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PROGRESS RELATING TO CIVILIAN APPLICATIONS
DURING FEBRUARY, 1957

by

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REPORTS RELATED TO CIVILIAN APPLICATIONS
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- BMI-1154 "Studies Relating to the Reaction Between Zirconium and Water at High Temperatures", by Alexis W. Lemmon, Jr.
- BMI-1156 "Aqueous Corrosion of Uranium Fuel-Element Cores Containing 0 to 20 w/o Zirconium", by Daniel R. Grieser and Eugene M. Simons.
- BMI-1158 "Characterization of Inclusions in Dingt Uranium", by Donald M. Cheney and Ronald F. Dickerson.
- BMI-1159 "Effect of Impurities on the Corrosion Behavior of Uranium-10 w/o Niobium Alloys in 680 F Water", by Edwin S. Hodge, Warren E. Berry, Glen H. Beatty, Stan J. Paprocki, and Robert S. Peoples.
- BMI-1161 "Progress Relating to Civilian Applications During January, 1957", by Russell W. Dayton and Clyde R. Tipton, Jr.

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A. DEVELOPMENT OF MATERIALS FOR HANFORD REACTORS

F. R. Shober

Design and construction of equipment for thermal-conductivity measurements of irradiated encapsulated uranium is being continued. Metallographic techniques used to confirm solubility limits of uranium in thorium, previously determined by electrical-resistivity and X-ray data, have been unsuccessful.

The determination of mechanical properties of zirconium and zirconium alloys at elevated temperature is continuing with creep tests on Zircaloy 2 and Zircaloy 3A in the 149 to 343 C range. The burst strengths of seamless zirconium and Zircaloy 2 tubes have been determined at 343 C. A good bond has been obtained between nickel-plated uranium cores and zirconium clad by hydrostatic pressing at 730 C for 2 hr under a 10,000-psi pressure. Preparation of single crystals of aluminum, molybdenum, and zirconium has been initiated.

Thermal Conductivity of Uranium

H. W. Deem and C. F. Lucks

A study of the effect of irradiation on the thermal conductivity of uranium clad with Zircaloy 2 is to be made. Thermal-conductivity measurements will be made prior to irradiation. Parts of the necessary measuring apparatus now completed include the thermocouple welder and welding jig, and the constant-temperature water bath. The design and detailing of the thermal-conductivity measuring apparatus and shielding should be completed during March.

The Constitution of Thorium-Uranium Alloys

A. A. Bauer and R. F. Dickerson

An investigation of the solubility of uranium in thorium is being conducted. Solubility limits, based on electrical-resistivity and X-ray data, have been determined and were reported earlier. Recent attempts to obtain confirmatory metallographic data have proved unsuccessful. No satisfactory method for permitting the metallographic identification of small amounts of uranium has been determined. As a result, work is being concluded on this program and a topical report will be written.

Mechanical Properties of Zirconium and Zircaloy 2

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

The mechanical properties of zirconium and zirconium alloys are being determined. These determinations include the burst strength of seamless zirconium and

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Zircaloy 2 tubes, the creep strength of annealed Zircaloy 2, and the tensile properties of Zircaloy 3A.

The burst strengths of seamless zirconium and Zircaloy 2 have been determined over the 75 to 650 F temperature range. The data obtained during this report period are shown in Table A-1. Several check tests which are needed will be run and data from all test temperatures will be summarized and evaluated.

Creep tests on a second lot of Zircaloy 2 are continuing. The initial creep tests on Zircaloy 3A have been initiated. These have been scheduled to determine the stress necessary to produce a creep rate of 10^{-5} per cent per hr. The results of creep tests in progress and those from tests on the Lot 1 material at comparable stress are given in Table A-2.

The tensile properties of annealed and 35 per cent cold-worked Zircaloy 3A are being determined.

Zirconium Cladding

F. R. Shoher and R. F. Dickerson

Several nickel-plated uranium cores have been bonded to zirconium cans by hot hydrostatic pressing. These are part of a series to investigate the effect of time and temperature under constant pressures.

Three additional nickel-plated uranium cores were canned and pressurized at 10,000 psi at 1200 F for 6 hr and at 1350 F for 2 and 6 hr. These have been sectioned and examined metallographically to determine the extent of bonding and diffusion occurring under these conditions. It is apparent that extensive diffusion occurred for these times and temperature combinations; however, some voids still exist after 6 hr at 1200 F. These are in the areas where irregularities occur in the nickel plate. At 1350 F, the zirconium is ductile enough to flow in and fill all depressions in the nickel plate for the times investigated. The diffusion is so extensive at 1350 F that a brittle diffusion zone of intermetallics is formed. This zone provides a site for the initiation and propagation of cracks and leads to ultimate failure of the bond.

Two additional nickel-plated uranium cores will be canned and pressurized to investigate the effect of shorter times at 1350 F. The surfaces of two other nickel-plated cores will be specially prepared prior to canning to investigate the effect of surface condition on bonding at 1200 F. Several unplated uranium cores will also be canned in zirconium and pressurized at 1200 and 1350 F in an attempt to determine time and temperature necessary for strong bonds.

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TABLE A-1. BURST STRENGTHS OF ZIRCONIUM AND ZIRCALOY 2 TUBES

Specimen	Material	Nominal OD, in.	Nominal Wall Thickness, in.	Measured OD, in.	Measured Wall Thickness, in.	Cold work, per cent	Rockwell Hardness	Burst Pressure, psi	Burst Stress(a), psi	Circumferential Elongation(b), per cent
<u>75 F</u>										
451-1	Zirconium	1.5	0.060	1.500	0.060	0	75.0-B	6750	77,680	21.9
451-2	Zirconium	1.5	0.060	1.501	0.060	0	75.0-B	6600	75,960	9.4(c)
447-1	Zirconium	1.5	0.060	1.502	0.061	40	90.0-B	9400	105,990	15.8
447-2	Zirconium	1.5	0.060	1.502	0.060	40	90.0-B	9600	102,500	16.1
<u>300 F</u>										
451-3	Zirconium	1.5	0.060	1.505	0.060	0	75.0-B	4650	53,380	42.1
451-4	Zirconium	1.5	0.060	1.501	0.060	0	75.0-B	4700	53,930	44.7
451-3	Zirconium	1.5	0.060	1.502	0.060	40	90.0-B	6800	78,085	16.4
447-4	Zirconium	1.5	0.060	1.499	0.060	40	90.0-B	6850	78,785	17.0
<u>650 F</u>										
245-7	Zirconium	1.5	0.020	1.499	0.020	0	16.1-30N	1100	40,150	32.4
245-8	Zirconium	1.5	0.020	1.502	0.020	0	16.1-30N	1100	40,175	32.5
249-7	Zirconium	1.5	0.020	1.495	0.020	40	32.2-30N	1200	43,740	17.4
249-8	Zirconium	1.5	0.020	1.500	0.020	40	32.2-30N	1250	45,625	16.6
451-7	Zirconium	1.5	0.060	1.501	0.060	0	75.0-B	2500	28,750	44.2
451-8	Zirconium	1.5	0.060	1.505	0.061	0	75.0-B	2900	32,805	14.2(c)
447-7	Zirconium	1.5	0.060	1.501	0.060	40	90.0-B	4600	52,940	17.4
447-8	Zirconium	1.5	0.060	1.501	0.060	40	90.0-B	4900	56,150	11.3
256-7	Zircaloy 2	1.5	0.020	1.496	0.019	0	15.4-30N	1200	46,135	19.2(c)
256-8	Zircaloy 2	1.5	0.020	1.495	0.020	0	15.4-30N	1650	60,260	37.0
254-7	Zircaloy 2	1.5	0.020	1.500	0.019	40	35.2-30N	1650	63,655	17.0
254-8	Zircaloy 2	1.5	0.020	1.505	0.019	40	35.2-30N	1750	65,450	18.6
389-5	Zircaloy 2	1.5	0.035	1.496	0.036	10-15	86.9-B	2600	51,385	34.5
381-6	Zircaloy 2	1.5	0.035	1.499	0.036	10-15	86.9-B	2600	51,600	39.8
401-7	Zircaloy 2	1.5	0.060	1.502	0.060	0	79.7-B	3600	40,090	57.0
401-8	Zircaloy 2	1.5	0.060	1.502	0.062	0	79.7-B	3550	40,185	57.8
405-8	Zircaloy 2	1.5	0.060	1.502	0.061	40	93.8-B	6050	63,025	20.0

(a) Calculated by Barrow's thin-wall tube formula, $S = \frac{Pd}{2t}$, where S = hoop stress, P = internal pressure, d = inside diameter, and t = wall thickness.

(b) Based on change in diameter at fracture point.

(c) Failed at defect.

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TABLE A-2. CREEP PROPERTIES OF ANNEALED ZIRCALLOY 2 AND ZIRCALLOY 3A

Lot	Specimen	Temperature, F	Stress, psi	Time at Test, hr	Deformation at Indicated Time, per cent					Minimum Creep Rate ^(a) , per cent per hr	
					Load on	50 Hr	100 Hr	500 Hr	1000 Hr		1500 Hr
<u>Zircaloy 2</u>											
1	--	300	23,000	1,000	0.39	0.90	0.97	1.09	1.15	--	0.00012
2	40-3	300	23,000	300 ^(b)	0.20	2.0	2.20	--	--	--	--
2	31-1	300	23,000	1,000	0.175	1.80	1.96	2.29	2.39	--	0.00020
1	--	450	21,000	1,500	0.48	0.915	0.93	0.96	0.98	--	0.00040
2	24-3	450	21,000	700 ^(b)	0.59	2.45	2.465	2.49	--	--	--
1	--	450	23,000	1,000	0.30	1.98	2.05	2.13	2.15	--	0.00003
2	40-1	450	23,000	200 ^(b)	1.85	3.85	3.90	--	--	--	--
1	--	450	24,500	22.3 ^(c)	0.90	--	--	--	--	--	--
2	40-4	450	24,500	150 ^(b)	2.40	9.00	9.90	--	--	--	--
2	40-6	550	24,500	500 ^(b)	7.50	15.75	16.00	16.05	--	--	--
2	40-7	550	22,500	350 ^(b)	2.65	4.60	--	--	--	--	--
1	--	650	9,000	3,400	0.032	0.06	0.072	0.072	0.081	0.090	0.00001
2	3-2	650	9,000	1,600 ^(b)	0.06	0.09	0.1	0.117	0.117	0.117	<0.00001
1	--	650	12,500	1,000	0.17	0.42	0.425	0.448	0.46	--	0.000024
2	3-1	650	12,500	1,175 ^(b)	0.15	0.23	0.245	0.282	0.335	--	0.000053
1	--	650	17,500	1,000	0.54	0.655	0.675	0.711	0.742	--	0.00006
2	34-2	650	17,500	725 ^(b)	1.385	1.54	1.55	1.594	--	--	--
2	34-4	650	17,500	100 ^(b)	1.37	1.62	--	--	--	--	--
<u>Zircaloy 3A</u>											
	Zr3-3	475	20,000	225 ^(b)	0.50	2.505	2.507	--	--	--	--
	Zr3-1	475	22,500	400 ^(b)	2.3	14.4	17.0	--	--	--	--

(a) Based on creep deformation between 500 and 1000 hr.

(b) Tests in progress.

(c) Ruptured.

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A-5 and A-6

Preparation of Aluminum, Molybdenum, and
Zirconium Single Crystals

F. R. Shober, E. J. Jablonowski, and R. F. Dickerson

As part of a metallurgical service program, Battelle has undertaken the preparation of single crystals of high-purity aluminum, molybdenum, and zirconium for use in irradiation studies. The single crystals are to be grown by the strain-anneal process. Initial work has been directed to the procurement of materials and a survey of available literature.

Preparation of single crystals of aluminum by the strain-anneal method will commence next month. High-purity aluminum (99.99 w/o aluminum), available in ingot form, is to be used. Following fabrication and heat treatment of the aluminum, the strain-anneal technique will be applied.

For the growth of molybdenum single crystals, modification of the strain-anneal process and annealing equipment will be necessary. It is expected that a modified Anorade furnace will be constructed and used. At present, no reference to single-crystal growth of zirconium by strain-anneal methods has been found. It is anticipated that considerable effort will have to be devoted to developing and evaluating the strain-anneal technique for the growth of zirconium single crystals.

