconium-iron and zirconium-nickel alloys, microstructures composed of a fine dispersion of compound particles in an alpha matrix are most resistant. These studies have been completed, whereas corrosion studies on other phases of the program are being continued.

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H. REACTOR-MATERIALS DEVELOPMENT

F. A. Rough

The general reactor materials development program supported by the Reactor Development Division and a program of assistance to Argonne National Laboratory are included in this section.

Development of enamel coatings for uranium and evaluation of enamel coatings for zirconium is continuing.

Several experiments to determine the kinetics of the reaction of zirconium and uranium dioxide are reported.

Oxidation studies of niobium have been made at 600, 800, and 1000 C. The oxidation was linear at 800 and 1000 C, but was parabolic for a time then linear at 600 C. Various alloy additions are being evaluated in an attempt to improve the oxidation resistance of niobium. Thus far, binary alloys with titanium are the most promising alloys studied.

Attempts to deposit sound coatings of molybdenum on the inside and outside of a small-bore stainless steel tube are continuing. Various procedures for deposition from mixtures of MoCl_5 vapor and hydrogen are being evaluated.

Enameling of Special Metals

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

Enamel coatings for uranium are being developed. In addition, current work includes thermal cycling tests of zirconium enamels previously developed in this program.

The major problem encountered in enameling uranium has been crazing of the coating during cooling. The reduction or elimination of this type of failure is currently being sought through the application of thin, partially crystalline coatings.

In work to date, the principal method of producing such coatings has been to exceed saturation of the enamel glass by solution of oxide from the base metal during firing. Possibly due to nonuniform oxidation of the base metal, it has been difficult to obtain thin uniform coatings in this manner. Another method of achieving crystal development in the coating might be to

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take into solution an oxide layer applied to the enamel as a cover coat. A few trials of this latter method were encouraging.

Thermal cycling tests of enameled zirconium are in progress. The results will be reported next month.

Future work will continue to emphasize methods of applying thin enamel coatings to uranium. Thermal cycling tests of enameled zirconium also will be continued.

Kinetics of the Zirconium-Uranium Dioxide Reaction

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

Fuel elements having UO_2 cores clad with zirconium are being considered for some reactor applications. The interaction of these materials in the range of 950 to 1600 F is being studied to aid in estimating the service life of such elements. The study is being made with experimental elements containing a plane surface of zirconium in intimate contact with a plane surface of a solid UO_2 pellet.

Thin-walled elements being heated at 950 and 1100 F have been removed from test after being heated under 5000 psi pressure for 249 and 260 days, respectively. These elements will be examined metallographically and, if warranted, machined into thin layers for oxygen and uranium analyses in the zirconium beginning at the interface. These data will be used to describe the transfer of oxygen and uranium to the UO_2 .

A large thin-walled element that was heated at 1200 F for 146 days, showed evidence in the cross section that the required intimate contact between the zirconium and the UO_2 had not been attained. At this temperature, the zirconium apparently is not plastic enough to deform under the 5000 psi pressure in the autoclave, although a thick-walled element heated at 1300 F under similar conditions, showed the desired contact. Thus, quantitative analytical data on the transfer of uranium and oxygen to the zirconium cannot be obtained on this 1200 F element. On the basis of this finding, it appears unlikely that quantitative data will be obtainable on the elements that were heated at 950 and 1100 F.

Zirconium- UO_2 elements were heated at 1525 F for 227 hr during the past month. One of these large elements is in the process of being machined into analytical samples.

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Attempts also are being made to obtain samples for analysis from a large element heated at 2000 F for 140 hr. It appears that this heating time was sufficient to embrittle the element with oxygen and it is doubtful if it will be amenable to machining.

Calculations were made to determine a diffusion coefficient for the transfer of oxygen to zirconium on the basis of the oxygen analyses obtained for the element heated at 1600 F for 95 hr. (Data reported last month.) The diffusion coefficient was found to be 3×10^{-10} cm² per second. This value is about one-tenth of that extrapolated for the diffusion coefficient of oxygen in Zircaloy 2 at the same temperature. The terminal solubility for oxygen in alpha zirconium calculated from these data is 6.7 w/o. This value agrees very well with the solubility (6.75 w/o) reported in the literature*. Calculations of this type will be made for other analytical data.

Elements are being prepared for some additional experiments with uranium foil at the original zirconium-UO₂ interface. These experiments should aid in better defining the role of uranium as a barrier for the diffusion of oxygen and zirconium.

Oxidation-Resistant Niobium Alloys

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

The high-temperature strength properties and low nuclear cross section of niobium make it attractive as a base material for high-temperature structural alloys in nuclear reactors. Pure niobium, however, suffers from lack of oxidation resistance. The effects of alloying additions on the oxidation behavior of niobium alloys is being investigated. The fabricability and mechanical properties of the more oxidation resistant alloys are also being evaluated.

