BMI-1259

METALLURGY AND CERAMICS

UNITED STATES ATOMIC ENERGY COMMISSION

PROGRESS RELATING TO CIVILIAN APPLICATIONS DURING MARCH 1958

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

April 1, 1958

Battelle Memorial Institute
Columbus, Ohio

Technical Information Service Extension, Oak Ridge, Tenn.

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Date Declassified: July 18, 1958.

Printed in USA. Price $2.00. Available from the Office of Technical Services, Department of Commerce, Washington 25, D. C.

AEC Technical Information Service Extension
Oak Ridge, Tennessee

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Contract No. W-7405-eng-92

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REPORTS RELATING TO CIVILIAN APPLICATIONS ISSUED DURING MARCH, 1958

BMI-1246 "Preparation of Low-Hydrogen Magnesium-Lithium Alloys", by Robert J. Jackson, Alvin M. Sabroff, and Paul D. Frost.

BMI-1252 "The Corrosion of Types 347 Stainless Steel in Boiling Digest Liquors", by Frederick W. Fink, Walter J. Braun, and Oliver M. Stewart.

BMI-1256 "Progress Relating to Civilian Applications During February, 1958", by Russell W. Dayton and Clyde R. Tipton, Jr.

A-1

A. DEVELOPMENTS FOR ZIRCONIUM-CLAD FUEL ELEMENTS

F. R. Shober

The thermal conductivity and electrical resistivity of uranium encapsulated in Zircaloy 2 with NaK as a heat-transfer material is being determined prior to irradiation. Final adjustments have been made to the apparatus constructed to measure the thermal conductivity of UO_2, and measurements will be started. Additional creep units are being used to evaluate the short-time rupture strength of 15 per cent cold-worked Zircaloy 2 at 290, 345, and 400 C.

Melting and fabrication of several series of ternary and quaternary zirconium-base alloys is in progress. Selection of the alloy with highest strength and most corrosion resistance at 300 C will be made on the basis of hardness and corrosion tests.

Thermal Conductivity of Uranium and UO_2

H. W. Deem and C. F. Lucks

A program to investigate the effect of irradiation on the thermal and electrical conductivities of uranium and on the thermal conductivity of uranium oxide is in progress.

Uranium

Radiographic examinations of the clad, unirradiated specimens of Zircaloy 2 and uranium show an unexplained material in the expansion chambers of the specimen assemblies. Judging from the amount of NaK introduced during filling, it is questionable if there is NaK in the annular spaces between the specimens and the Zircaloy 2 cladding. Vibration and heating failed to cause the material in the expansion chambers to flow down around the specimens. In view of the importance of good NaK contact between the specimens and the cladding walls, one of the Zircaloy 2 specimens will be opened and examined. The conductivity-measuring apparatus, recently damaged when a major vacuum leak developed while measuring hot uranium, has been repaired and is ready for service.

Uranium Oxide

An apparatus for making thermal-conductivity measurements on UO_2, both before and after irradiation, has been completed. A steady-state absolute method is being used. Briefly, accurately measured power is introduced into the top part of the specimen and the heat flows through the specimen into a heat sink. Compensated thermocouples at known positions measure the thermal gradients. The thermal conductivity of the specimen will be calculated from the heat flow, cross-sectional area, and the thermal gradients over measured lengths. Guarding to prevent stray heat flows has been provided.

A-2

Measurements on fused quartz have continued. The significantly lower thermal conductivity of fused quartz as compared to UO_2 provides a severe test for the apparatus. However, the modified guarding arrangements have produced a marked improvement. Over the temperature range 100 to 400 C, the measured values range from excellent agreement with literature values to 50 per cent above, depending upon guarding conditions.

During April, work will continue on guarding problems, the temperature range will be extended, and measurements will begin on the UO_2 specimens.

Mechanical Properties of Zirconium Alloys

F. R. Shober and J. A. VanEcho

Evaluation of the creep properties of 15 per cent cold-worked Zircaloy 2 at several temperatures up to 400 C has continued. The long time (up to 10,000 hr) creep and rupture properties are to be determined. The time for the initiation of third-stage creep and the creep deformation associated with it are of interest in determining design stresses.

Ten tests are now in progress in the 290 to 400 C temperature range. The total time at test is approximately 3500 hr for some of the longer tests. The results of the tests are given in Table A-1. Third-stage creep is evident from the results of one test at 345 C and 30,000 psi. Five additional creep units are to be used to determine short-time rupture properties at 290, 345, and 400 C. These tests will be started in April.

Development of High-Strength Corrosion-Resistant Zirconium Alloys

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

A research program to develop a zirconium alloy with greater strength than Zircaloy 2 at 570 F and good corrosion life in 570 F water is continuing. The nuclear properties, thermal conductivity, and expansion coefficient of the alloy are to be comparable to those of Zircaloy 2. Alloys are being prepared by arc-melting techniques using sponge zirconium. Alloys of interest may contain up to 2.0 w/o molybdenum, 3.0 w/o niobium, and 4.0 w/o tin. The better alloys will be selected on the basis of the results from corrosion tests in 570 F high-purity water and on the basis of room-temperature hardness. Hot-hardness data will be secured on alloys which show promising properties in the screening operation. If time permits, work on the mechanical and physical properties will be initiated.

All charges have been prepared and were submitted for arc melting. A first series of ternary zirconium-base alloys containing 2 w/o tin plus 0 to 2.0 w/o molybdenum, a second series of ternaries containing 0 to 3 w/o niobium, and a third series

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

Specimen	Temperature, C	Stress, psi	Time at Test[a], hr	Deformation at Time Indicated, per cent										Creep Rate[b], per cent per hr
				Load On	50 Hr	100 Hr	500 Hr	1000 Hr	1500 Hr	2000 Hr	2500 Hr	3000 Hr	3500 Hr	
7-4-2	290	40,000	935	0.269	0.510	0.550	0.800	1.00[c]	--	--	--	--	--	--
7-2-2	290	35,000	3700	0.353	0.495	0.520	0.595	0.625	0.675	0.692	0.705	0.726	0.741	0.00003
7-2-3	290	30,000	3600	0.275	0.375	0.385	0.415	0.440	0.445	0.470	0.476	0.483	0.495	0.000024
7-3-1	290	25,000	3800	0.205	0.267	0.282	0.305	0.323	0.330	0.335	0.340	0.347	0.353	0.000012
7-3-2	270	20,000	3800	0.178	0.223	0.227	0.245	0.250	0.265	0.265	0.270	0.272	0.280	0.000016
7-1-1[d]	345	30,000	3300	0.315	0.537	0.592	0.745	0.875	1.025	0.183	1.398	1.745	--	0.0694
7-2-1	345	25,000	3500	0.230	0.385	0.420	0.510	0.548	0.580	0.612	0.645	0.675	0.695	0.00004
7-3-3	345	20,000	3500	0.180	0.300	0.325	0.380	0.397	0.417	0.427	0.440	0.450	0.475	0.00005
7-4-1	345	15,000	2600	0.110	0.185	0.205	0.245	0.265	0.275	0.287	0.293	--	--	0.000012
7-4-3	400	15,000	1100	0.134	0.290	0.330	0.440	0.500	--	--	--	--	--	0.00015

(a) Tests in progress.
(b) Creep rate based on creep deformation occurring during the latest 500-hr period of test.
(c) Extrapolated value.
(d) Test discontinued at 2015.6 hr and reloaded after a 6-week rest period.

of quaternary alloys containing from 0.5 to 2.0 w/o molybdenum and 1.0 to 3.0 w/o niobium have been arc melted. A fourth, fifth, and sixth series containing 3 w/o tin and a seventh, eighth, and ninth series containing 4 w/o tin are being prepared. The niobium and molybdenum contents of the fourth through ninth series corresponds to the contents of the first, second, and third series.

Nineteen alloys of the first, second, and third series were hot rolled from a 900 C helium furnace. Due to excessive surface oxidation, the fabrication temperature was reduced to 850 C for the remaining thirteen alloys in the first, second, and third series. No difficulty was encountered in rolling at 850 C, and a lighter oxide film was evident. The same fabrication temperature (850 C) will be used for the fourth through ninth series of alloys. The majority of the alloys being investigated will be fabricated in a two-phase region. Rolling in a two-phase region has not produced any adverse effects in a similar alloy system; this plus the advantage of rolling at a lower temperature has prompted a lower rolling temperature.

B-1

B. DEVELOPMENTS FOR ALUMINUM-CLAD FUEL ELEMENTS

R. J. Carlson

Testing of the right-angle extrusion cladding tools has been concluded and a topical report is being prepared. Although the equipment was successfully used to apply 30-mil cladding to several 40-in.-long uranium plates, additional modification in the shape of either the mandrel or the die appears to be necessary for optimum results.

Pressure bonding of aluminum to nickel-plated uranium by temperature and gas-pressure technique has produced sound metallurgical bonds. Minimum time, temperature, and pressure necessary to obtain sound bonds is being investigated.

The evaluation of a mechanical extensometer designed and constructed to have sufficient sensitivity to determine the transverse mechanical properties of 3-in.-OD uranium tubing has been completed. It is judged to be satisfactory both in elastic and plastic deformation applications.

A series of 17 alloy compositions has been prepared for corrosion testing in an effort to develop a natural-uranium fuel alloy with improved corrosion resistance. Actual testing is about to begin.

Extrusion Cladding of Flat Plates

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

Tests to develop the right-angle method of extrusion cladding for flat plates were continued, using a modified mandrel tip. The bottom portholes of the mandrel were enlarged in an attempt to equalize the flow of aluminum from the top and bottom portholes and thus prevent edgewise cocking of the core. The 30-mil claddings applied to several 10-ft-long steel plates using the reworked mandrel show that the flow of aluminum from the portholes of the mandrel was somewhat improved. However, additional modification in the shape of either the mandrel or the die appears to be necessary for optimum results.

Claddings of 30 mils were applied to several 40-in.-long uranium plates. Attempts to clad over several uranium plates joined with M355 aluminum (19 w/o Al_2O_3) connectors were unsuccessful, because of fractures in the M355 aluminum.

Experimental work on this project was concluded. A topical report covering the research conducted is being prepared.

B-2

Preparation of Aluminum-Uranium Alloys

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

During March, the preliminary study was concluded. A more extensive development program on the preparation of aluminum-uranium alloys by centrifugal-casting techniques will be initiated in April.

Aluminum Cladding

S. J. Paprocki, E. S. Hodge, C. B. Boyer, and C. C. Simons

The cladding of internally and externally cooled fuel elements, which consist of a nickel-plated uranium core clad with aluminum, is being investigated. The method used to achieve a metallurgical bond between core and cladding is pressure bonding, a technique employing gas pressure and temperature.

Metallographic examination of an "I" and "E"-type slug bonded at 950 F for 1 hr at 5,000 psi revealed a sound metallurgical bond with the formation of interface reaction layers of Ni_2Al_3 and $NiAl_3$. The amount of Ni_2Al_3 and $NiAl_3$ formed at the interface was equivalent to that obtained with a similar specimen bonded at 925 F for 5 min at 10,000 psi.

Thermal-shock tests were run on the bond interface of the specimen bonded for 1 hr at 950 F at 5,000 psi. Metallographic examination of this specimen, after a thermal-shock test consisting of heating to 950 F for 20 min subsequent to water quenching, revealed no evidence of cracking in the bond interface.

Two 20-in.-long specimens were prepared for pressure bonding. These specimens consisted of nickel-plated uranium canned with aluminum. The conditions chosen for the pressure bonding of these specimens were 1 hr at 950 F and 10,000 psi for the first specimen, and 1 hr at 950 F and 5,000 psi for the remaining specimen. The as-bonded specimens were shipped to another site for further evaluation.

Sound metallurgical bonds have been obtained during pressure bonding for 1 hr at 870 F to 960 F and 10,000 psi, for 1 hr at 950 F and 5,000 psi, and for 5 min at 925 F and 10,000 psi. Additional specimens are being bonded in an effort to determine the minimum time, temperature, and pressure necessary to obtain a sound metallurgical bond.

Development of a Mechanical Extensometer

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

Evaluation of a mechanical extensometer designed and constructed to have sufficient sensitivity to determine the transverse mechanical properties of 3-in.-OD uranium tubing has been completed.

B-3 and B-4

The transverse properties of aluminum, copper, stainless steel, and uranium tubes were measured to evaluate the response of the extensometer. All testing was done at room temperature. The sensitivity of both the cantilever and loop-type strain gages has been determined. This was accomplished by determining the deformation produced per pound of internal pressure on the circumference of a tube. The deformation was measured by a SR-4, A-9 wrap-around type of electric strain gage. The corresponding movement of the mechanical extensometer for the same interval of load was established. Comparison of the movement measured by the wrap-around gage and the cantilever indicates the sensitivity of the mechanical extensometer. The cantilever gages designed to measure the elastic modulus of uranium showed a sensitivity of approximately 1 division on the SR-4 indicator for every 0.000001-in. movement on the circumference of the expanding tube. The calibration of the loop-type gages designed to measure the plastic portion of the stress-strain curve showed approximately 1-division movement on the indicator for 0.000035-in. movement on the circumference of the tube.

No further work is planned.

Development of a Natural-Uranium Fuel Alloy With Improved Corrosion Resistance

M. S. Farkas, A. A. Bauer, and R. F. Dickerson

Development of a high-uranium fuel alloy that possesses improved corrosion resistance in 300 C water is continuing. Design requirements state that the thermal-neutron cross section must be less than that of a uranium-4 w/o zirconium alloy, and the alloy must possess corrosion resistance better than that of a uranium-2 w/o zirconium alloy.

Seventeen alloy compositions were chosen by two methods. One group of alloys is of the composition, uranium-2 w/o zirconium plus a third element. The third element was added in the maximum amounts permitted by the cross-section limit. Additions chosen were aluminum, chromium, molybdenum, nickel, niobium, platinum, ruthenium, titanium, and vanadium. The other approach was to make up ternary and quaternary alloys by adding small amounts of low-cross-section elements to uranium for the purpose of alloying the alpha phase for improved corrosion resistance.

All alloys were arc cast, worked, and heat treated at 900 C for 1 hr and furnace cooled. The specimens have been machined to size and holes drilled in order to mount the alloys in the autoclave. The autoclave has been readied for operation and corrosion testing will commence upon completion of several test runs. The alloys will be exposed to 300 C water in a windowed autoclave and failure will be noted visually. The alloys that show comparatively good performance will be further evaluated by short-time corrosion-rate determinations.

C-1

C. PLANT ASSISTANCE TO MCW

D. A. Vaughan

Density measurements and X-ray-diffraction intensity data are being obtained to aid in understanding the miscibility gap between UO_2 and U_4O_9. A literature search is being made for quantitative methods of determining orientation in fabricated uranium.

The study of the effect of chloride-contamination on the corrosion resistance of Type 304 ELC stainless steel in less than 38 w/o nitric acid solutions has been discontinued. No serious corrosion was observed with 0.3 w/o or less chloride ion contamination in 4000 hr. In more concentrated nitric acid solutions (38 and 45 w/o), lower chloride contents were required to reach the threshold in the corrosion rate. Additions of sulfate, up to 5000 ppm, to boiling 38 w/o nitric acid have shown no evidence of increasing the corrosion rate of Type 304 ELC stainless steel. A marked increase was observed, however, when the fluoride concentration of 38 w/o nitric acid solutions was increased from 10 to 100 ppm.

The permeation of hydrogen through molten magnesium fluoride slag is being measured. A new reaction tube was fabricated, but the measurements have not been completed. The apparatus for surface-tension measurements of slag has been tested, and results are being obtained on MgF_2, MgF_2-MgO, and MgF_2-UO_2 mixtures at 1350 to 1370 C.