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B. DEVELOPMENTS FOR ALUMINUM-CLAD FUEL ELEMENTS

R. J. Carlson

A new mandrel for use in extrusion-cladding work has been constructed. To minimize edge cocking of the core, this mandrel has provision for a core guide located closer to the mandrel slot. An additional mandrel which is designed to reduce the amount of compression of the mandrel slot is under construction.

The transverse properties of beta-quenched ingot uranium as determined by the "ring test" were compared with the longitudinal properties obtained by standard sheet tensile tests at minus 75, 75, and 300 F. Elastic moduli obtained in the ring test were of the same order as moduli obtained by the longitudinal tensile tests at corresponding temperatures; however, the transverse yield-strength values were somewhat lower. A topical report is being prepared on this work.

Specimens of the 16, 30, 35, 40, and 45 w/o uranium ingots have been press forged at 800 and 1000 F to 50 per cent reduction without serious difficulty. These specimens were encased in heavy-walled 2S aluminum cans to approximate extrusion conditions. Radiographs of the specimens fail to show any evidence of hot tears or edge cracking. A topical report is being prepared on aluminum-uranium alloys.

Extrusion Cladding of Flat Plates

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

Additional evidence has been obtained in several recent tests indicating that cocking of the core causes it to be restrained, and results in excessive extrusion pressure. To minimize the cocking, a new mandrel has been constructed which will provide for a core guide located closer to the mandrel slot. The new mandrel also has a core slot (0.190 by 2.745 in.) with a 1/16-in. radius at the corners. This was done to minimize the possibility of the slot cracking at the corners.

An additional mandrel which is designed to reduce the amount of compression of the mandrel slot is under construction.

Mechanical Properties of Uranium Tubes

F. R. Shober, E. J. Jablonowski, and R. F. Dickerson

The investigation of a test method for determining the transverse mechanical properties of uranium tubing has been completed. A hydraulically loaded "ring test" has been developed and consists of internally pressurizing a section of uranium tubing and measuring the subsequent circumferential expansion of the tubing by means of

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electric strain gages. The transverse properties of beta-quenched ingot uranium as determined by the ring test were compared with the longitudinal properties obtained by standard sheet-tensile tests at minus 75, 75, and 300 F.

Six sections of beta-quenched ingot uranium tubing were nickel-plated (0.0005 in.) to provide an oxidation-resistant surface on which electric strain gages were mounted. Three of the nickel-plated uranium sections were tested at minus 75 F and three sections at 300 F. Paper-back strain gages protected with Pliobond insulation and heat-resisting Bakelite gages were used at minus 75 and 300 F to measure the strain. Results of these tests appear in Table B-1 along with some longitudinal tensile properties for comparison purposes.

TABLE B-1. COMPARISON OF ELASTIC MODULI OF BETA-QUENCHED INGOT URANIUM

Type of Test	Test Temperature, F	Elastic Moduli, psi	0.2 Per Cent Offset Yield Strength, psi
Transverse			
Ring Test	-75	25.6×10^6	41,000
Ditto	-75	29.2×10^6	38,700
Ditto	-75	26.3×10^6	44,250
Ditto	300	25.7×10^6	27,800(a)
Ditto	300	25.1×10^6	27,300
Ditto	300	24.4×10^6	27,500
Longitudinal			
Standard sheet			
tensile	-75	26.8×10^6	54,800
Ditto	-75	27.5×10^6	45,200
Ditto	300	24.5×10^6	34,900
Ditto	300	25.0×10^6	32,400

(a) Obtained by extrapolation.

Elastic moduli obtained in the ring test were of the same order as moduli obtained by longitudinal tensile tests at corresponding temperatures; however, the transverse yield-strength values were somewhat lower. The yield strength decreased with increasing test temperature from approximately 40,000 psi to 27,500 psi.

Experimental work on this project has been completed, and a topical report on the transverse and longitudinal properties of uranium tubes is being prepared.

Preparation of Aluminum-Uranium Alloys

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

The program of research concerned with the development of melting and casting techniques for the production of aluminum-uranium extrusion billets is being continued.

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At the present time, alloys containing 30 to 45 w/o uranium are being investigated. These alloys are of interest as possible fuels in reactors; therefore, the casting methods developed must be amenable to production techniques.

Because of the difficulties encountered in casting sound production-size extrusion billets of high-uranium-content alloys, efforts have been concentrated on producing 45 w/o uranium ingots 2 in. in diameter by 16 in. long. Sound material has been obtained on ingots melted and cast in a vacuum and in a dynamic helium pressure. The chemical analyses from these ingots are not complete; however, indications are that the average uranium variation from top to bottom of the ingot is on the order of 5 per cent of the contained uranium. It is felt that this segregation can be alleviated by further study.

Experiments have been performed in an attempt to determine the effect of pouring rate, pouring temperature, and crucible material on the quality of the 45 w/o uranium alloy ingots and the data are being evaluated. Chemical analyses have been completed and a sound full-scale extrusion billet has been successfully cast.

Specimens of the 16, 30, 35, 40, and 45 w/o uranium ingots have been press forged at 800 and 1000 F to 50 per cent reduction in length without serious difficulty. These specimens were encased in heavy-walled 2S aluminum cans to approximate extrusion conditions. Radiographs of the specimens fail to show any evidence of hot tears or edge cracking.

The fabrication evaluation completes the present study and a topical report is being prepared.

C-1

C. PLANT ASSISTANCE TO MCW

A. A. Bauer

A study of the relationship between residual nitrogen content and the reactivity of UO_3 and subsequently produced UO_2 is being made. Amorphous UO_3 containing high nitrogen contents was found to have a high hydration reactivity; UO_2 prepared by reduction of these samples was semiactive. Similar studies of MCW Type III UO_3 indicated no relationship between the nitrogen content of the UO_3 and either its hydration reactivity or to the oxygen reactivity of UO_2 subsequently prepared.

Studies of the effect of nitrogen additions, added in the form of $\text{UN}_{1.5}$ powder, on the electrical properties of UO_2 are being performed. The conductivity of UO_2 is found to decrease as nitrogen content is increased. The conductivity exhibits a minimum at 0.3 mole per cent $\text{UN}_{1.5}$ and a maximum at about 1 mole per cent $\text{UN}_{1.5}$. Additional property measurements are planned.

Corrosion tests are being performed on Type 304 ELC stainless steel in chloride- and fluoride-contaminated 5, 18, and 30 w/o nitric acid solutions. No severe corrosion has been observed when chloride alone is added in amounts of 0.30 w/o or less. Fluoride-chloride combinations produce much higher corrosion rates than chloride additions alone. With fixed chloride-fluoride contaminations, interface and vapor-phase corrosion increases with nitric acid concentrations between 5 and 30 w/o; liquid-phase corrosion decreases within this range. Corrosion tests of welded specimens indicate that corrosion resistance is unaffected by the welding process.

Preliminary measurements of hydrogen permeability through molten magnesium fluoride slag have been made. A tentative value of $0.001 \text{ cm}^3 \text{ (STP) hydrogen cm / (sec)(cm}^2\text{)}$ has been calculated.

Investigation of Uranium Oxides

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

A study of the reactivities of UO_3 and UO_2 and their relation to the residual nitrogen content of UO_3 is in progress. Previous results had indicated that UO_3 with a high nitrogen content and a high hydration reactivity reduces to a more reactive UO_2 .

The hydration-reactivity test of amorphous UO_3 was continued. The water pickup at 30 C was continued to equilibrium and the results are shown in Table C-1. These indicate that amorphous UO_3 with a high nitrogen content is more reactive to hydration as measured by the amount of water adsorbed. Reduction of these amorphous UO_3 samples yielded semiactive UO_2 . The activity toward oxidation was considerably less than observed previously in the case of supposedly similar preparations. It was found that these UO_2 materials continued to adsorb oxygen at different rates. Oxygen-uranium ratios, determined immediately after exposure to air and after 3 weeks, are

TABLE C-1. HYDRATION-REACTIVITY TEST OF AMORPHOUS UO_3

Sample	Treatment Prior to Denitration	Denitration		UO ₃ , per cent	N, per cent	UO ₂ Oxygen- Uranium Ratio After Indicated Exposure to Air		UO ₃ Hydrate X-Ray Type ^(a)	Total Percentage H ₂ O in Hydrate
		Temperature, C	Time, hr			1 Day	3 Weeks		
314A	UNH-vac-125 C	250	2	96.56	0.80	2.166	2.323	UO ₃ •H ₂ O	22.65
340A	UNH-vac-150 C	300	2	97.20	0.76	2.155	2.175	UO ₃ •H ₂ O	22.18
363A	UNH-vac-150 C	300	4	99.27	0.37	2.166	2.263	UO ₃ •2H ₂ O	15.21
365A	UNH-vac-150 C	400	4	99.72	0.39	2.183	2.335	UO ₃ •2H ₂ O	13.16
358A	UNH-belt	350	2	97.87	0.53	2.259	2.341	UO ₃ •2H ₂ O	16.30
357A	UNH-belt	400	2	98.97	0.34	2.108	2.137	UO ₃ •2H ₂ O	13.44
348A	UNH-belt	425	2	98.88	0.36	2.128	2.254	UO ₃ •2H ₂ O	12.44
362A	UNH-belt	450	2	99.08	0.36	2.093	2.185	UO ₃ •2H ₂ O	12.50

(a) The monohydrate structure takes up as much as 4 to 6 moles of H_2O . The dihydrate structure appears to be limited in the amount of water it can adsorb.

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C-3

included for comparison. The UO_3 hydrates were heated at 250 C for 18 hr, then reduced to UO_2 . The oxygen-uranium ratios differ very little among themselves, and have a lower value (average, $\text{UO}_2.09$) than UO_2 made from unhydrated amorphous UO_3 .

A similar study was carried out on six different lots of MCW Type III UO_3 . The results as given in Table C-2 show some variation in nitrogen content. However, no relation can be seen between the nitrogen content of the UO_3 and its hydration reactivity. The oxygen reactivity of UO_2 made from these UO_3 materials is low and does not appear to have any relation with the nitrogen content.

TABLE C-2. HYDRATION-REACTIVITY TESTS OF MCW-TYPE III UO_3

Lot	UO_3 , per cent	N, per cent	UO_2 Oxygen - Uranium Ratio	Total Percentage H_2O in UO_3 Hydrate
5	99.10	0.45	2.052	12.99
6	98.96	0.25	2.047	15.23
7	99.28	0.63	2.037	12.39
13	98.99	0.35	2.056	10.39
14	98.82	0.46	2.042	11.87
15	98.89	0.42	2.033	14.79

During the next period, it is planned to continue to study the effect of nitrogen in UO_3 . Attempts are being made to reduce the nitrogen content by washing in water. The progressive oxidation of active dioxide will be studied.

The Electrical Properties of Uranium Dioxide

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

Past work has indicated that nitrogen in the lattice of uranium dioxide might appreciably affect the activity and the electrical properties of the compound. In particular, there is an anomaly in the conductivity of those sintered specimens likely to contain nitrogen. At about 350 C the conductivity of these specimens suddenly decreases, in some cases by as much as an order of magnitude. This anomaly was not observed in those specimens which sintered to high densities and were ball milled and thoroughly washed before sintering.

Since the uranium dioxide used in these studies was prepared by the decomposition-reduction of uranyl nitrate, it was felt that the anomaly might be due to the presence of nitrogen in the inactive specimens. It is known that not all the nitrogen is removed by the decomposition of the nitrate and it is reasonable to assume that some nitrogen persists even after reduction. Washing the uranium dioxide reduces the nitrogen content and results in a more active material.

A previous attempt to "dope" uranium dioxide to study the effects of nitrogen was inconclusive. This was done by exposing active uranium dioxide to dry nitrogen gas. However, the absorption of oxygen on subsequent exposure to air overweighed the effects

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of any nitrogen doping. Even so the conductivities of these specimens were somewhat less than was to be expected from the measured oxygen content.

Recently another attempt to dope uranium dioxide with nitrogen was more successful. This was accomplished by intimately mixing uranium dioxide and uranium nitride powders before pressing into specimens for electrical measurements. The uranium dioxide used was normal MCW material, Lot No. 77016, having an oxygen-to-uranium ratio of 2.03. The uranium nitride was prepared at Battelle and had a composition of about $\text{UN}_{1.5}$.