Oxidation rates in air have been determined for six additional niobium alloys, as given in Table H-1. The niobium-30 a/o titanium alloy oxidized slightly faster than the niobium-25 a/o titanium, but slower than the niobium-35 a/o titanium alloy. These data indicate that 25 a/o titanium is optimum in this system for maximum oxidation resistance, with larger additions slightly increasing the oxidation rate.

The two niobium-vanadium-chromium alloys oxidized more rapidly than niobium-5 a/o vanadium but slower than niobium-5 or 10 a/o chromium. Comparison of the data for five niobium-vanadium-chromium ternary alloys with the niobium-vanadium and niobium-chromium binary alloys shows that

*Domagala, R. F., and McPherson, D. J., Trans. Journal of Metals, 6, page 238 (1954).

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none of the ternary alloys had better oxidation resistance than the best binary alloys. Chromium additions to the niobium-5 a/o vanadium base increased the oxidation rates at 5 and 10 a/o chromium, but had little effect at 20 a/o chromium. Thus, to date, the effects of chromium-vanadium additions on the oxidation rate of niobium appear to be averages of the effects of the individual additions, and no oxidation rate minimum has been found in the ternary system.

TABLE H-1. AIR OXIDATION RATES FOR NIOBIUM-BASE ALLOYS

Alloy Composition a/o	VHN	Oxidation Rate, mg/(cm ²) (hr)		
		600 C	800 C	1000 C
100Nb	115	5.7	33.7	24.2
Nb-25Ti ^(a)	156	0.05	0.6	1.9
Nb-30Ti	189	0.09	0.52	3.8
Nb-5V-5Cr	207	0.22	2.85	8.18
Nb-5V-10Cr	201	0.12	3.55	8.65
Nb-5V-5Ta	188	0.09	7.35	16.13
Nb-5V-5W	227	0.36	9.73	36.25
Nb-5V-20Zr	287	0.68	7.76	20.06

(a) Most oxidation-resistant alloy found to date.

Additions of 5 a/o tantalum, 5 a/o tungsten, or 20 a/o zirconium to a niobium-5 a/o vanadium base increased the oxidation rate in each case. None of these additions effected any significant improvement in oxidation resistance when added as binary additions to niobium or as ternary additions to the more oxidation-resistant binary alloys. Consequently, these elements are of little interest with regard to producing niobium-base alloys with high oxidation resistance.

Several oxidation tests have been made on pure niobium sheet in the recently completed continuous weighing oxidation device. These tests were conducted for 2 hr in slowly moving dry air. At 600 C, the oxidation was parabolic for about 40 min, after which the oxidation became linear, with a rate of 1.78 mg/(cm²)(hr). This rate is much lower than the rates measured by intermittent weighing of samples exposed to ambient, undried air, which ranged from 4 to 8 mg/(cm²)(hr). At 800 C, the oxidation was

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entirely parabolic, with an oxidation rate constant of $1.023 \times 10^3 \text{ mg}^2/(\text{cm}^4)(\text{hr})$. The 1-hr weight gain was $29.9 \text{ mg}/\text{cm}^2$, which is very close to the weight gains obtained by intermittent weighing in undried air. At 1000 C, two tests were conducted, both of which gave parabolic oxidation curves. The rate constants were 2.31×10^3 and $2.27 \times 10^3 \text{ mg}^2/(\text{cm}^4)(\text{hr})$, respectively. The weight gains in 1 hr were 45.4 and 43.8 mg per cm^2 , respectively, somewhat higher than the weight gains found earlier for undried air (about 25 to 30 mg per cm^2). Additional tests are now being conducted on pure niobium to confirm the oxidation curves reported here, and to investigate the effects of water vapor on the oxidation. Tests will be conducted on niobium alloys as soon as suitable material is available.

Initial cold fabrication tests have been performed on alloys from the niobium-titanium, chromium, molybdenum, and vanadium binary series. These samples were cold rolled at 10 per cent per pass. Alloys containing up to 35 a/o titanium were all quite fabricable. The hardnesses increased about the same amount for each alloy, indicating that titanium has little effect on the work hardening characteristics of niobium. Alloys containing up to 10 a/o chromium (nominal) were fabricable, while higher chromium alloys fractured during rolling. Molybdenum and vanadium-containing alloys were fabricable up to 5 a/o and 12.5 a/o, respectively. Vanadium additions alone appeared to increase the rate of work hardening during cold rolling. Fortunately, with the exception of chromium, the fabricable range for each of these binary additions extends to the level required for optimum oxidation resistance.

Initial hot-rolling experiments have been performed on several 40-g binary alloy ingots. A pure niobium ingot and three ingots of niobium-10, 20, and 30 a/o titanium were hot rolled at 1200 C at 10 per cent reduction per pass to 0.1 in., although the edges of the titanium alloy ingots suffered from much fine edge cracking which apparently was promoted by a white oxidation product which filled the cracks. Alloys of niobium-10, 20, and 30 a/o chromium and niobium-5 a/o molybdenum cracked badly and could not be fabricated to 0.1 in. The fabricable strips will be cold rolled to 0.03-in. strip after pickling and cleaning.