Investigation of Uranium Oxides

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

A study of the oxidation of uranium dioxide has been continued. Results of helium density measurements on oxygen-enriched uranium dioxide were reported in BMI-1256. These results indicated that the density of UO_{2+x} decreases with oxygen additions up to about $UO_{2.13}$ and then increases in the UO_{2+x} + U_4O_9 two-phase region.

Several samples were prepared in the region of $UO_{2.05}$ and annealed at 450 C. Density measurements were made and the results were in agreement with previous conclusions. Experiments are under way to prepare $UO_{2.19}$, to substantiate the increase in density for oxygen-rich materials of composition greater than $UO_{2.13}$.

X-ray spectrometer intensity measurements were made on oxygen-enriched uranium dioxide to determine the effect of oxygen addition on the structure of the materials. Although, as expected, no large changes in intensities were observed, the data are being compared with computed intensities based upon anion or cation concentration changes in the UO_2 structure.

A literature search has been begun and a bibliography is being prepared on measurement of the orientation of uranium.

C-2

The Electrical Properties of Uranium Dioxide

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

This work is being discontinued.

The Corrosion Resistance of Selected Stainless Steels

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

Nitric Acid Reconcentrator

The prolonged exposure studies of Type 304 ELC stainless steel in chloride-contaminated 5, 18, and 30 w/o nitric acid solutions, boiling under reduced pressure, were discontinued. No serious corrosion was observed with chloride contaminations of 0.3 w/o or less. All of these specimens were exposed for at least 4000 hr. Studies with 0.15, 0.20, and 0.25 w/o chloride in 38 w/o nitric acid have reached the 4000-hr mark with no serious corrosion, although the rate for the specimen exposed in the liquid containing 0.25 w/o chloride has slowly risen to a value of 0.39 mil per month. Only two studies (0.10 and 0.20 w/o chloride) are still under way in 45 w/o nitric acid. Very low rates of the order of 0.05 mil per month are measured after 3000 hr with 0.1 w/o chloride while, after 2500 hr with 0.2 chloride, much higher rates from 0.71 mil per month for the liquid specimen to 1.45 for that in the vapor are the rule. Both the 38 and 45 w/o nitric acid studies will be continued.

After 500 hr of exposure, there was still no evidence that up to 5000 ppm sulfate had any effect on the corrosion rate of Type 304 ELC stainless steel specimens exposed in 38 w/o nitric acid solutions boiling at 250 mm of mercury absolute pressure. The studies with 100 and 5000 ppm sulfate are being continued. Meanwhile, a comparative investigation with Type 304 ELC stainless steel specimens exposed in 38 w/o nitric acid, containing 0, 20, 100, and 5000 ppm sulfate, and boiling at atmospheric pressure has been carried to the end of six 48-hr exposure periods. Again, there is no clear-cut evidence of any effect from even the largest sulfate addition. However, these corrosion rates vary from 0.2 to 0.4 mil per month, while in similar solutions boiling at reduced pressure, the rates scarcely exceed 0.04 mil per month. Thus, the increase in temperature due to the different boiling points has resulted in, roughly, a five- to tenfold increase in corrosion rates.

A series of experiments has been initiated in 38 w/o nitric acid solutions boiling at atmospheric pressure to determine the concentration of fluoride alone at which the corrosion of Type 304 ELC stainless steel becomes severe. Additions of 0, 1, 10, and 100 ppm fluoride are being studied by means of 48-hr exposure tests as the first step in determining this break point. After seven such exposure periods, the pattern has become plain that the rate increases rapidly between 10 and 100 ppm fluoride. At 10 ppm, the corrosion rate fluctuates in the neighborhood of 0.3 to 0.5 mil per month, while with 100 ppm, the rate may vary from 1.0 to 2.7 mils per month. Future studies will be made on concentrations between 10 and 100 ppm fluoride. Similar studies are planned for titanium specimens in 15, 38, and 60 w/o nitric acid solutions.

C-3 and C-4

Container Materials for Proposed Solvent Extraction Process

The corrosion study of Types 304 and 304 ELC stainless steel in simulated solvent extraction solutions made from a composite sample of the Weldon Springs raffinate is being discontinued.

Gas-Metal Studies

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

A study is being conducted to assist in determining fundamental factors affecting the purity and yield of dingot uranium produced in thermite reactors. Present experiments are on the permeability of hydrogen through molten magnesium fluoride slag and on the surface tension of Mallinckrodt and synthetic slags.

Permeation of Hydrogen Through Molten Magnesium Fluoride Slag

The molybdenum reaction tube mentioned in BMI-1256 has been obtained and fabricated. Permeability measurements are under way.

Surface Tension

The experimental system described in BMI-1253 was tested using distilled water at room temperature. The agreement between experimental values and those reported in the literature was very good indicating that the apparatus and technique were satisfactory. Using this system, initial measurement of the surface tension of molten magnesium fluoride was started. After a few measurements were made, the molybdenum capillary became clogged. In order to overcome this difficulty the capillary was enlarged. Optical measurement of the diameter of the enlarged capillary showed irregularities in the periphery of the hole. Therefore, the capillary was calibrated with distilled water to obtain the effective radius.

Preliminary measurements indicate that the liquid density of Mallinckrodt slag is approximately 2.5 g per cm^3 at 1350 C. This density was used in calculating surface-tension values. It is quite likely that the density of the different compositions varies somewhat. When more precise density measurements have been made the surface tension values will be recalculated and reported.

D-1

D. PROCESSING OF FEED MATERIALS

E. L. Foster

Three programs relating to the processing of feed materials are in progress. Two of the programs ultimately are related to the improvement of uranium quality since they are concerned with the factors affecting the compositions of vacuum-induction-melted uranium and a theoretical study of the solidification of unalloyed uranium ingots. The remaining program has been devoted to determining the feasibility of centrifugal casting heavy-walled uranium tubes using apparatus that could, with small revision, be operated in air.

Solidification of Uranium

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

A fundamental study of the solidification of uranium is being undertaken. The program has as its objective a fuller understanding of the physical problems and the thermal considerations present in the casting of a uranium ingot. The importance of the various casting variables such as superheat, pouring rates and times, mold configurations, and mold materials will be investigated. The over-all effect of these factors on the soundness of the casting will be evaluated.

The variables present during the pouring and casting of uranium ingots will be studied by making small-scale melts under highly controlled conditions. Thermocouples, properly insulated from the melt, will be placed in the mold cavity and at positions in the mold walls. These thermocouples will be so positioned as to record the time-temperature patterns from the top of the casting to the bottom. From these temperature measurements, thermal gradients can be obtained as a function of time. Cylindrical castings with high length-to-diameter ratios will be cast during the initial investigations. Graphite molds (International Graphite Type 7100) will be used in the casting runs. The information and data collected from the casting runs will be evaluated and interpreted to give information that can be inserted into equations being developed in a mathematical study of the heat-transfer phenomenon. The role of the mold-casting interface in the mechanics of heat transfer from the casting will be studied as one phase of this program.

As a part of the study, the physical constants of the materials under consideration must be obtained. Investigation of the technical literature has not revealed sufficient data on the thermal properties of uranium at high temperature. This has necessitated the measurement of these properties by experimental means.

One of the physical properties to be determined is the total normal emissivity of uranium and graphite. Measurements will be taken at temperatures as high as 2000 F. For this test, a uranium specimen 0.5 in. in diameter by 11 inches long was prepared. The surfaces of the uranium tube were oxidized slightly in order to duplicate the as-cast surface of the ingot. In addition, the emissivity of graphite will be measured using a specimen 3/4-in. OD by 1/2-in. ID by 11 in. with the inside surface of the graphite

coated with MgO mold wash. The temperature dependency of such properties as thermal conductivity and linear thermal expansion of these materials will be determined up to 2000 F.

In connection with the study of heat transfer of the metal and mold material, a new computer program representing a 76-cell model of a pie slice of the casting and mold has been constructed. Some preliminary testing of the program has been completed, and the results are now being checked for accuracy. The temperatures computed for some of the smaller cells have shown tendencies to instability or lack of convergence, and some reformulation of the problem has been necessary to overcome this. It has been found that one cycle of temperature calculations requires 28 to 30 sec of computer time, whereas the earlier 20-cell model required about 28 sec for each cycle; although the number of computations made have been increased by a factor of over 3, the time required for a cycle of computations has remained about the same, this being due to the higher computational speeds possible through use of the magnetic-core storage and other features added to the computer.

The use of varying time intervals in computing the change of temperature is being tried as a method for reducing the number of cycles required to examine the temperature field from the time of pouring until solidification is completed, e.g., when the melt first contacts the colder bottom of the mold, the temperature-change rate is high, and it is necessary to use a short time interval in order to obtain an adequate idea as to the thermal field; however, continued use of this short time interval results in unnecessarily long computer times, so experiments are now being conducted to determine at what stages of the computation it is possible to go to larger intervals.

Examination of Factors Affecting the Quality of Induction-Melted Uranium

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

This program deals with a study of the reactions that may occur during the induction melting of uranium. Of particular interest are the various nonmetallic impurities that are associated with the metal and their relationship with melting-process reactions. An evaluation of experimental results through the application of the principles of thermodynamics and reaction kinetics is expected to provide a better knowledge of those reactions that ultimately may be useful in suggesting improvements in processing. A literature survey is being conducted concurrently with the experimental portion of an investigation centering about a 10-lb-capacity vacuum-melting furnace.

During March, the metal and gas analyses of a test series which was completed previously were obtained and are shown in Table D-1. The test series included (1) moisture-controlled blank tests with uncoated graphite crucibles, (2) moisture-controlled uranium-melting tests in which timed exposures of the molten metal in uncoated graphite crucibles were compared, and (3) melting tests conducted in a graphite-free system in which an attempt was made to compare the CO-uranium reaction under wet and dry conditions. An evaluation of these results in terms of thermodynamic considerations was made.

TABLE D-1. TEST CONDITIONS AND ANALYSES OF URANIUM VACUUM MELTED AT 2500 F

	Heat						
	1206-1	1206-2	1207	1208	1209	1210	1211
Uranium	Blank	Blank					
Weight, kg	None	None	4.33	4.37	4.335	4.405	4.37
Initial Analysis, ppm[a]							
Carbon			40	35	20	30	95
Nitrogen			30	20	20	25	20
Final Analysis, ppm[b]							
Carbon			1650	1600	60	130	85
Nitrogen			20	20	30	35	40
Crucible	Uncoated graphite	Uncoated graphite	Uncoated graphite	Uncoated graphite	Zirconia	Zirconia	Zirconia
Furnace Additions							
Water, cm^3	--	1.1	--	0.2	--	--	0.1 cm^3
CO (STP), liter	--	--	--	--	--	0.82	0.82
Time at Temperature, min	70	30	30	30	30	40	54
Sampling Pressure, μ							
McLeod	33	90	26	20	43.5	20.5	55
T. C. Gage	35	>500 <1000	47	160	71	34	110
Mass Spectographic Analysis, (volume, per cent)							
H_2	Nil	68.3	94	0.8	71	75	--[c]
CO	12.7	24.9	2.9	5.0	2.6	1.9	--
N_2	68.5	2.1	1.5	71	24.2	7.3	--
O_2	14.9	0.03	Nil	20.7	0.09	0.2	--
H_2O	2.2	3.7	1 to 3	1 to 3	1 to 3	1 to 3	--
A	0.9	0.05	0.15	0.9	0.2	1.3	--
CO_2	0.2	0.3	0.16	0.09	0.18	0.48	--
As N-pentane	0.6	0.7	0.94	0.2	0.3	2.0	--
As toluene	Nil	Nil	Nil	Nil	Nil	Trace	--

(a) Approximately 2 ppm hydrogen.
(b) Approximately 0.2 ppm hydrogen.
(c) Sample lost.
Note: Furnace volume = 1192 liters.

D-4

Early in the program there was concern that inherent disadvantages of equipment, procedure and analysis might yield only qualitative results. However, it was determined that evaluations, semiquantitative in nature, could be made of the data shown in Table D-1. In these tests, the three predominant and competing reactions under consideration were the water-gas reaction ($C + H_2O \rightleftarrows CO + H_2$), the water-uranium reaction ($2H_2O + U \rightleftarrows UO_2 + 2H_2$) and a secondary reaction between the carbon monoxide (from the first reaction) and the uranium. In the dry blank (Heat 1206-1), system leakage was low and no extraneous moisture other than that associated with the air (relative humidity of 70 per cent) entered the furnace as evidenced by the close correlation between McLeod and thermocouple vacuum-gage readings. A calculation of furnace atmosphere based only upon accountability of air entering the system gave the following theoretical composition (volume per cent): hydrogen = 1.9, CO = 9.1, nitrogen = 70.3, oxygen = 15.3, H_2O = 2.3, argon = 0.9, CO_2 = 0.2. Except for the failure to detect ydrogen, the actual analysis compared favorably with the theoretical. The companion wet test (Heat 1206-2) showed that a water gas reaction occurred; however, an explanation of the high hydrogen content of the gas (or low CO) was not resolved. In the timed exposures of molten uranium to the furnace environment, not enough water was admitted to the system to detect the carbon pickup in the melt resulting from the postulated water-gas reaction.

During the graphite-free tests in which measured quantities of CO were admitted to the furnace, pressure profiles of the system were obtained. A curve, Figure D-1, was obtained by plotting system pressure against time (Heat 1210), graphically illustrating the rapid reaction between CO and uranium. In Heat 1210, a degree of stirring of the melt was achieved that could not be reproduced for Heat 1211. Evidently this stirring was sufficient to yield a reliable posttest carbon analysis since the carbon pickup was approximately equal to the amount of carbon introduced as CO. In general, there were certain discrepancies in the gas analyses (e.g., Heat 1209) which appear to stem from experimental difficulties and which limit the effectiveness of an evaluation of the tests.

A theoretical treatment of the H_2O plus uranium and a CO plus uranium reaction (both at 2500 F) indicated that the equilibrium constant of the latter reaction is several magnitudes greater than the former. The equilibrium constant for the carbon plus H_2O reaction at the same temperature was found to be much less than either of the above reactions. According to thermodynamics, if equilibrium had actually been established, oxygen, H_2O, CO, and CO_2 would not be detected in the gas analyses of any of the uranium melting tests, and in the blank tests oxygen and H_2O would have been too low for detection. A material balance of the dry blank (Heat 1206-1) indicated that the gas analysis was essentially correct, yet if equilibrium had been reached the analysis according to thermodynamics was erroneous. Obviously, the system was dynamic instead of static, and the assumptions made for equilibrium did not apply. Consequently, an experimental approach is suggested that should be amenable to treatment by thermodynamics and reaction kinetics. By admitting adequately sized test reactants (alone or in combinations as was done in Heats 1210 and 1211) to the furnace in which a constant, low-level leak rate has been established, a steady state should be reached that should not be adversely affected by system leakage or outgassing.