The effect of nitrogen on the room-temperature conductivity of UO_2 was apparent even in the as-prepared specimens (which might be expected to be nonhomogeneous). As nitrogen content is increased the conductivity of UO_2 decreases and appears to pass through a minimum at about 0.3 mole per cent $\text{UN}_{1.5}$. Beyond the minimum the conductivity increases somewhat with nitrogen content up to about 1.0 mole per cent $\text{UN}_{1.5}$. As the nitrogen content is further increased the conductivity gradually decreases (at least up to 5.0 mole per cent $\text{UN}_{1.5}$).

A similar dependence of room-temperature conductivity on nitrogen content was found after annealing the specimens at 200 and 400 C. The conductivities of all the specimens were increased by annealing; the minimum conductivity at 0.3 mole per cent $\text{UN}_{1.5}$ and the decrease of conductivity above 1 mole per cent $\text{UN}_{1.5}$ became more pronounced. All the specimens were *p*-type regardless of nitrogen content or magnitude of conductivity. The values of the room-temperature conductivities of the annealed specimens as well as of the as-prepared specimens are listed in Table C-3.

TABLE C-3. ROOM-TEMPERATURE CONDUCTIVITY OF NITROGEN-DOPED URANIUM DIOXIDE

Nitrogen Content, mole per cent $\text{UN}_{1.5}$	Conductivity, $10^{-4}\text{-ohm}^{-1}\text{-cm}^{-1}$, After Indicated Heat Treatment		
	As Prepared	200 C Anneal	400 C Anneal
0.00	7.1	30	54
0.10	4.2	25	37
0.50	3.9	13	13
1.0	6.5	27	43
5.0	7.5	20	14

Since it is reasonable to assume that the mobility of charge carriers in these specimens, determined by grain-boundary scattering, is more or less constant, it appears that nitrogen reduces the effective number of carriers in UO_2 . Of especial interest is the minimum at about 0.3 mole per cent $\text{UN}_{1.5}$. However, an explanation of the mechanism by which the number of carriers is affected must await measurements of the temperature dependence of the conductivity and thermoelectric power of these specimens.

The amount of nitrogen doping was chosen arbitrarily for these experiments and it is obvious that there are certain gaps in the data. Additional specimens will be prepared to define the minimum and, after electrical measurements are completed, the structure of these materials will be determined by X-ray analysis.

C-5

The Corrosion Resistance of Selected Stainless Alloys

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

The corrosion studies of Type 304 ELC stainless steel specimens in chloride- and fluoride-contaminated nitric acid solutions of 5.0, 18.0, and 30.0 w/o were continued during the month of February.

The prolonged-exposure tests in the three concentrations of 5.0, 18.0, and 30.0 w/o nitric acid solutions containing various chloride contaminations have now reached exposure times of 1000, 2500, and 2000 hr, respectively. A résumé of the present status of these corrosion tests is presented in Table C-4. The results of the duplicate tests in 5.0 w/o nitric acid solutions are not given in this table, but the corrosion rates closely parallel those listed. No severe corrosion has been observed in chloride contaminations of 0.300 w/o or less. These specimens are now being examined at intervals of 500 hr. At the time of these inspections, the acid solutions are renewed. All of these tests will be continued.

Thus far, the set of specimens representing the material being used in the construction of the Weldon Springs reconcentrator are performing well in 18.0 w/o nitric acid containing 0.500 w/o chloride.

Seven 48-hr exposure periods were completed for Type 304 ELC stainless steel specimens, both welded and unwelded, which were exposed to nitric acid solutions contaminated with chloride or with combinations of chloride and fluoride. Chloride contaminations of 0.05 w/o and fluoride contaminations of 0.01 w/o were studied in 5.0 and 30.0 w/o nitric acid solutions boiling at atmospheric pressure. This completed the scoping experiments with fluoride contaminations in the three nitric acid concentrations. The same chloride and fluoride concentrations were studied in 18.0 w/o nitric acid solutions and reported in BMI-1152, although the concentrations were erroneously listed there as 0.50 and 0.10 w/o in some cases.

A summary of the results of these tests is presented in Table C-5. It is readily apparent that combined fluoride-chloride additions produce much higher corrosion rates than do chloride additions alone. In 5.0 w/o nitric acid, fluoride shows a strong effect in the liquid but not in the vapor or at the interface. As the nitric acid concentration is increased, the effect of fluoride in the vapor and at the interface increases, but falls away in the liquid.

Specimens containing weldments of Type 308 ELC stainless steel, produced by the shielded metal-arc process and with the weldment so positioned as to leave an area of the specimen which was not heat affected, were included at the interface position in these tests. These specimens were used in addition to regular unwelded interface specimens. The sizes of the vapor- and liquid-phase specimens were reduced accordingly to keep the ratio of surface area to volume of solution constant. Both weight-loss data and microscopic examination showed the welded specimens to be as resistant as the unwelded, with the exception of one welded specimen which exhibited a crack. This occurred adjacent to the weldment near the drilled hole and may have been due to stresses arising from the combination of cold working and heat. The weldments themselves seemed quite resistant to attack. None of the specimens exhibited the so-called knife-line attack in the heat-affected areas.

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TABLE C-4. CORROSION OF TYPE 304 ELC STAINLESS STEEL IN CHLORIDE-CONTAMINATED NITRIC ACID

(Boiling solutions, reduced pressure)

Chloride, w/o	Specimen Position	Corrosion Rates in 5, 18, and 30 w/o HNO ₃ Solutions at Indicated Temperature, mils per month							
		1000 Hr			1500 Hr		2000 Hr		2500 Hr
		5 w/o	18 w/o	30 w/o	18 w/o	30 w/o	18 w/o	30 w/o	18 w/o
0.000	Vapor	Weight gain	.001	0.005	.002	.004	.002	.006	.002
	Interface	0.002	.001	0.010	.002	.010	.002	.013	.002
	Liquid	0.001	.011	0.011	.002	.011	.002	.012	.002
0.025	Vapor	--	--	.007	--	.008	--	.009	--
	Interface	--	--	.013	--	.014	--	.015	--
	Liquid	--	--	.014	--	.012	--	.011	--
0.050	Vapor	0.003	.001	.002	.001	.002	.001	.003	.001
	Interface	0.002	.003	.012	.004	.012	.004	.013	.004
	Liquid	0.002	.001	.014	.002	.013	.002	.014	.002
0.100	Vapor	0.002	.001	.006	.001	.005	.001	.009	.002
	Interface	0.105	.002	.014	.002	.013	.002	.014	.002
	Liquid	0.002	.001	.015	.002	.014	.002	.015	.002
0.300	Vapor	--	--	.017 (1166)	--	.017	--	--	--
	Interface	--	--	.029 (1166)	--	.026	--	--	--
	Liquid	--	--	.017 (1166)	--	.016	--	--	--
0.500	Vapor	0.001	.002 ^(a)	.014	--	.014	--	.015	--
	Interface	1.973	.003 ^(a)	.024 (906)	--	.022 (1406)	--	.022 (1906)	--
	Liquid	0.002	.002 ^(a)	.022	--	.020	--	.023	--

(a) These specimens were cut from Type 304 ELC used in the Weldon Springs reconcentrator.

Note: Solutions of 5 and 18 w/o HNO₃ are boiling at 200 mm of mercury, 30 w/o HNO₃ at 250 mm of mercury absolute pressure. Numbers in parentheses indicate hours of exposure which differ from the column heading.

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C-7 and C-8

TABLE C-5. CORROSION OF TYPE 304 ELC STAINLESS STEEL IN NITRIC ACID CONTAMINATED WITH CHLORIDES AND FLUORIDES

(Boiling solutions, atmospheric pressure)

HNO ₃ , w/o	Cl ⁻ , w/o	F ⁻ , w/o	Corrosion Rate for Indicated Exposure, mils per month					
			Vapor		Interface		Liquid	
			A	B	A	B	A	B
5.0	0.05	0.00	0.00	0.00	0.00	0.00	0.28	0.08
18.0	0.05	0.00	0.04	0.03	0.03	0.04	0.03	0.03
30.0	0.05	0.00	0.12	0.11	0.14	0.10	0.15	0.13
5.0	0.05	0.01	0.02	0.02	0.04	0.06	9.70	8.84
18.0	0.05	0.01	0.25	--	0.38	--	4.12	--
30.0	0.05	0.01	0.78	0.93	1.00	1.61	3.19	2.81

Note: The corrosion rates are the averages for seven 48-hr exposure periods. Specimens A and B are from duplicate tests.

In addition to continuing the prolonged-exposure tests, it is planned to survey the range of nitric acid concentrations above 30.0 w/o during the next month to find the highest concentration at which chloride is retained in solutions boiling at 250 to 275 mm of mercury absolute pressure. Scoping experiments with various chloride contaminations will then be made in this concentration. Also, a study of the effect of aluminum additions on the corrosivity of fluoride-contaminated nitric acid solutions is planned.

Gas-Metal Studies

M. J. Trzeciak and M. W. Mallett

A study is being made of the relationships between hydrogen and materials used in a thermite reactor for producing uranium. This study is a part of an MCW program to develop an understanding of factors which influence the hydrogen content of dingot uranium. The present hydrogen-material relationship being studied is the permeation of hydrogen through molten magnesium fluoride slag.

Two successful preliminary experiments have been made for measuring permeation of hydrogen through slag under a 1-atm external pressure. The technique was described in BMI-1161. A tentative permeation value of 0.001 cm³ (STP) hydrogen cm/(sec)(cm²) has been calculated from the data of the two experiments. This value is tentative because the effects of some factors which might influence permeability have not been evaluated as yet. A refinement in technique is planned to give a more precise value for the permeability.

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D. STUDIES OF THE REACTION BETWEEN
ZIRCONIUM ALLOYS AND WATER

A. W. Lemmon, Jr.

Research on this subject has been completed, and a topical report on it has been issued.

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E. GENERAL FUEL-ELEMENT DEVELOPMENT

F. A. Rough

Various fuel-element development projects involving ceramics, metallurgy, and corrosion are presented in this section.

The loss of fission products from irradiated UO_2 -graphite fuel samples during thermal treatment is being evaluated. The effects of magnesium and calcium as contaminants in BeO powders are being evaluated in connection with the development of sinterable beryllium oxide.

In the studies of uranium alloys, the properties of uranium-niobium alloys are receiving further study, and a capsule containing 15 w/o zirconium and 10 and 20 w/o niobium samples is being submitted for irradiation. Enriched samples of uranium-5 w/o chromium-1 w/o molybdenum which was selected for its casting properties and microstructure have also been prepared for encapsulation.

The fabrication of compartmentalized fuel elements has been essentially completed, and enriched stainless-matrix samples, containing uranium nitride or uranium carbide, are being prepared.

In the study of uranium corrosion, a series of experiments intended to determine the oxygen-uranium ratio and the valence of uranium in the product of corrosion is in progress. Other corrosion tests are also being performed.

CERAMICSRefractory Fuel Elements

G. B. Engle, M. J. Snyder, J. F. Quirk,
D. N. Sunderman, and M. Pobereskin

This research on refractory fuel elements for high-temperature gas-cooled reactors is concerned with graphite and with dense BeO as matrices for UO_2 fuel.

BeO

Studies were continued on the diffusion of uranium through dense BeO. Previously, a BeO- UO_2 couple, prepared by reducing uranyl oxalate to UO_2 on one surface of a dense BeO disk, was heated at 2300 F for 20 hr in vacuo. Last month, a light concentration of uranium was detected at a depth of 0.001 in. below the treated face. Successive 0.001-in. cuts are being removed from this couple and photographic exposures made after each cut to determine the depth of penetration of uranium into the BeO.

Additional BeO-UO₂ diffusion couples will be prepared, using dense BeO tubes and wedge-shaped slabs in an effort to provide more precise information on the diffusion. The new specimens will be heated for various time periods in the temperature range 2000 to 3000 F.

Graphite

In developing UO₂-graphite fuel elements for possible use in a gas-cooled power reactor, experiments were continued on uranium losses and fission-product retention and on fabrication of sphere-shaped elements.

In fabrication studies, unfueled graphite spheres, 1.75 in. in diameter, were cured at 400 F, baked at 2200 F, and their strength in compression determined. The spheres were free from cracks and smooth except for a bisecting molding seam. Three spheres broke at an average of 1800 psi when the load was applied in a direction parallel to the direction of the molding pressure and one sphere broke at 1300 psi when the load was applied perpendicular to the molding pressure. Inasmuch as the strength of graphite increased with temperature and the load on a graphite sphere at the bottom of a 10-ft-high graphite pebble bed would be only about 13 lb, the spheres appear to be amply strong.