Work planned for the future includes:

- (1) Additional continuous-weighing oxidation tests on pure niobium.
- (2) Hot fabrication of the 40-g ingots of niobium-molybdenum and niobium-vanadium.
- (3) Cold fabrication of the strips from the hot-rolled 40-g ingots.

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- (4) Completion of the intermittent weighing oxidation tests on niobium alloys.

Uranium-Titanium Alloy Studies

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

An investigation of the uranium-rich end of the uranium-titanium alloy system is being conducted. This region of the phase diagram as it is shown in the literature appears to be inaccurate and should be redetermined in order to permit a careful study of the martensitic transformation. The mechanical properties of heat treated alloys will also be determined.

Differential thermal analysis of alloys containing up to 6 at/o titanium proved unsuccessful in the equipment recently constructed. Temperature gradients existed across horizontal sections of the furnace; these conditions caused the nickel standard to be 20 C higher than the alloy sample. It was felt that the equipment design could be vastly improved by placing the furnace itself in the vacuum chamber and by utilizing a large mass of metal as a heat reservoir. A copper cylinder will be used as a heat reservoir at temperatures up to 900 C. The specimens, 1/4-in.-diameter cylinders 1/2 in. high, will be placed in a 3/8-in.-diameter hole insulated by Alundum powder at a distance of 3/8 in. from the nickel reference standard in a similar insulated hole. The copper body will assure the two samples of being at the same temperature initially, and the insulation will prevent temperature equalization during a phase change for a sufficient length of time to permit a measurement of the small heat effect associated with the uranium alloy.

Construction of this equipment is nearing completion. Future work is dependent upon the phase diagram results.

Vapor Deposition of Molybdenum Coatings on
Stainless Steel Tubing

C. F. Powell and I. E. Campbell

As part of a program of assistance to ANL, Battelle has undertaken the development of methods for vapor depositing molybdenum on the inside and outside of small bore, Type 304 stainless steel tubing. During previous work, apparatus for applying uniform molybdenum coatings to the outside of 21-in. lengths of the tubing was developed and successfully tested. The cause of brittleness in the coatings was sought and appeared to be attributable to the presence of Mo₂N.

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During the past month, the coating of full (20 in.) lengths of the small bore tubing on the inside was attempted. The following technique was used in attempting to molybdenum-coat the small bore tubing internally.

A 21-in.-length of tubing was heated uniformly to about 200 C, temperature sufficiently high to prevent condensation of MoCl_5 from the coating atmosphere inside the tubing. Argon gas was saturated with MoCl_5 vapor at a low partial pressure and then mixed with hydrogen at the inlet end of the tubing, the mixture of argon, MoCl_5 vapor, and hydrogen passing through the tubing. A short, 1.5-in. section of tubing was heated to the deposition temperature of 900 C. This hot zone was then slowly moved from one end of the tubing to the other to effect molybdenum deposition throughout the entire length of tubing.

Two difficulties were encountered with this method of deposition. A small amount of reduction of MoCl_5 occurred at the point where hydrogen was added to the mixture of MoCl_5 vapor and argon. The lower chlorides produced condensed at the point of mixing and eventually plugged the tubing near the inlet end before the full length could be coated. Part of the MoCl_5 was incompletely reduced in the deposition zone, resulting in deposition of a very thin film of lower chlorides on the cooler tube walls downstream from the metal-deposition zone. As the metal deposition zone passed over the tubing, this deposit of lower chloride was reduced to a powdery layer of metal which rendered the molybdenum subsequently deposited over it nonadherent.

It appears that satisfactory deposition of molybdenum over the inside of a long length of small bore tubing will be obtained only by mixing hydrogen with MoCl_5 vapor at the center of a short hot zone which is passed over the tubing while the uncoated and coated portions of the tubing are protected by a flow of pure hydrogen. The apparatus for doing this has been assembled, but difficulty has been encountered in getting it to operate properly. This will be done during the coming month.

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I. PHYSICAL METALLURGY

F. A. Rough

Progress on several programs sponsored by the Research Division of the AEC is reported in this section. Included are basic studies of ceramics, metals, and gas-metal reactions.

In the study of uranium compounds, the principal effort this month has been directed toward preparation of samples of the uranium silicides.

The effect of strain rate on the tensile transition in alpha uranium has been investigated and found to be limited. Various aspects of the plastic deformation occurring are being considered further.

Preliminary data are reported for the constitution of uranium-zirconium-molybdenum alloys. Also, some success has been achieved in preparing thin rods of uranium carbide for high-temperature X-ray diffraction studies in this system.

Two mechanisms, diffusion and recrystallization, are being evaluated in the study of bonding fundamentals. Experimental data are in good agreement with diffusion theory, but further study is needed to determine which mechanism prevails.

Preliminary data on the reaction of hydrogen with niobium at 500 to 700 C are being evaluated.

PROPERTIES OF URANIUM COMPOUNDS

Some fundamental properties of refractory binary compounds of uranium are being investigated. These compounds are potential nuclear fuels.

