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1

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PROGRESS RELATING TO CIVILIAN APPLICATIONS DURING APRIL, 1958

by

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DISCLAIMER

TABLE OF CONTENTS

	Page
REPORTS RELATING TO CIVILIAN APPLICATIONS ISSUED DURING APRIL, 1958	5
A. DEVELOPMENTS FOR ZIRCONIUM-CLAD FUEL ELEMENTS	7
Thermal Conductivity of Uranium and UO_2	7
Mechanical Properties of Zirconium Alloys	8
Development of High-Strength Corrosion-Resistant Zirconium Alloys	8
B. DEVELOPMENTS FOR ALUMINUM-CLAD FUEL ELEMENTS	13
Preparation of Aluminum-Uranium Alloys	13
Aluminum Cladding	15
Development of a Natural-Uranium Fuel Alloy With Improved Corrosion Resistance	15
C. PLANT ASSISTANCE TO MCW	17
Investigation of Uranium Oxides	17
The Electrical Properties of Uranium Dioxide	18
The Corrosion Resistance of Selected Stainless Steels	20
Gas-Metal Studies	23
D. PROCESSING OF FEED MATERIALS	27
Solidification of Uranium	27
Examination of Factors Affecting the Quality of Induction-Melted Uranium	28
E. GENERAL FUEL-ELEMENT DEVELOPMENT	31
Development of Dispersed UC and UN Fuel Elements	31
Fueled Zirconium Hydride Moderator	31
F. STUDIES OF URANIUM AND URANIUM-ALLOY FUELS	33
Radiation Stability of Uranium-Zirconium Alloys	33
Development of Gamma-Phase Uranium Alloys	33
Preparation of Uranium-Niobium Alloys	34
Mechanism of Aqueous Corrosion	36
G. FATIGUE STUDIES OF INCONEL AND INOR-8	39
Fatigue Studies of Inconel	39
Fatigue Studies of Inor-8	39
H. REACTOR MATERIALS AND COMPONENTS	41
Oxidation-Resistant Niobium Alloys	41
Valence Effects of Oxide Solutions in Uranium Dioxide	44
High-Temperature High-Pressure Solid-State Studies	44
Rubbing Surfaces in Sodium Environments	45
Basic Studies of Pressure Bonding	46
Effect of Surface Preparation on Bonds Obtained During Pressure Bonding of Zircaloy 2	47
I. PHYSICAL RESEARCH	49
Preparation, Fabrication, and Physical Properties of Uranium Compounds	49
Constitution of Uranium-Base Ternary Alloys	51
Solid-State Study of Ternary System Uranium-Nitrogen-Carbon	51
Structure of UC_2	52

TABLE OF CONTENTS
(Continued)

	Page
J. CORROSION PROBLEMS ASSOCIATED WITH THE RECOVERY OF SPENT REACTOR FUEL ELEMENTS	53
The Darex Process	53
The Sulfex-Thorex Process	54
The Fluoride-Volatility Process	55
L. STUDIES OF SODIUM-TANTALUM COMPATIBILITY AT ELEVATED TEMPERATURES	57
Tantalum-Sodium Compatibility Studies	57
High-Temperature Mechanical Properties of Tantalum	59
Weldability of Tantalum for High-Temperature Systems	59
M. DEVELOPMENTAL STUDIES FOR THE PWR	61
Reactor-Flow Studies	61
X-Ray Photometric Examination of Fuel Elements	62
Pressure Bonding of Zircaloy 2-Clad Fuel Elements Containing Compartmented Oxide Fuel Plates	62
N. EVALUATION OF URANIUM MONOCARBIDE AS A REACTOR FUEL	65
Casting Techniques for the Preparation of Uranium Monocarbide	65
Irradiation-Capsule Design for Uranium Monocarbide	66
O. DEVELOPMENTS FOR NMSR	69
Fabrication of Urania Fuel Pellets for Loop-Test Studies	69
Fabrication of Loop-Test Fuel Pins	70
Simulation of Various Accident Considerations for the NMSR Program Using Analog Techniques	71

REPORTS RELATING TO CIVILIAN APPLICATIONS ISSUED DURING APRIL, 1958

BMI-1258 "Studies of Upper-Plenum Coolant Circulation in a Quarter-Scale Air-Flow Model of the PWR", by Alexander R. Orban and Herbert R. Hazard.

BMI-1259 "Progress Relating to Civilian Applications During March, 1958", by Russell W. Dayton and Clyde R. Tipton, Jr.

A-1

A. DEVELOPMENTS FOR ZIRCONIUM-CLAD FUEL ELEMENTS

F. R. Shober

Preliminary measurements of the thermal conductivity of clad uranium and Zircaloy 2 prior to irradiation have begun. The apparatus for making thermal-conductivity measurements of UO_2, both before and after irradiation, has been completed. The creep and rupture strengths of 15 per cent cold-worked Zircaloy 2 at 290, 345, and 400 C are being determined. Data indicate that the total deformation associated with the transition from secondary to tertiary creep is approximately 1.0 per cent.

The preparation of high-strength corrosion-resistant zirconium alloys is continuing. All alloy compositions have been fabricated at 850 C without difficulty. The 2 w/o tin-3 w/o niobium alloy, one of the harder alloys, had a room-temperature hardness of 360 DPH in the annealed condition. Corrosion data are not yet available.

Thermal Conductivity of Uranium and UO_2

H. W. Deem and C. F. Lucks

The effect of irradiation on the thermal and electrical conductivities of uranium and on the thermal conductivity of uranium oxide is being studied.

Uranium

Radiographic examinations of the clad specimens of uranium and Zircaloy 2 to determine if NaK surrounded the specimens were continued. In addition the cladding on one of the Zircaloy 2 specimens was opened. Kerosene was first admitted to the specimen chamber in a manner to trap any NaK that was around the specimen for examination when the capsule was sawed open. This examination showed that NaK was in the specimen chamber, but the degree of filling could not be determined. Examination of the surfaces showed wetting over most of the area. On the basis of this examination, it was decided to proceed with measurements on the unirradiated specimens. The first measurements on a Zircaloy 2 specimen were nullified by the omission of a key thermocouple. This is being remedied.

During the next month, measurements will be continued on the clad Zircaloy 2 and uranium specimens.

Uranium Oxide

Construction of 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.

Work has continued on guarding problems and on measurements of the fused-quartz standard. Measurements show the modified guard to have adequate control to balance out radial heat flows.

During May the UO_2 measurement will begin.

Mechanical Properties of Zirconium Alloys

F. R. Shober and J. H. VanEcho

The creep strengths of 15 per cent cold-worked Zircaloy 2 are being determined at temperatures up to 400 C. The demand for reactor materials to withstand higher operating temperatures has prompted this investigation to determine the creep strengths, the elongations associated with the initiation of third-stage creep and rupture, and the metallurgical stability of cold-worked Zircaloy 2 under load at elevated temperatures. The tests include long-time creep and stress-rupture tests.

Twelve tests are in progress in the 290 to 400 C temperature range with some tests having been in progress approximately 4400 hr. Six stress-rupture tests have been completed. The results of the creep tests are shown in Tables A-1 and A-2. The average total creep deformation from five tests, three short time and two longer term, at the beginning of third stage creep is 1.08 ± 0.15 per cent. The deformation observed at the transition to third-stage creep does not appear to be related in any way to the test temperature, stress, or the time associated with transition. The length of the tertiary-creep portion of the test is apparently a function of stress. The low total deformations to failure at 290 C are indicative of cold-worked Zircaloy 2. Values for annealed material have been reported to be approximately 40 per cent. The cold-worked properties are retained at 290 C for times as long as 1650 hr. It is thought that more softening will occur at the higher temperatures and the longer test times.

Sufficient additional tests will be run to establish design curves for the creep of Zircaloy 2 at 290, 345, and 400 C.

Development of High-Strength Corrosion-Resistant Zirconium Alloys

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

Zirconium alloys have been given considerable attention as materials which may have desirable properties for reactor components. In some instances, their lack of strength at elevated temperatures had been a handicap. The purpose of this program

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

Specimen	Temperature, C	Stress, psi	Time on Test, hr	Per Cent Deformation at Indicated Time: Load On	50 Hr	100 Hr	500 Hr	1000 Hr	1500 Hr	2000 Hr	2500 Hr	3000 Hr	3500 Hr	4000 Hr	4500 Hr	Creep Rate, per cent per hr
7-5-1	290	47,970	Failed on loading	--	(Total elongation 11.0 per cent)											--
7-5-3	290	45,000	0.1	0.66	(Total elongation 8.3 per cent)											--
7-6-2	290	44,000	0.3	--	(Total elongation 9.3 per cent)											--
7-6-3	290	42,000	123.3	0.46	0.85	(Total elongation 1.07 per cent)										0.0036[a]
7-A-3	290	41,000	190.0[b]	0.46	0.69	0.735	--	--	--	--	--	--	--	--	--	--
7-4-2	290	40,000	1690.0	0.269	0.510	0.550	0.800	1.00	1.415	--	(Total elongation 10.7 per cent)					0.0004[a] 0.00083[c]
7-2-2	290	35,000	4400[b]	0.353	0.495	0.520	0.595	0.625	0.675	0.692	0.705	0.726	0.741	0.757	--	0.00003[c]
7-2-3	290	30,000	4300[b]	0.275	0.375	0.385	0.415	0.440	0.445	0.470	0.476	0.483	0.495	0.503	--	0.000016[c]
7-3-1	290	25,000	4475[b]	0.205	0.267	0.282	0.305	0.323	0.330	0.335	0.340	0.347	0.353	0.365	0.375[d]	0.00002[c]
7-3-2	290	20,000	4460[b]	0.178	0.223	0.227	0.245	0.250	0.265	0.265	0.270	0.272	0.280	0.280	0.280[d]	<0.00001[c]
7-A-1	345	37,500	32	0.47	(Total elongation 10.7 per cent)											--
7-5-2	345	35,000	140.4	0.37	1.20	2.11	(Total elongation 12.7 per cent)									0.014
7-1-1[e]	345	30,000	4000[b]	0.315	0.537	0.592	0.745	0.875	1.025	1.183	1.398	1.745	2.390	3.77	--	0.00026[a] 0.0027[c]
7-2-1	345	25,000	4200[b]	0.230	0.385	0.420	0.510	0.548	0.580	0.612	0.645	0.675	0.695	0.715	--	0.00004[c]
7-3-3	345	20,000	4200[b]	0.180	0.300	0.325	0.380	0.397	0.417	0.427	0.440	0.450	0.475	0.475	--	<0.00001[c]
7-4-1	345	15,000	3150[b]	0.110	0.185	0.205	0.245	0.265	0.275	0.287	0.293	0.315	--	--	--	0.000044[c]
7-6-1	400	20,000	520[b]	0.200	0.500	0.580	0.930	--	--	--	--	--	--	--	--	--
7-4-3	400	15,000	1780[b]	0.134	0.290	0.330	0.440	0.500	0.550	--	--	--	--	--	--	0.0001[c]

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

TABLE A-2. TOTAL CREEP DEFORMATION AT THE BEGINNING OF THIRD-STAGE CREEP

Specimen	Temperature, C	Stress, psi	Time for Initiation of Third-Stage Creep, hr	Total Elongation at Initiation of Third-Stage Creep, per cent	Total Deformation at Fracture, per cent	Minimum Creep Rate, per cent per hr
7-6-3	290	42,000	70	1.00	10.3	0.0036
7-4-2	290	40,000	1250	1.15	10.7	0.0004
7-A-1	345	37,500	18	1.08	10.7	0.02
7-5-2	345	35,000	50	1.25	12.7	0.014
7-1-1	345	30,000	1200	0.92	--	0.00026

is to develop zirconium-base alloys having both twice the strength of Zircaloy 2 and good corrosion life at 570 F. It is necessary that these alloys have nuclear properties, thermal conductivities, and expansion coefficients similar to Zircaloy 2. It has been shown that small additions (less than 5 w/o) of molybdenum, niobium, and tin strengthen zirconium with only a slight detrimental effect on corrosion resistance in high-temperature water. With this in mind, nine groups of alloys were selected to be prepared and screened. The selection of the better alloys will be based upon results from corrosion testing for 1000 hr in 570 F high-purity water and room-temperature hardness tests. A maximum corrosion rate of 34 mg per dm^2 weight gain in 1000 hr in 570 F water and a minimum room-temperature hardness of 250 DPH have been selected for initial screening. Alloys which meet these requirements will be further screened with hot-hardness measurements, and the best alloys will be selected for mechanical- and physical-property studies.

The nine series of alloys consist of ternary zirconium-base alloys containing 2, 3, and 4 w/o tin plus 0 to 2.0 w/o molybdenum, ternaries containing 2, 3, and 4 w/o tin plus 0 to 3 w/o niobium, and quaternary alloys containing 2, 3, and 4 w/o tin plus 0.5 to 2.0 w/o molybdenum and 1.0 to 3.0 w/o niobium. All nine series have been arc melted and cast into buttons. About half of the alloys have been remelted and cast into 1 by 1 by 1/4-in. bars for rolling. These have been hot rolled at 850 C from a helium furnace to 70-mil sheet, annealed at 700 C for 4 hr, and furnace cooled. Hardness measurements were made, and specimens were prepared for corrosion testing. All of these alloys sheared readily with no evidence of brittleness.

Additions of 1 and 2 w/o molybdenum to the zirconium-2 w/o tin base produced alloys having higher hardnesses than annealed Zircaloy 2 (210 to 220 DPH). A zirconium-2 w/o tin-3 w/o niobium alloy had a hardness of 360 DPH, which is the highest hardness obtained among the 2 w/o tin alloys. This alloy rolled without difficulty at 850 C. The quaternary alloys containing 2 w/o tin, 2.0 w/o molybdenum, and 1, 2, and 3 w/o niobium showed hardnesses of around 3000 DPH. Corrosion data are not yet available for any of the above alloys. If the corrosion resistance of any of these hard alloys falls within the requirements noted above, it would appear that several will warrant further investigation. The most notable of these is the 2 w/o tin-3 w/o niobium alloy.

Casting and fabrication of the remaining alloys are in progress. Hot-hardness measurements will be made on any of the above 2 w/o tin alloys which show good corrosion resistance. Additional corrosion tests will be started as material becomes available.