Previously, several lots of rod-shaped graphite elements, containing UO₂ rods at their axes and differing in the fabrication methods used in their preparation, were irradiated at room temperature. The exposure was equivalent to 85 min at a flux of 1.06×10^{12} nv. The irradiated specimens have been heat treated in evacuated capsules for various times in the temperature range from 1650 to 2200 F. Following the heat treatments, bulbs on either end of the capsules were sealed off in liquid nitrogen. The sealed bulbs were counted in a well-type scintillation counter, and energy determinations were made with a gamma-ray spectrometer. These data are being analyzed to determine the fraction of the total fission gases produced during irradiation which diffused from the specimen during each heat treatment. Also, the gamma-ray spectra are being analyzed to identify the fission products by measuring the half-lives of the major gamma emitters.

Disintegration of the UO₂-graphite specimens as a result of oxidation has been a major problem in measuring uranium losses in flowing nitrogen at 2300 F. However, by using high-purity nitrogen and a vitrified alumina tube, the weight loss of a graphite specimen was decreased to an insignificant amount after the first 4 hr of a 16-hr run at 1800 F. This month, a run was made at 1950 F for 2 hr without significant loss by using the refined technique.

To permit long uranium-loss tests in flowing nitrogen at 2000 F, a pump will be installed in a closed system and the nitrogen recirculated over the sample after the uranium vapor has been removed in a cooled trap. The recirculating system will require the use of less nitrogen and should thereby reduce the total impurities introduced from the nitrogen.

For the present, no additional fabrication studies will be made. Experiments to measure fission-gas losses from irradiated UO₂-graphite elements will be continued and the effect of fabrication techniques on fission-gas retention will be assessed. Uranium loss tests will be continued with emphasis on long runs (50 to 100 hr) at 2000 F.

E-3

Characterization of Sinterable Oxide Powders

J. F. Quirk and N. Mosley

Basic properties that affect the sinterability of oxide powders are being assessed, currently with an investigation of BeO made from Be(OH)₂. Previous work showed that the sinterability of BeO powder is critically affected by the calcination treatment used in preparing it from Be(OH)₂. Recent work has indicated that impurities have an important influence on sinterability.

Last month samples of BeO showed a marked improvement in sinterability when purified Be(OH)₂ starting powder was deliberately contaminated by leaching with dilute MgSO₄ solution.

This month acid-leaching experiments were made on BeO samples prepared from the purified and from the MgSO₄-contaminated hydroxides, and from a lot of Brush Be(OH)₂ designated C5659. Each of the three BeO powders, calcined 2 hr in air at 1470 F, was leached three times in succession with 10 per cent HCl solution. The leaching solutions were examined spectrographically for dissolved impurities. Some were found to contain appreciable amounts of magnesium and calcium. Table E-1 shows the significant results of the leach-solution analyses and the densities of sintered compacts made from the unleached BeO powders. The results show that the two sinterable BeO powders contained appreciable amounts of acid-soluble impurities concentrated near the particle surfaces. Leachings from the nonsinterable purified powder contained no significant impurities.

TABLE E-1. ACID LEACHING OF SINTERABLE AND NONSINTERABLE BeO POWDERS

BeO Sample	Estimated ^(a) Total Impurities, w/o	Magnesium ^(a) Ion Content, w/o	Leaching Treatment	Dissolved in Leach Solutions, mg per ml ^(a)				Bulk Density of Sintered BeO Compacts ^(c)	
				Be	Mg	Ca	Mg-to-Be Ratio	G per Cm ³	Per Cent of Theoretical
28A	0.2	0.001	First	0.36	Nil	Nil	--	2.33	77.0
			Second	3.6	Nil	Nil	--		
			Third	3.6	Nil	Nil	--		
M28A ^(b)	0.9	0.7	First	2.0	1.4	Nil	0.700	2.85	94.2
			Second	5.0	0.36	Nil	0.072		
			Third	6.0	0.10	Nil	0.017		
C5659	1.0	0.4	First	0.07	0.43	0.86	6.100	2.96	97.8
			Second	1.45	0.18	0.15	0.120		
			Third	1.45	0.035	0.036	0.024		

(a) Estimated by spectrographic examinations.

(b) Purified Be(OH)₂ (Sample 28A) was contaminated by leaching with 5 w/o MgSO₄ solution.

(c) BeO was compacted at 50,000 psi and sintered 1 hr at 2600 F in 10 volume per cent hydrogen and 90 volume per cent argon.

E-4

Since the very readily sinterable BeO made from Brush hydroxide contained appreciable amounts of surface-concentrated calcium as well as magnesium, experiments will be made to determine the effect on sinterability of calcium added as a contaminant to purified Be(OH)₂. Also, experiments will be made to assess the effect of calcining temperature on the distribution of impurities in BeO particles.

METALLURGY

Uranium Alloys for High-Temperature Application

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

An evaluation of elevated-temperature physical and mechanical properties of binary uranium alloys containing additions of molybdenum, niobium, and zirconium is in progress. The alloys are considered as possible reactor fuels at beta-phase operation temperatures. An additional portion of the program is to irradiate, examine, and evaluate specimens of uranium-15 w/o zirconium and uranium-10 and 20 w/o niobium after 1 a/o total burnup.

Last month, elevated-temperature tensile properties were reported for uranium-7 and 15 w/o niobium alloys heat treated by water quenching from their rolling temperatures of 1450 and 1600 F, respectively. Additional tensile data are being obtained upon the same alloys heat treated at 1065 F to transform the gamma structures. In addition, specimens of uranium-10 w/o niobium in both gamma-quenched and transformed conditions will be tested. An ingot of uranium-20 w/o niobium, weighing approximately 2 kg, has been successfully prepared by induction-melting techniques. The charge was made up of prealloyed arc melts, heated to 3250 F and poured at that temperature into a 1-1/2-in.-diameter graphite mold. Attempts are being made to fabricate this ingot into tensile specimens.

The first irradiation capsule is being readied for shipment to the MTR. Contained within the capsule are three pins, individually sealed, of uranium-10 and 20 w/o niobium and uranium-15 w/o zirconium, respectively. Two other capsules planned for irradiation are also in preparation.

Preparation and Properties of Low-Melting Alloys

C. K. Franklin, A. W. Hare, W. E. Murr, A. A. Bauer,
and R. F. Dickerson

The development of a low-melting or castable uranium alloy for possible use as a power-reactor fuel is continuing. The alloy under present investigation is composed of uranium-5 w/o chromium-1 w/o molybdenum.

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Specimens of the as-cast alloys are to be irradiated in temperature-controlled capsules at 600 C and in capsules not temperature controlled at about 300 C. The specimens are to be irradiated to burnups of approximately 1 total a/o.

Fuel pins of this alloy have been prepared by casting in both cold graphite molds and heated (1000 F) graphite molds. Metallographic examination of alloys from the two casting operations show that microinhomogeneities are slight and general in distribution where present. The specimens cast in cold graphite molds will be used for the irradiation studies.

The test pins have been machined to size and the preirradiation measurements taken. The pins are to be encapsulated and shipped to the MTR for irradiation.

Compartmentalized Fuel Elements

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

With the completion of the fabrication development program, work has been directed to the preparation of irradiation specimens. All of the materials investigated appear promising for irradiation testing; however, because of limited funds, only two cermet-type systems, UC or UN dispersed in stainless steel and clad with stainless, have been selected for irradiation testing at this time.

These irradiation specimens will contain the amount of uranium which would be present in a fuel element of 27 w/o UO_2 (fully enriched) dispersed in stainless steel. Fully enriched UN and UC will be used in the irradiation specimens.

A series of dummy specimens using natural UC and UN is being prepared to establish the exact fabrication techniques which will be used. Picture-frame packs have been designed, and UC and UN powder is being prepared.

CORROSIONMechanism of Uranium Corrosion

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

The mechanism of aqueous uranium corrosion is being studied to provide data which will enable a corrosion-resistant alloy to be designed.

As part of a series of experiments aimed at determining the oxygen-to-uranium ratio and the valence of the products of corrosion, three samples of corrosion-produced oxide were dried and then ignited to U_3O_8 in a controlled-atmosphere microbalance.

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The oxygen-to-uranium ratios for the dry oxides were 2.19, 2.26, and 2.19. Similar tests are to be run with "inactive" UO_2 prepared by reducing U_3O_8 with hydrogen.

Corrosion tests with zone-melted and ingot material were continued at 200 C in a moist flowing-argon atmosphere. To date, results have not been of sufficient consistency to permit establishment of a plausible corrosion-reaction mechanism. An X-ray analysis of the residual corrosion product shows it to be UO_2 . Examinations of microsections of the metal following corrosion have not revealed the presence of hydrides or oxides as a result of the corrosion.

Floating-zone-melting runs were completed on two ingots of uranium during February. Ingot 12169-11 was given five passes at a rate of 1 in. per hr. Previous ingots have been submitted for spectrographic analysis, but results are not yet available.

Two experiments are planned for the near future:

- (1) To employ slower rates of zone travel, i. e., 1/4 to 1/2 in. per hr to improve segregation.
- (2) To attempt to purify an ingot by heating only to the plastic state of uranium rather than the melting point.

The second experiment will be performed because it is felt that diffusion of impurities in the plastic state of uranium is high. It is planned to give an ingot a large number of passes (perhaps 50) at 1 in. per hr. This is not practicable if the ingot is to be melted, since constant attention is required and the ingot bends out of shape during each pass. It is felt that segregation will result by heating slightly below the melting point. The process can be made continuous and will require a minimum of attention.

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F. STUDIES OF ZIRCONIUM-URANIUM ALLOYS

F. A. Rough

The broad study of zirconium-uranium alloys is continuing with emphasis on further development and understanding of their mechanical properties, corrosion behavior in high-temperature water, and performance in radiation.

Studies of the corrosion of zirconium-uranium alloys include further determinations of the temperature dependence of corrosion of bare samples and evaluation of clad samples. A 70 w/o uranium ternary, resistant to water, is also being sought.

Preliminary results on the irradiation of 22 w/o uranium samples having three heat treatments are reported.

Heat Treatment and Mechanical Properties of Zirconium-Uranium Alloys

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

The isothermal decomposition of beta zirconium-uranium alloys containing 0.094 and 0.29 w/o oxygen is being studied by the determination of time-temperature-transformation diagrams.

A determination of the beta/beta plus alpha transus for alloys containing 7, 10, and 15 w/o uranium for both oxygen levels has been undertaken by quenching the alloys from temperatures of 1200, 1300, and 1400 C under high vacuum. Heat treatments are complete, but the metallographic examination of the quenched samples is incomplete. The transus will be located on the basis of the presence of equilibrium alpha in the microstructures. Solution treatments for the interrupted-quench samples will still be performed at 1000 C as reported previously. The location of the transus will, however, enable the composition of the beta phase to be determined at the solution-treating temperature.

An analysis of the microstructures of the samples for the TTT curves is currently under way, but complete evaluation is contingent upon additional heat treatments. It may be said qualitatively, however, that the addition of oxygen to the alloys increases the kinetics of the precipitation of alpha zirconium at all temperatures investigated.

Corrosion of Zirconium-Uranium Alloys

W. Chubb, R. F. Dickerson, R. S. Peoples, and W. E. Berry

Evaluation of Clad Samples

In order that the corrosion behavior of clad zirconium-uranium alloys may be understood, a program has been instituted to show the effects of cladding and heat

treatment upon representative zirconium-uranium alloys. The cores will be zirconium-22, 50, and 70 w/o uranium alloys made from sponge zirconium; the cladding will be Zircaloy 2.

The core alloys have been obtained and are being machined into disks for insertion into Zircaloy 2 picture frames which have been prepared. Cladding will be done by hot rolling the zirconium alloys in evacuated cans made of titanium-deoxidized steel. These cans are in process of preparation. The roll-cladding operation will be performed in the near future.

Evaluation of Bare Samples

Alloys being studied range in content from 7 through 70 w/o uranium and were arc-melted from crystal bar, sponge, and high-oxygen-sponge zirconium.