Since it appears from the various tests made to date that hydrogen, nitrogen, CO, CO_2, oxygen, and H_2O are the main gas components found over the molten uranium, a series of tests appears warranted in which melts would be made under a low-pressure

D-5

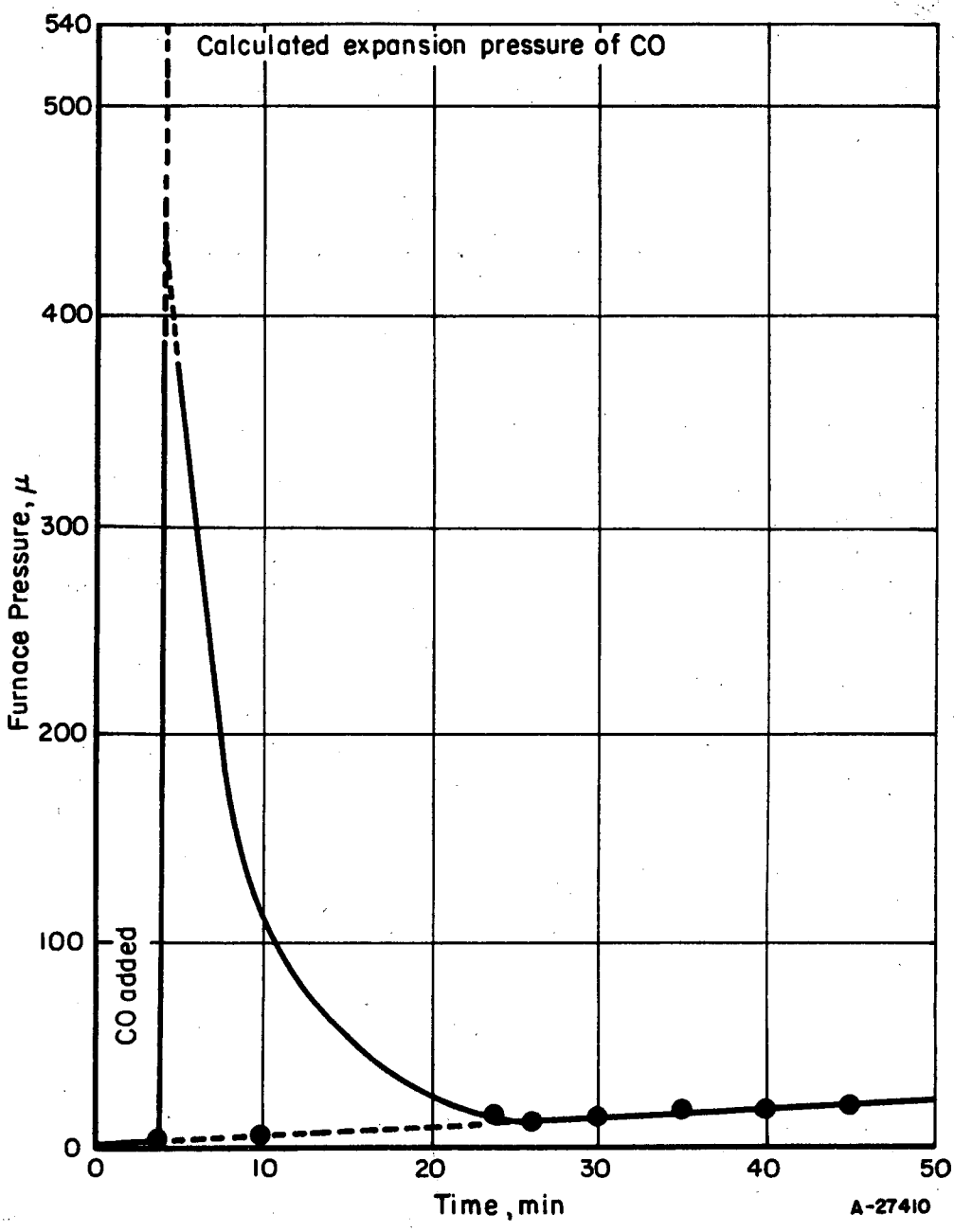

FIGURE D-1. PROFILE OF SYSTEM PRESSURE SHOWING EFFECT OF CO ADDITION DURING VACUUM MELTING OF URANIUM AT 2500 F

Heat 1210.

(500 μ) blanket of these gases alone and in various combinations. Samples for gas analysis would be taken initially and at intervals from the time of gas injection to the furnace. Future work may be indicated by variations in analyses of gas and metal in trial melts made from ingot croppings, derby chips, and briquetted turnings. Tests based on this approach should supply practical equilibrium and reaction-rate data for the most probable reactants.

Preparation of Thick-Walled Uranium Tubes by Centrifugal Casting

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

Natural-uranium elements in the shape of hollow tubes are of interest for natural-uranium reactors. A fabrication technique currently being considered for the production of this type element consists of extruding tubes from solid billets and drawing the extrusion to the desired size. Such a process would involve high capital and process costs. If uranium could be cast directly into the shape of a high-quality hollow tube which in turn could be reduced easily to the required final dimensions, considerable savings could be accomplished.

With this in mind, a brief feasibility study on centrifugal casting of uranium was initiated. Since this process has been applied commercially in the production of such items as iron pipe and large-caliber gun barrels, it was thought to be worthy of consideration as a possible technique for uranium. This feasibility study was to be performed using air-melting induction techniques and existing horizontal centrifugal-casting equipment.

Because of the problems associated with air melting uranium, modifications of the existing equipment were necessary. The major change involved was adapting the equipment so that the melt could be bottom poured. This was done in an attempt to minimize pickup of impurities by the reaction of the pour stream with air. This modification would also allow the melt to be poured from beneath the dross present when melting uranium in air.

The pouring cup and spout were constructed of graphite and designed so that they could be filled with inert gas to provide some measure of protecting the molten uranium from oxidation during pouring. The mold chamber was also made of graphite and constructed in such a way that a protective atmosphere would be present during pouring.

Six experimental heats were performed. Since the objective of the study was to evaluate feasibility on the basis of existing basic equipment, a mold speed of 550 rpm was used in all cases. The variables examined were mold temperature, melt temperature, and pouring-spout position.

Evaluation of the castings produced is complete. While some areas of the castings were sound, no casting possessed acceptable quality over its complete length. The outside surfaces of the castings were not of the quality achieved in prior centrifugal casting

work with alloys of uranium and aluminum. Surfaces varied in quality along the length of the castings. At the position of the pouring spout the quality was good but deteriorated as the distance from the spout was increased. It is theorized that a combination of factors may be responsible. These factors include pickup of impurities from the atmosphere existing in the mold, the fixed position of the pouring spout, and temperature of the metal as it enters the mold.

The wall thickness of these initial castings varied along the length, and metal soundness was not consistent. Again the temperature of feed metal and the techniques used to feed the metal into the mold cavity are believed to be critical.

The evaluation of the castings also showed that the inside surfaces were very rough and were composed of a mixture of oxidized and sound metal. The presence of the oxidized material indicates that contamination with the air occurred during the pour and in the mold. It is also believed that the method of feeding the molten metal to the mold cavity is very important in achieving good casting surfaces.

Although the feasibility study was narrow in scope because of equipment limitations, certain specific conclusions can be reached. These are as follows:

(1) If uranium is to be centrifugally cast in air, it will be necessary to devise techniques of providing positive protection of the molten metal from atmosphere contamination.

(2) The pouring temperature of the uranium (in the equipment used for this study) must be at least 2600 F.

(3) The method of feeding the molten metal into the mold is critical. It would seem that a technique is required which would provide even feed along the length of the mold.

In general, it can be stated that the production of cylindrical castings of uranium by the specific techniques and the equipment employed in this study would not be feasible. However, it is believed that with the proper development this technique of casting could be applied in the production casting of uranium.

This concludes the study.

E-1

E. GENERAL FUEL-ELEMENT DEVELOPMENT

F. A. Rough and D. C. Carmichael

In this section, various programs of fuel-element development sponsored by the AEC Division of Reactor Development are reported.

Specimens of enriched UN or UC dispersed in stainless steel have been clad with stainless steel for irradiation testing. Results of tensile tests on similar specimens are presented for temperatures from room temperature to 1650 F.

The conclusions of a study of the properties and methods of fabrication for fuel elements containing high loadings of fuel compound dispersed in a metal matrix are presented this month. Satisfactory hot-pressing techniques have been determined for preparing cermets of high density. It has been found that the mechanical strength, the resistance to thermal shock, and probably the thermal conductivity of ceramic fuels can be improved with a cermet structure.

A study is being made of the feasibility of using the hydride of a uranium-zirconium alloy as a fueled moderator. Additional results from pressure-composition-temperature studies are reported; an electrical analog analysis of the heat flow in an irradiation capsule containing specimens of 2 w/o uranium-zirconium alloy hydride was performed.

Development of Dispersed UC and UN Fuel Elements

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

Specimens containing 24 w/o of UN or UC dispersed in stainless steel and clad with stainless steel are being investigated to determine tensile properties at elevated temperatures and resistance to irradiation damage. Irradiation specimens have been subjected to preirradiation leak tests, density measurements, and radiographic examination. In addition, the microstructures of typical specimens have been examined and the specimens to be used have been marked and photographed. Specimens are being encapsulated and will be shipped to the MTR for testing. Specimens will be irradiated to three different burnups at a temperature of 1650 F.

Tensile properties of specimens containing cores of 24 w/o UN or UC dispersed in Type 302B stainless steel and clad with Type 347 stainless steel are shown in Table E-1. The specimens were in the fully annealed condition and edges of the cores were exposed in the test area. Specimens were 0.060-in.-thick plates with 0.050-in. cores. Tensile bars were held at temperature 20 min before applying the load.

E-2

TABLE E-1. TENSILE PROPERTIES OF 24 w/o UN AND UC

Fuel Compound	Dispersion Test Temperature, F	0.2 Per Cent Offset Yield Strength[a], psi	Ultimate Tensile Strength[a], psi	R[b]	Elongation[a] In 2 In., per cent
UN	Room	36,900	69,300	0.99	14.3
UN	1100	25,400	48,900	1.07	10.3
UN	1300	20,000	34,500	1.08	12.0
UN	1500	14,900	18,100	0.97	16.5
UN	1650	10,800	13,000	1.12	18.1
UC	Room	42,400	67,500	0.94	4.6
UC	1100	30,300	42,500	0.93	5.0
UC	1300	26,900	32,200	1.01	8.8
UC	1500	16,900	20,000	1.07	16.9
UC	1650	9,700	12,000	1.03	25.3

(a) Average of two values.

(b) Ratio of ultimate tensile strength of dispersion element to ultimate tensile strength of stainless steel multiplied by volume per cent of stainless steel.

Fabrication of Cermet Fuel Elements

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

A limited study has been made to determine the feasibility and advantages of producing fuel elements which contain 60 to 90 volume per cent ceramic fuel supported by a continuous or semicontinuous metallic matrix. Most of the work has been conducted using UO_2 and stainless steel. However, other metals such as molybdenum and niobium look promising as skeleton materials, and UC and UN appear promising as fuel materials. The study has included an investigation of sintering, infiltration, and hot-pressing techniques as methods of obtaining dense cores. Mechanical-property data have been limited to the calculation of room-temperature tensile strength from bend-test data and the measuring of resistance to thermal shock. The only physical property obtained was the electrical resistivity of the cermet. Methods of cladding the dense cores were not thoroughly investigated, but the most feasible method appears to be the gas-pressure bonding technique.

Fabrication studies have indicated that of the commonly used powder-metallurgy procedures, only the hot-pressing method will consistently produce stainless steel – UO_2 compacts of higher than 90 per cent of theoretical density. Sintering of the mixtures which contain high loadings of UO_2 was not shown to be feasible. Since UO_2 does not sinter at the temperatures normally used for sintering stainless steel, the void space between the UO_2 particles is not decreased during sintering and consequently the total UO_2 loading is dependent upon the maximum packing which can be attained by cold pressing. Although calculations show that loadings as high as 88 volume per cent UO_2 are possible by arranging spherical UO_2 particles of two different sizes in a close-packed arrangement, cold compaction of powder commercially available has not resulted in more than 75 per cent of the space being filled with UO_2. A second complication in the sintering process is the tendency of the stainless steel to shrink away from the UO_2 and even in a 75 volume per cent UO_2 compact, full density cannot be realized by sintering. Apparently the stainless steel sinters into a continuous skeleton but the force created by

the shrinkage of the stainless steel is not sufficient to rearrange the UO_2 and overcome the bridging effect which occurs during cold pressing.

If infiltration were feasible, however, UO_2 could be readily pressed to a density of 75 per cent of theoretical, and sufficient stainless steel could be added to give a 100 per cent dense compact containing 75 volume per cent UO_2. By the use of special UO_2 powders even higher loadings could be attained. Initial attempts at infiltrating by sintering above the melting point of stainless steel were not successful because the stainless steel did not wet the UO_2. Nevertheless, future investigations may develop suitable sintering and infiltration procedures. Such studies will include the use of metallic-coated particles and additives which are known to promote the wetting of ceramic materials by various alloys.

All specimens used for mechanical and physical testing were made by the hot press-forging procedure. However, it was found that the structure of the fabricated core was not only dependent upon the compacting method but also dependent upon UO_2 particle size and the blending procedure used. The best results were obtained by the use of minus 200 plus 270-mesh UO_2. If larger size UO_2 particles are used, severe fracturing occurs. Smaller particle sizes result in increased porosity. At the hot-pressing temperatures very little sintering of the UO_2 occurs and the final density is mostly dependent upon compacting the UO_2 into as small a space as possible and surrounding it with a continuous stainless steel skeleton. Therefore, relatively large, dense UO_2 particles with a smaller surface to volume ratio can be more easily surrounded by the limited amount of metal available, provided they are not fractured during the process. Little or no difference could be noted in the structure when minus 200-mesh stainless steel was used rather than minus 325-mesh stainless steel. The materials used were Mallinckrodt Hi-Fired Ceramic Grade UO_2 and Type 302B prealloyed stainless steel powder. The most satisfactory blending procedure consists of mixing the powders dry for two hr and then mixing two hr with less than 1/2 w/o Ceremul C (Mobilcer). A V-shaped twin-shell blender was used for all mixing operations.

The blended compacts were cold pressed at 30 tsi and then degassed at 600 F in a vacuum to remove the binder and residual gases. The compacts were placed in stainless steel picture frames and MgO-coated cover plates were welded on to seal the packs. This operation was performed in an argon-filled dry box. The welded packs were then press forged at temperatures of 1800 to 2100 F to a reduction of 30 to 35 per cent in thickness. A pressure of approximately 50 tsi was required. After removal from the pack, test specimens approximately 1.0 by 0.020 by 0.090 in. were obtained by grinding to final size.

In order to ascertain whether continuous stainless steel skeletons were being obtained, specimens were leached 24 hr in a warm 50 per cent nitric acid solution and examined. Both metallographic examination and density measurements were made before and after the leaching operation. In all of the specimens containing 50 to 87 volume per cent UO_2, a continuous skeleton was obtained, although in the very high loadings there appeared to be some segregation of the phases.

Results of electrical-resistivity measurements and tensile tests are shown in Table E-2. Resistivity was measured with a Kelvin bridge; the tensile strength was calculated from bend-test data. Tensile results indicate that, at the very high UO_2

loadings, the strength is primarily due to the amount of stainless steel present, but at loadings of approximately 50 volume per cent UO_2, the UO_2 also apparently contributes to the strength. For specimens containing less than 50 volume per cent UO_2, the cermet always fails with considerable elongation and hence the bend-test data cannot be considered as reliable for computing the actual tensile strength. Only a limited number of specimens were available for testing. However, both resistivity and tensile values appear to fall within a narrow scatter band. Tests on similar specimens show that both electrical conductivity and tensile strength are improved with decreasing porosity.

TABLE E-2. ELECTRICAL RESISTIVITY AND TENSILE STRENGTH OF UO_2-STAINLESS STEEL CERMETS AT ROOM TEMPERATURE

UO_2, volume per cent	Per Cent of Theoretical Density	Electrical Resistivity, μohm-cm	Ultimate Tensile Strength[a], psi
40	95.5	208.	63,400
50	93	150.	61,800
63	92	526	22,500
70	90.8	831	16,600
74	90.4	1,250	16,700
80	93	1,850	15,200
87	88.9	6,900	9,200

(a) Calculated from bend-test data.