B-1

B. DEVELOPMENTS FOR ALUMINUM-CLAD FUEL ELEMENTS

R. J. Carlson

A development program on the preparation of aluminum-25 to 40 w/o uranium alloys in the form of hollow extrusion billets by centrifugal-casting techniques has been initiated. In addition, ternary additions will be studied to determine if fabricability of the alloys can be improved by suppression of UAl_4 formation or by refinement of the UAl_4 particle size.

A technique has been developed whereby hydrostatic pressure bonding can be used to clad nickel-plated uranium slugs with aluminum with a sound metallurgical bond between core and cladding. Efforts are currently being directed toward determining minimum time-temperature-pressure relations which will result in satisfactory fuel elements.

Efforts to develop a high-uranium fuel alloy possessing improved corrosion resistance in 300 C water by a factor of 3 or 4 over that of the uranium-2 w/o zirconium alloy and having a thermal-neutron-absorption cross section equal to or less than a uranium-4 w/o zirconium alloy are continuing.

Preparation of Aluminum-Uranium Alloys

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

Aluminum-uranium alloys clad with aluminum are of interest as fuels for low-temperature, water-cooled, and water-moderated reactors. Alloys in this system containing low concentrations of uranium have proved themselves as reactor fuels and have been used as such for some time. However, it is desirable to raise the uranium concentration in order to increase fuel loading and decrease parasitic neutron capture. Two major difficulties are encountered in melting and casting these alloys. They are: (1) porosity from gas and shrinkage, and (2) segregation due to the density differences between the phases present and to the great temperature difference between the liquidus and solidus lines of the phase diagram. These difficulties must be overcome if the high-uranium alloys of this system are to be cast into other than the simplest shapes. For certain applications, it is desirable to cast these alloys into the form of heavy-walled tubes suitable for coextrusion into tubular fuel elements.

As a result of previous studies, it was determined that centrifugal casting techniques could be developed into a satisfactory production technique for casting aluminum-uranium alloys containing uranium in amounts up to 25 w/o and above. During these investigations, single-length extrusion billets of the 25 w/o uranium alloy were prepared. These billets, cast from air-melted alloy, were relatively homogeneous and exhibited extremely good exterior surfaces. The only evidence of porosity was found at one area around the inside surface of the castings. This band, approximately 1 in. wide,

was located about equidistant from each end of the casting and represented the last portion of the melt to solidify. Studies of this area indicated that the porosity was due to shrinkage. It is believed that proper mold design and mold feed will correct this problem. Further improvement of the interior surface of the castings can be expected with the use of improved equipment and casting techniques.

In an effort to obtain the desired improvements of the interior surfaces of the cast shapes, various mold designs and pouring techniques will be employed. For the latter purpose, a pouring mechanism is being designed which will permit the operator to direct the pour stream at any point along the axis of the mold. This will permit the investigation of various pouring techniques which cannot be investigated utilizing a stationary pouring spout. Mold designs to be used in conjunction with the improved pouring mechanism include those having variable wall thicknesses and insulated walls. With these variations, investigations can be made of the effect of various cooling rates on the ingot quality. It is believed that these studies will result in a mold and pouring technique that will produce sound homogeneous extrusion blanks.

Previous experience with the high-uranium alloys has indicated that they exhibit relatively poor fabrication characteristics. This is due in part to the large UAl_4 particles present in the alloys. A logical approach to the improvement of the fabrication characteristics is through the suppression of UAl_4 formation, thereby retaining UAl_3 and increasing the amount of ductile matrix present in the alloys. If sufficient UAl_3 cannot be retained, fabrication properties may be improved by the refinement of the UAl_4 particle size. It is possible that alloying additions may accomplish these objectives and also improve the casting properties.

The choice of additions to be made to the alloys will be governed by their compatibility with the chemical processing step, by their thermal-neutron cross section, and by experience with additions to aluminum-uranium or other aluminum-alloy systems. Among the additions now under consideration are tin, titanium, and zirconium. All of these are known to suppress UAl_4 formation in aluminum-uranium alloys. It is planned to prepare small melts containing up to 3 w/o of the ternary addition in alloys containing 25, 35, and 45 w/o uranium.

The alloys containing ternary additions will be evaluated by metallographic examination, X-ray diffraction, and thermal analysis. Alloys that exhibit favorable characteristics will be screened further by corrosion testing in 300 F water. Upon completion of the screening program, promising alloys will be compared to the equivalent binary alloys on the basis of castability and fabricability.

Future work will be concerned with the evaluation of mold designs and pouring techniques. This work will be confined to single-length 25 w/o uranium-alloy ingots. When satisfactory techniques have been developed for the production of the above material, representative castings of 25 and 35 w/o uranium alloys will be forwarded to the production site for further evaluation and testing.

B-3

Aluminum Cladding

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

The technique, whereby gas pressure and temperature are used to obtain a metallurgical bond, is being employed for the cladding of internally and externally cooled prototype fuel elements. These fuel elements consist of a tubular nickel-plated uranium core clad with aluminum.

Various temperatures have been employed to date in an effort to determine the minimum temperature which can be used to obtain a sound metallurgical bond using a constant time and pressure of 1 hr and 5000 psi, respectively. The latest specimen to be pressure bonded was run for 1 hr at 850 F and 5000 psi. This sample has been sectioned and is being evaluated metallographically. The integrity of the metallurgical bond obtained from this test will be used as a guide in determining the conditions to be chosen for future specimens.

Once the minimum bonding temperature has been obtained, pressure and time will be varied in an effort to ultimately determine the minimum time, temperature, and pressure necessary to obtain a sound metallurgical bond.

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 by a factor of three or four over that of the uranium-2 w/o zirconium alloy is being undertaken. This alloy must also have a thermal-neutron cross section that is equivalent or less than that of a uranium-4 w/o zirconium alloy.

Seventeen alloy compositions, consisting mostly of uranium-2 w/o zirconium-base alloys, plus the allowable amount of a low-cross-section element, have been cast, worked, and heat treated at 900 C for 1 hr and furnace cooled. Preliminary corrosion testing in a windowed autoclave has indicated that visual observation of the corrosion process is not feasible, as the corrosion products which spall off obstruct the view. Consequently, short-time corrosion tests will be employed to evaluate the corrosion resistance of the alloys.

The extreme rapidity of uranium corrosion at 300 C makes it necessary that the following method be used. The tests will be carried out in an autoclave that has been flushed with argon and evacuated, this process being repeated several times. Water at 300 C will be admitted to the preheated autoclave and corrosion allowed to proceed, initially for approximately 15 min. Use of a hydrogen diffuser will be employed to permit the escape of hydrogen generated in the corrosion process. Cooling of the autoclave will be carried out by release of the pressure and introduction of argon. After the autoclave has reached 150 C, it will be water quenched. Because it is difficult to reproduce cooling rates, and the period of cooling may approximate the intended time of

testing, all specimens will be corrosion tested simultaneously so that comparative data can be obtained. Based upon the results obtained during the initial tests, those alloys which exhibit promising behavior will be subjected to controlled corrosion tests for increased periods of time.

C-1

C. PLANT ASSISTANCE TO MCW

D. A. Vaughan

The programs which have been in progress during Fiscal Year 1958 have been terminated during the past month, with the exception of a study of the orientation of uranium. This study has been limited, to date, to an evaluation of published methods for quantitizing the amount of orientation by X-ray diffraction. It is planned to test modifications of the diffraction techniques in order to select a suitable procedure for production control.

The experimental work on the electrical properties of uranium dioxide was discontinued last month. The significant results on the effect of additions (calcium, molybdenum, nitrogen, and zirconium) on the electrical properties of UO_2 bodies are reviewed.

Final corrosion rates were measured for specimens of Type 304 ELC stainless steel in 38 and 45 w/o nitric acid solutions and in these acid solutions containing chloride, fluoride, and sulfate additions. No significant changes in corrosion rates were observed for the acid solutions containing chloride or sulfate additions. The corrosion rates of this steel in 38 w/o nitric acid containing fluoride continued to increase with increasing fluoride concentrations up to 100 ppm.

A final test was made of hydrogen permeation through molten MgF_2 slag. From the one valid test, it would appear that molten slag is impermeable to hydrogen. Surface-tension and density measurements on MgF_2 and mixtures of MgF_2, MgO, and UO_2 were completed.

Investigation of Uranium Oxides

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

During April a literature search was made on the quantitative determination of preferred orientation, to select a suitable procedure for production control. The majority of the methods evaluated were modifications for the method of Schulz*. This method results in the preparation of a pole figure. A large number of measurements are required for each crystallographic plane, which makes the procedure very time consuming. Automatic instrumentation is used for this reason, but this is still time consuming.

Harris and several other workers use a modified method to construct a "reciprocal pole figure".** This method, however, is still rather lengthy if several directions are to be studied in the fabricated body.

*Schulz, L. G., J. Appl. Phy., 20, 1030-3 (1949)

**Harris, G. B., Phil. Mag., 43 (336), 113 (1952).
Mueller, M. H., Knott, H. W., and Beck, P. A., ANL-5194 (1954).
Stucken, E. F., DP-251 (1957).

C-2

It is possible that a simplification of the published methods may be devised to satisfy the requirements of the intended application.

The Electrical Properties of Uranium Dioxide

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

The incorporation of foreign atoms in the uranium dioxide lattice results in a change of lattice constants and of the valence of some of the U^{+4} ions. It is to be expected, then, that the presence of even small amounts of impurities would have a gross effect on such structurally sensitive properties as reactivity, sinterability, electrical characteristics, etc. Early work was concerned with the effect of excess oxygen atoms on the electrical properties of uranium dioxide, and it was shown how the magnitude and type of electrical conductivity could be related to the phase relationships in the UO_2-U_3O_8 system (BMI-1135). More recently, this work was extended to include the effects of nitrogen and various metallic impurities on the electrical properties of UO_2. The significant findings of this work are summarized in the succeeding paragraphs.

Nitrogen

Since uranyl nitrate is used as an intermediate in the usual preparation of UO_2, it is reasonable to suppose that nitrogen is a common impurity in UO_2. Three methods were used to deliberately "dope" UO_2 with nitrogen. The first of these methods involved exposing freshly made "active" UO_2 to dry nitrogen gas. In general, the electrical conductivities of these specimens were lower and the activation energies were higher than that observed for inactive specimens of comparable excess oxygen content. The structure of the samples was cubic. Since *n*-type conductivity was observed in every case, these results were interpreted as indicating the presence of a cubic modification of UO_3. Subsequent work with the samples revealed that they were absorbing oxygen during handling, and reproducible results of electrical properties were difficult to obtain.

Uranium dioxide was also doped with nitrogen by adding uranium nitride to normal MCW UO_2 before pressing the powders into specimens for electrical measurements. Again a reduction of the magnitude of the conductivity of UO_2 was noted. If nitrogen is accommodated in the UO_2 lattice in interstitial or oxygen positions, the *p*-type conductivity of the compound should be increased, not decreased. Since the composition of the nitride used in these experiments was uranium-rich, it was believed that part of the excess oxygen of the oxide might have combined with the excess uranium of the nitride, resulting in a decrease of the conductivity. However, this hypothesis was not proven.

A third method used to dope UO_2 with nitrogen was the addition of uranyl nitrate to normal MCW UO_2 powders. Room-temperature electrical measurements on the as-prepared specimens revealed a surprising decrease of conductivity with increasing nitrate content. Where between 3 and 5 mole per cent of the nitrate was added, the

conductivity of the oxide changed from *p*-type to *n*-type. These results indicate the ease by which UO_2 may be doped by the nitrate. Nitrogen was lost from these specimens when measured at elevated temperatures.

Due to the difficulties of obtaining reproducible electrical measurements and the lack of an independent method of assaying the nitrogen content, the effect of nitrogen on the electrical properties of UO_2 is not clearly understood. However, the results of the three methods of doping were consistent in that nitrogen caused a reduction of *p*-type conductivity and the appearance of *n*-type conductivity when present in sufficient amounts.

Calcium

Normal MCW UO_2 was intimately mixed with various amounts of CaO and the mixtures were sintered at 1600 C for 2 hr. Calcium is known to be soluble in the UO_2 lattice to about 10 mole per cent. It enters the lattice by substituting for uranium atoms. The accommodation of a Ca^{+2} ion in a site normally occupied by a U^{+4} ion introduced additional acceptor states and enhanced the *p*-type conductivity of UO_2. Activation energies measured for calcium-doped UO_2 were slightly lower than those of undoped material.

Zirconium

Zirconium dioxide was added to UO_2 in a manner similar to that used for calcium doping. It forms a substitutional solid solution with UO_2. The substitution of a Zr^{+4} ion for U^{+4} (up to 1 mole per cent) resulted in no detectable effects on the electrical properties of sintered specimens of UO_2.

Molybdenum

Molybdenum trioxide was added to UO_2 in an effort to dope the compound with an ion of +6 valence. However, room-temperature measurements of the electrical conductivities of specimens containing molybdenum were not significantly different from those of "pure" UO_2. Evidently the Mo^{+6} ions were reduced by the UO_2 and molybdenum entered the lattice as Mo^{+4}.

The temperature dependence of the conductivity of the molybdenum-containing samples showed an anomalous decrease in conductivity at about 800 C. It is believed that this anomaly is associated with a change of the oxidation states of uranium and molybdenum ions.

C-4

The Corrosion Resistance of Selected Stainless Steels

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

Nitric Acid Reconcentrator

During April the corrosion investigations carried on as part of a program of assistance for the design and operation of the Weldon Springs plant were terminated.

The final corrosion rates measured for specimens of Type 304 ELC stainless steel in 38 and 45 w/o nitric acid solutions boiling at 250 mm of mercury absolute pressure are given in Tables C-1 and C-2, respectively.

The only significant change in any of the corrosion rates in 38 w/o nitric acid occurred in the case of the specimen exposed in the vapor-phase position in the acid containing 0.20 w/o chloride. Here a sudden fivefold increase occurred during the 209 hr following the 4000-hr measurement. However, similar increases occurred in the case of the liquid-phase specimens in the other solution containing 0.20 w/o chloride and in the solution containing 0.25 w/o chloride between the 1500- and 2000-hr examination. While none of these rates are beyond the range of useful service life, these sudden changes indicate that concentrations of 0.20 w/o chloride, and greater, may result in metastable conditions in 38 w/o nitric acid solutions boiling under these conditions.

The results with 45 w/o nitric acid solutions continue to show that, at the 0.10 w/o chloride level, corrosion is relatively insignificant but becomes important at the 0.20 w/o level.