Preparation, Fabrication, and Physical Properties

L. D. Loch, W. D. McKee, and M. J. Snyder

This month's effort concerned vacuum sintering of powder compacts, preparation of USi and UC, measurement of the specific heats of some

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uranium silicides, and preparation of uranium hydride for use in making other compounds.

Powder compacts of two compounds, USi_2 and UAl_2 , were sintered under a high vacuum. No noticeable nitriding or oxidation occurred. In both cases, somewhat porous specimens resulted, and it is anticipated that higher densities can be obtained by increasing the time and/or temperature of sintering.

An attempt was made to prepare USi by sintering a hydrostatically pressed compact of UH_3 and silicon under a high vacuum. The starting materials were mixed by ball milling in petroleum ether containing 3 w/o paraffin. X-ray diffraction examination of the resultant nonmetallic-appearing specimen showed a high UO_2 content. A like result was obtained from a similarly processed compact sintered in flowing argon, except that external oxidation (or nitriding) also was evident.

Uranium carbide, UC , was made by reaction of uranium with methane. The product was contaminated with UO_2 .

A likely source of the UO_2 contamination of the sintered USi and of the UC was UO_2 found to be present in the UH_3 . Steps will be taken to obtain purer UH_3 .

Determination of the specific heats of USi_2 , USi_3 , and USi was undertaken. Results are expected in November.

During the next two months, primary effort will be devoted to the following:

- (1) Determination of the optimum vacuum-sintering conditions for UAl_2 , USi_2 , and the other uranium silicides, and formation of sintered specimens for use in physical-property investigations.
- (2) Metallizing silicide specimens for use in thermal diffusivity measurements.
- (3) Determination of thermal-expansion properties of materials successfully sintered.
- (4) Preparation of UH_3 of higher purity for use in preparing other compounds by solid-solid, high-temperature reaction.
- (5) Finding a source for, or means of preparation of, the uranium borides.

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Reactions With Gases

W. M. Albrecht and M. W. Mallett

A fundamental study is being made of the reactions of certain uranium compounds with some of the common gases.

An investigation was made to determine the nature of the surface film formed on U_3Si by reaction with oxygen at 400 C for 1-1/2 hr. Metallographic and X-ray examinations of the film showed that it was a single-phase layer of UO_2 . No silicon or SiO_2 could be detected by the X-ray analysis. Although it appeared that only the uranium reacted with oxygen, there remains a strong possibility that SiO_2 had been produced but that its quantity was below the limit of detection of X-ray diffraction.

Future work will be done as other uranium compounds become available.

Heat-of-Formation Measurements

J. W. Droege, A. W. Lemmon, Jr., and R. B. Filbert, Jr.

A study is being made to determine what method of measuring heat of formation is most likely to be successful. ORNL is planning to make similar measurements and will be consulted in connection with this study.

INVESTIGATION OF THE TENSILE TRANSITION
IN ALPHA URANIUM

L. L. Marsh and G. K. Manning

Uranium undergoes a transition from ductile to semibrittle failure in tension in the temperature region around room temperature. A program is being pursued to learn more about this transition, particularly with regard to the cause.

The effect of tensile strain rate on the transition temperature has been examined over the range of crosshead speeds from 0.005 to 0.05 in. per min. Increasing the strain rate raises the transition temperature slightly. The activation energy, H , associated with the deformation process to

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fracture is approximately 30,000 to 35,000 cal per mole. However, a determination of the activation energy associated with the flow stress at a true plastic strain of 0.01 (Zener-Hollomon relation $\sigma = \dot{\epsilon} \exp H/RT$) yielded a value for H of approximately 5,000 cal per mole. In the above relation, σ is the flow stress, $\dot{\epsilon}$ is the strain rate, R is the gas constant, and T is the absolute temperature. The reason for the tremendous difference in the activation energy calculated from the flow stress and the elongation at fracture is not known. It is interesting to observe that the use of the value of 5,000 cal per mole in connection with Stroh's* relation for predicting the temperature of the transition produced a value of approximately 100 C, in good agreement with experiment. Stroh's relationship is

$$T = \frac{U(\sigma)}{k \log (f t_0 \ell / b)} ,$$

where U (σ) is the activation energy, k is Boltzmann's constant, f is an atomic frequency of vibration (10^{12} per sec), t_0 is the time to form a pile-up of dislocations, and ℓ/b ($\sim 10^3$) is the number of points at which the breakaway of dislocations can start. This equation was derived on the basis of anchoring of dislocations by impurity atoms and suggests that quenching from elevated temperatures, where atmospheres are not stable, would lower the transition temperature. This speculation is being checked further.

CONSTITUTION OF URANIUM ALLOYS

Uranium-Base Ternary Alloys

R. F. Dickerson and A. A. Bauer

The investigation of the phase relationships between the delta phases of the uranium-zirconium and uranium-molybdenum systems is proceeding.

Thermal analysis of a series of alloys ranging in composition from uranium-72 at/o zirconium to uranium-31.5 at/o molybdenum has been completed. On the basis of these data, it is tentatively concluded that the gamma phase in zirconium-rich alloys is stabilized to a temperature of about 455 C by molybdenum additions.