Resistance to thermal shock was not determined quantitatively. However, comparison of a 74 volume per cent UO_2 cermet was made with UO_2 of 95 per cent of theoretical density by quenching into water from elevated temperatures. No visible cracking occurred in the cermet when quenched from 2300 F while a 100 per cent UO_2 compact visibly cracked when quenched from 1600 F.

In addition to work with UO_2, a small number of specimens containing UN and UC have been fabricated. A cermet containing 80 volume per cent UN in stainless steel, which contains more uranium than a 100 per cent dense UO_2 compact, shows a tensile strength of 23,800 psi, while in comparison a value of 15,200 psi is obtained for an 80 volume per cent UO_2 cermet. The examination of microstructures indicates that some fusion of the UN occurs. Densities of 94 per cent of theoretical are readily obtained. UC cermets with a molybdenum matrix were successfully fabricated but no mechanical- or physical-property data are available.

Results of these experiments indicate that both the mechanical strength and the resistance to thermal shock of ceramic fuel cores can be improved by the use of cermet structures. Fuel materials which appear promising include UO_2, UN, and UC, while chromium, molybdenum, nickel, niobium, and stainless steel all may be useful as skeleton materials.

E-5

Fueled Zirconium Hydride Moderator

H. E. Bigony and J. B. Vetrano

Work has continued on the investigation of hydrides of uranium-zirconium alloys as fueled moderators. The hydrogen sorption-isotherm study planned for the zirconium-1 w/o uranium alloy was finished by obtaining additional data at 534 C.

Sheets of zirconium-1 w/o uranium alloy and the zirconium-50 w/o uranium alloy approximately 0.015 in. thick were fabricated from thicker stock for a source of specimens to be used in the X-ray diffraction study.

An electrical analog of the heat flow in the capsule for irradiation was performed, and the temperature drops expected across various reference points were calculated.

Structure and Pressure-Composition-Temperature Studies

The second transition point for the hydrogen sorption isotherm of the zirconium-1 w/o uranium alloy at 534 C occurred at a hydrogen uptake of 171 cm^3 per g of sample at an equilibrium pressure of 0.014 cm. Only two transition points were detected at 534 C because this temperature is below the eutectoid temperature.

A series of isochores were constructed from the isotherms previously reported. Using these data, the $\beta \rightarrow \alpha + \delta$ eutectoid temperature was determined and the heats of solution of hydrogen in the alloy were calculated as a function of hydrogen concentration. These data are summarized in Table E-3. Included also for comparison are literature data for pure zirconium and for a zirconium-50 w/o uranium alloy. The effect of the added uranium is apparently to raise both the eutectoid temperature and the heat of solution in the two-phase regions.

TABLE E-3. THERMAL PROPERTIES OF THE ZIRCONIUM-HYDROGEN SYSTEM AND OF TWO ZIRCONIUM-URANIUM ALLOY HYDRIDE SYSTEMS

Uranium Content, w/o	$\beta \rightarrow (\alpha + \delta)$ Eutectoid		ΔH, kcal per mole	
	Temperature, C	Hydrogen Content, a/o	$\alpha+\beta$ Two-Phase Region	$\beta+\delta$ Two-Phase Region
0	574	32	--	45.8
1	565	32.5	15.3	47.2
50	608	--	36.4	53.9

E-6

Effort during the coming period will center around the preparation of hydrides of 1 and 50 w/o uranium-zirconium alloys for X-ray diffraction examination at 500, 600, 700, and 800 C. Specimens for this work will contain approximately 10, 30, and 50 a/o hydrogen, based on the zirconium and hydrogen atoms.

Encapsulation and Irradiation

The change in the temperature pattern of the capsules as a result of mechanical shifting of the fueled specimens was analyzed by setting up an electrical analog. It was found that a 15-mil shifting of the specimens could cause a 100 F drop of the center temperature, and set up a 70 F gradient across the diameter of the specimens.

F-1

F. STUDIES OF URANIUM AND URANIUM-ALLOY FUELS

F. A. Rough and A. W. Hare

Research and development programs sponsored by the Reactor Development Division of the AEC are reported in this section.

The results of a metallographic examination by light microscopy techniques on three specimens of irradiated zirconium-22 w/o uranium alloy are reported. Irradiation of Capsules BMI-8-5 and BMI-8-6 are nearing completion and are tentatively scheduled for discharge from the MTR in May.

In the investigation concerned with the development of gamma-phase uranium alloys, results of thermal-analysis data on various uranium-molybdenum-zirconium alloys are discussed.

In the research concerned with the development of suitable techniques for the preparation of homogeneous uranium-niobium alloys, it is reported that banding in arc-melted uranium-20, -40, and 80 w/o niobium alloys is caused by arc variations and subsequent segregation in a relatively shallow pool of molten metal. A possible technique to alleviate this condition is proposed.

Experimental data of corrosion studies on uranium in 100 C water and 200 C steam are reported and discussed in the program designed to investigate the mechanism of uranium corrosion.

Radiation Stability of Uranium-Zirconium Alloys

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

The irradiation of Capsule BMI-8-5, a temperature-controlled capsule, containing two specimens of zirconium-50 w/o uranium is continuing. The capsule has completed 11 cycles of irradiation at the MTR and it is estimated that two more cycles will be required to attain the design burnups of about 2 total a/o. The capsule has been operating at a control-thermocouple temperature of 510 C, which has been stable since the termination of the use of the low-enrichment core in the MTR in mid-December, 1957. This thermocouple temperature corresponds to a calculated specimen temperature of 675 C.

Capsule BMI-8-6, a nonlead capsule which contains three specimens of zirconium-22 w/o uranium alloy, has completed six cycles of irradiation at the MTR and is scheduled for an additional two cycles after which it will be discharged with a calculated burnup of 2 total a/o. The tentative discharge of both irradiation capsules has been scheduled for May.

The postirradiation metallographic examination by light microscopy techniques of three specimens of zirconium-22 w/o uranium alloy irradiated to burnups of about 0.9 total a/o has been completed. Prior to irradiation, the specimens were given three different heat treatments to produce three different microstructures. The resultant

microstructures were (1) fine alpha zirconium and epsilon grains, (2) coarse alpha zirconium in an epsilon matrix, and (3) alpha zirconium outlining a fine epsilon and alpha zirconium matrix. The examination of the three specimens showed no significant changes in the microstructure as a result of irradiation. No fission gas porosity or microcracks were observed in the three specimens which were examined.

An examination of this material by electron-microscopy techniques is being continued. Replicas of the microstructures of the irradiation specimens and of duplicate unirradiated specimens have been made and are presently being prepared for examination with the electron microscope.

Development of Gamma-Phase Uranium Alloys

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

In an effort to develop a gamma-phase uranium alloy of increased thermal stability, ternary and quaternary alloys of uranium with chromium, molybdenum, niobium, ruthenium, vanadium, and zirconium are being investigated.

Thermal-analysis data indicate that molybdenum additions to uranium-20 w/o zirconium alloys have approximately the same effect as niobium in lowering the temperature at which alpha uranium forms in conjunction with gamma solid solution. Temperatures of 674 and 639 C were obtained for uranium-20 w/o zirconium-1 w/o molybdenum and uranium-20 w/o zirconium-5 w/o molybdenum alloys, respectively. Zirconium added to uranium-7.5 w/o molybdenum alloys apparently raises the temperature of gamma decomposition from 615 C for an alloy with 3 w/o zirconium to 643 C for an alloy with 10 w/o zirconium. Apparently, zirconium additions to uranium-7.5 w/o molybdenum alloys impair gamma stability as transformation kinetic studies at 500 C indicate that increasing zirconium additions decrease the time for transformation.

Corrosion data on gamma-quenched alloys in 680 F water are still being obtained. After 672 hr of testing, surviving alloys have corroded as tabulated below.

Alloy Composition (Balance Uranium), w/o	Total Weight Loss, mg per cm^2
20Zr-5Nb	532.0
10Nb-3Mo	72.2
10Nb-5Mo	185.0
15Nb-3Mo	169.0
20Nb	19.5
20Nb-3Zr	106.0
20Nb-5Zr	4.92
7.5Mo-2Ru	10.9

All the surviving alloys have generally shown good gamma stability in transformation kinetic studies.

Additional uranium-molybdenum alloys containing ternary and quaternary additions of ruthenium and niobium have been prepared and are now being heat treated. These alloys were chosen on the basis of data which indicated a gamma-stabilizing effect by ruthenium and niobium on uranium-7.5 w/o molybdenum alloys. Also, uranium-12 w/o

molybdenum alloys with ternary additions of 0.18 w/o cerium and 0.25 w/o lanthanum have been prepared to determine the effects of these elements on gamma stability.

Preparation of Uranium-Niobium Alloys

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

The relatively high strength of niobium-uranium alloys at elevated temperatures makes them of interest as possible enriched fuel for high-temperature gas-cooled reactors. In view of this, a program is in process which has as its over-all objective the complete evaluation of these materials for such an application. The first phase of this study is concerned with development of suitable techniques for the preparation of these alloys and is currently in progress.

Because of the high alloying temperatures required and the reactivity of both alloying constituents with normal crucible materials, the investigation has been concentrated on arc-melting techniques. Binary alloys containing 20 and 80 w/o niobium have been twice melted by the consumable-electrode arc-melting technique. These alloys exhibited the type of segregation known as banding.

At present, a series of alloys containing 20, 40, and 80 w/o niobium is being evaluated for homogeneity and the degree of banding which exists after a single consumable-electrode arc melt. Radiographic examination indicates that banding is present. It has been shown that this banding is caused by arc variations and subsequent segregation in a relatively shallow pool of molten metal. A possible technique for eliminating the banding could be to increase the pool depth so that the effect of arc fluctuations is not nearly so critical.

With this in mind, preparations are being made to make the second consumable melts in a crucible lined with an insulating sleeve. This technique should provide a cold bottom with insulating sides, thereby not only producing directional solidification but also providing a deep pool of molten metal.

Small melts of the same alloys have been produced by inert-electrode arc-melting techniques. Hot-hardness determinations on these small ingots have been made up to a temperature of 900 C. These data indicate that the 20 w/o niobium alloy might be fabricated at temperatures above 650 C. The 40 w/o niobium alloy would probably have to be hot worked at temperatures above 1200 C. This alloy is a two-phase alloy and will probably be very difficult to cold work. The 80 w/o niobium alloy can probably be cold worked once the cast structure has been broken down by suitable hot work. Actual fabrication tests will be performed after a metallographic examination of the alloys has been completed.

Evaluation of melting techniques and fabricability will be continued.

F-4

Mechanism of Aqueous Corrosion

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

The reaction products of aqueous corrosion of uranium are being investigated to aid in understanding the corrosion mechanism. Previous studies on the composition of the corrosion products have failed to account for all the weight loss of the metal. Valence studies on the solid corrosion product, by chemical methods, had indicated that the average valence of uranium in the oxide is less than U^{+4}. This could account for the difference between the metal consumed and the amount of hydrogen evolved. However, X-ray diffraction and X-ray absorption edge studies indicate that the bulk of the corrosion product has a valence of 4 or greater.

During the past month, X-ray and microscopic studies on this film and bulk corrosion products were continued in an attempt to resolve the question of material balance. The initial corrosion of uranium in 100 C water produced a thin oxide film with a preferred growth habit which appeared to be independent of the matrix orientation. The (110) plane of UO_2 was found to be parallel to the metal surface. As corrosion proceeded, the preferred orientation of the film was destroyed. The metal was not attacked uniformly during corrosion, indicating that some areas in the metal are more corrosion resistant than others.

In view of the lack of a material balance in the corrosion reaction and the apparent nonuniform attack, the bulk oxide was examined microscopically and by X-ray diffraction for unoxidized metal particles which were separated from the base. Dissolution of the bulk oxide in dilute nitric acid, increasing the acid concentration as the reaction slowed, left a residue of feathery-shaped particles. These were identified by X-ray diffraction as metallic uranium. Thus, in experiments involving dissolution of the oxide on corrosion specimens to obtain weight-loss data for comparison with the amount of hydrogen evolved, it is possible that some unoxidized metal was computed as oxide. An error of this type would account for the lack of material hydrogen balance in the corrosion reaction.

During the next period, studies in water at 100 C will be made to confirm the presence of metallic uranium in the solid corrosion product and to determine the reason for the corrosion resistance of these particles.

Studies are continuing on the nature of the freshly formed corrosion product in tests conducted in steam at 200 C. Based on material balances, tests conducted during the past month have indicated an oxygen content in the newly formed corrosion product of $UO_{2.06}$. Upon admitting room-temperature air to the reaction chamber, this product was oxidized further to $UO_{2.39}$. Heat was evolved during this reaction. Further ignition to U_3O_8 at 400 C revealed an oxide ratio of $UO_{2.67}$ and no loss in material. The above results are to be compared with values of $UO_{2.18}$, $UO_{2.38}$, and $UO_{2.64}$ obtained at similar stages in tests reported in BMI-1256.

The amount of hydrogen collected from the above steam reaction was 94 per cent of the theoretical amount assuming $UO_{2.0}$ to be the corrosion product. Small amounts of hydrogen were collected during the room-temperature-air and 400 C-ignition oxidation steps. This additional hydrogen raised the total amount of hydrogen collected

to 96.5 per cent of the theoretical amount. An unexpected development was the collection of small amounts of water during these oxidation steps. The source of the water has not yet been established. However, the quantity was sufficiently large to rule out the possibility of incomplete drying after the steam reaction.

In future work, an X-ray diffraction analysis will be made to determine the nature of the newly formed oxide in 200 C steam. The oxide will be formed in a capillary quartz tube which can be sealed and removed from the reaction train.

G-1 and G-2

G. FATIGUE STUDIES OF INCONEL

W. S. Hyler and R. J. Favor

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

The scope of the program includes temperatures of 1200, 1400, and 1600 F. In BMI-1220, the data for the 1600 F investigation were reported. The conditions that were to be investigated at 1200 and 1400 F were not as comprehensive as those at 1600 F. The experimental phase of the program was completed during March. The data for the 1200 and 1400 F investigations are being analyzed and, following the completion of the evaluation, will be reported.

H-1

H. REACTOR MATERIALS AND COMPONENTS

F. A. Rough and A. W. Hare

Investigations concerned with reactor materials and components which are supported by the Reactor Development Division of the AEC are reported in this section.

Oxidation data on niobium and niobium alloys tested in dry air at 1000 and 1200 C are reported and discussed. Hardness and hot-fabricability data are reported on various niobium alloys.

Routine progress is reported on the investigation of valence effects of oxide solutions in uranium dioxide.

Preliminary results of high-temperature and high-pressure solid-state studies on oxides of beryllium, uranium, and lanthanum indicate that pressures in excess of 1 million psi appear feasible with the right-circular cylindrical die units.

The preliminary tests to evaluate the various phases of operation of an apparatus which was designed to test rubbing surfaces in sodium environments have been completed. Details of these initial runs are discussed.

In the analytical investigation concerning the phenomena of solid-phase bonding, a rational method of correlation is currently being studied to determine if hot-hardness data will provide an economical method of indicating bonding parameters. In the experimental phase of the program, it is reported that the data obtained from pressure-bonding experiments can be correlated with theoretical values derived from the basis of mathematical models.