As reported in BMI-1259, the presence of up to 5000 ppm sulfate as a contaminant in 38 w/o nitric acid solutions does not seem to have any deleterious effect on the corrosion of Type 304 ELC stainless steel. The final results for solutions boiling at 200 mm of mercury absolute pressure and at atmospheric pressure are given in Table C-3. A larger effect results from the higher boiling temperature than from increases in sulfate concentrations. There is a definite indication that a higher corrosion rate will occur at the interface than in the vapor or liquid phases.

A series of experiments has been completed in which the effect of additions in the range from 1 to 100 ppm fluoride was studied in 38 w/o nitric acid solutions boiling at atmospheric pressure. This study was made to determine the concentration of fluoride contamination alone at which corrosion becomes severe. Seven 48-hr exposure periods were completed using specimens of Type 304 ELC stainless steel, and the corrosion rates calculated on the total exposure are tabulated in Table C-4.

TABLE C-1. THE EFFECT OF CHLORIDE CONTAMINATIONS ON THE CORROSION OF TYPE 304 ELC STAINLESS STEEL IN BOILING 38 w/o NITRIC ACID

(250 mm of mercury absolute pressure)

Chloride, w/o	Specimen Position	Corrosion Rate at Indicated Exposure, mil per month		
		3500 Hr	4000 Hr	4209 Hr
0.00	Vapor	0.017	Discontinued	--
	Interface	0.027	Discontinued	--
	Liquid	0.016	Discontinued	--
0.05	Vapor	0.023	Discontinued	--
	Interface	0.031	Discontinued	--
	Liquid	0.026	Discontinued	--
0.10	Vapor	0.026	Discontinued	--
	Interface	0.035	Discontinued	--
	Liquid	0.024	Discontinued	--
0.10	Vapor	0.024	Discontinued	--
	Interface	0.032	Discontinued	--
	Liquid	0.028	Discontinued	--
0.15	Vapor	0.028	0.027	0.026
	Interface	0.037	0.037	0.035
	Liquid	0.061	0.056	0.055
0.20	Vapor	0.029	0.030	0.149
	Interface	0.033	0.034	0.033
	Liquid	0.032	0.046	0.082
0.20	Vapor	0.022	0.023	0.024
	Interface	0.034	0.033	0.033
	Liquid	0.191	0.223	0.231
0.25	Vapor	0.029	0.031	0.031
	Interface	0.043	0.068	0.067
	Liquid	0.375	0.389	0.411

C-6

TABLE C-2. THE EFFECT OF CHLORIDE CONTAMINATIONS ON THE CORROSION OF TYPE 304 ELC STAINLESS STEEL IN BOILING 45 w/o NITRIC ACID

(250 mm of mercury absolute pressure)

Chloride, w/o	Specimen Position	Corrosion Rate at Indicated Exposure, mils per month	
		3000 Hr	3500 Hr
0.00	Vapor	0.023	Discontinued
	Interface	0.045	Discontinued
	Liquid	0.031	Discontinued
0.05	Vapor	0.040	Discontinued
	Interface	0.040	Discontinued
	Liquid	0.035	Discontinued
0.10	Vapor	0.055	0.053
	Interface	0.053	0.051
	Liquid	0.049	0.053
0.20	Vapor	1.213	Discontinued
	Interface	0.481	Discontinued
	Liquid	0.625	Discontinued

TABLE C-3. THE EFFECT OF SULFATE CONTAMINATIONS ON THE CORROSION OF TYPE 304 ELC STAINLESS STEEL IN BOILING 38 w/o NITRIC ACID

Sulfate, w/o	Specimen Position	Corrosion Rate at Indicated Exposure, mil per month			
		200 mm Hg Absolute Pressure		Atmospheric Pressure	
		336 Hr[a]	500 Hr[a]	336 Hr[a]	500 Hr[a]
0.0000	Vapor	0.011	0.011	0.176	0.170
	Interface	0.022	0.022	0.216	0.210
	Liquid	0.023	0.023	0.181	0.163
0.0005	Vapor	0.016	0.016	--	--
	Interface	0.026	0.026	--	--
	Liquid	0.024	0.025	--	--
0.0020	Vapor	0.019	0.018	0.185	0.180
	Interface	0.026	0.026	0.245	0.237
	Liquid	0.025	0.026	0.187	0.167
0.0100	Vapor	0.016	0.016[b]	0.187	0.187
	Interface	0.029	0.029	0.270	0.264
	Liquid	0.026	0.027	0.186	0.169
0.5000	Vapor	0.029	0.029[b]	0.262	0.257
	Interface	0.044	0.043	0.427	0.407
	Liquid	0.041	0.040	0.247	0.241

(a) The 336-hr exposure actually consisted of seven 48-hr periods, with solutions changed for each period, followed by one period of 164 hr to give the 500-hr exposure.

(b) These two tests were continued until a total exposure of 1500 hr was reached. The results were: 0.0100 w/o sulfate - 0.021, 0.038, and 0.030; 0.5000 w/o sulfate - 0.039, 0.049, and 0.041 mil per month, respectively.

C-7

TABLE C-4. THE EFFECT OF FLUORIDE CONTAMINATIONS ON THE CORROSION OF TYPE 304 ELC STAINLESS STEEL IN BOILING 38 w/o NITRIC ACID

(Atmospheric pressure)

Fluoride Addition, ppm	Corrosion Rate[a] at Indicated Position, mils per month		
	Vapor	Interface	Liquid
0	0.18	0.25	0.22
1	0.28	0.28	0.26
10	0.41	0.43	0.34
20	0.48	0.59	0.45
40	1.05	1.04	1.00
60	1.18	1.29	1.51
80	1.03	1.50	2.08
100	1.35	2.03	2.56

(a) These corrosion rates for 20, 40, 60, and 80 ppm F^- have been calculated on the basis of 336 hr of exposure consisting of seven 48-hr periods; those for 0, 1, 10, and 100 ppm F^- on the basis of 321 hr of exposure due to one period of only 33 hr.

The corrosion rate is seen to increase in all three positions with increasing fluoride concentration. The variation of the rates for the vapor and interface specimens is somewhat erratic, but a plot of corrosion rate as a function of fluoride concentration for the liquid specimen results in a smooth curve. From 20 to 100 ppm fluoride, the relationship is nearly linear. There is no abrupt change in the curve, and the threshold value of fluoride contamination which results in severe corrosion would have to be selected after an arbitrary limit of the corrosion rate was imposed for the operation at hand.

Gas-Metal Studies

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

To assist in understanding fundamental aspects in the production of dingot uranium, a study is being made of factors influencing yield and purity of product. Present experiments are on the permeability of hydrogen through molten magnesium fluoride slag and on the surface tension of Mallinckrodt and synthetic slags.

Hydrogen Permeation

An attempt was made to measure hydrogen permeation using the experimental setup previously described (BMI-1256). In the blank run, rates were obtained at 1420 and 1350 C. A third rate (the last determined) at 1300 C was considerably higher than that obtained at 1350 C. A later visual examination of the reaction tube suggested a possible explanation for this erratic behavior. Two cracks extending through approximately half the wall thickness had developed at the slag-metal interface. Because

of the higher blank rate at 1300 C, it was presumed that the cracks had formed during or just prior to this run. Next, the tube was fitted with a 3-mil molybdenum diaphragm and permeation values were determined at 1300, 1350, and 1420 C. These data appeared normal in that the logarithm of the rate increased proportionately with temperature. The rate obtained at 1300 C was the same as that obtained for the blank within the limits (about 5 per cent) of experimental error. The other permeation values could not be evaluated for lack of reliable blank data. From the one possible valid rate, it appears that the molten slag is impermeable to hydrogen.

Surface Tension

Densities of Mallinckrodt slag and several MgF_2-base materials were determined by measurement of slag depth in a tantalum crucible. The crucibles were regular cylinders which were calibrated with water for volume per unit depth at room temperature. Corrections for the thermal expansion of tantalum at the operating temperature were made. The position of the slag surface was found using the surface-tension capillary as a probe. With argon flowing through the capillary, an abrupt rise in pressure was noted when the capillary was sealed off by touching the slag surface.

The experimental slag-density data are tabulated below:

Slag Composition, w/o			Temperature, C	Density[a], g per cm^3
MgF_2	MgO	UO_2		
100	--	--	1350	2.27
98.8	1.2	--	1350	2.48
96.1	3.9	--	1365	2.54
94.1	5.9	--	1350	2.54
98.8	--	1.2	1365	2.56
97.7	--	2.3	1365	2.51
96.8	--	3.2	1365	2.59
95.5	--	4.5	1365	2.56
94.4	--	5.6	1365	2.55
92.2	--	7.8	1370	2.61
Mallinckrodt slag			1375	2.42

(a) The estimated experimental error is ± 5 per cent.

The surface-tension values calculated using the densities listed above are tabulated on the following page.

Slag Composition, w/o			Temperature, C	Average Surface Tension[a], dynes per cm	Number of Determinations	Average Deviation, dynes per cm
MgF_2	MgO	UO_2				
100	--	--	1350	236	7	6
100	--	--	1425	233	2	1
98.8	1.2	--	1350	221	8	1
96.1	3.9	--	1370	241	2	5
93.2	6.8	--	1370	244	2	2
98.8	--	1.2	1365	218	2	0
96.4	--	3.6	1365	217	2	1
93.0	--	7.0	1365	212	2	0
Mallinckrodt slag			1350	222	3	2

(a) The estimated error in these measurements is ± 5 per cent.

From a knowledge of the surface tension of molten Mallinckrodt slag, calculations were made to determine the maximum size of a uranium sphere which could be supported on its surface. The force supporting such a particle is $2\pi r\gamma$ and the downward pressure, P, of the sphere is equal to the pressure exerted by the uranium particle minus the upward pressure of the displaced slag:

$$P = \frac{(V\, d_u\, g) - (1/2\, V\, d_s\, g)}{\pi r^2} ,$$

where

V = volume of sphere

d_u = density of uranium

d_s = density of slag

g = acceleration of gravity.

The limiting condition for displacement is when the sphere is one-half immersed. The resultant force is equal to the pressure, P, times the diametrical cross section of the sphere, $\pi r^2 P$. For the largest sphere supportable by the surface tension of the slag, the pressure may be designated as P_{max} and the following equations hold:

$$2\pi r\gamma = \pi r^2 P_{max}$$

$$P_{max} = \frac{2\gamma}{r}$$

$$\gamma = \frac{r}{2}(P_{max}) .$$

C-10

Calculations from the data show that Mallinckrodt slag with a surface tension of 222 dynes per cm will support uranium spheres with radii up to 0.138 cm. It should be emphasized that these uranium particles would be located on the slag surface. Thus, the data offer no explanation for the uranium particles found randomly distributed in a typical sample of Mallinckrodt slag.

This concludes the current work on a series of studies on three properties of molten magnesium fluoride slag: (1) its permeation by hydrogen, (2) its viscosity, and (3) its surface tension. As indicated before, experimental data show that neither viscosity nor surface tension of the slag could have an appreciable effect on the yield of uranium metal. Therefore, other factors should be studied as possible causes of low yield. One plausible explanation which merits study is that at high temperatures uranium may form a complex low-valence fluoride with magnesium, thus retaining uranium in solution in the slag. Upon cooling, disproportionation may take place, producing a dispersion of uranium in MgF_2. This may occur at or near the melting point of the slag so that the uranium has no opportunity to settle out. Such reactions have been noted in other slag-metal systems.

D-1

D. PROCESSING OF FEED MATERIALS

E. L. Foster

Two programs now in progress relate to problems concerning the processing of feed materials. The programs are concerned with two specific lines of study: one pertaining to the factors affecting the quality of vacuum-melted uranium and the other the theoretical considerations involved in the solidification of unalloyed uranium ingots. The resolution of the factors affecting the quality of vacuum-melted uranium could make an immediate contribution to the improvement of fuel-slug quality, and the solidification study will provide an evaluation of mold variables for future casting needs.

Solidification of Uranium

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

A basic study of the governing mechanisms present during the casting of uranium metal is being made. Variables such as pouring rates, superheat, mold shapes, mold materials and others will be investigated and evaluated as to their effect on the internal soundness of ingots. Small-scale melts of uranium will be poured under controlled conditions to study the individual variables. The casting and mold will contain thermocouples in such a manner as to measure and record the temperatures of the metal and mold material during the cooling period. These data will be used to further refine the mathematical expressions being developed to describe heat transfer from the metal and mold.

To study the heat-flow phenomena a mathematical model of a metal-mold system consisting of 76 cells was prepared. This model represents a pie slice of the casting and mold materials. Preliminary tests of the model have been made by use of an IBM 650 computer. Corrections have been made to the model on the basis of one of these tests in which solidification of the entire casting was completed. All checks made to date indicate that the information fed to the computer correctly represents the mathematical model. The number of cells have been reduced from 76 to 72 due to elimination of some small cells at the bottom of the casting; this was done to permit use of a larger time interval in computing the temperature change in a particular cell.

Present efforts are being directed toward improving the values of the constants used in the mathematical expressions and a limited amount of computing will be done to produce preliminary data to indicate the nature of the results obtainable. Extensive computational work is being delayed until correlation with the experimental program is attempted.

Although the previously used 20-cell model does not contain the variable thermal conductivity and the gap formation, the results of computation with this smaller model are being compared with the 72-cell model for indications as to the convergence of the solution. A further test of the mathematical method being employed would be to

compare the 72-cell solution with the solution obtainable with a larger number of cells, e.g., 500. However, if results from the 72-cell model obtained are favorable compared with the experimental results, it will be assumed to be adequate.

In connection with improving the mathematical constants, various physical-property measurements on the materials are being made. Measurements being made include the thermal conductivity of uranium and graphite, each in two different orientations; thermal resistance of a layer of mold wash; total normal emissivity of wash-coated graphite and of oxidized uranium; and linear thermal expansion of graphite and uranium.

The total normal emissivity of oxidized uranium has been measured in the temperature range between 1540 to 1975 F. The measured values during the first heating varied from about 0.55 at 1540 F to about 0.56 at 1875 F. Upon reheating to 1975 F, the emissivity dropped to about 0.54. During subsequent cooling to 1588 F and then heating to near the melting point, the emissivity increased with temperature from about 0.53 to 0.54.