Corrosion tests in 600 and 680 F high-purity water have been terminated. Studies in 500 F water are being continued in an attempt to establish corrosion rates of alloys low in uranium content (less than 30 w/o). Since temperature-dependency plots of the logarithm of the linear corrosion rate versus the reciprocal of absolute temperature do not result in straight lines, corrosion tests are now under way in 550 and 640 F water to more definitely establish the effect of temperature. Exposure time at these temperatures is not yet sufficient to establish the desired corrosion rates.

Development of Corrosion-Resistant 70 w/o Uranium Alloys

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

The possibility of improving the corrosion resistance of the zirconium-70 w/o uranium alloy either by heat treatment or by ternary alloying is being studied.

Molybdenum, silicon, and titanium additions were made to the base alloy with the objective of tying up the free alpha uranium present in this alloy at equilibrium in the form of a compound or intermediate phase. The molybdenum additions were also made with the aim of stabilizing the beta zirconium or gamma-uranium phase. Ternary additions were substituted for zirconium in order to keep the uranium concentration constant.

Corrosion tests of these alloys have been completed; alloy specimens were exposed bare in 680 F water in a variety of heat-treated conditions. The treatments included quenching from gamma-uranium temperatures, furnace cooling, isothermal-transformation treatments at temperatures ranging from 360 to 575 C, and quench-and-anneal treatments. The zirconium-uranium-silicon alloys were given an epsilonizing treatment designed to produce U_3Si prior to these treatments.

In all conditions of treatment, the zirconium-uranium-silicon specimens were found to disintegrate during test in 680 F water within 24 hr. The majority of specimens had corrosion lives of less than 6 hr. Metallographic examination of sections of corroded specimens indicated that corrosion was proceeding along stringers of compound

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present in the alloy, eating out the matrix material. These results suggest that formation of the compound has produced alloy depletion in adjacent areas. Possibly homogenization treatments would result in improved corrosion performance.

Similarly, the corrosion life of zirconium-uranium-molybdenum specimens was found to be extremely short. While the majority of specimens looked excellent and had low weight losses after a 24-hr exposure, within the next 24-hr period the specimens began to crack. The single exception was a specimen which was furnace cooled after 24 hr at 900 C; it lasted 96 hr before cracking. Metallographic examination of corroded specimens indicated that the cracking was associated with hydride formation. This behavior may limit the application of zirconium-uranium-molybdenum alloys in general.

The zirconium-uranium-titanium alloys tested also were found to have poor corrosion resistance. However, it was felt to be encouraging that corrosion proceeded by a uniform surface attack as determined by metallographic study. A single specimen of those tested had a corrosion life in excess of 48 hr. This specimen had received a slow furnace cool from 800 C which is believed to produce the most nearly equilibrium structure obtained as a result of the various heat treatments. Additional specimens are being heat treated in an attempt to increase the degree of equilibrium with the expectancy of improved corrosion resistance.

The base binary zirconium-uranium alloy appears on the basis of these results to have the best bare corrosion resistance of the alloys tested to date. The optimum treatment for the base alloy appears to be an isothermal transformation at 500 C for about 100 sec after solution treatment at 800 C. Corrosion results on the base alloy were reported in BMI-1161.

Meanwhile alloys are being prepared for corrosion study in the clad condition. These include alloys identical to those already described as well as zirconium-uranium alloys containing niobium additions.

Radiation Stability of Zirconium-Uranium Alloys

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

The work on the program concerned with the study of the effect of irradiation on zirconium-uranium alloys is being continued. The initial radiation-effects experiment has been done on 12 zirconium-22 w/o uranium specimens. Further work is planned for the zirconium-22 w/o uranium alloys and zirconium-50 w/o uranium alloys.

The postirradiation measurements have not been completed in the 12 zirconium-22 w/o uranium alloys to date. The density measurements, dimension measurements, and photomicrographs of each specimen have been completed. However, until the burn-up determinations have been calculated, a complete evaluation of the radiation data cannot be made.

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The necessary equipment to make postirradiation heat treatments and to measure the rate of fission gas released during heat treatment of the specimens is now being assembled. The heat treatment and measurements of the rate of fission gas release will probably be completed in the next 2 months.

The zirconium-50 w/o uranium irradiation-test specimens have been fabricated. Preirradiation measurements are now being completed on these specimens. When these measurements are completed, the specimens will be encapsulated and shipped to the MTR for irradiation to a burnup of about 2 a/o total.

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G. CORROSION STUDIES OF ZIRCONIUM

R. S. Peoples

This section describes research supported by the AEC Reactor Development Division pertaining to a study of the corrosion properties of zirconium-base cladding materials in elevated-temperature water and steam.

During the past month, long-term corrosion studies have been continued for samples of Zircaloy 2 and related alloys exposed to 600 and 680 F water and 750 F steam.

Corrosion Studies of Zirconium and Zirconium Alloys

W. K. Boyd and R. S. Peoples

After exposure periods of more than 40 months in 600 F degassed water, no evidence of transition or breakaway in corrosion rate has been observed for samples representing seven different melts of Zircaloy 2. Total weight gains are slightly in excess of 50 mg per dm².

Corrosion data obtained for intentionally contaminated Zircaloy 2 samples exposed a total of 20 months in 680 F water continue to indicate that (1) corrosion resistance is not affected by hydrogen additions in the range of 500 to 1500 ppm; (2) oxygen additions of more than 6000 ppm destroy corrosion properties; and (3) nitrogen in excess of 200 ppm destroys corrosion properties of Zircaloy 2.

Zirconium Corrosion Committee Program

Long-term corrosion studies on sponge-base zirconium alloys are being conducted in cooperation with the Zirconium Corrosion Committee's program of alloy development. Modified Zircaloy 2 compositions (lower tin with iron and/or nickel) are being studied in 680 F water and 750 F steam. Corrosion rates after a total exposure of 560 days are of the same order as those tabulated in BMI-1152. Trends observed to date may be summarized as follows:

- (1) Alloys containing 0.25 to 0.5 w/o tin with 0.25 to 0.50 w/o iron show a progressive decrease in corrosion resistance as the nitrogen level is increased from 70 through 300 ppm.
- (2) Aluminum additions of 200 ppm lower corrosion resistance of the modified Zircaloy 2 composition.
- (3) The corrosion behavior of tin-iron and tin-nickel alloys is not significantly affected by heat treatments consisting of a slow cool from 775 C or a water quench from 900 C.

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- (4) Alloys containing 0.2 to 0.5 w/o tin and 0.2 to 0.5 w/o iron are more resistant to 680 F water than are tin-nickel alloys of similar composition; however, the reverse is true in 750 F steam.

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H. REACTOR MATERIALS DEVELOPMENT

F. A. Rough

A program of assistance to ANL and various reactor materials development programs supported by the AEC are included in this section.

A variable-composition phosphate enamel is being investigated as a coating for uranium. Further studies are intended to eliminate crazing of the enamel coatings.

Nickel has been found to be unsuitable, either as a binary or ternary additive, for improving the oxidation resistance of niobium.

Preliminary data are reported for the solubility of titanium in beta uranium. These studies of uranium-rich alloys are continuing.

Difficulties continue to be encountered in the vapor deposition of molybdenum on the inside of small-bore Type 304 stainless steel tubes. New procedures are being evaluated to improve the process, and the deposition of niobium by similar means is to be attempted.

Enameling of Special Metals

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

In this research on developing enamel coatings for uranium, a major problem has been crazing of the coating during the cooling period of the firing cycle. The aluminum phosphate enamel developed, which had otherwise satisfactory adherence properties, could not be altered sufficiently to correct this defect. The solution to this problem was sought this month through the use of a different phosphate enamel with a composition that could be varied over wide ranges and still retain excellent adherence and wetting properties. With this enamel, it would be possible to evaluate more completely the effect of the thermal expansion of the enamel on crazing.

The phosphate enamel used in this investigation contained lead oxide, iron oxide, and sodium oxide. Four compositional groups were evaluated, based on their calculated P_2O_5 content. The fixed molar percentage of P_2O_5 for these groups was 45, 50, 55, or 60. Initial compositions studied indicated that the lead oxide, iron oxide, or sodium oxide contents could be varied considerably without causing devitrification in the groups having either 50 or 55 mole per cent of P_2O_5 .

Crazing was not eliminated, but more compositions will be tested in the effort to eliminate it.

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Oxidation-Resistant Niobium Alloys

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

Niobium is attractive as an elevated-temperature structural material because of its good high-temperature mechanical properties, but it suffers from a high oxidation rate. This program is concerned with the oxidation behavior of pure niobium and various niobium-base alloys.

Air-oxidation tests by the intermittent-weighing method have been completed on two niobium-nickel binary alloys and four niobium-base ternary alloys containing nickel. The oxidation rates for these alloys in undried air are given in Table H-1. Binary additions of 10 and 20 a/o nickel promoted a slight decrease in oxidation rates at 600 and 800 C, but the alloys oxidized faster at 1000 C as compared with pure niobium. Ternary additions of 5 a/o nickel raised the oxidation rates of niobium-25 a/o titanium, niobium-5 a/o molybdenum, and niobium-10 a/o vanadium by about 50 per cent, and raised the oxidation rates of the niobium-25 a/o chromium alloy by factors of 3 to 6. Thus, binary and ternary additions of nickel are not of interest to improve the oxidation resistance of niobium.

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

Alloy Composition, a/o	Cast Hardness, VHN	Oxidation Rate at Indicated Temperature, mg/(cm ²)(hr)		
		600 C	800 C	1000 C
Nb-10Ni	276	1.92	29.8	38.0
Nb-20Ni	330	0.98	14.5	32.6
Nb-25Ti-5Ni	253	0.10	0.67	2.94
Nb-5Mo-5Ni	256	0.445	3.22	7.17
Nb-10V-5Ni	299	0.15	1.06	4.05
Nb-25Cr-5Ni	258	1.50	35.8	23.0
100Nb (a)	115	5.7	33.7	24.2
Nb-25Ti (a)	156	0.05	0.6	1.9
Nb-5Mo (a)	166	0.25	2.1	4.6
Nb-10V (a)	172	0.05	0.7	3.5
Nb-25Cr (a)	345	0.5	5.1	6.1

(a) Data from previous tests included for comparison.

Two continuous-weighing oxidation tests have been completed on pure niobium in controlled-humidity air at 800 C. These tests were conducted for 5-1/2 and 6 hr compared with 2 hr for previous tests, to further investigate the time-dependent nature of the oxidation weight gains. The results, given in Table H-2, indicate that the weight gains in wet air for the present test are similar to those for dry air in previous tests. The sample oxidized in dry air gained about 20 per cent more weight than either the wet-air test or the previous dry-air tests.

The results also indicate that the time law determined in the previous 2-hr tests is applicable for exposures up to 6 hr. The weight gains are expressed by the equation

$$W = Kt^n,$$

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where n is between 0.5 and 1.0. The fact that the weight gains cannot be expressed by either a simple linear ($n = 1.0$) or parabolic ($n = 0.5$) time law is not yet explainable.

TABLE H-2. AIR-OXIDATION RATES FOR PURE NIOBIUM AT 800 C

Water Vapor Pressure, mm of mercury	Duration of Test, min	Values of Constants		Weight Gain, mg per cm ²					
		$K,$ mg/(cm ²)(min ⁿ)	n	1 Hr	2 Hr	3 Hr	4 Hr	5 Hr	6 Hr
0	325	2.10	0.677	34.9	56.5	74.8	90.6	104.3	--
100	360	1.93	0.657	28.9	46.6	60.9	71.9	82.7	92.8
0(a)	120	2.17	0.635	29.9	46.0	--	--	--	--

(a) Average data from two previous tests included for comparison.

X-ray diffraction measurements have been made on both the loose white outer scales and the adherent black subscales from four pure niobium samples and six niobium-titanium samples. The results, given in Table H-3, indicate that in all but one case the only identified oxide in either scale was Nb₂O₅. Pure niobium oxidized at 1000 C and showed traces of oriented NbO in the adherent subscale. The major difference between the outer scale and the subscale appears to be preferred orientation of the latter. Additions of titanium up to 30 a/o do not change the phases present in the scales.