Oxidation-Resistant Niobium Alloys

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

The objective of this program is to study the oxidation of pure niobium and the mechanisms by which various alloying additions affect oxidation behavior. Present work includes oxidation testing of niobium ternary alloys, metallographic examination of previously oxidized binary alloys, and preparation of additional binary and ternary alloys.

Niobium-titanium ternary alloys have been oxidation tested at 1000 and 1200 C, with results given in Table H-1. These results indicate that the oxidation behavior of binary alloys can be significantly improved by ternary additions. Additions of chromium, vanadium, and molybdenum to niobium-titanium bases decreased the oxidation weight gains as much as 68 per cent at 1000 C and 56 per cent at 1200 C, compared to similar binary additions. The greatest improvement was obtained on niobium-10.5 a/o titanium-3 a/o molybdenum, where the weight gains were 68 and 56 per cent lower at 1000 C than those for niobium-10 a/o titanium and niobium-2.5 a/o molybdenum, respectively, and 43 and 34 per cent lower, respectively, at 1200 C. The least improvement was obtained on the niobium-25.5 a/o titanium-6 a/o chromium alloy, where the weight gains were 31 per cent lower at 1000 C and 34 per cent greater at

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

Sample	Composition[a] (Balance Niobium), a/o	Test Temperature, C	Parabolic Rate Constant, (mg per cm^2)^2/hr	Transition to Linear Rate, hr	Linear Rate Constant, mg/(cm^2)(hr)	Weight Gain in Time Indicated, mg per cm^2					
						1 hr	2 hr	3 hr	4 hr	5 hr	6 hr
O-30	100Nb[b]	1000	100	0.1	30.0	30.0	61.3	89.8	114.2	136.9	158.6
O-37	25Ti[b]	1000	54.0	2.2	2.56	7.4	10.5	13.1	15.7	18.2	20.8
O-109	19Ti-2.5Cr	1000	7.9	1.0	2.98	3.0	4.8	7.3	10.7	13.6	16.4
O-112	25.5Ti-6Cr	1000	11.4	0.75	2.33	3.6	6.9	9.2	11.0	12.6	14.0
O-114	10.5Ti-3Mo	1000	68.3	>6	--	9.5	12.8	14.9	16.7	18.3	19.9
O-116	17Ti-6.5V	1000	31.2	3	2.33	5.8	8.5	11.2	13.4	15.8	18.0
O-77	100Nb[b]	1200	--	0	(93)[c]	107.7	--	--	--	--	--
O-82	25Ti[b]	1200	193	0.45	10.6	15.8	26.8	37.4	47.4	57.0	67.0
O-110	19Ti-2.5Cr	1200	(96)	0.05	16.3	23.3	39.7	55.2	69.9	83.8	96.8
O-113	25.5Ti-6Cr	1200	68.4	0.2	15.5	15.4	31.7	48.3	63.7	78.5	92.8
O-115	10.5Ti-3Mo	1200	170	0.15	15.5	23.9	40.0	55.2	69.6	82.2	--
O-117	17Ti-6.5V	1200	260	0.7	9.3	17.6	27.2	36.0	45.2	54.8	63.6

(a) Compositions of ternary alloys are corrected to nearest 0.5 a/o on basis of weight losses during melting.
(b) Data from previous tests are included for comparison.
(c) Estimated linear rate.

1200 C, compared to niobium-25 a/o titanium. This is still a significant improvement at 1000 C, since niobium-25 a/o titanium is one of the best binary alloys tested.

Samples of binary alloys which were oxidized previously at 1200 C have been examined metallographically. Severe intergranular oxide penetration was observed in alloys containing molybdenum, tungsten, and vanadium. Subscales were observed in alloys containing titanium and zirconium, as at 1000 C. Intergranular oxidation and cracking occurred in alloys containing up to 25 a/o titanium, but did not occur in the zirconium alloys. Thus, high-titanium and high-zirconium alloys may be more attractive at 1200 C, where embrittlement of the metal core by oxygen diffusion is more severe than at 1000 C. The oxide scales adhered only on the niobium-zirconium alloys. These scales are being examined to determine if a correlation can be established between the appearance of the scales and the oxidation behavior.

Hot fabrication has been completed on a number of ternary and binary alloys, with the results as given in Table H-2. The fabricability limits for niobium-molybdenum and niobium-tungsten alloys are 10 a/o and 12.5 a/o, respectively. Titanium is not detrimental to fabricability in ternary combination, as all ternary alloys containing titanium were fabricable. Four previously unfabricable alloys, nominally niobium-15 and 25 a/o chromium, niobium-5.5 a/o molybdenum-11 a/o chromium, and niobium-6 a/o molybdenum-9 a/o vanadium, have been remelted and will be oxidation tested as cast.

TABLE H-2. HARDNESS AND FABRICABILITY OF NIOBIUM ALLOYS

Composition[a] (Balance Niobium), a/o	Hardness, VHN		Fabricability at 1000 C[b]
	Cast	Rolled and Annealed	
16.5Ti-4.5Mo	192	227	Good
-21.5Ti-6Mo	206	260	Good
7.5Ti-0.5Cr	136	240	Excellent
10Ti-3V	175	268	Excellent
-24Ti-11V	243	287	Good
12.5W	256	299	Fair
-15W	299	--	Not fabricable
11.5Mo	247	--	Not fabricable
-14Mo	268	--	Not fabricable

(a) Compositions corrected to nearest 0.5 a/o on basis of weight losses during melting.
(b) Hot rolled in evacuated stainless steel packs.

Future work will include oxidation testing of the above binary and ternary alloys, examination of the scales, and correlation of the oxidation behavior in terms of the atomic size and valence and properties of new scales.

H-4

Valence Effects of Oxide Solutions in Uranium Dioxide

W. B. Wilson, A. Gerds, and C. M. Schwartz

Microbalance studies of the oxidation and vaporization characteristics of UO_2 and UO_2 with 30, 40, 50, and 60 w/o La_2O_3 have been completed. UO_2 was found to oxidize nearly instantaneously when held in air at 2500 and 2800 F. The resulting U_3O_8 volatilized at 2500 F and above and redeposited as single crystals of U_3O_8 at 2200 F. The solid solutions, which were ground to minus 325-mesh powder, were also instantaneously oxidized, in accord with previously discussed considerations. Following the initial oxidation, however, the weight loss or volatility of the solid solution was found to decrease with increasing La_2O_3 content. At 60 w/o La_2O_3, little or no change in weight was detected after the initial oxidation.

Weight-change analysis on more massive ceramic-type bodies yielded similar results to the microbalance data and were used for X-ray diffraction studies.

X-ray diffraction studies of the UO_2-La_2O_3 solid solutions indicated that they were of the fluorite structure both before and after air oxidation. Air oxidation, however, did produce a decrease in lattice parameter in accord with the change in uranium valence from the plus four to plus six valence state. Thus, although the stabilized materials may be oxidized or reduced with a resulting change in lattice parameter, the structure is retained as cubic.

Work will continue to determine if the uranium-to-lanthanum ratio is altered during oxidation and to determine the effects of oxidation upon the electrical properties.

High-Temperature High-Pressure Solid-State Studies

W. B. Wilson and C. M. Schwartz

The preliminary calibration of both right-circular-cylinder die units has been essentially completed. The bismuth transition was found to occur under identical pressure conditions in both the 150- and 700-ton presses. The results indicate that approximately 20 per cent excess force is required to overcome friction and produce the transition. The thallium transition was not run since it occurs near the probable failure point of these particular units. Temperature was calibrated to 1560 C without pressure by inserting a thermocouple into the sample chamber, and the calibration curve extrapolated for temperature estimates at extreme temperature.

Three samples, BeO, UO_2, and La_2O_3, were given trial runs, under varying circumstances, which served in demonstrating operational characteristics of the units. The most striking characteristic found in the preliminary tests is related to the pressure effects of friction "hysteresis" or reversal which occurs upon heating. Under ordinary circumstances it is possible to produce a predetermined pressure by pushing the plunger into the die. Friction opposes this plunger advance and requires, as mentioned, about 20 per cent excess force. When heat is generated in the sample volume, it expands, tending to reverse the original motion of the plunger. This reversal of

direction means that the friction then supplements the primary force of the press. Since the carbide plunger may withstand 700,000 to 900,000 psi directly, approximately 40 per cent additional pressure may be obtained by utilizing this friction "hysteresis" effect. A direct calibration to determine more accurately the pressures generated, using this technique, has not yet been attempted, but pressures in excess of 1 million psi appear to be feasible.

The three trial runs have disclosed limitations in the sample configuration utilized and have pointed to the need for more support from the multiple binding rings, since sufficient pressure was exerted during the BeO experiment to produce cracks in the carbide die inserts. It is estimated that 650,000 psi at 3000 C was obtained for a duration of 10 min. Analysis of the samples has not been completed.

A superior method of electrical insulation has been devised for the "geometrical-advantage"-type die, and the design should be completed soon. Construction of this die should begin in June.

Rubbing Surfaces in Sodium Environments

Several tests of a 1/2-in.-diameter, M-1, tool steel ball sliding against an Armco iron, lapped, flat plate were performed during March with the inert-atmosphere, friction-test apparatus designed for sodium-immersed rubbing-surface experiments. The first series of these tests employed a solid lubricant. The results obtained were similar to those found previously with like conditions and served to confirm the effectiveness of several minor modifications recently incorporated into the apparatus. For the second series of tests, the specimen surfaces were thoroughly cleaned, lapped, and degreased and friction tested without benefit of lubrication. Base-line data were thus procured for the third series of experiments in which sodium was introduced between the rubbing surfaces; the latter were the first experiments that have been conducted with sodium and, thus, were exploratory in nature.

The unlubricated runs produced coefficients of friction which consistently increased with temperature; the minimum and maximum values being 0.18 at 76 F and 0.95 at 1000 F. After the sodium was added, the friction increased, reaching a maximum coefficient of 1.59 at 1110 F. Friction runs at 1000 F were repeated after several days of conditioning in sodium at various temperatures. In these runs, the coefficients dropped to values only slightly greater than 1. In general, the increased friction following the introduction of sodium is thought to be the result of the removal of surface oxide films by the molten sodium.

After these runs, the flat specimen was washed in alcohol to remove the sodium and examined for wear. Wear tracks, indicating a marked degree of galling, were evident for the dry friction runs made at temperatures above 800 F. However, despite the higher friction characteristics prevailing in the runs involving sodium, wear tracks were not observable. The absence of wear tracks in this case was unexpected, since any treatment of a rubbing surface that decreases contamination should increase the opportunity for momentary welding resulting in the formation of distinguishable wear tracks. Reasons for this anomalous situation are not, at present, apparent.

H-6

The tests with sodium described above concluded the preliminary program which has had the over-all objective of evaluating the various phases of operation of the test apparatus. In the series of tests now under way, the sodium-immersed rubbing members are fabricated of WC plus 20 w/o cobalt binder. Past experience with such cermets indicates that they should be superior to metals with respect to rubbing behavior.

Basic Studies of Pressure Bonding

S. J. Paprocki, E. S. Hodge, S. D. Beck, and M. A. Gedwill

This investigation is concerned with obtaining a fundamental understanding of the phenomena of solid-phase bonding under hydrostatic pressure. Particular emphasis is being placed on analyzing the deformations associated with the collapse of voids, in order to obtain an understanding of the mechanism by which surfaces attain the intimate contact necessary for bonding.

Analytical Studies of Pressure Bonding

In the analytic phase of the pressure-bonding study, an analysis is being made of the behavior of a thick-walled circular cylinder under external pressure. Deformations are described in terms of creep parameters which are obtained experimentally. It is anticipated that the creep parameters thus determined for a given material may be applied to the case of the collapse of a spherical hole due to external pressure. If the assumption is made that the roughness of a surface to be pressure bonded can be represented by a set of spherical voids, then the deformation of these voids can be predicted. It remains to prescribe the amount of deformation required to insure that the surfaces have attained sufficiently close contact.

It is conceivable that hot-hardness data may provide an economical method of indicating bonding parameters. The hardness and variation of hardness with time of indentation can be easily measured, and probably are somewhat related to the creep behavior of the material under hydrostatic load. The relationship may of necessity be empirical or qualitative, but if a valid relationship can be found it will be a simple matter to obtain the appropriate hardness data for a given material. A rational method of correlation is being studied.

Experimental Studies of Pressure Bonding

In the experimental phase of the program, thick-walled tubular aluminum specimens are evacuated, sealed, and subjected to various sets of pressure-bonding parameters in order to study the flow characteristics of metals during a hydrostatic pressure-bonding process. The experimental data can be correlated with theoretical values calculated on the basis of postulated mathematical models. Duplicate specimens are pressurized for each condition.

H-7

In order to determine the dependency of deformation on the time, pressure, and temperature during pressure bonding, aluminum specimens have been subjected to pressure bonding parameters of 4,000 psi at 500 F for periods of 4 and 6 hr; 4,000 psi at 700 F for periods of 4 and 6 hr, and 6,000 psi at 500 F for periods of 1/2 and 1 hr. The amount of deformation occurring during each of these tests is being measured and will be compared with data from previous samples. Additional specimens will be pressurized using various pressure-bonding conditions as prescribed by the analytical studies.

In support of the proposal to attempt to find a relation between hot hardness and creep behavior of metals, hot-hardness tests have been planned. Measurements may be made at a constant temperature with varying times of load application. Time-dependent Vickers hardness determinations will be made on two to five flat-plate aluminum specimens at temperatures of 500 and 700 F. Calculations based on these data will be compared with the results obtained by pressurizing the tubular specimens.

Effect of Surface Preparation on Bonds Obtained During Pressure Bonding of Zircaloy 2

In support of the study of the pressure-bonding process, an investigation has been initiated to study the effect of surface preparation of Zircaloy on the quality of the bonds obtained. Previous experience has indicated that the quality of bond obtained during pressure bonding is dependent on the surface condition of the Zircaloy. This is to be expected as a minimum amount of deformation occurs between the mating surfaces during the pressure-bonding operation. It has been demonstrated that specimens prepared by machining or belt-abrading processes yield the best bonds. Poor bonds are produced when Zircaloy is finished by cold working, pickling, and vapor blasting. The bonds do not possess complete grain growth across the interface and exhibit what appears to be bond-line contamination. Differences in quality of bond have also been observed between rolled and annealed Zircaloy. From these observations, surface conditions for obtaining good bonds have evolved; however, the results are not understood. This study is intended to give a better understanding of the relationship between surface preparation and bonding so that the optimum and least costly surface-preparation process can be selected.

Zircaloy 2 that has been pickled does not bond properly during pressure bonding. Preliminary investigations have indicated that a surface film is formed during pickling that does not disappear during subsequent pressure bonding. In addition, this film appears to block grain growth across the original interface during pressure bonding. Pickled surfaces will be cold worked in order to determine if the film can be disrupted sufficiently to produce a surface that is more easily bonded.

During the early pressure-bonding studies, it was believed that a cold-rolled structure was desirable; however, tests indicated that more consistent and satisfactory bonds were produced with annealed material. A study will be made of the effect of cold work. Zircaloy will be subjected to different increments of cold reductions between 2 and 67 per cent by cold rolling between protective plates to avoid contamination.

H-8

Surface layers of carbon, chromium, iron, niobium, nickel, titanium, and zirconium oxide will be applied to Zircaloy prior to bonding to study their effect on bonding and to observe the movements of these layers during pressure bonding. Layers 1 and 2 μ thick will be used in this investigation.

Information on the effect of surface roughness on bonding will also be obtained by using annealed and carefully machined surfaces with a roughness in the range of 50 to 600 rms. Additional insight into the pressure-bonding process will be obtained by observing the behavior of different types of surface-prepared material at several time intervals during the pressure-bonding cycle. All packs for this investigation will be pressure bonded at the same pressure and temperature as used for the preceding parts of the investigation.