Uncorrected values for the emissivity of graphite painted with mold wash have been obtained from 1500 to 3000 F. Corrections must be made for the temperature gradients through the relatively thick walls of the graphite-tube specimens, and the effect of flaking of the MgO from the graphite in this temperature range also must be evaluated. As soon as the thermal conductivity of the graphite is determined, the corrections will be applied and emissivity values will be reported. Other measurements to be taken are the linear thermal expansion and thermal conductivity of the materials. Data obtained from the determination of these physical properties will be used in the mathematical model.

Examination of Factors Affecting the Quality of Induction-Melted Uranium

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

This program is concerned with the reactions that occur during the induction melting of uranium. Of particular interest are those nonmetallic impurities which can vary from charge to charge both in kind and in magnitude. The experimental portion of the investigation is being conducted in a 10-lb-capacity vacuum-melting furnace which has been equipped with a gas-sampling manifold. A better knowledge of the reactions that may occur within the furnace during melting should lead to improved methods of process control.

A series of experimental melts has been in progress in which the gases nitrogen, hydrogen, oxygen, CO, CO_2, and H_2O have been admitted to the furnace in significant amounts so as to obtain pressure profiles (the change of furnace pressure with time) over pure uranium held at a temperature of 2500 F and contained in uncoated graphite crucibles. Gas analyses are being omitted in the initial profiles, but are being obtained at the apparent reaction end point in two succeeding replicate tests. The

initial profiles are used to indicate the gas-sampling points and to indicate whether the gas reacted. The above-mentioned gases were chosen because they have been found as the predominant background gases in previous tests and because they stem from two important operational impurities: air and water. It is believed that a knowledge of the behavior of these impurities in the presence of molten uranium must be obtained before an intelligent evaluation can be made of the effects of impurities which stem from the various charge materials.

During April, the initial profiles and one replicate series of profiles were obtained from oxygen, nitrogen, CO, CO_2, and hydrogen. All gases except hydrogen appeared to react with various degrees of rapidity. The indicated relative rates of reaction place oxygen as most reactive and nitrogen second. CO and CO_2 were each less than nitrogen in reactivity and approximately equivalent to each other. After hydrogen was admitted to the furnace, the pressure remained constant, which indicated that hydrogen was inert at this temperature and pressure to the carbon-uranium system. The tests with water vapor were deferred until all other tests have been completed so that inaccuracies arising from absorbed water on the furnace and sample-bottle walls are avoided.

Agreement of pressure data appears to be reasonably good for these tests. Results of the various gas analyses are now being processed. Preliminary thermodynamic considerations of a nitrogen reaction with carbon to form cyanogen indicate that a nondetectable amount of cyanogen would be formed at a temperature of 2500 F. On the other hand, reaction between nitrogen and uranium is expected to take place, since the equilibrium constant is calculated to be, $K_{2500F} = 9.1 \times 10^6$.

Preparations are under way to repeat these tests for the third time (three replicate tests each). Because of its apparent inertness to the system, hydrogen is to be omitted. The water-vapor tests in triplicate are to follow. An indication of the importance of the type study presently being conducted is to be found in a theoretical thermodynamic treatment of reactions in molten uranium by E. H. Roland of Westinghouse (WAPD-TM-99). He states that the role played by the presence of CO on the impurity level of carbon and oxygen in uranium and its alloys is very important. Roland believes that the variability of furnace pressures over the working range in vacuum-melting techniques can account for the difference in oxygen and carbon contents from melt to melt.

E-1

E. GENERAL FUEL-ELEMENT DEVELOPMENT

F. A. Rough and D. C. Carmichael

Various studies of fuel-element development are reported in this section. These studies are part of the program of the AEC Division of Reactor Development.

No additional results of a study of dispersions of UN or UC in stainless steel will be reported until specimens prepared for this program have been irradiated and examined.

An investigation is being made to determine the feasibility of a fueled zirconium hydride moderator. Specimens are being prepared for irradiation testing and high-temperature structural studies by X-ray diffraction.

A program has been initiated to study the effect of surface preparation of Zircaloy 2 on the quality of bonding obtained between the surfaces. The pressure-bonding technique being employed utilizes a high gas pressure at elevated temperatures to achieve bonding.

Development of Dispersed UC and UN Fuel Elements

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

Stainless steel-clad irradiation specimens containing 24 w/o UC or UN dispersed in matrix composed of 18 w/o chromium, 14 w/o nickel, 2.5 w/o molybdenum, and the balance iron have been fabricated and are being prepared for insertion in the MTR. Specimens will be irradiated at 1650 F at various burnups up to 15 a/o of the uranium-235. No additional fabrication studies are planned for the remainder of Fiscal Year 1958.

This study will be recessed until postirradiation study begins.

Fueled Zirconium Hydride Moderator

H. E. Bigony and H. H. Krause

The hydrides of uranium-zirconium alloys are being investigated as fueled moderators for potential use in gas-cooled reactors. Efforts during April were directed toward preparation of samples for structural studies. Encapsulation of specimens for irradiation is still in progress.

E-2

Structure and Pressure-Composition-Temperature Studies

Samples of uranium-zirconium hydrides are being prepared for high-temperature X-ray diffraction in order to identify the condensed phases more completely. Alloys containing 1 and 50 w/o uranium will be examined at temperatures of 500, 600, 700, and 800 C. Leaks which developed in the hydriding apparatus resulted in oxidation and nitriding of the first set of specimens prepared, making them unacceptable for X-ray studies. A second set will be hydrided during the next period. The zirconium-25 w/o uranium alloy required for the remaining hydrogen-absorption-isotherm study is being prepared.

Progress is continuing on the encapsulation of irradiation specimens in Capsule BMI-20-1, which is designed to operate at a temperature of 1500 F. Most of the capsule components have been fabricated. The planned date for shipment of the irradiation capsule is May 12, 1958, in order that it arrive in time for MTR Cycle 106, scheduled for June 16, 1958. The decision was reached to discontinue work on Capsule BMI-20-2, which was designed to operate at 1200 F. A topical report for this program is being prepared.

F-1

F. STUDIES OF URANIUM AND URANIUM-ALLOY FUELS

F. A. Rough and A. W. Hare

The various studies of uranium-alloy fuels are reported in this section. This research is part of the program of the AEC Reactor Development Division. The programs currently being investigated are concerned with the effects of radiation zirconium-uranium alloys, development of gamma-phase uranium alloys, development of techniques for the preparation of homogeneous uranium-niobium alloys, and the mechanism of uranium corrosion.

Radiation Stability of Uranium-Zirconium Alloys

D. J. Hamman, A. W. Hare, A. A. Bauer, and R. F. Dickerson

No work was done in April on the metallographic examination of irradiated zirconium-22 w/o uranium alloys by electron-microscopy techniques. It is currently planned to complete this phase of the investigation during May.

Capsule BMI-8-5, which contains two specimens of zirconium-50 w/o uranium, is continuing to operate at the control thermocouple temperature of 950 F, giving an approximate specimen center-line temperature of 1145 F. The capsule is scheduled for discharge during MTR Cycle 104 shutdown in May with a calculated burnup of about 2.1 total a/o.

Capsule BMI-8-6, which contains three specimens of zirconium-22 w/o uranium, is operating at a calculated specimen center-line temperature of approximately 550 F. This experiment is scheduled for discharge from the MTR during Cycle 104 shutdown with a calculated burnup of 1.9 total a/o.

Development of Gamma-Phase Uranium Alloys

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

Ternary and quaternary alloys of uranium with chromium, molybdenum, niobium, ruthenium, vanadium, and zirconium are being investigated in an effort to develop an improved metastable gamma-phase alloy.

Hot-hardness data are being obtained on all alloys to gain an indication of hot strength. Some general statements can be made concerning the effect of alloying on hardness. Increasing niobium and molybdenum content in gamma-quenched uranium-20 w/o zirconium and uranium-40 w/o zirconium alloys usually results in lower room-temperature hardness and increased high-temperature hardness. The decreased room-temperature hardness is probably due to improved gamma stability, while the increased high-temperature hardness is a solid-solution hardening effect. Among uranium-niobium-base alloys it is very difficult to make any general statements concerning

effects of alloying on hardness as results have been inconsistent. For instance, a uranium-20 w/o niobium-5 w/o zirconium alloy apparently resists softening at temperatures as high as 900 C while uranium-20 w/o niobium-3 w/o zirconium and uranium-20 w/o niobium-10 w/o zirconium alloys begin to soften appreciably at 500 C. Zirconium additions to uranium-7.5 w/o molybdenum alloys increased hardness at temperatures up to 500 C, but at 900 C showed practically no effects.

From thermal-analysis data, zirconium appears to lower the gamma-to-alpha plus gamma transformation from 634 C in a uranium-10 w/o niobium alloy to 594 C for a uranium-10 w/o niobium-10 w/o zirconium alloy, while 1 to 5 w/o molybdenum additions do not appear to have any appreciable effect. Niobium additions to uranium-40 w/o zirconium alloys lower the temperature of gamma decomposition from 606 C in the binary alloy to around 583 C for a uranium-40 w/o zirconium-3 w/o niobium alloy. Additions of either 3 w/o niobium or molybdenum lower the gamma-decomposition temperature of uranium-30 w/o zirconium alloys from 606 C to 585 C.

Corrosion tests of gamma-quenched alloys in 680 F water are continuing. After 1008 hr of exposure, surviving alloys exhibit weight losses as tabulated below:

Alloy (Balance Uranium), w/o	Total Weight Loss, mg per cm^2
10 niobium-3 molybdenum	392.0
20 niobium	33.7
20 niobium-5 zirconium	13.9
7.5 molybdenum-2 ruthenium	13.6

Transformation-kinetics studies are continuing, but studies of the additional uranium-molybdenum-base alloys prepared are incomplete, as are the studies being made at 480 C on uranium-niobium-base alloys. Final data are expected shortly.

Preparation of Uranium-Niobium Alloys

J. B. Melehan, E. L. Foster, and R. F. Dickerson

The uranium-niobium system is being studied to find and develop alloys for use in reactor fuel elements. A notable benefit to be gained by adding niobium to uranium is the improvement of high-temperature mechanical properties without an intolerable increase in neutron-absorption characteristics. The principal objectives of this study are the development of techniques for obtaining the alloys in satisfactory form, purity, and metallurgical condition, and the determination of certain properties such as mechanical properties and corrosion resistance in various media.

At Battelle and other sites previous efforts in the preparation of uranium-rich uranium-niobium alloys have encountered difficulties in obtaining homogeneous material. The extreme reactivity of the molten alloys with ceramic crucibles and mold materials results in undesirable contamination. Impurity pickup is minimized by employing the consumable-electrode arc-melting method. However, a disadvantage of this technique is the segregation of the alloy during solidification with the formation of a banded macrostructure. At an alloy content of 10 w/o niobium, the segregated material

exhibits nonuniform corrosion resistance in superheated water and it is expected that similar nonuniformities exist in mechanical physical properties. Recent work has shown that the banding phenomenon persists throughout the composition range 20 to 80 w/o niobium. The present efforts in this program have been concerned with eliminating or minimizing alloy segregation by modification of the melting techniques and/or by fabrication or heat treatment.

Melting studies consisted of preparing ingots of the alloys uranium-20, -40, and -80 w/o niobium by the consumable-electrode method. The ingots, 4 to 6 in. long by 2 in. in diameter, were generally of uniform composition but exhibited local segregation with banding transverse to the ingot axis. An attempt was made to melt the uranium-20 w/o niobium alloy by the consumable-electrode method using a ZrO_2 sleeve to prevent contact between the ingot and the walls of the water-cooled furnace crucible. The ZrO_2 liner was attacked and melted and the ingot was of poor quality. Because of the higher melting temperatures required, this experiment was not extended to the higher niobium alloys.

Fabrication experiments have been restricted to the rolling of uranium-20 and -80 w/o niobium alloys. Two cylinders of the former, 3/8 in. in diameter by 3/4 in. long, were sealed in titanium and hot rolled at 650 C. The final specimen thickness was about 0.080 in. No difficulty was encountered in fabricating under these conditions; however, the specimen surfaces were rough with substantial waviness. The specimen edges were dressed on an emery wheel to remove larger imperfections and fabrication was then continued by cold rolling. Only minor reductions were possible at room temperature and both specimens eventually cracked. A single specimen of the alloy uranium-80 w/o niobium similar in geometry to the uranium-20 w/o niobium specimens was sealed in molybdenum and rolled at 1000 C with 10-mil reductions per pass. The capsule cracked in the early stages but fabrication was continued until the alloy specimen was exposed. The final specimen, 165 mils thick, was fractured during removal from the capsule; however, it is apparent that efforts to roll the uranium-80 w/o niobium alloy were at least partially successful, as were experiments with the uranium-20 w/o niobium alloy.

Experiments are under way to study the elimination of segregation by homogenization heat treatments. Heat treatments carried out to date are tabulated below:

Niobium Content (Balance Uranium), w/o	Specimen	Temperature, C	Time at Temperature, hr	Atmosphere	Cooling Rate
20	20-2A	1000	4	Hydrogen	Water quench
20	20-1A	1000	24	Hydrogen	Water quench
20	20-3A	1200	8	Vacuum	Furnace cool
40	40-3A	1223	8	Vacuum	Furnace cool
80	80-3A	1650	8	Vacuum	Furnace cool

Microstructure examination revealed that dendritic structures remained in all specimens after heat treatment. However, the uranium-20 w/o niobium specimens show an increasing deterioration of the cored structure with increasing severity of heat-treatment conditions. Heating at 1200 F for 8 hr is sufficient to remove all but a few traces of the dendritic structure. Despite the removal of the microscopic coring, radiographic evidence shows that macrosegregation of the constituents remains and that interdiffusion has not significantly reduced concentration gradients responsible for banding.

F-4

Melting studies are being continued with attention being directed to the skull-melting technique as a possible means of preparing homogeneous ingot material. If efforts to produce small experimental ingots are successful, the design of equipment for larger scale experiments may be worthwhile. Investigations into the best techniques for fabricating the alloys will be continued, and some additional experiments are at this time already in progress. Additional homogenization heat treatments are under way and others are being planned. The present plan is to increase the homogenization temperatures to as close to the solidus temperatures as is practicable to determine if it is possible to eliminate alloy segregation by heat treatment. Corrosion and oxidation studies are in the planning stages, and a limited amount of material is now available to begin such experiments.