TABLE H-3. RESULTS OF X-RAY DIFFRACTION ANALYSES OF NIOBIUM SCALES

Alloy Composition, a/o	Oxidation Conditions		Phases Present in Scales
	Temperature, C	Atmosphere	
100Nb	500	Dry oxygen	T-Nb ₂ O ₅
100Nb	600	Dry air	T-Nb ₂ O ₅
100Nb	800	Dry air	T-Nb ₂ O ₅ with a small amount of M-Nb ₂ O ₅
100Nb	1000	Dry air	M-Nb ₂ O ₅ and H-Nb ₂ O ₅ ; NbO possibly present in adherent scale
Nb-10Ti	1000	Dry air	M-Nb ₂ O ₅ and H-Nb ₂ O ₅
Nb-10Ti	1000	Wet air	Ditto
Nb-20Ti	1000	Dry air	Ditto
Nb-20Ti	1000	Wet air	Ditto
Nb-30Ti	1000	Dry air	Ditto
Nb-30Ti	1000	Wet air	Ditto

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Twelve 50-g niobium-base ingots have been arc melted to provide material for continuous-weighing tests. Cold rolling of these ingots to strip was attempted, with results as given in Table H-4. Four niobium-zirconium ingots, prepared from niobium sheet containing 1 w/o zirconium as an impurity, were unfabricable and have been remelted for encapsulation and hot rolling at 1000 C. Niobium-titanium alloys prepared from zirconium-free niobium were easily fabricable, and have been cold rolled to 0.05-in. strip. Niobium-7.5 a/o vanadium was also fabricable, but the niobium-10 and 12.5 a/o vanadium ingots cracked in two attempts at cold rolling. Restrained cold rolling will be attempted to break up the cast grain structure and increase fabricability.

TABLE H-4. COLD FABRICATION OF NIOBIUM-BASE ALLOYS

Alloy Composition, a/o	Cast Hardness, VHN	Initial Reduction, per cent	Results	Annealing Temperature, C	Final Reduction, per cent	Results
Nb-10Zr	187	7	Cracked	--	--	--
Nb-25Zr	212	10	Cracked	--	--	--
Nb-35Zr	283	5	Cracked	--	--	--
Nb-45Zr	289	36	Cracked	--	--	--
Nb-10Ti	123	73	Excellent	1500	50	Excellent
Nb-20Ti	145	73	Excellent	1500	50	Excellent
Nb-25Ti	145	74	Excellent	1500	50	Excellent
Nb-30Ti	151	72	Excellent	1500	50	Excellent
Nb-35Ti	155	72	Excellent	1500	50	Excellent
Nb-7.5V	168	71	Good	1500	50	Good
Nb-10V	196	19	Cracked	--	--	--
Nb-12.5V	209	14	Cracked	--	--	--
Nb-10V(a)	--	32	Cracked	--	--	--
Nb-12.5V(a)	--	16	Cracked	--	--	--

(a) The original niobium-10 and 12.5 a/o vanadium ingots were remelted and rerolled at 3 per cent reduction per pass instead of 10 per cent.

Plans for future work include:

- (1) Conduction of 6-hr continuous-weighing tests on wrought and annealed niobium at 600 to 1200 C, and on annealed niobium-titanium at 1000 C in wet and dry air.
- (2) Fabrication of niobium alloys containing chromium, molybdenum, tungsten, vanadium, and zirconium for oxidation testing.
- (3) Investigation of the niobium-oxygen reaction at 400 and 550 C.

Uranium-Titanium Alloy Studies

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

A study of the phase diagram in the vicinity of the eutectoid decomposition of gamma to beta plus epsilon (U_2Ti) is currently in progress by means of dilatometry, hot hardness, and metallographic techniques.

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Hot-hardness tests have been run at temperatures ranging from 650 to 770 C. A plot of log hardness versus temperature will show discontinuities where a phase change occurs. The curve will show a change in slope at the intersection of a one-phase region and a two-phase region in the equilibrium diagram. An analysis of the data shows a change of slope at 750 C for a 0.6 a/o titanium alloy. This point represents the solid solubility of titanium in beta-uranium at 750 C. The solid solubility of titanium in uranium is 1.1 a/o at 735 C. The eutectoid horizontal was detected at 722 C and compares closely with Knapton's* value of 723 C. A subsequent run of each alloy will be made to check these results.

Dilatometric data are unavailable due to difficulties in the vacuum system. It is hoped that the temperature-length change curves may be obtained during March.

Metallographic examination of samples quenched from several equilibration temperatures is currently in progress. Results will be used to supplement the other tests.

Vapor Deposition of Molybdenum Coatings
on Stainless Steel Tubing

C. F. Powell and I. E. Campbell

As part of a program of assistance to ANL, Battelle has undertaken the development of processes for vapor depositing molybdenum on the inside and outside of small-bore Type 304 stainless steel tubes.

In prior work, adherent molybdenum coatings were applied to the inside and outside of 20-in. lengths of small-bore Type 304 stainless tubing by hydrogen reduction of MoCl_5 vapor at a total pressure of 10 to 50 mm of mercury. Uniform coatings were obtained on the outside of this tubing, but the coatings on the inside were highly non-uniform, covering only a 2 to 3-in. length of tubing.

One type of coater designed to coat the inside of the tubing was operated at atmospheric pressure and at reduced pressure. The results were not satisfactory because of recurrent breakage of the fragile parts of the apparatus, and plugging of the small passages involved with lower molybdenum chlorides. In some instances, iron or nickel was extracted from the specimen tube by reaction with MoCl_5 , or with the reduction product HCl , and then redeposited on the downstream sections of the specimen as a porous, poorly adherent layer which would form a poor base for a subsequent molybdenum deposit.

Work for February was concerned with (1) deposition of molybdenum by reduction of MoCl_5 vapor with mercury vapor, (2) preparation of niobium pentachloride preparatory to depositing niobium on the inside of the small-bore tubes, and (3) reassessment of the entire coating problem in the light of the difficulties which have been encountered and data which have been obtained to date.

* Knapton, A. G., "The System Uranium-Titanium", Journal of the Institute of Metals, 83, 497 (1954).

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Molybdenum was deposited on the inside of tubing by reduction of MoCl_5 vapor with mercury vapor at reduced pressure, to see if this reaction would avoid codeposition of iron or nickel from their respective chlorides formed by reaction of the tube walls with the MoCl_5 . The molybdenum deposit was more uniform than the comparable deposit obtained by hydrogen reduction, but it was poorly adherent and contained traces of incompletely reduced molybdenum chlorides. There was no evidence of appreciable codeposition of iron or nickel, even though the weight loss in the specimen indicated the formation of considerable amounts of chromium, iron, and nickel chlorides. No further work with mercury reduction is planned in view of the poor-quality deposit obtained thereby.

Examination of the data obtained in past coating experiments with the small-bore tubing, with respect to gas-flow conditions, deposition patterns, deposition rates, deposition products, and temperature zones involved, has led to the design of two types of apparatus which, it is hoped, will avoid the difficulties encountered with previous apparatus. The simpler of these uses a moving temperature gradient of controlled intensity and size, to effect molybdenum deposition from a homogeneous gaseous coating mixture which is passed through the specimen tube. Construction of this unit is nearly completed and it will be tested during the coming month.

The other coating unit will use a new principle of operation, viz., a rapidly oscillating zone of mixing of two separate gas streams (without use of an injection nozzle) within the homogeneously heated specimen tube. This principle of operation will be tested first in the form of its hydraulic analogue (flow of liquids in glass tubes) since this will be quicker and cheaper than construction and operation of the coating unit itself. The model for this study has been completed and the study itself will be made during March. If results of this study are promising, the coating apparatus will be built.

Niobium will be deposited on the inside of the small-bore tubing in one of the coating units available.

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I. PHYSICAL METALLURGY

F. A. Rough

Several basic research programs, sponsored by the Research Division of the AEC, are reported in this section.

The study to determine the properties of various uranium compounds includes the preparation of the silicides, UB_4 and UAl_2 . Data are reported for the reaction of USi , USi_3 , and UAl_2 with oxygen at temperatures of 200 to 400 C. Also Parr oxygen-bomb calorimeters are being modified to determine heats of formation for these compounds.

Study of the constitution of uranium systems includes uranium-zirconium-molybdenum, uranium-zirconium-silicon, and uranium-carbon alloys. Additional high-temperature X-ray data are presented for uranium sesquicarbide (U_2C_3). Study is continuing in order to produce $U_2C_3 + UC_2$ structures and to determine the upper temperature limit of the immiscibility region between UC and UC_2 at high temperatures.

The tensile transition in uranium is being studied. As anticipated, the elongation at fracture of uranium is quite sensitive to strain rate. No serrations were observed in stress-strain curves as reported by others and attributed to twinning and kinking. This may result from a finer grain size where the deformation twins are very fine.

Current experiments in bonding fundamentals, using gold samples, are concerned with the effect of applied bonding pressure on the bond formed instantaneously upon contact of microscale areas.

An improved equation expressing temperature-pressure-composition equilibrium data for niobium-hydrogen is reported. These data are the bases for additional kinetics studies.

PROPERTIES OF URANIUM COMPOUNDS

The fundamental properties of some refractory uranium compounds are being investigated in this program.

Preparation, Fabrication, and Physical Properties

W. D. McKee and M. J. Snyder

It was reported last month that powders made from arc-melted U_3Si_2 , USi , USi_2 , or USi_3 had close to stoichiometric uranium-silicon ratios (± 0.4 w/o) but were low in total uranium plus silicon (96 to 99 w/o). Spectrographic analyses this month showed

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no appreciable metallic impurities were present, indicating oxygen may be the principal impurity. This possibility will be investigated further.

A powder compact of USi_3 sintered at 1475 C (USi_3 melting point is reported as 1500 C) apparently lost some component by volatilization, as a surface crust was formed. Another sample will be sintered to obtain weight-loss data, and chemical analyses will be obtained, if the data warrant it.

Sintering and melting-point studies of the uranium silicides are continuing. To date, bulk densities greater than 95 per cent of theoretical have been obtained by sintering powder compacts of USi , USi_2 , or U_3Si_2 in high vacuum. No apparent volatilization of either uranium or silicon occurred, indicating that all of these compounds have low dissociation pressures.

An attempt to sinter powder compacts of UB_4 at 2000 C failed owing to equipment breakdown, resulting in loss of the specimen by oxidation. More UB_4 powder is being prepared.

Sintering studies of UAl_2 are being continued. An arc melt of UAl_3 has been made, and sintering studies of this compound will be started.

Reaction With Gases

W. M. Albrecht and M. W. Mallett

The reactions of several common gases with certain uranium compounds are being studied.

Sintered compacts of USi , USi_3 , and UAl_2 were reacted with oxygen in the temperature range 200 to 400 C for a period of 3 to 4 hr. The reactions were found to follow the general equation:

$$w = kt^n,$$

where

w = weight gain in g per cm^2

k = rate constant

t = time in sec.

The value of n depends upon the rate law that is followed, for example $n = 1$ for the linear law, $n = 0.5$ for the parabolic law, and $n = 0.33$ for the cubic law. However, for the present materials no common rate law was followed, and the value of n varied with the uranium compound.

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The values of n and k obtained at various temperatures are given in the following tabulation:

<u>Compound</u>	<u>Temperature, C</u>	<u>n</u>	<u>k</u>
USi	200	0.84	0.19
	300	0.71	4.2
	400(a)	--	--
USi ₃	300	0.45	4.9
	400	0.35	25.0
UAl ₂	200	0.32	13.7
	250	0.30	33.2
	300(a)	--	--

(a) Samples burned nonisothermally.

The reaction of oxygen with USi follows a reaction rate between the linear and the parabolic laws. Apparently an imperfect protective film is formed on the USi during oxidation. Protective films were formed on both the USi₃ and UAl₂ compounds. The film formed on UAl₂ was most protective, compared with those on the other compounds.

Additional rate data are being obtained.

Heat-of-Formation Measurements

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

Preliminary work has proceeded during the past month on the use of bomb calorimetry for determining the heat of formation of USi₂ and other refractory uranium compounds.

Parr oxygen-bomb and peroxide-bomb calorimeters are being modified for use. The oxygen bomb will be provided with electrodes and a fusion cup of platinum to withstand high temperatures without oxidation. Platinum fuse wire will be used with a time switch in order that the firing energy may be made reproducible. Temperatures will be measured with a platinum-resistance thermometer and Mueller bridge. The water jacket, which completely surrounds the calorimeter, is thermostatically controlled.

The peroxide bomb will be used in the same isothermal jacket. This bomb is being modified to allow thermoelectric measurement of fusion-cup temperature. The temperature and duration of the fusion are expected to be important considerations

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with regard to both the completeness of the reaction and the extent of unwanted reaction with the nickel cup.