I-1

I. PHYSICAL RESEARCH

F. A. Rough

Physical research in metallurgy and ceramics is reported in this section. These studies are supported by the AEC Division of Research.

Last month, in BMI-1256, reports of results were included for several programs, including the determination of physical properties of uranium compounds, the study of uranium-base ternary-alloy constitution, the study of uranium-nitrogen-carbon solid-state characteristics, and the determination of the structure of uranium dicarbide. No detailed report is made on these subjects this month.

The investigation into the fundamentals of bonding is nearing completion, and a paper is being written.

Degassing experiments at 450 to 650 C have been successfully performed on niobium-hydrogen, permitting calculation of diffusion coefficients. At 500 to 650 C, an activation energy of 19,140 cal/(mole)(C) was determined from the diffusion coefficients.

In a fundamental study of the mechanism of migration of hydrogen in zirconium hydride, the theory of alternate mechanisms is being considered, and necessary diffusion data needed for critical experiments are being determined.

Study of Bonding Fundamentals

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

During this report period, the experimental phases of work on the study of solid-state bonding have been completed. Efforts presently are directed toward the further refinement of theory, and the preparation of a topical report.

The theoretical model for this work is based on the volume-diffusion mechanism. Using a simulated single asperity, the rate of bond growth between a gold needle point and a gold flat has been studied by experimental and theoretical methods. Experiments recently have been conducted to determine the initial contact area by electrical resistivity, direct measurements on the flat surface, and sections through bonded couples. Further observations of sections through bonded couples have shown no evidence that recrystallization has occurred; they do show a definite movement of the initial interface, however. The presence or absence of grain boundaries, which are thought to provide paths for the rapid diffusion of vacancies, may be an important factor in determining bond growth.

Further modifications of the theoretical bond-growth equation are being made, based on the results of recent observations on initial bond area and specimen geometry.

I-2

Niobium-Gas Reactions

W. M. Albrecht and W. D. Goode

A fundamental study is being made of the kinetics and mechanism of the reaction of hydrogen with niobium. Kinetic data for the formation of solid solutions of hydrogen in niobium with hydrogen-niobium ratios in the range 0.05 to 0.70 have been reported. As previously reported, these data show that a surface reaction and not diffusion in the metal controls the rate of sorption of hydrogen.

Degassing experiments have been made at temperatures from 450 to 650 C to determine the diffusion coefficients of hydrogen in niobium at hydrogen-niobium ratios of 0.03 to 0.06. The desorption-rate curves indicate that hydrogen removal is controlled by diffusion in the niobium. The diffusion coefficients obtained are given in Table I-1 and are shown on an Arrhenius-type plot in Figure I-1. The data obtained below 500 C indicate that a surface effect may be affecting the degassing rate at 450 C or below. The 450 C diffusion coefficient, which is much lower than would be expected, is an indication of this effect. Similar surface effects at low temperatures have been reported for the degassing of hydrogen from zirconium.* The diffusion coefficient of 2.4×10^{-5} cm^2 per sec obtained at 600 C by degassing is in agreement with the previously reported value of 2×10^{-5} cm^2 per sec estimated by the concentration-gradient method.

TABLE I-1. DIFFUSION COEFFICIENTS FOR HYDROGEN IN NIOBIUM OBTAINED BY A DEGASSING METHOD

Temperature, C	Diffusion Coefficient, 10^{-5} cm^2 per sec
650	4.3
600	2.4
550	1.3
500	0.52
500	0.57
450	0.078

The temperature dependence of the diffusion coefficient for hydrogen in niobium in the range 500 to 650 C was calculated from the Arrhenius plot, Figure I-1, to be

$$D = 1.5 \exp [(19,140 \pm 200)/RT] \quad ,$$

where the activation energy of the diffusion process is 19,140 cal/(mole)(C).

*Mallett, M. W., and Albrecht, W. M., J. Electrochem. Soc., 104 (3), 142-146 (1957).

I-3

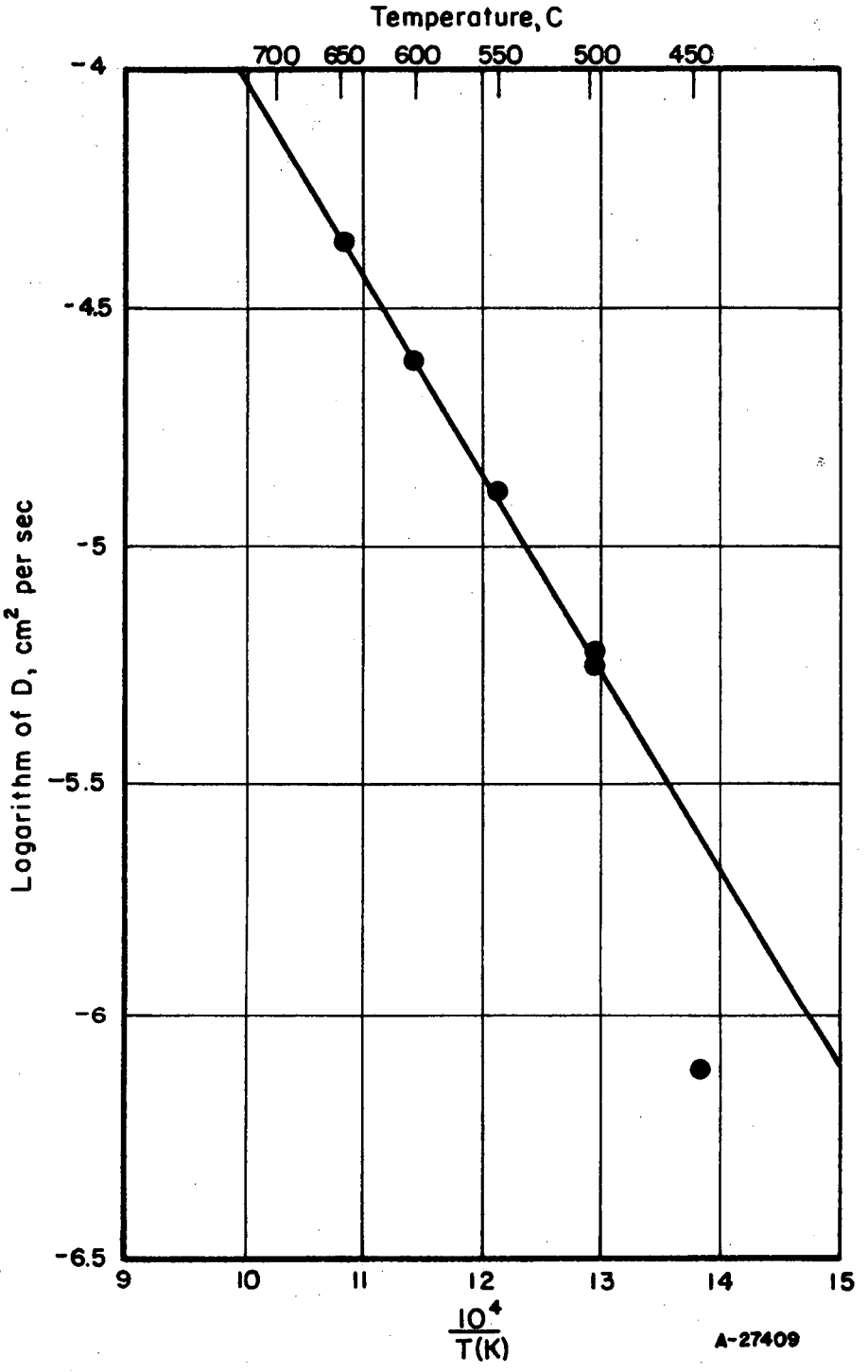

FIGURE I-1. DIFFUSION COEFFICIENTS FOR HYDROGEN IN NIOBIUM

I-4

Diffusion coefficients for hydrogen in niobium have been reported by Paxton and Sheekan.* These were obtained from permeation experiments. The values reported for 300 to 700 C which are in the range 10^{-11} to 10^{-7} cm^2 per sec, are considerably lower than those obtained in the present study. However, Paxton and Sheekan report formation of a dark film on the surfaces of their samples. This is an indication of contamination and may account for the low diffusion coefficients reported.

Paxton and Sheekan also report data for the equilibria in the niobium-hydrogen system at 1 atm p at 300 to 800 C. Their equilibrium concentrations for below 600 C are considerably lower than those obtained in the present study and by Sieverts and Moritz.** On the basis of high-temperature X-ray studies, Paxton and Sheekan report a hydride, Nb_2H, having a close-packed-hexagonal structure. The presence of such a hydride is not indicated by the present study. Such a hexagonal structure has been attributed to impurities, probably nitrides, by Brauer and Hermann.***

A low-pressure equilibrium study of the niobium-hydrogen system is being continued. The results obtained to date at 250 to 600 C and 0.1 to 10 mm of mercury pressure are consistent with the equilibrium data previously reported. Elevated temperature X-ray studies of niobium samples with 0.097, 0.24, and 0.54 hydrogen-uranium ratios show only the single-phase niobium above 150 C. The lattice expands with increasing hydrogen concentration. At 100 C, two phases were detected, but only in the niobium sample with a hydrogen-niobium ratio of 0.24. Further equilibria data are being obtained.

Migration of Hydrogen in Zirconium Hydride

J. B. Vetrano, R. J. Harrison, and J. F. Foster

A theoretical analysis of the factors affecting the diffusion of hydrogen in zirconium and zirconium hydride is continuing.

Experimental work on the determination of the diffusion coefficient for hydrogen in delta-phase zirconium hydride has been completed. Measurements in the beta-phase will probably be made with a permeation technique.

Theoretical Analysis

Work has continued on the examination from a theoretical viewpoint, of some of the processes that might be important in the description of the migration of hydrogen in the zirconium-hydrogen system. The ultimate aim of the program of research is to determine the basic processes that are involved in the phenomenon in order to enable the prediction of rates of diffusion and hydrogen migration in an arbitrary complex situation of specified thermal gradient and other relevant metallurgical conditions as might be met in practice. The more limited aim of the study that has been made up to

*Paxton, H. W., and Sheekan, J. M., "A Study of the Niobium-Hydrogen System", NYO-8040.

**Sieverts, A., and Moritz, H., Z. anorg. u. allgem. chem., 247, 124-30 (1941).

***Brauer, G., and Hermann, R., Z. anorg. u. allgem. chem., 274, 11-23 (1953).

this point is to determine what can be learned from experimental information obtained to date; what further information needs to be gained from experiment; what are the most relevant experiments and how experimental data should be handled to be of greatest theoretical significance. A primary question in the present study involves determining the correct phenomenological equation to describe the experimental situation.

A possible answer to this question is the equation commonly written to describe the Soret effect or thermal-diffusion effect in solids; namely

$$-J_H = D \text{ grad } C_H + D' C_H (1-C_H) \text{ grad } T \quad , \qquad (I-1)$$

where J_H, the "matter current" of the hydrogen, is assumed proportional to the gradient of the concentration C_H of hydrogen and to the gradient of temperature, and D and D' may be functions of composition and temperature. J_H is zero when a steady state has been reached, and the Soret coefficient S_T is defined in terms of the ratio of grad C to grad T by

$$S_T = - \text{grad } C_H / \text{grad } T [C_H(1-C_H)] \quad . \qquad (I-2)$$

It should be pointed out, however, that it is not a trivial point to establish by experiment that this equation is the correct and complete phenomenological description. This has not yet been done in a complete manner, although the results that have been obtained do not, to the extent that they have been analyzed, contradict Equation (I-1).

There are theoretical arguments in support of Equation (I-1), and it is well to say something about these. First, the development of theories of the thermodynamics of the steady state, stimulated in recent years by the work of Onsager and others, lends confirmation to the fact that Equation (I-1) as well as more general equations are consistent with thermodynamic reasoning. A further result of these theories is that in a situation where Equation (I-1) holds, an analogous equation may be written relating the flow of heat to the same gradients, with the Onsager symmetry relations connecting the cross coefficients in the two equations. The theory cannot however be used to derive the values of either D or D' from purely thermodynamic information. Other theoretical studies of the microscopic or kinetic mechanism of diffusion have further clarified the nature of D and D', relating them to activated processes. At this stage no attempt has been made to apply such a kinetic argument to the zirconium-hydrogen system. While there is work in the literature discussing the kinetics of ordinary diffusion of hydrogen in other systems, no treatment of the thermal diffusion of hydrogen in hydrided metals has been found. However, Darken and Oriani point out in a paper* on thermal diffusion in alloys, that a positive Soret coefficient means in the case of interstitial-vacancy diffusion that a solute atom takes with it a larger fraction of the activation energy than does the vacancy. For a positive Soret coefficient, the concentration gradient of solute is opposite in sign to the temperature gradient so that the solute tends to accumulate in the region of lower temperature. The latter is characteristic of the zirconium-hydrogen system and is at least qualitatively consistent with Darken and Oriani's

*Acta Met., 2, 841 (1954).

criterion, since, for small solute atoms and a relatively open structure, only a small amount of relaxation about a vacancy and hence small activation energy associated with its motion would be expected.

An alternate explanation of the migration of hydrogen to the colder end of the hydride bar may also seem just as plausible; namely the partial pressure of hydrogen in zirconium hydride of a fixed composition is strongly dependent upon temperature, and it would seem natural that there would be a tendency for the composition to alter in such a way as to tend to equalize the partial pressure of hydrogen throughout the bar. It is true that in the experimentation, the hydride bars are clad to prevent the escape of hydrogen, and it would have to be assumed that there were some internal channels of fair size within the bar in order to provide a specific mechanism to equalize the partial pressure of hydrogen. Apart from how reasonable this assumption might seem — a microscopic metallurgical examination may help prove or disprove it — it is true that the assumption is roughly consistent both with the sign and magnitude of the observed hydrogen migration. Van't Hoff, in a paper published in 1887, referred to and criticized in the article by Ballay*, developed a theory of thermal diffusion with essentially this same assumption regarding the equality of partial pressures. An alternative assumption leading to not very much different results, is based on a model in which it is assumed that longitudinal channels exist in the hydride bar, but are narrow with respect to the mean free path of the gas. Instead of the assumption that the hydrogen partial pressure is equal throughout the bar, it would be assumed that the partial pressure varies as the square root of absolute temperature.

If either of the two models just described is chosen, the steady-state distribution of hydrogen is predictable on the basis of thermodynamic data alone. Thus, if the data are interpreted using the phenomenological Equation (I-1), it is true that the apparent value of Soret coefficient follows from thermodynamic data together with the assumed model, and depends upon the model.

It is concluded, therefore, that along with experiments aimed at determining the constants in Equation (I-1) as a function of temperature and composition, attention should be given to the question of whether this equation is adequate. Some of the uncertainty may arise if porosity of some type may develop, whether of a type similar to that of the models described or along grain boundaries. Even if only solid-state volume diffusion can take place, inadequacies in Equation (I-1) may arise from the same type of complications that can enter in ordinary diffusion, i.e., phenomena giving rise to a Kirkendall effect, or effects due to the fact that diffusion may be governed by nonequilibrium defect distributions.

Experimental Study

The diffusion rates of hydrogen in beta and delta zirconium hydride are being determined.

*Rev. mét., I. Mém., 25, pp 427-454, 509-520 (1928).

I-7 and I-8

The diffusion coefficients for hydrogen in delta zirconium hydride were determined by the moving-boundary technique. The values obtained at 200 to 700 C are given in Table I-2. The temperature dependence of the diffusion coefficient from 200 to 700 C is

$$D = 0.40 \exp [(-20,700 \pm 750)/RT] ,$$

where 20,700 cal/(mole)(C) is the activation energy for the diffusion process.