In addition to standard chemical analysis, a nondestructive method is being employed to measure concentration gradients in the segregated material. A narrow beam (2 μ in diameter) of electrons incident on the alloy specimen results in an X-ray emission, the character of the emission at any given region being dependent on the concentration of the alloying elements. With this method, it should be possible to determine the alloy composition across the banded areas.

Mechanism of Aqueous Corrosion

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

The aqueous corrosion of uranium is being investigated to aid in understanding the corrosion mechanism. Since previous analysis of the corrosion products failed to account for all the metal consumed, assuming the solid products to be UO_2, the studies during the past year have been concentrated on a better identification of the solid corrosion product. Chemical analyses indicated an average valence of uranium in the oxide of less than +4, while X-ray absorption methods indicated the bulk of the corrosion product has a valence of +4 or greater. More recent X-ray diffraction studies have revealed particles of metallic uranium dispersed in the oxide produced at a temperature of 100 C. Thus, it appeared that the lack of a material balance in the corrosion reaction may have been due to incorrect assumptions in regard to the amount of metal oxidized.

During April, studies were continued on the phases present in the solid corrosion product from boiling-water corrosion of dingot uranium. The identification of metallic uranium in the corrosion product was verified. However, in order to retain the metallic particles by preferential dissolution of the oxide, it was found necessary to maintain careful control of the nitric acid concentration. Acid solutions containing more than 10 cm^3 HNO_3 to 100 cm^3 H_2O tend to dissolve the small metallic particles, whereas too dilute a solution fails to dissolve some of the oxide particles. In nearly all samples examined after the dissolution treatment, unidentified diffraction lines were observed. During the next month, the source of the unidentified phases will be sought.

37

F-5 and F-6

Studies are continuing on determining the nature of the newly formed oxide on uranium exposed in steam at 200 C. A thin wire of uranium inserted in a glass capillary tubing was reacted with 200 C steam until completely converted to oxide. The tubing was then sealed. X-ray diffraction analysis of the corrosion product revealed only UO_2. Because of the high density of UO_2, the X-ray beam was able to identify reaction products at the surface. Any subsurface reaction products would not be revealed by this method. A modified technique is being considered for further study.

G. FATIGUE STUDIES OF INCONEL AND INOR-8

W. S. Hyler and R. J. Favor

Fatigue Studies of Inconel

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 first phase of the over-all program has been completed. This includes conventional axial-load studies at 1200, 1400, and 1600 F. The results of this phase are being summarized in a topical report.

The current phase of this program is concerned with the measuring and recording of strain associated with the cyclic portion of a combined load. During April, work was centered on the design of a suitable specimen and extensometer system. It is expected that during May fabrication of a specimen and extensometer system will be completed. In addition, some modification of the fatigue machine is planned.

Fatigue Studies of Inor-8

A program to evaluate the fatigue properties of the alloy Inor-8 has been initiated. The broad implications of this program include exploration of the effects of stress concentrations and metallurgical variables.

During the remainder of the fiscal year, modification of fatigue machines and furnaces to accommodate temperatures up to about 1500 F are planned. Initial evaluation of the alloy will be made at 1250 F. In addition, exploration of the effect of speed of testing will be carried out in an effort to arrive at maximum feasible speed at which the machines can be operated without affecting results.

In April, the test material was received. This has been heat treated and is now being fabricated into specimens. The furnace has been reworked to accommodate testing temperatures up to about 1500 F. Other modifications to the fatigue machine are also being completed.

During May it is expected that assembling and checking of equipment will be completed. Subsequently, initial studies of Inor-8 will begin.

H. REACTOR MATERIALS AND COMPONENTS

F. A. Rough and A. W. Hare

Various parts of the program of the AEC Division of Reactor Development are reported in this section.

Routine progress is reported on the research concerned with the development of oxidation-resistant niobium alloys. Oxidation data for niobium and various niobium alloys in dry air are reported.

Experimental work is reported on the investigation of valence effects of oxide solutions in uranium dioxide. Also reported is the routine progress on the programs concerned with high-temperature high-pressure solid-state studies, rubbing surfaces in sodium environments, and the basic studies of pressure bonding, both analytical and experimental.

Oxidation-Resistant Niobium Alloys

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

This investigation is concerned with the oxidation reactions of pure niobium and the mechanisms by which various alloying additions affect these reactions. Current work includes oxidation testing of various binary and ternary alloys, material-balance calculations on previously oxidized alloys, and preparation of new alloys.

Binary alloys containing chromium, iron, rhenium, and tungsten were oxidized by continuous weighing to confirm previous tests and test the application of some oxidation principles previously suggested. Results are given in Table H-1. The niobium-4.5 a/o chromium alloy, tested in the as-cast condition, formed a partially protective scale at 1000 and 1200 C and oxidized slower than pure niobium, although not as slow as the best binary alloys. These tests partially confirm earlier intermittent weighing-test-results, which indicated a minimum oxidation rate in this system at 15 a/o chromium. Niobium-5 a/o iron oxidized linearly at a slightly greater rate than niobium-1 a/o iron. Iron additions were investigated on the basis of the smaller size of Fe^{3+} (0.64 A) compared with Nb^{5+} (0.69 A), which would suggest improved oxidation resistance through the "size-effect" principle. The decrease in oxidation resistance probably indicates the presence of Fe^{2+} (0.74 A) rather than Fe^{3+}, which would increase the oxidation rate. The addition of 5 a/o rhenium significantly increased the oxidation rate of niobium. Since these alloys were smoking on removal from the test furnace, it is probable that volatilization of low-melting (297 C) Re_2O_7 caused the decrease in oxidation resistance. This factor obscured the possible beneficial effects which might be expected of rhenium because of its high valence (+7) and small ionic size (0.56 A). A niobium-12.5 a/o tungsten alloy oxidized linearly at 1000 C, but formed a scale which was protective at 1200 C for at least 6 hr. These tests confirm previous results which indicate that tungsten is more effective at 1200 than at 1000 C, and also show that the period of protection at 1200 C increases with increasing tungsten content. If the Goldschmidt ionic radius for W^{6+} (0.62 A) is used rather than the

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

Sample	Composition (Balance Niobium)[a], 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 Indicated Exposure, 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-131	4.5Cr	1000	59.4	0.25	6.8	10.4	17.6	24.1	30.3	36.2	41.8
O-111	5Fe	1000	--	0	26.1	31.5	57.1	79.5	99.5	--	--
O-119	5Re	1000	--	0	77.7	73.7	--	--	--	--	--
O-129	12.5W	1000	114	0.1	34.1	32.5	--	--	--	--	--
O-123	16.5Ti-4.5Mo	1000	49.7	>6	--	8.0	10.8	12.9	14.8	16.2	17.7
O-121	21.5Ti-6Mo	1000	46.3	>6	--	6.6	9.3	11.5	13.6	15.3	17.0
O-127	10Ti-3V	1000	54.6	1.2	2.89	7.5	11.3	14.5	17.5	20.3	23.3
O-125	24Ti-11V	1000	49.3	0.45	10.1	8.3	16.4	25.7	36.1	46.5	56.4
O-133	5.5Mo-8V	1000	38.5	>6	--	7.0	9.4	11.2	12.7	14.0	15.3
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-132	4.5Cr	1200	576	0.15	23.2	31.0	56.2	79.4	101.9	122.0	141.1
O-118	5Fe	1200	1900	0.25	47.6	59.5	99.0	--	--	--	--
O-120	5Re	1200	--	0	(67)	70.9	--	--	--	--	--
O-130	12.5W	1200	786	>6	--	26.5	38.6	47.8	55.4	61.9	68.0
O-124	16.5Ti-4.5Mo	1200	235	0.05	(13)	24.0	39.4	52.4	63.6	73.5	82.0
O-122	21.5Ti-6Mo	1200	238	0.25	15.6	19.6	30.5	38.7	45.4	52.0	57.4
O-128	10Ti-3V	1200	535	0.4	16.6	27.0	44.2	59.6	74.2	87.0	--
O-126	24Ti-11V	1200	271	0.15	18.5	23.2	43.2	60.2	74.6	--	--
O-134	5.5Mo-8V	1200	365	4	5.5	17.8	26.7	33.0	37.9	43.7	--

(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 included for comparison.

(c) Rates in parentheses are estimated.

extrapolated Pauling crystal radius (0.83 A), the 1200 C improvement in oxidation behavior can be correlated with the size-effect principle. Tungsten appears to be an excellent addition for improving the 1200 C oxidation behavior.

Oxidation tests have also been completed on four niobium-titanium ternary alloys and one niobium-molybdenum-vanadium ternary alloy. All five alloys exhibited comparatively high oxidation resistance, but only the niobium-5.5 a/o molybdenum-8 a/o vanadium showed superior oxidation behavior compared with the best binary alloys. The scale on this alloy was protective for at least 6 hr at 1000 C and 4 hr at 1200 C. The behavior of this alloy suggests that the beneficial effects of those elements which improve oxidation resistance via size effects in the scale may be additive.

Niobium-16.5 a/o titanium-4.5 a/o molybdenum and niobium-21.5 a/o titanium-6 a/o molybdenum had greater oxidation resistance than niobium-10.5 a/o titanium-3 a/o molybdenum, reported in BMI-1259, but crystals which appeared to be MoO_3 were noted near the top of the furnace after testing these latest two alloys. The absence of an improvement over the best binary alloys plus this indication that MoO_3 is volatilizing from the scale suggests that molybdenum is not a good ternary addition to niobium-titanium alloys.

The two niobium-titanium-vanadium alloys were less oxidation resistant than niobium-17 a/o titanium-6.5 a/o vanadium, reported in BMI-1259. The optimum composition in this system thus lies between 10 and 24 a/o titanium and 3 and 11 a/o vanadium.

Several conclusions may tentatively be drawn from the results on ten ternary alloys tested to date:

(1) The solubilities of chromium, molybdenum, and vanadium are lower in Nb_2TiO_7 than in Nb_2O_5.

(2) The niobium-titanium-chromium and niobium-titanium-vanadium alloys are most attractive, since the parabolic rates which were followed for 60 to 80 min at 1000 C indicate weight gains as much as 60 per cent lower than weight gains on the best binaries.

(3) The solubilities of molybdenum and vanadium in Nb_2O_5 are not appreciably reduced in ternary niobium-molybdenum-vanadium alloys.

Material-balance calculations on niobium-zirconium binary alloys have shown that formation of the visible outer scale at 1200 C is not the predominant reaction, as was previously assumed. Instead, these calculations indicate that at 25 a/o zirconium 30 per cent of the oxygen reacted to form ZrO_2 subscale, while at 45 a/o zirconium 55 per cent of the oxygen was reacted into the subscale. The rates of exterior-scale formation on these alloys are appreciably lower than previously indicated.

Future work includes:

(1) Completion of oxidation tests on two remaining ternary alloys.

(2) Preparation and testing of cast niobium-15 a/o molybdenum and niobium-10 and -20 a/o chromium alloys (unfabricable) to complete tests on binary alloys.

(3) Continuation of material-balance calculations.

Valence Effects of Oxide Solutions in Uranium Dioxide

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

In microbalance studies, UO_2 with 50 w/o ThO_2 in solid solution was compared with the prior UO_2-La_2O_3 bodies. It was found that upon exposure to air at 1540 C, the sample started to decrease in weight at a linear rate of 3.5 μg per min over a period of 7 hr.

Since the microbalance sample was too small for accurate chemical analysis, massive samples are being fired in air at 1375 C to determine the cation ratio before and after extensive air oxidation. This is being done to determine what difference there is, if any, between the volatile components arising from solid solutions containing trivalent and tetravalent additives. While replacing a heating element which failed after 42 hr, the samples were visually inspected. The UO_2-60 w/o La_2O_3 was intact but had changed color to deep red, indicating oxidation, whereas the UO_2-50 w/o ThO_2 had shattered. The reason for the behavior of the UO_2-ThO_2 is not as yet clear, but would appear to arise from the fact that oxidation had either changed and produced internal strains, or had effected a high-temperature transformation.

High-Temperature High-Pressure Solid-State Studies

W. B. Wilson and C. M. Schwartz

Trial runs at high temperatures and high pressures were carried out on UO_2, BeO, and La_2O_3 samples previously. These preliminary tests were conducted in the right-circular-cylinder die apparatus to establish if the sample heater and insulator configuration would perform satisfactorily. The tests indicate that the BeO and BeO-plus-UO_2 reactions may be studied using the present configuration.

In some instances use of a graphite heater would result in conversion of the sample material to carbide, and modification would be required to avoid such undesirable side reactions.

Since it was believed desirable to determine the effect of pressure and more moderate temperatures on pure materials with greater freedom from contamination

problems, a simple "Bridgman anvil" unit with furnace has been assembled. This unit will make available facilities for use in another area of the pressure-temperature region. It is capable of higher pressures than the unsupported cylinder at low temperature, but is limited where high temperatures are needed for reactions involving refractory materials.

Additional work was conducted testing the Bridgman anvil unit and attempting to reduce the 18 per cent friction found in the right-circular-cylinder die unit.

Rubbing Surfaces in Sodium Environments

J. W. Kissel and J. H. Stang

Coefficient-of-friction data were obtained for a 1/4-in.-diameter WC-20 w/o cobalt polished ball sliding across a horizontally moving flat plate of the same material. The normal load at the contact area was about 145,000 psi maximum and 98,000 psi average. Dry friction coefficients were obtained at various temperatures up to 800 F; at this point, molten sodium was dropped on to the lower (flat) specimen. Coefficients for the sodium-immersed surfaces were than obtained at numerous temperatures for several temperature cycles during a week's period. Friction coefficients were around 0.3 for dry sliding at temperatures up to 800 F and 0.3 to 0.45 for sodium-lubricated surfaces, over the same temperature range — both in an argon atmosphere. Measurements made at higher temperatures, for sodium-lubricated tests, indicated a rapid increase in friction above the 1000 to 1100 F range. The maximum coefficients recorded were about 0.83 at 1200 F.

The most interesting aspect of the data for the sodium-immersed specimens is the marked increase in friction at the higher testing temperatures. After the runs, wear tracks could not be found on the flat specimen for runs involving dry friction. On the other hand, clearly defined tracks resulted for all of the sodium-lubricated runs; these were more pronounced at the high temperatures. After alcohol and water washes, these tracks became quite faint and were found, by microscopic examination, to be confined to a layer of fine crystals, regularly distributed over the surface. In the wear-track area, these crystals had a polished appearance indicating that sliding took place between layers of crystals rather than between the base specimen materials. The composition and source of the deposited crystals is unknown, although their disposition suggests an intergranular corrosion product.