Meanwhile, specimens have been heat treated and are now being prepared for metallographic examination. Selected specimens will then be examined by X-ray diffraction techniques.

*Stroh, A. N., Phil., 968 (May, 1955).

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

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

Thin wires of uranium dicarbide have been prepared which are suitable for high-temperature diffraction analysis. The technique adopted consists of enclosing fine dicarbide powder in combustible thin-walled plastic capillaries and hydrostatically pressing these at 100,000 psi. Following pressing, the capillary is sintered, while supported on uranium dicarbide, to produce the wire sample. Microscopic and diffraction analysis have shown the material produced to be quite suitable for the intended high-temperature diffraction studies.

Work has started on preparation of the remaining compositions to be examined and preliminary high-temperature tests have been made to select holders for the specimen. Spectrographic graphite rods and sintered BeO appear suitable for use, since the junction to the uranium carbide will be held at temperatures lower than those at which the specimen will be examined.

The specimen-preparation technique currently being used appears suitable for preparing other ceramic materials for high-temperature diffraction analysis.

STUDY OF BONDING FUNDAMENTALS

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

This program is a study of the mechanisms involved in the solid-state bonding of metals. During October, tests on the bonding of gold needles to gold flats were continued. Emphasis during this period has been placed on studies on the relationships between temperature, time, and cold work on the bonding process.

For the simulated single-asperity experiments being used in this program, the bonding process is thought to consist of two parts: (1) formation, or nucleation, of an initial bond when the needle point is brought into contact with the flat and (2) growth of the bond area. Extending this concept to the bonding of massive flats, the initial bonding of contact areas corresponds to the first process, and the subsequent growth of these bonded areas to eliminate voids corresponds to the second process. The present

work is an effort to relate these processes first to the controllable test variables (i. e., temperature, time, load, geometry, and cold work) and second, to derive an expression that will describe the bonding process in terms of fundamental properties of the materials (i. e., strength, energy of cold work, diffusion rate, and recovery).

In order to reach these objectives, it is necessary first to propose a hypothesis, or model, for the bonding process, and then to obtain reliable experimental data that can be used to confirm or reject the model. At the present time, the proposed mechanism for growth of the bond area is based on the work of Kuczynski*, which has been applied successfully to the sintering of metal powders. In this case, the increase in bond area results from the diffusion of atoms from surfaces of low to high curvature. For the bonding of a sphere to a flat surface, Kuczynski has developed an expression for the radius of the contact area: $x^5 = 40\sigma a^2 \delta^3 Dt/kT$, in which x is the radius of the contact area, σ is the surface tension, a is the radius (of the needle tip), δ is the interatomic distance, D is the diffusion coefficient, t is time, k is Boltzmann's constant, and T is the absolute temperature. For tests made at constant temperature and with needles of a constant tip radius, this expression can be simplified to the form $x^5 = C_1(T)Dt$, where $C_1(T)$ is a constant. Further, if the bond strength is assumed to be proportional to the area of contact, then the bond strength, S , can be expressed: $S = S_0 + C_2(T)Dt^{0.4}$, where S_0 is the initial bond strength and $C_2(T)$ is a temperature-dependent constant. Logarithmic plots of bond strength versus time have given values for the exponent of t that are close to the predicted value of 0.4.

The major experimental difficulty has been, and is, the attainment of reproducibility. In the earlier experiments, the scatter was so excessive that it was not possible to correlate theory and experiment. More recently, the reproducibility has been improved greatly by removing the worked surface layer from the flats by electropolishing. The influence of cold work on diffusion rates has long been recognized; in particular, the diffusion of zinc into copper has been shown to be increased by burnishing the copper surface. Because the diffusion coefficient enters the expression for bond strength directly, this effect was judged to be important enough to warrant further study. The amount of deformation introduced into the surface by mechanical polishing is difficult to measure or control. Accordingly, varying degrees of cold reduction up to 90 per cent have been given to sections of the gold flats, which are subsequently electropolished and tested. Isochronal annealing curves, where hardness is plotted as a function of annealing temperature for various degrees of cold work, have been obtained. Also, metallographic studies were used to determine the recrystallization temperatures for the various conditions. These data are being considered in conjunction with bonding test data to determine the influence of cold work on bond strength.

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

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Two other theories have been proposed to explain the time dependence of bond strength. In the first of these, an increase in the bond area caused by creep under the applied load was postulated. This was checked by tests in which a load was initially applied and then removed (or, actually, reduced to a very low value) during the remainder of the test. The results continued to show an increase of bond strength with time, thereby eliminating creep as a primary mechanism. A second mechanism is recrystallization, as proposed by Parks*. This mechanism likewise is influenced by time, temperature, and cold work, and provides a model that is at least qualitatively consistent with the test data.

In summary, two mechanisms for the growth of solid-state bonds, the diffusion model and the recrystallization model, are being considered. Experiments are being continued so that data to confirm or disprove these models can be obtained.