Preliminary experiments with the two calorimeters will be continued. When several oxidations have been carried out by each method with apparent success, the products will be examined to determine the completeness of reaction.

INVESTIGATION OF THE TENSILE TRANSITION IN
ALPHA URANIUM

L. L. Marsh and G. K. Manning

The effects of grain size and strain rate on the tensile properties of uranium over the temperature range defining the tensile transition are currently being studied. Accompanying this study is an investigation of the metallography of plastic deformation as affected by these variables. A parallel study is also being made on polycrystalline magnesium and zinc in order to better define the nature of the transition in uranium.

Testing is in progress on uranium over the temperature range of 200 F to minus 80 F for ASTM grain sizes of 0 and 3. The variation in strain rate presently being studied is 0.008 to 1.0 per sec. As anticipated, the sensitivity of uranium to strain rate is large, amounting to a decrease of approximately 50 per cent in the total elongation at fracture for the fastest of strain rates mentioned. A particularly interesting observation is that no serrations in the stress-strain curve have been observed as was reported by Lloyd and Chiswick.* The sudden dropping of the load was attributed to twinning and kinking by these authors. However, since twinning is favored by a large grain size, the absence of such behavior in the current tests may be due to the fine grain size where the deformation twins are extremely fine.

CONSTITUTION OF URANIUM ALLOYS

Uranium-Base Ternary Alloys

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

An investigation of delta-phase relationships in the uranium-zirconium-molybdenum system is being carried out. X-ray diffraction and metallographic studies of heat-treated specimens, varying in composition between the delta phases of the uranium-zirconium and uranium-molybdenum systems are nearly complete. High-temperature X-ray diffraction studies are being planned for more complete information of the phase regions present. Metallographic examination of heat-treated specimens

* Lloyd, L. T., and Chiswick, H. H., Trans. AIME, 203, 1206 (1955).

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to determine the extent of solid solubility near the ends of the ternary section has begun. A tentative diagram should be available and will be reported shortly.

Investigation of the uranium-rich corner of the uranium-zirconium-silicon system is proceeding. Metallographic examination of heat-treated specimens has been initiated, and X-ray diffraction studies are being planned.

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

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

Previous monthly reports have treated the behavior of UC_2 and UC when examined at elevated temperatures by X-ray diffraction. Preliminary results of the behavior of U_2C_3 at elevated temperatures were reported in BMI-1161.

Continued work in the region between UC and UC_2 has provided information in the following areas: (1) the stability of U_2C_3 as an equilibrium phase, (2) the expansion characteristics of U_2C_3 , (3) the relative volatility of the phases involved, and (4) some information on the mutual solubilities of UC and UC_2 at elevated temperatures.

A second sample containing UC plus U_2C_3 was prepared from finely ground UC and UC_2 powders. At 1850 C, the U_2C_3 decomposed to UC and cubic UC_2 and exhibited the same behavior as previously reported. The sample was then returned to 1750 C. After holding 15 hr at this temperature, no U_2C_3 was observed to have reformed, indicating that U_2C_3 requires some stress or pressure for its ready formation, as previously reported.

The mean coefficient of expansion of U_2C_3 was determined from precision parameter data at temperature; it followed a linear plot varying from 9.0×10^{-6} per deg C at 1000 C to 11.30×10^{-6} per deg C at 1800 C.

Further attempts to produce samples yielding diffraction patterns of U_2C_3 plus UC_2 have failed to date. This fact and comparison of previous metallographic and chemical analyses with the diffraction data have pointed up a difficulty in performing high-temperature diffraction work. The results indicate the UC_2 has a higher vapor pressure than UC, with U_2C_3 being intermediate to both. This property means that in any two-phase system of unequal vapor pressure the diffraction pattern from the sample surface will indicate less of the high-vapor-pressure phase than actually is in the bulk composition. Hence, although higher carbon samples than U_2C_3 have been prepared, the X-ray diffraction patterns correspond to lower carbon contents.

The above difficulty has prevented the determination of solubilities in the conventional manner using lattice parameters. To circumvent the problem, a modified approach was undertaken. Since UC and UC_2 are cubic and interstitial-like in character, a uniform variation in lattice parameter with carbon composition should be found for intermediate compositions.

I-6

When the U_2C_3 decomposed to UC and UC_2 at 1800 C, the parameters were determined and used, together with those of the stoichiometric compositions, to determine the solubility limits of UC and UC_2 at 1800 C. The solid-solution region for UC was 4.9 to 5.9 w/o carbon and for cubic UC_2 from 8.7 to 9.1 w/o carbon.

While the above technique assumes a linear variation between UC and cubic UC_2 parameters, deviations are small enough to allow such estimation of solubility. It is interesting to note that the value so obtained is in good agreement with the Bureau of Standards' determination using relative intensities of phases involved.

Some consideration has been given to the carbon-atom positions in the structures of UC and cubic UC_2 . Space considerations and X-ray intensities require, respectively, two separate structures, if the normal metallic radii are assumed. The positions of the carbon atoms in the transition of UC to cubic UC_2 is likewise of considerable interest and a knowledge of this may shed more light on the uranium "interstitials".

Work to determine the upper temperature limit of the immiscibility region of the phase diagram and to obtain data on samples between UC_2 and U_2C_3 will continue. In addition, further consideration of the carbon positions in these structures appears warranted

STUDY OF BONDING FUNDAMENTALS

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

Investigations into the mechanism and variables operative in the solid-state bonding process have been continued. Experiments in February were concerned with the effect of applied bonding pressure on the bond formed instantaneously upon contact at microscale areas. Measurements were made of the rupture strengths of contact regions between gold needle points and plane gold surfaces. To approximate an instantaneous bonding condition, the loading-unloading-rupture sequence was carried out in the minimum time possible with the present apparatus. Loads ranging from 50 to 1000 mg were applied at 600 C; the resulting bond was then tested.

Results to date indicate a slight load dependence of the instantaneous bond strength, with average values ranging between 1100 and 2200 mg (corrected to room temperature). The variation of applied load in the range between 100 and 600 mg appeared to influence bond strength only slightly; strengths were increased with a further increase in applied load. A significant difference in bond strength was observed for a series of tests made on a second gold flat, although the material had been given the same initial treatment. This suggests an uncontrolled variable, possibly an orientation effect.

Efforts were continued in the modification of an apparatus for direct microscopic examination of specimens under testing conditions. To a similar end, preliminary experimental techniques are being devised for metallographic sectioning and examination of the as-bonded specimens. If either of these procedures can be sufficiently

I-7 and I-8

refined, additional information from direct measurements of the contact regions will be available for use in developing a rational expression for bond formation and growth.

NIOBIUM-GAS REACTIONS

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

A study is being made of the kinetics and mechanisms of the reactions of nitrogen and hydrogen with niobium. Investigations of the niobium-hydrogen reaction are being conducted at the present time. Determination of the temperature-pressure-composition equilibrium diagram of the niobium-hydrogen system is being continued.

Additional data have been obtained using niobium foil (0.012 in. thick) and rod (1/8 in. in diameter) over a wider temperature and pressure range than reported previously. An improved expression of the data is given in the equation below.

$$\log_{10} \frac{S_{\text{ppm}}}{P_{\text{mm}}^{1/2}} = \frac{2030}{T} - 0.568.$$

This equation applies to the range 10 to 1000 mm of mercury at 500 to 900 C and at hydrogen concentrations up to 1600 ppm. The heat of solution for hydrogen in niobium is minus 9270 cal per g atom.

Further equilibrium experiments are being continued at lower temperatures and higher hydrogen concentrations. Experiments based on these equilibria are being planned to obtain diffusion and kinetic data.

J-1

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

P. D. Miller, C. L. Peterson, R. S. Peoples, F. W. Fink,
E. L. White, E. B. Friedl, and O. M. Stewart

In a program of assistance to ORNL, investigations concerning the corrosion problems associated with the reprocessing of spent reactor fuel elements have been continued.

Zircex Process Studies

The preliminary tests of various materials in four compositions of nitric acid have been completed.

The results in 0.5 M HNO_3 are included in Table N-1 of this report and in Table N-1 of BMI-1152. The results show that tantalum, titanium, Type S-816, Haynes 25, Vitallium, and Hastelloy C have corrosion rates less than the arbitrary limiting value of 3 mils per month. Results in other solutions were reported earlier.

Table N-2 summarizes the results of those materials resistant in the four solutions tested. It can be seen that tantalum is the only material resistant in all solutions. Unfortunately tantalum will not withstand the hydrochlorination conditions at temperatures of 400 to 600 C.

Figures N-1, N-2, N-3, and N-4 are graphical representations of the corrosion resistance of all the materials tested in the four solutions. The results are similar to those in Table N-2 except that values for poorly resistant materials are also included.

Exposure tests of the five materials resistant to 5 M H^+ , 0.4 M UCl_3 , 4.6 M NO_3^- solutions have now been run for an additional 4 weeks with no appreciable change in results.

Eleven materials are being evaluated in a new type of Zircex elimination test in a solution of 5 M HNO_3 , 0.4 M $\text{UO}_2(\text{NO}_3)_2$, and 500 ppm chloride. Results will be reported in detail at the conclusion of the test. On the basis of tests conducted to date, Hastelloy C is the only nonresistant material. Experiments are under way to analyze the gaseous constituents above 11-15 M HNO_3 -HCl systems.

Hydrochlorinator. Furnace equipment has been assembled for tests of materials subjected to an atmosphere of HCl, hydrogen, and ZrCl_4 at 400 to 600 C. These tests will also incorporate introduction of the same materials into boiling acid solutions in a cyclic manner.

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TABLE J-1. ZIRCEX BOILING NITRIC ACID ELIMINATION-TYPE TESTS (ca 0.5 M HNO₃, ca 0.4 M UC1₃)

Specimen	Specimen Position	Weight Loss, mg	Corrosion Rate, mils per month	Weight Loss, mg	Corrosion Rate, mils per month	Weight Loss, mg	Corrosion Rate, mils per month	Weight Loss, mg	Corrosion Rate, mils per month
		168 Hr		335 Hr		502 Hr		669 Hr	
Vitalium	Vapor	49.0	1.21	64.9	0.81	74.9	0.62	86.2	0.54
	Interface	0.6	0.02	1.0	0.01	2.0	0.02	2.2	0.01
	Liquid	0.2	0.01	1.1	0.01	3.6	0.03	12.2	0.08
Haynes 25	Vapor	3.6	0.02	6.0	0.02	9.6	0.02	10.6	0.02
	Interface	94.6	0.62	100.3	0.33	104.9	0.23	109.0	0.18
	Liquid	117.2	0.78	124.1	0.41	131.6	0.29	141.5	0.24
Type S-590	Vapor	24.3	0.18	67.1	0.25	102.5	0.25	153.8	0.29
	Interface	48.1	0.36	48.8	0.18	50.3	0.13	54.3	0.10
	Liquid	1869.0	13.99	3188.4	11.97	3174.1	7.95	3272.0	6.15
Hastelloy C	Vapor	101.0	0.63	131.4	0.41	149.5	0.31	160.2	0.25
	Interface	192.6	1.37	258.3	0.92	359.6	0.86	445.0	0.80
	Liquid	301.9	2.11	601.0	2.11	743.0	1.74	912.7	1.60

Note: Specimens of Carpenter 20 and Carpenter 20 stabilized were eliminated from this series of tests after 168 hr of exposure, and specimens of Type 304 ELC after 4 hr of exposure because of excessive corrosion rates.

TABLE J-2. MATERIALS RESISTANT TO ZIRCEX ELIMINATION-TEST SOLUTIONS

Elimination Test	Material	Maximum Corrosion Rate, mils per month	Specimen Position(a)	Exposure Time, hr
ca 0.5 M HNO ₃ , ca 0.4 M UC1 ₃	Titanium	Weight gain	V, I, L	658.5
	Tantalum	0.00	I	658.5
	Type S-816	0.13	I	658.5
	Haynes 25	0.24	L	669
	Vitalium	0.54	V	669
	Hastelloy C	1.60	L	669
3.0 M H ⁺ , 0.4 M UC1 ₃ , 2.8 M NO ₃ ⁻	Tantalum	Weight gain	V, I, L	674
	Titanium	0.02	I	674
	Vitalium	0.15	I, L	661
	Type S-816	0.34	L	674
	Carpenter 20	0.37	L	662
	Type S-590	0.42	L	662
	Haynes 25	0.47	L	662
	Carpenter 20 S	1.04	L	662
5.0 M H ⁺ , 0.4 M UC1 ₃ , 4.6 M NO ₃ ⁻	Tantalum	0.00	V, I, L	1332
	Titanium	0.20	V	1332
	Vitalium	0.42	L	1326
	Type S-816	1.88	L	1332
	Type S-590	2.92	I	1302
15.0 M HNO ₃ , 0.4 M UO ₂ (NO ₃) ₂ , H ₂ gas	Tantalum	Weight gain	V, I, L	656
	Carpenter 20	1.57	V	648

(a) V indicates vapor, I - interface, and L - liquid.