Pure molybdenum will be utilized for the next pair of test specimens. Because of the inertness of molybdenum in elevated-temperature sodium, the opportunity for surface films formed through a corrosion process should be minimized. Thus, data on the molybdenum specimens may, when compared with the previous data, help to provide an understanding of the contribution of surface films to friction behavior.

H-6

Basic Studies of Pressure Bonding

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

An investigation is being conducted in an effort to obtain an understanding of the mechanisms of pressure bonding. Particular emphasis is placed on the analysis of the deformations associated with external hydrostatic pressure, in order to determine the conditions under which surfaces will attain the intimate contact required for bonding.

Analytical Studies of Pressure Bonding

The deformations of surface irregularities are considered in terms of the creep properties of the materials. If the original surface roughness is thought of as a set of hemispherical voids it is possible to apply creep theory to predict the amount of collapse which will occur under prescribed bonding conditions. While the creep mechanism alone cannot account for complete closure of the holes, it may provide a basis on which to select the bonding conditions.

In order to obtain the material constants needed to analyze the creep behavior of the materials a simplified model has been utilized. The collapse of an axial hole in a circular cylinder can be analyzed in terms of the creep constants of the material. Steady-state creep, and a simple dependence of creep rate on a power of the stress are assumed.

The experimental measurements of collapse were used to determine the creep constants for 2S aluminum at 500 F. On account of wide scatter in the experimental results it is difficult to determine whether or not the steady-state assumption is valid. Experiments are being planned in which the predicted closure of voids in terms of the creep constants can be compared with the actual amount of closure. These experiments should indicate the reliability of the creep model used.

The cylindrical model used to obtain the creep constants has certain inherent disadvantages. One of these is the changing geometry of the specimen while the deformation is taking place. Secondly, it is impossible to measure the creep rate; only the final deformation can be measured. These disadvantages are counterbalanced, somewhat, by the advantage that the cylindrical specimen is subjected to a combined stress state similar to that which acts on the surfaces to be bonded; the extent to which this advantage outweighs the disadvantages is unclear. It is possible that an alternative model could be used which will give the desired information with greater accuracy and with fewer experimental difficulties. Consideration is presently being given to the finding of such an alternative.

Experimental Studies of Pressure Bonding

The work on this program is directed toward acquiring experimental data which can be correlated with the theoretical values calculated on the basis of postulated mathematical models. As prescribed by the analytical studies, thick-walled tubular

aluminum specimens are externally pressurized under various sets of pressure-bonding parameters in order to study the flow characteristics of metals during a pressure-bonding process.

During April, metallographic measurements of deformation were completed for specimens which had been previously subjected to pressure-bonding parameters of 4000 psi at 500 F for periods of 4 and 6 hr; 4000 psi at 700 F for periods of 2, 4, and 6 hr; and 6000 psi at 500 F for periods of 1/2, 1, and 6 hr. The results of these tests and the comparison with previous data indicate that the extent of deformation is most significantly affected by pressure, and least by temperature for the parameters which have been studied.

Additional specimens are being subjected to a pressure of 6000 psi at 700 F for periods of 1/2, 1, 2, 4, and 6 hr. Flat-plate aluminum specimens which will be subjected to time-dependent Vickers hardness determinations at 500 and 700 F are being machined from the bar-stock material used in the preparation of the tubular aluminum specimens. The calculations based on the hot-hardness data obtained from these specimens 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

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

An investigation has been initiated to study the effect of surface preparation on the quality of the bonds obtained during pressure bonding of Zircaloy 2 to Zircaloy 2. From previous experience, it is believed that the bond quality is dependent on prior surface condition of the Zircaloy 2, since a minimum amount of deformation occurs between mating surfaces during the pressure-bonding operation. The objective of this study is to acquire a better understanding of the relationship between surface preparation and bonding, so that an optimum and economical surface-preparation process can be selected. Bonding variables which appear to have an influence on the extent of bonding, such as the cold-worked condition of the metal, surface contamination, surface roughness, and recrystallization and grain growth, will be isolated, and their effect on pressure bonding will be determined. A belt-abraded surface has been selected as the base condition for this investigation.

The Zircaloy 2 stock-plate material being used in this investigation has been obtained from the same ingot and hot rolled at 1150 F from a helium-atmosphere furnace with a total reduction of 2 to 1 followed by alpha annealing under helium at 1550 F for 1-1/2 hr in flattening dies. After annealing, the majority of the plates have been belt abraded on the surfaces to be used subsequently for the surface-preparation studies, and are now in the process of being sheared to specimen size.

In order to obtain information on the effect of surface roughness on bonding, the few remaining plates have been sheared to specimen size, and the specimens are now being individually machined to a different surface roughness.

I-1

I. PHYSICAL RESEARCH

F. A. Rough

Various parts of the program of the AEC Division of Research are reported in this section.

BMI-1259 reported various studies, including those on bonding fundamentals, niobium-hydrogen reactions, and migration of hydrogen in zirconium hydride. Progress on the balance of the projects is reported this month.

In the study of the physical properties of uranium compounds, the thermal-expansion coefficients of UBe_{13} and of UC have been secured.

In the study of uranium ternary constitution, final details of research on uranium-zirconium-silicon alloys are in progress, and research has begun on the effects of oxygen on uranium-niobium alloys.

Additional details of the ternary uranium-nitrogen-carbon system are reported. A determination by neutron diffraction of the structure of UC_2 and further calculations of the carbon-carbon bonding parameter are in progress.

Preparation, Fabrication, and Physical Properties of Uranium Compounds

A. B. Tripler, Jr., M. J. Snyder, and W. H. Duckworth

Methods of ceramic fabrication and fundamental properties of some refractory uranium compounds which are potential nuclear fuels are being studied.

Linear-thermal-expansion measurements were made in the range 68 to 1800 F on sintered specimens of UBe_{13} and UC. The bulk densities of the specimens were 97 and 95 per cent of theoretical, respectively. The measurements were made in a recording, vertical, quartz-tube dilatometer under a vacuum of approximately 5×10^{-5} mm of mercury. A heating and cooling rate of approximately 5 F per min was maintained throughout the measurements. Table I-1 contains the mean-linear-thermal-expansion coefficients for the specimens over the temperature ranges shown. Both materials show a larger coefficient than UO_2 (about 5.6×10^{-6} per F in the range 32 to 1800 F) and a smaller coefficient than uranium (11×10^{-6} per F for the range 80 to 1220 F as determined by X-ray, and 10.9×10^{-6} per F for the range 68 to 1100 F as determined by dilatometer).

Preparatory to measuring the thermal expansion, the specimens were machined by grinding. No difficulty was encountered in grinding the UBe_{13}. With the UC specimen there was a tendency to pull out tiny particles, and although this tendency was minimized by taking small cuts, it was not overcome.

TABLE I-1. MEAN-LINEAR-THERMAL-EXPANSION COEFFICIENTS FOR SINTERED UBe_{13} AND UC SPECIMENS

Temperature Range, F	Mean Coefficients Over the Temperature Ranges Shown, 10^{-6} per F			
	First Cycle Heating	First Cycle Cooling	Second Cycle Heating	Second Cycle Cooling
		UBe_{13}		
68-200	7.2	7.3	7.1	7.7
68-400	7.6	7.6	7.4	8.0
68-600	8.0	7.9	7.8	8.3
68-800	8.4	8.2	8.3	8.5
68-1000	8.7	8.4	8.6	8.7
68-1200	8.9	8.7	8.9	8.9
68-1400	9.1	8.9	9.0	9.1
68-1600	9.1	9.1	9.2	9.2
68-1800	9.1	9.4	9.3	9.5
		UC		
68-200	6.9	6.7	7.1	7.0
68-400	7.0	7.0	7.1	7.1
68-600	7.2	7.2	7.3	7.2
68-800	7.3	7.3	7.6	7.5
68-1000	7.6	7.5	7.7	7.7
68-1200	7.6	7.6	7.9	7.8
68-1400	7.6	7.7	7.9	7.9
68-1600	7.6	7.9	8.0	8.0
68-1800	7.4	8.1	8.0	8.1

I-3

The electrical resistivity of sintered UBe_{13} has been determined as 113 microhm-cm at 27.6 C.

A method has been developed for electroplating nickel on the sintered UBe_{13}. The nickel electrodeposit makes it possible to tin the ends of the specimens for thermal-conductivity measurements. Attempts to electroplate on UC have not been successful. In order to insure good thermal contact with the sintered UC, the ends will be coated with indium, applied by a loaded-wheel technique.

Constitution of Uranium-Base Ternary Alloys

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

An investigation of the uranium-zirconium-molybdenum system has been confined to alloys whose compositions lie on a ternary cut joining the delta phases of the two uranium binary systems. Phase relationships in the ternary cut have been determined and are essentially as shown in BMI-1220. Work on this system has been concluded and a topical report is being prepared.

The phase relationships existing in the high-uranium portion of the uranium-zirconium-silicon system are also being studied. Data from all the alloys are complete with the exception of those being studied to establish the solid solubility of U_3Si_2 and Zr_3Si_2 and to establish the existence of Zr_4Si. Alloys for these determinations, prepared from electrolytic uranium, crystal-bar zirconium and transistor-grade silicon, have been cast and heat treated. They are now being prepared for metallographic and X-ray diffraction examination.

Phase relationships in the uranium-niobium system are being determined. High-purity niobium and uranium are the starting materials. The effect of oxygen on the gamma-phase immiscibility loop will also be studied. Electrolytic uranium and iodide and bromide niobium are to be employed in the study. The niobium is being prepared. Iodide niobium will be used in preparing the first alloy castings because it is available immediately in limited amounts.

Solid-State Study of Ternary System Uranium-Nitrogen-Carbon

A. E. Austin, A. F. Gerds, and C. M. Schwartz

The objective of this study is to determine existence regions of solid-solution phases of uranium carbides and nitrides. Solid solution extends along the binary join between UN and UC. There is essentially no solid solution of nitrogen in UC_2 or of carbon in U_2N_3. Several compositions were obtained in the two-phase field UC_2 + U(C,N). Reactions of the carbides with nitrogen up to 1600 C gave U_2N_3 + C.

Additional reactions have been carried out to yield compositions in the three-phase field UC_2, U(C,N), and C. Table I-2 gives the heat treatment, final compositions, and phases. According to the unit-cell size, the U(C,N) phase would be about

70 mole per cent UC and 30 mole per cent UN. This composition is about the same as the terminal U(C,N) solid solution for the compositions in the two-phase field UC_2 + U(C,N), as should be expected for a three-phase field.

TABLE I-2. COMPOSITIONS AND PHASES IN URANIUM-NITROGEN-CARBON SPECIMENS

Starting Material	Heat Treatment	Composition, a/o			Phases
		Uranium	Carbon	Nitrogen	
9 g UN + 1 g C	2 hr at 1800 C in argon	30.8	63.3	5.85	U(C,N) a_o = 4.9417 A, + UC_2 + C
1.95 g UN + 7.7 g UC_2	Ditto	31.0	68.5	0.58	UC_2 + U(C,N) + C
UC_2	2 hr at 1800 C under nitrogen at 760 mm mercury	32.0	39.8	28.5	U(N,C) a_o = 4.8923 A, + C
UC_2	2 hr at 2000 C under nitrogen at 760 mm mercury	40.2	48.5	11.35	U(C,N) a_o = 4.9416 A, + UC_2 + C

UC_2 as powder and solid chunks was reacted with nitrogen at 1-atm pressure at 1800 and 2000 C. Table I-2 gives the final compositions and phases. The U(N,C) phase formed at 1800 C is about 90 mole per cent UN according to its unit-cell size. The U(C,N) phase formed at 2000 C is about 70 mole per cent UC. Metallographic examination showed that the reaction at 1800 C gave a single uranium carbonitride phase plus free carbon, while the reaction at 2000 C formed a shell of U(C,N) material around UC_2. The decrease in nitrogen content and presence of UC_2 at 2000 C indicates that between 1800 and 2000 C the nitride becomes less stable than the carbide.

Structure of UC_2

A. E. Austin and C. M. Schwartz

The structure of UC_2 is being reinvestigated in order to determine the positions of the carbon atoms. This information should lead to an interpretation of its thermal behavior and type of uranium-carbon bonding. X-ray and neutron diffraction data have been obtained from UC_2 powder. The data confirm the body-centered tetragonal structure and indicate that the carbon-carbon bonding is of a type between the double and triple bond. Further calculation of the carbon parameter is in progress to refine the positions.

Neutron diffraction data were obtained for uranium sesquicarbide, U_2C_3. According to X-ray data the compound is body-centered cubic in space group $I\bar{4}3d$. However, the neutron-diffraction pattern showed a detectable (200) reflection, which means that the space group choice is incorrect. The data are being further analyzed.

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, W. C. Baytos, 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.

Titanium continues to be a promising material for use in the construction of both the dissolver and the feed-adjustment tank for the Darex process.

Nionel showed sufficient promise during scouting experiments to merit further consideration for evaluation as a container material in the Sulfex-Thorex dissolution process. Carpenter 20 Cb is being evaluated by alternate exposure to the Sulfex and Thorex solutions. At present, the data are not sufficient to draw conclusions as to its merit.

The Inor's, 1 and 8, are under investigation in the molten ZrF_4-NaF bath at present. The new Hastelloy B melt containers for this bath appear to function well.

The Darex Process

Uranium can be recovered from fuel elements containing stainless steel as a diluent or 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 flowing dissolver has been kept in operation, but no examination of the specimens was conducted during the past month.

FAT Studies With Titanium

The various plain, welded, and stressed specimens of Titanium 55A and 75A were examined following 16 weeks of exposure to boiling solutions representing the initial conditions in the feed-adjustment tank. The corrosion rates were small and of the same order as measured at the end of 12 weeks.

One of the hairpin-shaped steam tubes of unalloyed Titanium 55A was removed following slightly over 10 weeks of exposure to the Final FAT solution. A portion of the tube on both sides of the meniscus under the large deposit that accumulates there was removed and sectioned. Metallographic examination revealed no necking down of the thickness of the specimen tube nor any changes in its microstructure that might indicate

serious attack occurring beneath this deposit. The tube was welded together and replaced on test.