NIOBIUM-GAS REACTIONS

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

The kinetics and mechanisms of the reactions of niobium with hydrogen and nitrogen are being investigated. The study includes the determination of the rates of diffusion of hydrogen and nitrogen in niobium.

Preliminary experiments obtained for the reaction of niobium with hydrogen at 1-atm pressure in the range 500 to 700 C indicate that no surface hydride film is formed. Apparently, the reaction proceeds by absorption of hydrogen in the metal, and the rate of absorption of hydrogen should be dependent upon the diffusion of the gas in niobium. An equation has been derived from Fick's second law for diffusion in which the rate of hydrogen absorption is a function of the diffusion coefficient for hydrogen. Calculations are being made with the preliminary data to determine whether the derived diffusion equation can be used to describe the rate of hydrogen absorption of niobium.

*Parks, J. M., "Recrystallization Welding", Welding Research Council of the Engineering Foundation, Supplement to the Welding Journal, 209s-221s (May, 1953).

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J. DEVELOPMENTAL STUDIES FOR THE PWR

R. W. Dayton

Air-flow mixing studies in a model of the PWR core show that there is only a limited amount of mixing between the flow in various loops of the reactor. Flow studies in the upper-plenum region are continuing, with a limited amount of work remaining to be done.

Preliminary tests of the X-ray photometric method of void detection suggest that the method will have adequate sensitivity but show the need for better control of the voltage supplied to the X-ray tube.

Air-Flow Studies on PWR Pressure Vessel

L. J. Flanigan and H. R. Hazard

Air-flow studies in a quarter-scale flow model of the PWR are being conducted at Battelle as part of the engineering analysis of the reactor. Work previously reported as complete includes the study of flow distribution in the reactor core and studies of coolant flow in reactor thermal-shield passages; study of flow in the upper-plenum region is in progress. In October, the study in progress was continued, mixing studies related to cold-water-accident analysis were carried out, and preparation of topical reports was begun.

Mixing Studies

In order to study mixing effects to provide data for evaluating the effects of a cold-water accident, a study was made in which SO₂ was introduced as a tracer into one inlet of the quarter-scale flow model, and flow from this inlet traced quantitatively throughout the core. The SO₂ was mixed with air, then injected into a 20-point distributor in the inlet duct, to maintain a concentration of about 10 ppm at one reactor inlet. Air samples were then withdrawn from the upstream pressure tap of the flow-measuring orifice in each of the 145 simulated fuel clusters in the model for immediate analysis in a Consolidated Instrument Company Titri-log recorder. By using this technique, it was possible to run a complete traverse of the core in less than one day. The traverse included systematic checking of inlet concentration and background concentration. Data were obtained under three test conditions, simulating operation with (1) two adjacent loops, (2) two opposed loops, and (3) three loops, plus, in each case, the "cold-water" loop carrying the tracer gas. Studies showed that under each of the

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three test conditions the concentration of SO_2 was very high in a few fuel clusters immediately above the area of impaction of the inlet jet on the flow baffle, and then dropped off rapidly with distance from the center of impaction. Concentrations were generally moderate outside the quadrant in which the traced inlet impacted, being lowest where other inlets impacted, and higher around the circumference where coolant from the thermal shield passages discharged. Calculated values of the percentage of coolant from the traced inlet varied from 84 per cent, above the point of impaction, to values below 10 per cent, with large areas in the range of 20 to 40 per cent. Good reproducibility of data was found in repeating the four-loop test.

Upper-Plenum Studies

Flow studies in the upper-plenum region were continued through October. Velocities and direction of flow through openings in the hold-down barrel and along surfaces of the upper dome were determined for four-loop, three-loop, and two-loop operating conditions, and measurements of velocities and pressure differentials for determination of forces acting on control-rod guides were completed. Some work remains in determining exact flow patterns throughout the upper plenum space; this is being done with TiCl_4 smoke as a tracer.

Reports

Drafts of topical reports on flow distribution in the core and on flow in thermal-shield coolant passages have been prepared.

The first draft of a report on cold-water-accident mixing studies has been prepared. It is anticipated that this report draft will be completed in November.

Future Work

Two major studies will be undertaken in November: a study of flow in the upper-plenum region, with a revised hold-down barrel installed, and extended studies of flow distribution in the reactor core. Core distribution studies will extend and supplement previous studies, following model modifications and calibrations to improve accuracy, and will be carried out both with and without the flow baffle. Core distribution studies will be started early in November. They will be interrupted at a convenient time after the modified hold-down barrel is received, then resumed when upper-plenum studies are begun with the modified hold-down barrel.

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X-Ray Photometric Method of Void Detection
in Fuel-Rod Welds

J. B. Schroeder and C. M.. Schwartz

X-ray photometric techniques are being studied as a possible non-destructive test technique to detect weld porosity. The specifications call for an instrument capable of detecting all voids with a diameter greater than 10 mils.