TABLE I-2. DIFFUSION COEFFICIENTS FOR HYDROGEN IN DELTA ZIRCONIUM HYDRIDE DETERMINED BY THE MOVING-BOUNDARY TECHNIQUE

Temperature, C	Diffusion Coefficient, cm^2 per sec
700	1.5×10^{-5}
600	2.2×10^{-6}
500	3.4×10^{-7}
400	1.1×10^{-7}
300	3.1×10^{-9}
200	1.5×10^{-10}

Concentration-gradient, moving-boundary, sorption-rate, and desorption-rate techniques have been considered as means to determine the rate of diffusion of hydrogen through beta zirconium. Experiments by several of these methods gave an estimated diffusion coefficient for hydrogen in the beta phase of the order of 10^{-4} cm^2 per sec at 700 C.

Because diffusion is very rapid, further experiments are being made using a permeation technique. This should prove more suitable for determining higher diffusion coefficients than the techniques previously tried. Presently a permeability cell is being designed for this work.

J-1

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

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

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

The use of titanium as a construction material continues to appear promising for both the dissolver and the feed adjustment tank for the Darex process.

Limited evidence indicates that aluminum additions may be more suitable than thorium additions for controlling the corrosiveness of initial Thorex solutions.

The Darex Process

Uranium can be recovered from fuel elements containing stainless steel as a diluent, or as a cladding, by means of the Darex process. The elements are first dissolved in dilute aqua regia. The chlorides are stripped from the solution with concentrated nitric acid and, following suitable adjustment, the dissolved uranium is recovered by conventional solvent extraction.

Dissolver Studies With Titanium

The various plain, welded, and stressed specimens of Titanium 55A and 75A were removed from the flowing dissolver and examined following 1061 hr of exposure. Representative stressed and welded specimens were freed from scale by a caustic cleaning. Weight changes resulting from the exposure of these specimens were negligible. Sectioning and metallographic inspection revealed no evidence of intergranular attack, stress cracking, or preferential attack at the weldments. The remaining specimens were returned for further exposure. To this point, a total of 9.15 kg (20.2 lb) of Type 304 stainless steel has been dissolved in 157 liters (41.4 gal) of acid during the exposure of these specimens.

FAT Studies With Titanium

Following 12 weeks of exposure to boiling solutions representing initial conditions in the feed-adjustment tank, the various plain, welded, and stressed Titanium 55A and 75A specimens were cleaned and examined. The weight changes measured were small and of little consequence, except for specimens exposed in the vapor-phase positions. These rates are by no means excessive (0.04 to 0.14 mil per month), but are considerably higher than the rates for specimens exposed in other positions, this latter rate averaging approximately 0.002 mil per month. No intergranular attack, stress cracking, or preferential attack at the weldments was observed

upon metallographic examination. The remaining specimens were returned to fresh solutions for continued exposure.

A hairpin-shaped Titanium 40A unalloyed steam tube was removed after 5 weeks of exposure to the initial FAT solution. A thin, easily removable crystalline coating had formed beneath the liquid line. At and above the liquid line, an appreciable build-up of very adherent dried salts had occurred. No apparent attack was noted upon removal of most of this deposit. The tube was replaced in fresh solution and the exposure continued.

Titanium 40A and 55A steam-tube specimens were also inspected after 5 and 8 weeks of exposure to solutions representing final conditions in the feed-adjustment tank. A much greater build-up occurs at and above the meniscus in the more concentrated final solutions. The deposit is much more difficult to remove than the crystalline coating which forms on the portion submerged in the liquid phase. These tubes were given a crude cleaning and again no attack was apparent. The tubes were returned to fresh solutions and continued exposure.

The Thorex Process

Carpenter 20 stabilized is being evaluated as a container material for the dissolution step of a proposed Thorex-Sulfex process. In this particular process, stainless-clad fuel elements of thorium or thoria would be dejacketed by dissolution in sulfuric acid. Following this, the thorium or thoria would be dissolved by a solution of 13.0 M HNO_3, 0.05 M F^-. At the end of this dissolution, the final Thorex solution would be about 8.5 M HNO_3, 0.05 M F^-, and 1.0 M $Th(NO_3)_4$.

Additional scouting experiments have been completed in which the effects of thorium additions on the corrosion rates of specimens of Carpenter 20 stabilized in boiling initial Thorex solutions were determined. Thorium additions decrease the corrosion rates significantly but appear to be no better than aluminum additions for this purpose. For some reason, presently not understood, the corrosion rates were higher with 0.2 M Th^{+4} than with 0.1 M additions.

Special equipment has been assembled to handle boiling acid-fluoride solutions and cyclic studies are under way in these units. Specimens of welded Carpenter 20 stabilized are being cycled from boiling sulfuric acid solutions to solutions representing either the initial or final conditions of the nitric-fluoride dissolution containing 0.2 M Al^{+3} additions.

Scouting experiments are also planned to see if Nionel specimens show promise in the 4 and 6 M sulfuric acid solutions of the Thorex-Sulfex process.

J-3 and J-4

The Fluoride-Volatility Process

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

Corrosion investigations were delayed during the month while the three new Hastelloy B assemblies were in the process of being filled with salt. However, flowmeters were calibrated in preparation for runs with the new containers. Also, samples of HF were collected at various points in the gas line so that the effect of hot nickel (600 C), the molten salt, and the melt container on the sulfur content of the gas might be measured.

L-1

L. STUDIES OF SODIUM-TANTALUM COMPATIBILITY AT ELEVATED TEMPERATURES

J. H. Stang

This section reports the progress of studies designed to furnish information to Los Alamos Scientific Laboratory (in connection with the LAMPRE development program) on several facets of the behavior of tantalum at elevated temperatures. Recent findings suggest that tantalum specimens simultaneously stressed and exposed to 1200 F sodium circulating in forced-convection loops are not subject to stress-corrosion effects of any kind. In inert-atmosphere creep experiments conducted during March, tantalum specimens displayed no measurable deformation during 300 hr under the following conditions: 900 F - 20,000 and 25,000 psi, 1500 F - 5,000 and 6,000 psi.

Welding studies are now indicating that porosity in tantalum welds is influenced by the carbon content of the base material. The evidence on hand was gained from tests in which tantalum stock, taken from a batch that normally yielded welds of excessive porosity, was coated with graphite and subsequently welded; the welds thus produced were free from porosity. The use of ultrasonic excitation during tantalum-welding operations has been encouraging with respect to grain refinement; however, such excitation consistently results in the formation of a second phase at grain boundaries. Resistance-welding experiments continue to indicate promise for utilization of this method in making tube-to-header joints. In several cases, leak-free joints with good strength have been obtained.

Tantalum-Sodium Compatibility Studies

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

Experiments are under way to provide information pertinent to the effects of sodium exposure on the creep behavior of tantalum. Exposures of arc-cast and sintered tantalum specimens to 1200 F low-oxygen-content (normally >10 ppm) sodium are being conducted with the sodium circulating in small forced-convection polythermal loop systems fabricated of Type 316 stainless steel. Facilities are provided for stressing the specimens and measuring their creep.

To date, several 500 to 1130-hr-long corrosion-creep experiments employing stresses in the 12,000 to 18,000-psi range have been terminated. A principal finding is that sodium exposure does not greatly affect the creep behavior of tantalum. However, the actual creep rates thus far obtained (several were reported in BMI-1256) are most certainly high inasmuch as it is now apparent that the grip portions of the specimens have been deforming during the runs. In the creep-measuring system being employed, this results in error since total specimen deformation rather than gage-section deformation is being registered. It now appears that the actual creep rates of sodium-immersed specimens should closely approximate those of their inert-atmosphere counterparts. To substantiate this, experiments will be conducted with specimens which have been strengthened in the grip portions by spot welding an additional thickness of metal on both sides of each grip.

Although, as discussed in BMI-1256, initial information indicated a possibility that stressed sodium-exposed specimens suffer somewhat higher weight losses than similarly exposed unstressed specimens, it now seems evident that such a tendency must be attributed to another factor, the leading candidate being minute system contamination. For example, an arc-cast tantalum specimen stressed for 1100 hr at 18,000 psi recently inspected exhibited a weight loss equivalent to a penetration of 0.1 mil per year. This represents the amount of corrosion that would be expected for an unstressed specimen exposed to 1200 F high-purity flowing sodium. The contamination level present in the system in which the low-weight-loss specimen was exposed was obviously ultralow since (1) the specimen was not discolored as would be the case if trace impurities had been present, and (2) the specimen hardness was reduced from the original 180 VHN to 152 VHN (5-kg load). The latter shows that the tantalum lost oxygen to the sodium, an event indicative of low impurity level in the liquid metal.

High-Temperature Mechanical Properties of Tantalum

D. H. Wood, M. E. Langston, C. J. Slunder, and J. G. Dunleavy

Degassing experiments to provide tantalum stock of sufficient size and thickness for cold rolling to strip, recrystallizing to produce a fine-grained structure, and machining into creep test specimens, have recently met with difficulty. The factor primarily responsible is size of specimen being handled. While the vacuum-induction furnace being used can handle specimens of 100-g size at the 4800 F degassing temperature, the heat output necessary for the large (several hundred grams) specimens of current interest results in failures such as crucible cracking (a water-cooled Vycor jacket has been used) even when carefully placed radiation shields are present. As a result of this situation, it was recently decided to alter the furnace design in a fairly major way. The revised unit is now being assembled and should be ready for initial checkouts early in April.

If difficulties persist with the new unit, tantalum degassed by an electron-beam melting technique will be cold rolled and recrystallized as outlined above and used for specimen preparation. A lot of such material has been ordered and should be delivered early in May. According to the manufacturers' specifications, the product to be supplied will be quite low in interstitial content and will have a hardness corresponding to the 40 to 60 VHN range.

Creep tests in inert atmosphere have been initiated on annealed arc-cast tantalum sheet specimens at 900 and 1500 F. At 900 F, creep has not been apparent during the first 300 hr of loading to 20,000 and 25,000 psi. At 1500 F, the results are similar with loadings of 5,000 and 6,000 psi. The loads at both temperatures will be increased. Extensive creep testing at temperature levels other than 1200 F is not planned since the test furnaces will be needed for exposures of fine-grained degassed material when it becomes available.

L-3

Weldability of Tantalum for High-Temperature Systems

J. J. Vagi, S. M. Silverstein, and R. P. Sopher

An investigation is being made of causes of porosity in welds of some lots of tantalum. Analyses of an unweldable tantalum base plate and weld metal in the plate referred to in BMI-1256 were essentially the same except for minor differences in carbon, nitrogen, and oxygen. While the amounts of these elements were higher in the weld metal, probably because of imperfect shielding and incomplete specimen cleaning prior to welding, it is believed that the changes found were too small to be responsible for porosity. In recent porosity studies, using tantalum susceptible to gross porosity when welded, results have been obtained which indicate that carbon content is a governing factor. The test welds involved here were made with the base stock covered with graphite; metallographic examinations of these welds, which had a fairly high carbon content, indicated that virtually no porosity was present. Work is now being conducted to gain specific information about the effectiveness of carbon. The amount required to render tantalum weldable will no doubt change from lot to lot, depending on the oxygen content in the tantalum. Attempts are being made to add carbon to tantalum using methane gas (CH_4) at elevated temperature. It is anticipated than any hydrogen pickup owing to this treatment can be removed by evacuating the heated specimen immediately after ingassing.

Continuing studies on the grain refinement of arc welds by ultrasonic techniques have shown that optimum grain refinement can be obtained by exciting tantalum during welding and for 5 to 10 sec after welding. Specimens so treated show grain sizes one-half to one-quarter that of tantalum unexcited during welding; however, weld-metal expulsion may at times occur during excitation.

As mentioned in BMI-1256, ultrasonic excitation during welding leads to the precipitation of a second phase at grain boundaries. Since this tendency was observed for welds made with a single lot of weldable tantalum with a high carbon content (190 ppm), it was suspected that the precipitate was a carbide. In line with this reasoning, the amount of precipitate should be less in low-carbon material. To substantiate this, ultrasonic energy was supplied during welding to tantalum containing 10 ppm carbon. Pertinent information was not gained from this study since the test welds were too porous to allow satisfactory grain-boundary examinations. At the present time, the precipitate problem is being pursued using different lots of tantalum.

Resistance-welding studies of a flanged tantalum tube welded to a tantalum header indicated that the major difficulty with this type of joint is lack of bonding throughout the entire contact area. In an effort to solve this problem, a ring-type projection was machined on the flange. Results of tests of several such joints indicated that solid-phase bonding was obtained over the entire circumference of each. However, this occurred only in the projection-to-header interface which was approximately 10 mils wide.

A stored-energy capacitor-discharge welding machine was used for additional studies of tube-to-header butt joints. For these joints, the ends of the tubes were machined square or were beveled to form a ring-projection joint configuration. Best results were obtained with the bevel design since solid-phase bonding occurred over the

L-4

entire tube cross section. Helium leak tests of three beveled joints indicated that two were leak-free. Tension tests on others showed that an 80 per cent joint efficiency was obtained. It was found also that a correlation existed between the voltage to which the condensers were charged and weld strength. The suitability of ring-projection joints for multiple tube-to-header joints is being studied.

M-1

M. DEVELOPMENTAL STUDIES FOR THE PWR

R. W. Dayton

Apparatus for a continuation of the mixing studies in the PWR flow model has been installed and checked. Testing is about to be resumed.

Preliminary tests of the X-ray photometer have been made with satisfactory results. Only a little more work remains to be done.

Pressure-bonding studies of plate-type UO_2 fuel elements are continuing, with emphasis on a two-step bonding process, in which preliminary bonding is done at minimum pressure, temperature, and time; this is followed by a beta-phase anneal to complete the bonding operation. No results from this work are yet available.

Reactor-Flow Studies

L. J. Flanigan and H. R. Hazard

Air-flow studies in a quarter-scale model of the PWR are being conducted to determine the effects of lower-plenum geometry on mixing and flow distribution in Core 2. Previously reported work includes completion of all flow studies with the 9-ft core design, and moving the model and test apparatus into a new laboratory building.

Installation of the PWR model in the new laboratory building was completed in March.

The perforated flow baffle, to be used to simulate a 7-1/2-ft core design, was received in March and was immediately installed in the model. Preliminary studies of core-flow distribution and mixing were made in runs to check out the model and test equipment, with excellent results.

Next month, core-flow distribution and lower-plenum mixing will be studied with the basic 7-1/2-ft core design and with modified lower-plenum geometry designed to improve mixing.

X-Ray Photometric Examination of Fuel Elements

J. B. Schroeder and C. M. Schwartz

Work on the development of an X-ray photometer for the inspection of fuel elements has been essentially completed. The apparatus has been assembled and tested briefly. The initial tests appeared satisfactory.

This project has been recessed. Final testing and minor adjustments will be carried out as soon as possible.

M-2

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

S. J. Paprocki, E. S. Hodge, and D. C. Carmichael

A flat-plate Zircaloy 2-clad fuel element containing compartmented uranium dioxide fuel is being considered for use in PWR Core 2. An investigation is being conducted to study the preparation of these elements by a gas-pressure bonding technique. In this process, the components are fabricated to final size, cleaned, and assembled into a stainless steel or Ti-Namel envelope which is then evacuated and sealed. The assembly is then subjected to a helium gas pressure at elevated temperatures to obtain bonding of the components. Results of the program have indicated that satisfactory bonds can be obtained by pressure bonding at 10,000 psi and 1550 F for 4 hr using Zircaloy 2 bonding surfaces which have been belt abraded.