A Titanium A-40 steam tube was cleaned and examined for the first time after 9 weeks of exposure to the Final FAT solution. The usual accumulation of deposit had occurred at the meniscus, and the crystalline coating had formed beneath the surface of the liquid, but removal of these revealed a surface, unattacked, as far as could be discerned.

Other steam tubes are still being exposed and were not examined during the month. A study of the problems associated with the removal of the crystalline deposit which occurs below the surface of the solution on these tubes will be started soon. It is thought that this deposit may interfere with heat transfer, and a suitable means of remote removal will be desirable.

The Sulfex-Thorex Process

Various metals are being evaluated for use as container materials for the dissolution step of a proposed Sulfex-Thorex 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 $Th(NO_3)_4$.

Scouting experiments with Nionel specimens have indicated that this alloy merits further evaluation for use as a container material. Other experiments, in which Carpenter 20 Cb specimens were exposed to Final Thorex solutions containing 0.1 and 0.2 M thorium additions, show that 0.2 M additions reduce the corrosion more than 0.1 M, but neither are so effective as corresponding additions of aluminum.

A cyclic study has been started with Carpenter 20 Cb specimens being cycled between boiling Sulfex and Thorex solutions. Twenty cycles have been completed. In Study 1, the specimens are exposed for 3 hr in 6 M H_2SO_4 followed, after careful rinsing, by a 5-hr exposure in Final Thorex solution containing 0.2 M aluminum. In Study 2, a similar time cycle is maintained between boiling solutions of 4 M H_2SO_4 and Initial Thorex containing 0.2 M aluminum additions.

In both studies, the highest corrosion rates were measured for the liquid-phase specimens. All the corrosion rates are decreasing with continued exposure. In Study 1, the rate in the liquid started at about 3 mils per month and is now below 2, while in Study 2 the rate has been consistently higher, starting near 5 and decreasing nearly to 2. The corrosion rates based on the combined weight losses of two sets of specimens which have not been cycled but which, taken together, have endured the same amount and type of exposure as the cycled specimens, are always higher than those based on the comparable cycled specimens. In other words, cycling does not impose a more severely corrosive sequence than the combined forces of the two conditions.

There is an indication that at least the particular Carpenter 20 Cb stock being used for these specimens shows transcrystalline corrosion after exposure in the sulfuric acid solution at points subjected to deformation stress prior to the beginning of the exposure. The exact nature and severity of this attack is one of the objectives of investigation at present.

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. An alternate bath of molten LiF-NaF may be employed. A material of construction for this hydrofluorinator is being sought.

Two runs are under way in the new melt containers constructed from Hastelloy B. Both are being conducted in the molten ZrF_4-NaF bath. Specimens of Inor-1 and Inor-8 are under study. Present plans call for inspection of these specimens at the end of 500 hr of exposure. At this time, specimens will also be inserted in the vapor phase. The third melt container will be filled with a LiF-NaF mix and one of the two Inor's will be studied in this system. The new design of the melt container seems to be functioning well. If this performance continues, several more will be constructed along the same design.

L. STUDIES OF SODIUM-TANTALUM COMPATIBILITY AT ELEVATED TEMPERATURES

J. H. Stang

Studies to determine creep characteristics of tantalum in sodium and in inert-gas environments and an investigation of problems associated with the welding of tantalum are being supported by Los Alamos Scientific Laboratory. The information sought is pertinent to the LAMPRE development program; this reactor concept is based on the containment of a plutonium-alloy fuel in a small sodium-cooled all-tantalum vessel.

Recently, creep data for tantalum specimens simultaneously stressed and exposed to 1200 F flowing sodium have indicated that the sodium environment has a beneficial effect on strength. Reasons for this unexpected trend cannot be advanced on the basis of present knowledge. In inert-atmosphere creep tests, additional data for tantalum specimens stressed at 900 and 1500 F are reported. At the lower temperature, creep has been negligible at 20,000 and 25,000 psi; the same is true at 1500 F for loadings up to 8,000 psi.

Currently, an objective of the welding research is to demonstrate conclusively that a relatively high carbon content improves the soundness of tantalum welds. Also of interest are further explorations into the use of ultrasonic excitation to reduce weld grain size. During April, an apparatus capable of introducing a large amount of ultrasonic energy was constructed and successfully run.

Tantalum-Sodium Compatibility Studies

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

Small forced-convection polythermal loop systems fabricated of Type 316 stainless steel are being employed to procure information related to the effects of sodium exposure on the creep behavior of tantalum. In each of these loop systems, a tantalum specimen is simultaneously stressed and exposed to 1200 F low-oxygen-content (<10 ppm) flowing sodium. The creep of the specimen is monitored during the exposure.

At the end of April, four of the five experiments conducted during the month were still in progress. These experiments utilized arc-cast tantalum specimens strengthened to prevent deformation in the grip portions (as was discussed in BMI-1259). Creep data from these experiments are presented in Table L-1. The creep rates are somewhat lower than those previously established for 1200 F arc-cast tantalum stressed in helium. This evidence of increased strength in sodium is surprising. The only known major change in tantalum from exposure to low-oxygen sodium is a reduction in oxygen level and a corresponding decrease in hardness. In general, such changes in a material should produce lowered strength at elevated temperatures.

TABLE L-1. CREEP DATA FOR ARC-CAST TANTALUM OBTAINED DURING EXPOSURE TO HIGH-TEMPERATURE SODIUM

Loop Conditions:

Exposure Temperature	1200 ± 10 F
Fluid Temperature Cycle	Approximately 80 F and 160 F
Flow Rate	Approximately 1/2 fps

Stress, psi	Time in Progress, hr	Time to Reach Indicated Percentage Deformation, hr				Total Deformation, per cent	Minimum Creep Rate, per cent per hr
		0.1	0.2	0.5	1.0		
20,000[a]	258[c]	2	5	--	--	0.40	<0.0001
22,000[b]	537	4	240	--	--	0.40	<0.0001
26,000[b]	367	0.6	3	12	264	1.07	0.0014
26,000[b]	211	0.5	1.8	7	18	1.65[d]	0.0006
26,000[a]	65	0.3	0.8	4	--	0.90	--

(a) Fluid temperature cycle, 160 F.

(b) Fluid temperature cycle, 80 F.

(c) Terminated because the creep was negligible (remaining experiments still in progress).

(d) The first-stage creep for this experiment was higher than was the case for its duplicate. Thus, the total deformation at the end of 211 hr was relatively high.

While it is difficult to see how either the particular lot of tantalum employed or the specimen-loading and creep-monitoring system being used could be responsible for this unexpected effect, these possibilities are to be thoroughly checked out. In addition, consideration will be given to planning of experiments that can provide information which can help to explain the apparent increase in strength caused by sodium exposure.

High-Temperature Mechanical Properties of Tantalum

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

Preliminary experiments with the recently modified vacuum-induction furnace have indicated that fairly large (several hundred grams) tantalum specimens can be degassed at 4800 F without difficulty. Substitution of clear quartz for Vycor in the water-cooled furnace jacket and elimination of radiation shields have provided substantial improvement in operating characteristics. Work is in progress to obtain a sufficient stock of thermally degassed tantalum for cold rolling to strip, machining into creep-test specimens, and recrystallizing by annealing to produce a fine-grained structure.

A lot of tantalum, which was produced by the electron-beam melting technique, has been received. According to the manufacturer's specifications, the product supplied was to be quite low in interstitial content and was to have a hardness corresponding to the 40 to 60 VHN range. Hardness measurements on a transverse section of the ingot, however, showed values of about 83 VHN. Chemical analyses are being made to determine whether certain interstitials are contributing to the higher-than-expected hardness.

Creep tests (in helium) on annealed arc-cast tantalum sheet specimens at 900 and 1500 F are continuing. The loads at both temperatures have been increased after periods of about 300 hr. The results have indicated that at 900 F creep was negligible at loads of 20,000 and 25,000 psi; loadings of 30,000 and 40,000 psi produced minimum creep rates of approximately 0.00004 and 0.00046 per cent per hr, respectively. Data obtained at 1500 F show negligible creep with loadings of 5000, 6000, and 8000 psi. A loading of 10,000 psi produced an approximate minimum creep rate of 0.00003 per cent per hr.

Weldability of Tantalum for High-Temperature Systems

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

Recently, the investigation of the cause of porosity in welds of tantalum has been concerned primarily with ascertaining the influence of various carbon levels. Prior tests indicated that porosity in tantalum welds can be reduced markedly merely by covering the weldment surfaces with graphite before welding. The recent studies were

designed to increase the carbon content of a low-carbon unweldable lot of tantalum by exposing the sheet material to a CH_4 atmosphere at elevated temperature. As a result of this treatment, carbon was adsorbed on the surface of the tantalum specimens; however, subsequent heat treatments at 1000 C (in argon) did not diffuse the carbon to the center of the sheet. It is suspected that any oxygen in the system during the homogenization treatment could have removed some of the added carbon from the samples since, at 1000 C, tantalum carbide will react with oxygen to produce tantalum oxide and carbon monoxide. At present, additional studies are in progress to add an excess of carbon to combine with any oxygen that might be in the system at the time of homogenization. Plans are to study the effects of three levels of carbon. Once the carbon is diffused into the tantalum, an analysis of the material will be made and welding studies will be performed.

The use of ultrasonic excitation has reduced the grain size of arc welds of tantalum. However, weld-metal expulsion (when excitation takes place during welding) and reproducibility have been a problem. These difficulties have been attributed to the method of coupling the acoustical horn (ultrasonic source) to the test specimen. To obtain a better couple, a new horn containing a slit to accommodate the tantalum specimens has been designed and evaluated. This newly designed horn has given specimen displacements of approximately 1 mil at a 20 per cent power factor, whereas the old horn was capable of imparting a maximum motion of only 0.5 mil at a power factor of 100 per cent. In addition, the new design has minimized extraneous transverse motion, which appears to have caused weld-metal expulsion. At present, studies are being made of the effect of stress imparted by the new acoustical horn on grain size.

The major effort in resistance welding consisted of the preparation of tubes and header stock for an evaluation of the most promising joint designs. Most of the machining work has been completed, and it is expected that additional welded samples will soon be available for testing and examination.

M-1

M. DEVELOPMENTAL STUDIES FOR THE PWR

R. W. Dayton

Flow studies in the PWR model have been resumed with attention being concentrated on mixing in the lower plenum. Improvements in mixing have been obtained, but at the expense of increases in pressure drop. Studies are being continued to obtain more efficient design configurations.

Studies of the X-ray photometer are continuing. The shielding is being improved; sensitivity tests are in progress.

Studies of the gas-pressure bonding of plate-type oxide elements are continuing with the study of a two-step process, alpha-phase bonding at a low temperature to produce a partial bond followed by beta annealing to complete the bonding. Early results are encouraging, and several radiation samples have been prepared.

Reactor-Flow Studies

L. J. Flanigan and H. R. Hazard

Studies in a quarter-scale air-flow model of the PWR are being conducted to determine the effects of lower-plenum geometry on mixing and on flow distribution in Core 2. Previously reported work includes flow studies with the 9-ft core design, relocation of the model and test apparatus in a new laboratory building, installation of a perforated flow baffle to be used to simulate a 7-1/2-ft core design, and preliminary core-flow distribution and mixing studies.

During the past month, mixing in five different lower-plenum configurations was studied. The first configuration was the basic 7-1/2-ft core design. The mixing was poor. The major portion of the flow from the traced inlet passed through the core in the quadrant adjacent to that inlet. The maximum concentration of air from the traced inlet found in one simulated fuel assembly was 99 per cent. The static pressure drop between the inlet pipe and a point downstream of the flow baffle was 8.1 in. of water.

In the second configuration, turning vanes were attached to each inlet to produce a vortex in the lower plenum. A 4-in.-ID ring having straight vanes 1 in. wide, spaced 11/16 in. apart, and inclined 45 deg was installed over each inlet. These vanes directed the flow tangentially around the bottom dome. With this configuration the maximum amount of fluid from the traced inlet found in any fuel assembly was reduced to 79 per cent, but the static pressure drop between the inlet duct and downstream of the flow baffle was 31.2 in. of water.

Configuration 3 was designed to maintain vortex flow in the lower plenum, but with lower pressure loss. A ring of 18-3/4-in. diameter was installed on the flow baffle; sixty vanes 3/4 in. wide were attached to the ring at 1-in. intervals. The vanes were positioned at an angle of 60 deg from a radius and extended from the flow baffle to a circle on the bottom dome tangent to the bottoms of the inlets. With this configuration

the maximum amount of fluid from the traced inlet found in any fuel assembly was 65 per cent. The static pressure drop between the inlet pipe and downstream of the flow baffle was 16.7 in. of water. With Configuration 3, some of the fluid passed through holes in the flow baffle located outside the turning-vane ring, without flowing through the vanes. In Configuration 4, these holes were plugged with masking tape. Results of the fourth mixing study showed that the maximum amount of fluid from the traced inlet was 58 per cent. The fluid from the traced inlet was well distributed over the core with the exception of an area in Regions 3 and 4 about 45 deg from the traced inlet opposite from the direction of rotation of the fluid. The static pressure drop between the inlet and the bottom of the core was 18.7 in. of water. An analysis of pressure distribution data indicated that the fluid from any inlet flowed about 45 deg in each direction in the space between the vanes and the bottom dome and then passed through the vanes.

In Configuration 5, to obtain both traced air and clean air 90 deg in each direction from an inlet, horizontal dividers were placed in the space outside the vaned ring, extending from the top of one inlet to the bottom of the adjacent inlet. This configuration eliminated the high concentrations in Regions 3 and 4, 45 deg from the traced inlet, and opposite from the direction of rotation, but over-all mixing was not so good, with a maximum concentration of fluid from the traced inlet of 70 per cent.

Because the high concentrations of fluid from the traced inlet were located near the periphery of the core, studies in May will be made to determine the effect of thermal-shield coolant flow on mixing results. In addition, other devices will be studied in an attempt to obtain adequate mixing with lower pressure loss.

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 resumed. The apparatus is essentially completed, and initial tests have indicated satisfactory operation.

Minor modification of the X-ray shielding is being made to provide adequate safety. Sensitivity tests on flat-plate filler material and on fuel-pin end closures are in progress. These tests will complete the work planned.

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

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

Flat-plate Zircaloy 2-clad fuel elements containing compartmented uranium dioxide fuel are being considered for PWR Core 2. An investigation is being conducted to study the preparation of these fuel elements by gas-pressure bonding, in which helium gas pressure at elevated temperatures is used to obtain metallurgical bonding of the components.