A 250-kv X-ray generator and a scintillation detector have been used in tests to date. The detector is shielded with 2 in. of lead on all sides. The sample is placed between two collimating holes (13 mils in diameter) which have been machined in the top shield.

Results have shown that (1) fluctuations in the line voltage produce serious changes in the counting rate and (2) at 155 kv a 1-mil tantalum foil (roughly comparable to 3 mils of zirconium) inserted above the collimator reduces the counting rate through a 0.425-in. diameter Zircaloy rod from 9500 to 9200 counts per min.

Because of the difficulty in reproducing the X-ray output, a simple feed mechanism is being built to move actual weld samples in a helical path through the X-ray beam. In addition, a voltage regulator is being obtained to eliminate the counting-rate changes caused by line-voltage changes.

K-1

K. EVALUATION OF A REFLECTOR-CONTROLLED
HETEROGENEOUS BOILING REACTOR

J. W. Chastain

Previous analyses by Battelle have shown a reflector control system to be a stable and feasible method for controlling a boiling heterogeneous reactor. In this system an annular water reflector is connected intimately with the core and, through a pipeline, to a surge tank. Increases in the reactor power cause increased boiling which forces water from the reflector to the surge tank. This lowering of the reflector level causes a decrease in the reactivity and, consequently, in the power which tends to return the reactor to its previous power level.

To verify this system experimentally, two separate experiments are planned. Data on the reactivity effects will be obtained from a critical-assembly experiment. The kinetics of the control system will be checked by a full scale mock-up of the hydraulic system driven by an electronic reactor simulator.

During the month, construction and wiring of the critical experiment was completed. Testing of the components should be completed by the middle of November and loading of the first core will begin.

Critical Experiment

W. C. Ballowe, F. J. Jankowski,
and J. W. Chastain

The purpose of this experiment is to measure the worth and effectiveness of the reflector system of control. This information will be used as input data to the reactor simulator to evaluate the transient behavior of the reactor system.

The reflector tank for containing the remotely-driven reflector material has been installed. The installation of the reactor support tables is now complete. The wiring of the table drive and source drives to the console has also been finished. Testing of these units should be completed by the first week in November.

The core parts have been assembled on the table and are ready for loading. The extruded plastic for the core has been delivered and a

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sufficient number of strips have been cut to length for the first loading of the reactor core. The total fuel inventory of 10 kg of uranium foil has been delivered and is ready for loading.

It has been necessary to order more plastic blocks to insure the flexibility of the reflector design. These blocks as well as the control rods and the other materials for the core are expected within 1 week.

If the above items arrive as they are now scheduled the loading will begin about the middle of November.

Simulator Studies

B. B. Gordon and J. J. Stone

The simulator study is being done to obtain information on the hydraulic system of the reactor. The hydraulic system has been reproduced in a full scale mock-up. Dynamic operation is duplicated by driving this system with an operational analog simulating the reactor. Information on the reactivity worth of the reflector will be supplied to the simulator from the critical experiments.

All construction is complete and the start-up and shut-down procedures have been made up and reviewed. Initial operation was planned for the end of October, but the pressure recorder-controller was not delivered. The delivery of this equipment is promised for early November, and then operation can begin immediately.

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L. STUDIES OF SODIUM-TANTALUM COMPATIBILITY AT ELEVATED TEMPERATURES

J. H. Stang

A program of research has recently been initiated at Battelle on several problems which stem from the containment by tantalum of flowing sodium at temperatures ranging from 1000 F to 1800 F. Four separate areas of investigation (corrosion problems, mechanical-property evaluations of tantalum at elevated temperatures, tantalum welding studies and oxygen determinations for very pure sodium) are of interest. This work is associated with the development of a fast reactor (LAMPRE I) system at Los Alamos Scientific Laboratory.

During October, the various phases of the Battelle program were concerned primarily with the design of experimental equipment. Another item of major concern, the procurement of a fairly large supply of tantalum of known history, was also actively pursued. It was found that such material carries a long time delivery. Hence, until a uniform-quality batch is obtained it will be necessary to employ material from several sources for experimental purposes.

Tantalum-Sodium Corrosion Studies

C. V. Weaver, D. R. Grieser, and S. L. Fawcett

An investigation is under way to evaluate the behavior of tantalum subjected to long-time high-temperature-sodium exposures. The temperature range of interest is 1000 F to 1500 F. Two general effects are of particular interest. The first concerns corrosion behavior in polythermal experimental systems, and the second concerns change in physical and mechanical properties of the materials as a result of corrosion or other deleterious factors. The role of oxygen content in the sodium will be of special importance because it is known that tantalum will getter oxygen from sodium at elevated temperatures.

The initial effort is being aimed at providing a sodium-production facility which can supply sodium of varying oxygen levels. The corrosion and mechanical-property experiments will utilize this controlled-purity sodium as the test fluid in basically simple test apparatus such as static or tilting-furnace capsules. At present, a design for the production system, using the techniques of cold trapping and distillation, is nearly finished. In this design, the two purification techniques are employed consecutively. It

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is felt that, in this way, the oxygen content of the sodium can be reduced below 10 ppm. If higher impurity levels are desired in particular batches, metered amounts of oxygen can be introduced into the system to achieve specified conditions.