A study is now being made of a two-step bonding process using pressure bonding followed by a heat treatment. The pressure-bonding step will be used to obtain an intimate bond which can then be heat treated at about 1850 F to obtain complete beta-phase transformation and grain growth across the bond interface. Previous results have indicated that specimens with incomplete grain growth across the bond interface can be heated into the beta-phase region for Zircaloy 2 for a very brief period of time to obtain 100 per cent grain growth across the interface. A determination will be made of the minimum temperature and pressure for pressure bonding which will result in completely satisfactory bonding after a subsequent heat treatment. Cold-rolled and pickled Zircaloy 2 strips will be principally used for this study; belt-abraded plates will be bonded as control specimens. The components will be enclosed in Ti-Namel envelopes during bonding. Pressure-bonding temperatures from 1200 to 1500 F and pressures from 2000 to 5000 psi will be investigated. After pressure bonding, specimens will be heat treated in a salt bath at 1850 F for 2 to 5 min and air cooled. Evaluation of the specimens will be based on metallographic examination, destructive bend and peel tests, and corrosion tests. Specimens in an additional group which have been sealed by edge welding of the cladding components are being pressure bonded under various conditions, followed by a heat treatment to determine the feasibility of this technique. The specimens do not have protective cans and are not evacuated.

Tests have been run on specimens to determine the effect of the thickness of the cores on the extent of bonding obtained. Specimens were bonded containing cores which ranged from 0.006 in. thinner to 0.004 in. thicker than the receptacle plate. The cores were the proper length and width. Metallographic examination revealed no difference in the bonds obtained using the various core thicknesses; however, the thickness of the cladding varied with the dimensions of the core.

Several irradiation specimens have been prepared by the two-step bonding process. These specimens were pressure bonded at 1500 F and 10,000 psi for 4 hr and then heat treated in a salt bath at 1850 F for 5 min. The edges of each of the specimens were examined metallographically after heat treating. Examination of the first specimen, which had pickled cladding plates, revealed complete grain growth across the bond interface but slight bond-line contamination. A second specimen with clad plates finished by belt abrading possessed complete grain growth across the bond interface and no

contamination after pressure handling and beta heat treatment. Two additional irradiation specimens are being prepared with belt-abraded cover plates. These specimens will be used as control specimens.

N-1

N. EVALUATION OF URANIUM MONOCARBIDE AS A REACTOR FUEL

F. A. Rough

Uranium monocarbide is generally the most attractive reactor fuel now in the development stage. It has high thermal conductivity, high uranium content, and appears amenable to fabrication by casting.

In the present program, excellent progress has been made in the fabrication by casting, and well-formed specimens up to 5/8 in. in diameter and 4 in. long have been made. Preliminary compatibility tests have been completed prior to making capsules for irradiation.

As a result of this progress and a desire for irradiation data as soon as feasible, irradiation specimens will be prepared soon for May 15 loading of the first capsule. The casting process will not be fully developed before these initial samples are made, but 2- and 6-week compatibility will be available on which to base the capsule design. This initial capsule will be irradiated to about 1000 MWD/T in the MTR and is roughly scheduled for return to the Battelle hot cells in October.

Casting Techniques for the Preparation of Uranium Monocarbide

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

Excellent progress has been made on the first phase of a program concerned with the evaluation of uranium monocarbide as a possible fuel material. Well-formed castings of uranium monocarbide measuring 5/8 in. in diameter by 4 in. long have been prepared. These castings did not fracture upon cooling or in subsequent grinding. The castings were prepared in a bench scale, arc-melting furnace using graphite thimble molds and a helium atmosphere.

Specimens for thermal-conductivity and -expansion tests have been prepared, and the tests are in progress. In order to obtain preliminary data on the thermal-shock properties of UC, cast and machined specimens were heated slowly to 1500 F and furnace cooled to room temperature. The specimens were then reheated to 1500 F and cooled at the rate of 100 F per min. None of the specimens cracked as a result of these thermal treatments. Some of the specimens were in contact with Type 304 stainless steel and some with molybdenum. No reaction with the metals was observed in either case.

Immediate plans are to study the physical properties and microstructures of small charges of "off" composition material, to study the effects of heat treatments, and to improve casting techniques. Emphasis will shift to the production of enriched specimens as soon as the enriched material is received.

N-2

Irradiation-Capsule Design for Uranium Monocarbide

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

NaK compatibility tests, basket design, and irradiation-capsule design are under way with a target date of May 15, 1958, for the completion of the fabrication of two capsules. Target dates for the irradiation of the first capsule are: (1) reactor loading - July 7, 1958, (2) reactor discharge - September 29, 1958, and (3) hot cell delivery - October 15, 1958. Due to an acceleration of the program, the burnup for the first irradiation has been reduced from 2000 MWD/T to 1000 MWD/T. The schedule for the balance of the original program (6 capsules) remains unchanged except for a possible reduction in planned burnup for all capsules.

NaK compatibility tests of 4.8 w/o carbon specimens in stainless steel containers, tabulated below, are under way. Preliminary results from Tests 1, 3, and 4 are available. These capsules were opened and observations were made of the baskets and specimens. The specimens remained intact and no penetration by NaK was observed; however, weight losses of the order of 5 mg occurred for each specimen. No weight changes were observed on the baskets except a 4-mg loss on the basket in Test 4. However, discolorations occurred on all specimens and all baskets. Further examination of the test materials is being performed.

Test	Basket Material	Exposure Time, weeks	Temperature, F
1	Molybdenum	2	1100
2	Molybdenum	8	1300
3	Molybdenum	2	1300
4	Stainless steel	2	1100

O-1

O. DEVELOPMENTS FOR NMSR

A. W. Hare and R. F. Dickerson

The various research and development programs concerned with the Nuclear Merchant Ship Reactor program are reported in this section. This work is sponsored by The Babcock & Wilcox Company.

Experimental fabrication data for urania fuel pellets have been determined and these conditions will be used in the preparation of urania fuel pellets for loop-test studies. Data on ball-milling time, forming pressures, and sintering temperatures of uranium oxide of three different enrichments are reported.

The fabrication procedures of three short and one long dummy fuel-pin assemblies for dynamic flow tests in the B&W test loop at the MTR are described.

In the research concerned with the safety aspects of foreseeable accident types for the NMSR, an analysis of the startup accident is discussed.

Fabrication of Urania Fuel Pellets for Loop-Test Studies

H. D. Sheets, C. Hyde, and A. G. Allison

The objective of this program is to prepare suitable UO_2 specimens for irradiation testing. Specimens containing 3 to 7-1/2 per cent $U^{235}O_2$ with bulk densities of about 91 per cent of theoretical are desired.

Four lots of UO_2 powder were received for use in this program. Spectrographic analyses of sintered UO_2 pellets made from each of these powders are given in Table O-1.

TABLE O-1. SPECTROGRAPHIC ANALYSES OF UO_2 SAMPLES

$U^{235}O_2$ Enrichment, per cent	Impurity Content, ppm														
	Fe	Be	B	Si	Mn	Mg	Sn	Ni	Mo	Cu	Co	Ca	Al	Cr	Ba
2.83	80	2	1	60	2	40	1	>500	200	10	10	200	80	20	--
4.06	50	<1	1	40	1	--	5	>200	30	40	5	150	100	30	1
6.05	45	<1	<0.5	30	<1	15	15	50	20	1	1	40	100	10	2
7.48	40	<1	0.5	60	<1	60	1	25	10	10	50	80	160	<5	--

In order to choose fabrication conditions for making the required specimens, a series of experiments, in which ball-milling time, forming pressure, and sintering temperature were varied, has been carried out. The results are presented in Table O-2. The UO_2 was ball milled in 100-g batches in a 1-qt mill liner with natural rubber, using Al_2O_3 balls. The milled powder was mixed with 3 w/o camphor, pressed in a steel die, and sintered at the indicated temperatures in a hydrogen-atmosphere molybdenum-wound resistance furnace.

O-2

TABLE O-2. EFFECT OF PROCESSING VARIABLES ON BULK DENSITY OF SINTERED UO_2 PELLETS

Trial	Ball-Milling Time, hr	Forming Pressure, psi	Bulk Density As Formed[a], g per cm^3	Sintering Temperature, F	Diametral Shrinkage, per cent	Bulk Density[a]	
						G per Cm^3	Per Cent of Theoretical[b]
			Sample A: UO_2 Containing 2.83 Per Cent $U^{235}O_2$				
1	2	10,000	5.6	2600	15.8	9.36	85.3
2	2	20,000	5.9	2600	15.3	9.59	87.4
3	4	5,000	6.0	2600	16.3	10.10	92.0
4	4	10,000	6.2	2600	15.8	10.24	93.3
5[c]	4	10,000	6.2	2600	15.9	10.16	92.6
6	4	20,000	6.3	2600	15.5	10.28	93.7
7[c]	4	20,000	6.3	2600	15.2	10.26	93.5
8	4	10,000	6.2	2500	14.7	9.99	91.1
9[d]	4	10,000	6.1	2500	14.9	9.86	89.9
10	4	10,000	6.1	2400	12.7	9.13	83.2
11	4	20,000	6.3	2400	14.4	9.32	85.0
			Sample B: UO_2 Containing 4.06 Per Cent $U^{235}O_2$				
12	2	10,000	5.4	2600	18.8	9.99	91.1
13[c]	2	10,000	5.6	2600	18.3	10.11	92.2
14[d,e]	2	10,000	5.4	2600	18.3	9.92	90.4
15	2	20,000	5.7	2600	17.6	10.13	92.3
16[c]	2	20,000	5.8	2600	17.4	10.13	92.3
17[d,e]	2	20,000	5.7	2600	17.4	10.01	91.2
18	4	10,000	5.8	2600	17.7	10.28	93.7
19	4	20,000	6.0	2600	17.0	10.32	94.1
20	4	10,000	5.8	2400	12.8	8.60	78.4
21	4	20,000	5.9	2400	12.6	8.78	80.0
			Sample C: UO_2 Containing 6.05 Per Cent $U^{235}O_2$				
22	4	10,000	6.0	2600	16.0	9.70	88.4
23[c]	4	10,000	5.6	2600	16.8	9.66	88.1
24	4	20,000	6.0	2600	15.9	9.81	89.4
25[c]	4	20,000	5.9	2600	15.1	9.53	86.9
26[c]	4	20,000	5.9	2600	16.0	9.80	89.3
27	4	40,000	6.2	2600	14.7	9.75	88.9
28[c]	4	40,000	6.1	2600	15.1	9.91	90.3
29	15	10,000	6.1	2600	16.0	10.16	92.6
30	15	20,000	6.2	2600	15.8	10.13	92.3
			Sample D: UO_2 Containing 7.48 Per Cent $U^{235}O_2$				
31	4	10,000	6.0	2600	15.5	9.87	90.0
32	4	10,000	6.0	2600	15.7	9.81	89.4
33	4	20,000	6.2	2600	15.5	9.89	90.2
34	4	20,000	6.2	2600	15.3	9.95	90.7
35	4	20,000	6.2	2600	15.3	9.99	91.1
36	4	40,000	6.4	2600	15.3	10.07	91.8
37	4	40,000	6.4	2600	14.6	10.08	91.9
38	15	10,000	6.6	2600	13.3	9.85	89.8
39[d]	15	10,000	6.5	2600	13.9	9.97	90.9
40	15	20,000	6.8	2600	12.6	9.97	90.9
41[d]	15	20,000	6.7	2600	13.3	10.03	91.4
42	15	40,000	6.9	2600	13.5	10.16	92.6

Footnotes appear on the following page.

Footnotes for Table O-2:

(a) Calculated from the weight and size of the pellet.
(b) Theoretical density of UO_2 was taken as 10.97 g per cm^3.
(c) Trials 5, 7, 13, 16, 23, 25, 26, and 28 were fabricated from the same batch of ball-milled material as Trials 4, 6, 12, 15, 22, 24, and 27, respectively, and were sintered separately.
(d) Trials 9, 17, 39, and 41 were fabricated from different batches of ball-milled material than Trials 8, 15, 38, and 41, respectively, and were sintered separately.
(e) Trials 14 and 17 were made from different batches of ball-milled material than Trials 13 and 16, respectively, and were sintered at the same time.

On the basis of these data, the conditions tabulated below have been established for fabrication of the required specimens:

Sample	$U^{235}O_2$ Enrichment, per cent	Ball-Milling Time, hr	Pressure, psi	Sintering Temperature, F
A	2.83	4	10,000-20,000[a]	2500
B	4.06	2	10,000-20,000[a]	2600
D	7.48	15	20,000	2600

(a) It is planned to vary forming pressure from batch to batch in order to minimize differences in as-pressed densities.

Conditions for fabricating suitable specimens from Sample C (6.05 w/o $U^{235}O_2$) have not yet been established.

One hundred and twenty pellets about 1/4 in. in diameter and 1/4 in. high have been fabricated from the sample containing 7.48 per cent $U^{235}O_2$. Measurement of bulk density and open porosity of representative pellets is not yet complete.

Future work will include continuation of the effort to find suitable conditions for fabrication of specimens from Sample C, and fabrication of the pellets required for the in-pile tests.

Fabrication of Loop-Test Fuel Pins

S. Alfant, A. W. Hare, A. A. Bauer, and R. F. Dickerson

The fabrication and assembly of the UO_2-containing fuel pins for the Babcock & Wilcox test loop at the MTR is continuing.

During March, three short and one long dummy fuel-pin assemblies were fabricated and sent to the MTR for preirradiation dynamic flow tests in the loop. The dummy fuel pins which contained no UO_2 pellets and fuel-pin assemblies were manufactured with the techniques which are currently planned for the fueled irradiation test pins. Each pin was prepared by arc welding the stainless steel end caps to the stainless steel tubes in a helium atmosphere. The pins were placed in a vacuum chamber and leak checked with a helium leak detector, and the weld areas were radiographed. Several weld areas were sectioned and examined metallographically to determine the weld penetration and the integrity of the weld area. The completed dummy test pins were assembled in four-pin clusters, identified with the appropriate RFI number, and shipped to the MTR for the flow tests.

Preliminary work has begun on the fabrication of the UO_2-containing test pins. One fueled pin has been fabricated and is currently being examined for weld defects and the relative position of the active fuel length with respect to the center of the pin. Fabrication of the in-pile, out-pile, and manufacturing control specimens will be begun after examination of this initial fuel pin has been completed.

O-5 and O-6

Simulation of Various Accident Considerations for the NMSR Program Using Analog Techniques

J. J. Stone, B. B. Gordon, and R. S. Boyd

Research is being conducted on the safety aspects of foreseeable accident types in connection with the Nuclear Merchant Ship Reactor program. Four accidents have been selected for analysis by analog simulation techniques. These are: continuous rod withdrawal, startup, loss of coolant flow, and cold-water accident. The continuous-rod-withdrawal accident study has been completed.

During March, an analysis of the startup accident was undertaken. This accident was studied in three phases. First, a linear simulation was used to study the system during a change from an initial subcriticality to criticality. Next, an exponential simulation was used to study the system during the change in power from source level to low operating-power level. Finally, the system was simulated linearly again for study at operating-power levels and higher. The third phase was studied for a number of parameter variations including reactor temperature coefficients, rod-withdrawal rate, high-flux scram variables, and period scram variables.

In addition, preliminary setup of the loss-of-coolant-flow accident was carried out.

Work during April will involve completion of the loss-of-coolant-flow accident and portions of the cold-water-insertion accident.

RWD:CRT/all