Presently, this study consists of developing a two-step bonding process. Gas-pressure bonding is used to obtain a strong bond in the initial step, and heat treatment at 1350 F to promote complete grain growth across the bond interface is the final step.

Six edge-welded specimens with vapor-blasted and pickled components and containing natural uranium dioxide cores were bonded at 1200 and 1350 F and 3500 psi and at 1400 to 1500 F and 5000 psi. Bonding time was 4 hr.

After the gas-pressure-bonding operation, the specimens were wrapped in molybdenum foil and heat treated in a barium chloride salt bath for 5 min at 1850 F. After heating, the specimens were quenched to approximately 1200 F in a helium blast and then water quenched to room temperature. The specimens were sectioned and metallographically examined for core-to-clad reaction and bond integrity. The results of this examination disclosed that the specimens bonded at 1200 F did not experience any core-to-clad reaction; however, the specimens did not bond properly at this temperature. The specimen bonded at 1350 F exhibited much better bond integrity with no apparent reaction; however, the bond was questionable in areas. The best bonding results in this series were obtained with the specimens bonded at 1500 F; nearly equivalent bonding was observed in specimens bonded at 1400 F. The average core-to-clad diffusion for the specimen bonded at 1400 F was 0.0006 in., while the amount of diffusion obtained at 1500 F during gas-pressure bonding and subsequent heat treatment was 0.0017 in.

The results obtained with these specimens suggest that the two-step process may be feasible, since fairly good bonds were obtained even though the surface preparation by pickling has previously been proven to be detrimental to bonding. Therefore, arrangements will be made to prepare and gas-pressure bond more of these edge-welded-type specimens. However, in this case, the surfaces of the specimens will be belt abraded prior to edge welding.

In an attempt to determine the most suitable surface for specimens that are bonded in the alpha followed by a beta treatment, several flat-plate specimens have been run, using different surface preparations and pressure-bonding conditions. The surface preparations included a hydrofluoric acid pickle followed by immersion in boiling sodium hydroxide, a hydrofluoric acid pickle followed by a sulfuric acid pickle, and the belt-abraded surface preparation. The belt-abraded specimens were used as control specimens, since this type of surface preparation was previously shown to produce a favorable bond. Temperature was varied between 1400 and 1500 F for these tests, while pressure was varied between 5,000 and 10,000 psi. A constant-pressure bonding time of 4 hr was employed.

After pressure bonding, the samples were heated in barium chloride for 5 min at 1850 F, as previously described. These specimens have been metallographically prepared and are being examined to determine the optimum bonding conditions.

Several sets of irradiation specimens have been bonded, heat treated, examined, and shipped out for testing during this month. In all cases, the pressure-bonding conditions used were 4 hr at 1500 F and 10,000 psi followed by a 5-min heat treatment at 1850 F. Additional irradiation specimens will be prepared and bonded during May.

M-4

A series of 75 large-size specimens with uranium dioxide cores are being processed for bonding studies, to determine whether unexpected problems are encountered with larger specimens.

Studies of the core-to-clad reaction, clad ductility, fragmentation of the oxide core during bonding and heat treatment, and the effects of the 1850 F heat treatment on the bond integrity are also being investigated with these large-size specimens.

N-1

N. EVALUATION OF URANIUM MONOCARBIDE AS A REACTOR FUEL

F. A. Rough

The development of casting techniques for the preparation of uranium monocarbide samples is a key factor in this program. Thus far the development has proved quite successful, and techniques have been adopted for grinding and drilling samples. Considerable physical testing remains to be done, but the first steady-state conductivity data for the cast carbide are reported. The values are comparable to those of uranium.

Specimens are being prepared for the first irradiation experiments.

Casting Techniques for the Preparation of Uranium Monocarbide

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

The initial phase of a program to study and evaluate uranium monocarbide as a possible reactor fuel material is well under way and is proceeding on an accelerated schedule.

Thermal-conductivity data have been obtained on cast UC during the past month. Thermal conductivity was found to be almost as high as that for uranium metal and many times higher than values reported for UO_2 in the same temperature range. It is interesting that while the thermal conductivity of UO_2 decreases with increasing temperature over the range of 100 to 700 C, these preliminary data show that UC reaches a minimum at about 400 C and increases again up to 700 C. Tentative values under steady-state conditions at 100, 400, and 700 C were 0.060, 0.054, and 0.059 cal/(sec)(cm)(C), respectively. Additional conductivity measurements will be made to determine the reproducibility of these data.

In the preparation of specimens, better-formed castings are being made as the result of a 1/64-in. hole drilled through the bottom of the graphite mold. This hole allows entrapped or absorbed gas to escape when the molten monocarbide is poured into the mold.

The problem of occasional spalling of UC surfaces during grinding has been resolved. The spalling was found to be caused by the procedure followed during the machine-grinding operation. The grinding wheel became "loaded" and particles of carbide were torn from the castings. Dressing of the wheel at more frequent intervals eliminated this "loading". Substitution of a diamond wheel for the Alundum wheel formerly used completely eliminated the spalling tendency.

All specimens to be used in the next series of tests have been prepared and radiographed. The present and planned testing programs include long-term compatibility studies with NaK, thermal-shock tests on specimens in NaK-filled capsules, and impact tests on drilled and undrilled specimens. These tests are reported in the next section. In addition, thermal cycling of as-cast and ground specimens, heat-treatment studies at

elevated temperatures, modulus-of-elasticity measurements, and a room-temperature-resistivity determination are to be made.

As a result of a desire for irradiation data as soon as possible, irradiation specimens will be prepared very shortly for loading the first capsule. This initial capsule will be irradiated to about 1000 MWD/T in the MTR. Because of the accelerated schedule, the desired enriched fuel will not be available for the first specimens. Therefore, it will be necessary to blend different enrichments to produce uranium enriched to about 8.3 w/o uranium-235. These efforts have been initiated. A total of two specimens (3/8-in. diameter by 2 in. long) and three controls will be required for this first capsule.

A total of 12 enriched specimens (1/4-in. diameter by 1/2 in. long) and six control specimens will be required for another capsule to be irradiated in the Battelle Research Reactor. This capsule will be of simple design and will operate at a relatively low temperature. After several hundred MWD/T irradiations, specimens will be heated at various temperatures to obtain preliminary data on the gas-releasing characteristics of the carbide.

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 the first capsule. The irradiation schedule will depend to a considerable degree on the experimental plutonium-core test at the MTR tentatively scheduled to begin May 26, 1958. Target dates for the scheduled two-cycle irradiation of the first capsule are:

(1) Reactor loading - July 7, 1958
(2) Reactor discharge - August 18, 1958
(3) Hot-cell delivery - September 1, 1958.

The insertion schedule for the six additional capsules in the original program remains unchanged except for the substitution of one capsule in the Battelle Research Reactor for one of the MTR capsules.

The NaK compatibility tests of uranium-4.8 w/o carbon specimens in stainless steel containers which have been completed are tabulated below:

Test	Basket Material	Exposure Time, weeks	Temperature, F
1	Molybdenum	2	1100
2	Molybdenum	6	1300
3	Molybdenum	2	1300
4	Stainless steel	2	1100

Specimens in all tests remained intact and no penetration of NaK was observed. However, one specimen from Test 1 spalled slightly after standing about 1 week in a desiccator following the test period. Weight losses of the order of 5 mg occurred for each specimen. There was a slightly greater weight loss at 1300 than at 1100 F. The weight losses were about the same for both the 2- and the 6-week tests at 1300 F. This indicates that no continuing attack occurred after the initial weight loss which possibly resulted from specimen-surface cleanup, saturation of NaK with carbon or depletion of oxygen from the NaK. The systems UC-Mo-NaK and UC-stainless steel-NaK appear to be compatible at the test temperatures.

The following long-term NaK compatibility tests of uranium-4.8 w/o carbon specimens in stainless steel containers are under way:

Test	Basket Material	Exposure Time, weeks	Temperature, F
5	Molybdenum	To be determined	1100
6	Stainless steel	To be determined	1100

Thermal-shock tests, ten cycles from 1300 F to room temperature in a few minutes, of two new and two previously tested specimens (Tests 1 through 4) are being prepared. Two of these specimens will be drilled ultrasonically. Also physical drop tests of new solid and ultrasonically drilled specimens will be made.

Further compatibility tests of UC specimens with organic liquids were conducted. A remotely operated UC-CCl_4 compatibility test was conducted at 70 and 120 F to determine the possibility of reaction, but no reaction was observed. Subsequently, a UC specimen was immersed in CCl_4 for 1, 3, and 5 hr with no resultant weight change. Likewise, specimens were tested in acetone and methyl alcohol with no weight changes.

As a check on part of the preirradiation-inspection procedure, specimens were cleaned in CCl_4, weighed, baked at 500-μ pressure and 180 F for 2 hr, and reweighed with no significant weight change.

Specimen-basket and irradiation-capsule design and fabrication drawings have been completed. Fabrication of these components should be completed by May 15.

O-1

O. DEVELOPMENTS FOR NMSR

A. W. Hare and R. F. Dickerson

The research and development reported in this section is part of the Nuclear Merchant Ship Reactor Program sponsored by the Babcock & Wilcox Company. The current work is being directed toward the fabrication and subsequent irradiation of prototype fuel pins in the Babcock & Wilcox Company's dynamic test loop at the MTR. Also, research is being conducted on the safety aspects of this reactor by simulation of various accident considerations with analog techniques.

Fabrication of Urania Fuel Pellets for Loop-Test Studies

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

This program is aimed at the preparation of UO_2 specimens containing 3 to 7-1/2 per cent $U^{235}O_2$ for irradiation testing for the NMSR program. Bulk densities of about 91 per cent of theoretical are desired.

Previously, processing conditions for fabrication of pellets having the desired density were established for three of the four lots of UO_2 being used in this work. One hundred and twenty pellets about 1/4 in. in diameter and 1/4 in. high were made. Bulk density and open porosity of representative pellets are given in Table O-1.

TABLE O-1. BULK DENSITIES AND POROSITIES OF UO_2 PELLETS CONTAINING 7.46 PER CENT $U^{235}O_2$

Furnace Run	Bulk Density		Open Porosity, per cent	Closed Porosity, per cent
	G per Cm^3	Per Cent of Theoretical		
1	10.04	91.5	4.8	3.7
2	9.88	90.1	7.3	2.6
3	10.16	92.6	0.8	6.6
4	10.12	93.2	1.3	6.4

Note: Results reported are average of two measurements. Bulk densities of duplicate specimens agreed within 0.08 g per cm^3, or better. Per cent open porosities agreed within 1 per cent, or better. Bulk densities and open porosities were measured in accordance with ASTM C-373-55T, with the following exceptions:

(1) Specimens were dried at 80 C prior to measurement of dry weight.
(2) The balance used was an analytical balance capable of measuring to 0.0001 g.
(3) Specimens weighed about 2-1/2 g.
(4) Specimens were measured as they came from the furnace.

O-2

Additional trials were made during the past month in the effort to establish fabrication conditions for the sample of UO_2 containing 6.05 per cent $U^{235}O_2$ (Sample C). The results of these trials are given in Table O-2. On the basis of these data, 4-hr ball milling, 20,000 to 40,000-psi forming pressure, and 2600 F sintering temperature were established as satisfactory conditions for the required specimens. Fifty-five specimens about 1/2 in. in diameter and 1/2 in. high were prepared. Measurement of bulk density and open porosity is not yet complete.

TABLE O-2. EFFECTS OF PROCESSING VARIABLES ON SINTERED (2600 F) DENSITY OF UO_2 CONTAINING 6.05 PER CENT $U^{235}O_2$

Trial	Ball-Milling Time, hr	Forming Pressure, 10^3 psi	Bulk Density as Formed, g per cm^3	Diametral Shrinkage, per cent	Sintered Bulk Density, G per Cm^3(a)	Sintered Bulk Density, Per Cent of Theoretical(b)
43	4	10	5.6	16.8	9.66	88.0
44	4	20	5.9	16.0	9.79	89.2
45(c)	4	20	5.9	16.0	9.80	89.2
46	4	40	6.1	15.1	9.91	90.3
47	8	10	5.9	17.0	10.21	93.1
48	8	20	6.2	16.1	10.30	93.9
49	8	40	6.4	15.2	10.34	94.3

(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 44 and 45 were fabricated from the same batch of ball-milled material, and were sintered separately.

Future work will include fabrication of the additional pellets required for the in-pile capsule-irradiation tests.

Fabrication of Loop-Test Fuel Pins

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

Previous work on this program has resulted in the completion of four dummy fuel-pin assemblies for preirradiation dynamic fuel tests in the loop. These assemblies contained no UO_2 pellets, but were fabricated and assembled using the same techniques as were planned for the fueled pins.

At the present time all the in-pile test specimens have been fabricated. The fuel pins were loaded with enriched urania pellets in a helium atmosphere and were welded.

Upon completion of the welding, the fuel pins were given a fluorescent penetrant inspection to detect any discontinuities such as cracks, shrinkage, or pores. This was followed by a check for any helium leaks, and X-ray radiography to determine the extent of the fuel areas in the tubes. X-ray radiography was also used to study the penetration of weld on each fuel pin. Metallographic examinations were made on various

welds to determine the penetration. Results of all tests indicated 100 per cent penetration of the weld. No helium leakage or discontinuities in the weld areas, caps, or tubes were observed.

Final assembly of the fuel pins will be initiated upon completion of measurements of length, diameter, and apparent densities of each specimen.

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

J. J. Stone, Jr., 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 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 first two accidents were reported when completed previously.

During April, the effect of total loss of coolant flow was studied. Two cases were considered: (1) four pumps at full speed, coasting to no pumps, and (2) two pumps, one per loop, at half speed, coasting to no pumps. The first case represented total loss of flow under normal operating conditions, and the second a total flow loss under the conditions of startup at sea. This study involved an analysis of the variations of scram parameters and the moderator-temperature coefficient.

The cold-water accident was also investigated during this period. Conditions of immediate-idle-loop startup and gradual valve opening were considered. An analysis was made on the system for no safety action, high-flux trip, and period trip with the following parameter variations: scram characteristics, fuel-temperature coefficient, moderator-temperature coefficient, trip level, and initial cold-loop temperature. This analysis was carried out over a period of less than one loop time. Thus, the effect of the boilers was not considered.

This concludes the work to be carried out under the scope of this research program.

RWD:CRT/all