The fabrication and purchase of components for the production system (to be made principally of Type 316 stainless steel) will be started in early November. It is probable that trial runs can commence by mid-December. The design of the experimental equipment will be carried on as the construction of the purification system progresses.

The High-Temperature Mechanical Properties of Tantalum

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

This investigation has the basic objective of providing information on the mechanical properties of tantalum at temperatures between 1000 and 2000 F. A study of the prior literature indicates that a primary problem will be the control of gaseous contamination of the tantalum and maintenance of gas-content levels in the metal during high-temperature mechanical-property experiments such as creep-behavior evaluations. Visits were made to the Los Alamos Scientific Laboratory and to ORNL to obtain information on this problem and background for the research.

Delivery of a tantalum lot, fabricated in various shapes, but having the same chemical analysis with respect to solid impurities, was informally quoted at about 6 months by the Fansteel Metallurgical Corporation. In view of this situation, the following steps have been taken to provide material for preliminary tests:

- (1) A lot of tantalum tubing (3/16-in. OD by 0.015-in. wall) and of 0.030-in. -thick sheet has been transferred from Los Alamos Scientific Laboratory to Battelle.
- (2) Odd-size pieces of high-purity tantalum from various lots have been ordered from Fansteel.
- (3) An inquiry has been made regarding availability of tantalum in Europe.

Planning of the test program is continuing so that experimental work may be started as soon as tantalum is received. Initial work will involve determination of room-temperature properties with material which is obtained from the various sources.

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Weldability of Tantalum for High-Temperature Systems

S. M. Silverstein and R. P. Sopher

The objective of this research is to design and join a small (roughly 6-1/2 in. in diameter by 6-1/2 in. long) tube-and-shell container made of tantalum for use at high temperatures. It appears that a leading problem in this study will be the joining of a large number of 15-mil-wall, 3/16-in. - diameter tubes to a relatively thin header. These tubes have a nearest distance of approach of approximately 3/64 in.

According to present plans, the tube-to-header joints will be made by rotating the assembly under a stationary inert-gas-shielded tungsten-arc welding torch. The necessary jigs for this welding process are on order. The probable conditions for welding are as follows:

Shielding gas - argon

Current - approximately 95-amp direct current with a
superimposed high-frequency arc

Polarity - straight

Studies on small pieces of tantalum tubing and sheet will determine whether these conditions are correct. Commercial-grade tantalum will be used for this preliminary work in view of the long delivery period for special high-purity material.

Determination of Oxygen in Sodium

P. H. Goble, M. J. Trzeciak, and M. W. Mallett

A study is being made to develop an analytical method for oxygen in sodium with a sensitivity of 0.0001 w/o. At present, an amalgamation apparatus in which the reactions will take place in vacuum is being built. The information obtained from this method will serve as a guide in the development of the more sensitive method. The 0.001 w/o sensitivity of the amalgamation method will also be satisfactory for evaluation of sodium used in corrosion and mechanical-property studies, particularly at high oxygen levels.

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As was pointed out in BMI-1136, it is planned to utilize gettering techniques for oxygen determinations in the 0.0001 w/o range. The apparatus to be employed is now being designed. Stainless steel will be used as the material of construction in those components that will contact liquid sodium. A major problem in the design is posed by the extreme care that must be taken in sampling and handling of sodium at very low oxygen concentrations to avoid contamination prior to analysis.

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M. PROCESSING OF FEED MATERIALS

E. L. Foster, Jr.

During Fiscal Year 1956, a program of research concerned with the selection and evaluation of materials suitable for use in molten-salt baths for the heat treatment and processing of uranium was conducted for the National Lead Company of Ohio (NLO). The main objective of the program was to select a salt-bath system that would minimize the pickup of hydrogen by uranium. As a result of this study, a new program has been initiated at Battelle. It will be devoted to larger scale evaluation of the salts that showed promise during the initial investigation.

Two binary salt systems will be studied, the 50 w/o sodium chloride-50 w/o potassium chloride and 50 w/o potassium chloride-50 w/o sodium carbonate. These baths, plus controlled additions of salts from the baths now in use, will be evaluated.

This study was resumed during the latter part of October and at this time there are no data to report.

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N. CORROSION PROBLEMS ASSOCIATED WITH RECOVERY
OF SPENT REACTOR FUEL ELEMENTS

C. L. Peterson, P. D. Miller, and R. S. Peoples

As part of a program of assistance to ORNL, Battelle is undertaking various investigations associated with corrosion problems which have arisen in some of the envisioned processes for the recovery of spent reactor fuel elements.

Presently, tests are being designed to supply data of use in selecting materials of construction for the hydrochlorinator vessel in the proposed Zircex system, and for the dissolver vessel and off-gas system in the proposed Darex system of fuel-element recovery. Preliminary elimination tests will be followed by tests in which actual operating conditions will be simulated as nearly as practical.

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