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FIGURE J-1. CORROSION RESULTS IN 0.5 M ZIRCEX SOLUTIONS (BOILING)

Four weeks of exposure unless noted otherwise.

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FIGURE J-2. CORROSION RESULTS IN 3 M ZIRCEX SOLUTIONS (BOILING)

Four weeks of exposure unless noted otherwise.

FIGURE J-3. CORROSION RESULTS IN 5 M ZIRCEX SOLUTIONS (BOILING)

Four weeks of exposure unless noted otherwise.

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FIGURE J-4. CORROSION RESULTS IN 15 M ZIRCEX SOLUTIONS (BOILING)

Four weeks of exposure unless noted otherwise.

J-7

Darex Process Studies

A total of 4 weeks of exposure has been completed with tantalum, titanium, and Type S-816 specimens exposed to the beginning dissolver concentration of the Darex process. The corrosion results and solution composition are given in Table N-3. It can be seen that the rates for Type S-816 are relatively high. However, the rates are lower in the midpoint and final solutions (see Table N-4 in BMI-1161 for the results in the midpoint solution).

Three weeks of exposure of tantalum, titanium, titanium alloy (6 w/o aluminum-4 w/o vanadium), zirconium, Zircaloy 2, and Type S-816 specimens have been completed in solutions corresponding to the final Darex dissolver composition. All materials show low corrosion rates. These data will be tabulated next month when 4 weeks of exposure has been completed.

In connection with the Darex process, tests were completed in which specimens of Type S-816 were exposed to boiling 2, 6, and 15 M HNO_3 with no foreign ions added. As shown in Table N-4, the only serious attack occurred in the cases of the specimens exposed at the interface and in the liquid phase of the 15 M HNO_3 .

Galvanic Effects. During the dissolution of clad fuel elements in a tantalum-lined container, it is likely that the tantalum would be cathodic to the dissolving metal. Tests are being made to evaluate the possible harmful effects of the absorption of the hydrogen discharged on the tantalum surface. Half-cell and open-cell potentials have been measured in 2 M HCl -5 M HNO_3 solutions at boiling for uranium, stainless steel, and tantalum. The half-cell potentials of the uncoupled electrodes with respect to a saturated calomel electrode were: tantalum, +0.90 v (noble); Type 304 stainless steel -0.24 v (active); and uranium -0.71 v (active). Visible evolution of hydrogen on the tantalum surface was observed when uranium was coupled to the tantalum.

An apparatus has been constructed in which long-time tests can be run where an impressed voltage across tantalum and inert carbon electrodes will simulate the half-cell potentials occurring during dissolution.

Chloride Stripper Studies. Tantalum specimens are being tested under conditions simulating those which could occur when chloride is stripped from final Zircex and Darex solutions.

Purex Acid-Extraction Studies

Unstressed specimens of Type 347 stainless steel have been exposed to chloride-contaminated (up to 1 w/o chloride) Purex acid solutions for 4 weeks. The corrosion rate was negligible. These tests are being continued and similar tests with stressed specimens are ready to be started.

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TABLE N-3. DAREX BOILING BEGINNING DISSOLVER-SOLUTION(a) TESTS

Specimen	Specimen Position	Corrosion Rate(b), mils per month							
		A	B	A	B	A	B	A	B
		162 Hr		331 Hr		494 Hr		661 Hr	
Tantalum	Vapor	0.00	0.00	0.00	G(c)	0.00	0.00	0.00	G
	Interface	0.00	0.00	0.00	G	G	G	G	G
	Liquid	0.00	0.00	G	G	G	G	G	G
Titanium	Vapor	0.17	0.27	0.17	0.22	0.16	0.27	0.19	0.27
	Interface	0.43	0.55	0.44	0.60	0.45	0.60	0.53	0.68
	Liquid	0.85	0.93	0.86	0.91	0.90	0.93	0.92	0.94
Type S-816	Vapor	3.22	3.90	2.47	2.84	2.00	2.23	1.96	2.08
	Interface	7.30	7.43	6.33	6.54	5.96	6.10	5.68	5.80
	Liquid	7.24	8.27	6.83	7.27	6.49	6.74	6.35	6.52

(a) These solutions are: 7.00 M H⁺, 2.00 M Cl⁻, 5.05 M NO₃⁻, 0.0110 M Fe³⁺, 0.0030 M Cr³⁺,
0.0012 M Ni⁺⁺, 0.0040 M U⁶⁺.

(b) Specimens A and B are duplicate specimens.

(c) G indicates a small weight gain of less than 4 mg.

TABLE N-4. EXPOSURE OF TYPE S-816 TO BOILING UNCONTAMINATED NITRIC ACID

HNO ₃ Molar	Specimen Position	Corrosion Rate, mils per month, For Indicated Exposure Time			
		167 Hr	334 Hr	502 Hr	669 Hr
2.00	Vapor	0.13	0.08	0.06	0.05
	Interface	0.40	0.24	0.18	0.14
	Liquid	0.42	0.26	0.19	0.16
6.00	Vapor	0.41	0.23	0.27	0.25
	Interface	0.28	0.20	0.22	0.23
	Liquid	0.67	0.46	0.42	0.40
15.00	Vapor	2.17	1.66	1.82	1.86
	Interface	1.83	1.88	4.73	7.67
	Liquid	2.23	2.34	7.90	14.80

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K-1

K. EVALUATION OF A REFLECTOR-CONTROLLED HETEROGENEOUS
BOILING REACTOR

J. W. Chastain

A control system which makes possible long-time unmanned operation of a reactor possible is being investigated. This system of control makes use of the height of the water reflector surrounding the core. The annular reflector tank is connected to a pressurized surge tank and water is exchanged, depending on which has the higher pressure.

During the month of February, data were obtained for a number of reflector heights. These data include critical mass and reactivity worth of the reflector. The worth of the reflector can be obtained quite accurately by remotely changing the height by a small amount and measuring the resulting period.

The simulator system was operated during the month but was unstable. A modification of the system is being made and it should be operating by the end of the month.

Critical Experiment

W. C. Ballowe, D. A. McPherson, R. G. Wilson,
F. J. Jankowski, and J. W. Chastain

The experimental results obtained in the operation of this critical assembly will be used to evaluate the worth and effectiveness of the reflector system of control. Specifically, it will serve as input data to the reactor simulator in order to determine the transient behavior of the reactor system.

During the month of February, experiments were performed on the reactor to determine the movable-reflector worth for two conditions. In one system, a 1/8-in.-thick sheet of polyethylene containing boron carbide was sandwiched between the 6 in. of movable reflector and the stationary reflector. In the second case, this plastic sheet was removed. These two cases are termed the poisoned and unpoisoned cases. During these experiments the core had an aluminum-hydrogen atomic ratio of 0.358. Both the axial and radial reflectors were unvoided, solid polyethylene with a density of 0.91 per cm³.

The results of the experiments are listed in Tables K-1 and K-2. As the experiments on this moderator reflector configuration are not complete, the results given in the tables must be considered as tentative.

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K-2

TABLE K-1. REACTIVITY AND CRITICAL MASS FOR UNPOISONED CASE

Reflector Position, in. from the bottom of the core	Critical Mass, g	Reflector Worth, reactivity per in.
24	5062	$5.6 \pm 0.3 \times 10^{-4}$
0	5584	8.9 ± 1.1

TABLE K-2. REACTIVITY AND CRITICAL MASS FOR POISONED^(a) CASE

Reflector Position, in. from the bottom of the core	Critical Mass, g	Reflector Worth, reactivity per in.
24	5060	6.8 ± 3.0
18	5172	23.8 ± 0.3
12	5383	38.7 ± 1.7
10	5465	35.5 ± 0.7
0	5964	7.0 ± 1.0

(a) The poison consists of 1/8-in. -thick sheet polyethylene containing 0.119 g per cm³ of boron in the form of B₄C forming an annular ring between the inner and outer reflectors.

Experiments are planned which will yield more information on both the poisoned and unpoisoned cases. The reproducibility of the data given above is now being checked and more accurate results will be given at a later date.

Expanded (low density) polyethylene will be used for the reflector in the hot non-power-producing case. Nuclear properties equivalent to water at 417 F and 300 psi will be simulated. Sufficient moderator plastic has been voided for the "hot" case by making random cuts across the width of the strips. The axial reflector will be voided in the same manner.

During March, the present experiments will be completed and the "hot"-water case will begin.

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K-3 and K-4

Simulator Studies

B. B. Gordon and J. J. Stone

The simulator studies mock-up the hydraulic system associated with a reflector-controlled reactor. Dynamic operation is duplicated by driving this system with an operational analog.

During February the mock-up was connected to the computer and the entire system was studied. With no damping the system was unstable and divergent oscillations occurred. The addition of damping improved the system but still did not make it stable. This instability is due to a phase lag in the control system. Two inserts, to convert the control valves from 1/4 to 1/2-in. needles, have been ordered. This should speed up the operation of the control system and eliminate the undesirable phase lag. Delivery of the inserts is expected late in March.

After installation of the inserts the system will be checked again to determine proper damping. Data from the critical assembly can then be included in the simulation.

L-1

L. STUDIES OF SODIUM-TANTALUM COMPATIBILITY
AT ELEVATED TEMPERATURES

J. H. Stang

A program to provide information applicable to several materials problems associated with LAMPRE I is under way at Battelle. LAMPRE I is a fast reactor system being developed at Los Alamos Scientific Laboratory. Its fuel container is to be fabricated from tantalum and cooled by flowing high-temperature (to, perhaps, 1500 F) sodium. The work at Battelle includes corrosion problems posed by the tantalum-sodium combination and tantalum-metallurgy studies.

The first corrosion-test loop (a Type 316 stainless steel system with tantalum inserts) was assembled during February and initial check-out tests were made with 1500 F sodium. Performance was satisfactory, although some mechanical difficulties prevented long-time runs. The system is now being revised slightly and should be in full operation by mid-March. The assembly of five other loop systems is also progressing.

The construction of four inert-atmosphere stress-rupture furnaces for high-temperature experiments in which tantalum will be the test material is nearly complete. This equipment is now being assembled for test runs. Also, during February, improvements were made in the apparatus for degassing tantalum at temperatures in the 500 F range.

Porosity is evident in many welds (by the tungsten-arc process) recently made on sintered tantalum sheet and small tube-to-header assemblies. As pointed out in BMI-1161, it is probable that lack of soundness of the base materials is the chief contributor to porosity. Information obtained during February indicates that factors such as extent of gas shielding, welding procedures, and gas content of the test materials are responsible only in a minor way, if at all.

In the studies to develop a sensitive method for determining oxygen in sodium, the first analytical run was made using titanium to getter oxygen from a sodium sample at 525 C. Since the reaction appeared to be too slow at this temperature, higher exposure temperatures are planned for runs now scheduled.

Tantalum-Sodium Compatibility Studies

D. R. Grieser, C. V. Weaver, and W. H. Goldthwaite

These studies are being conducted to establish the effects that tantalum can experience (corrosion, mass transfer, resulting loss of high-temperature strength, etc.) when exposed to 1500 F peak temperature sodium containing oxygen up to 100 ppm in amount. Polythermal forced-convection (by electromagnetic pumps) Type 316 stainless steel flow loops with tantalum inserts are to be used as the basic test apparatus. Each loop features a built-in cold-trap and gettering circuit incorporated to control the oxygen content of the sodium within fairly narrow limits. Emphasis during February was

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L-3

As discussed in BMI-1161, welds made with 40-mil sintered tantalum sheet exhibited porosity (at the outer edges of welds adjacent to heat-affected zones) while welds made with 30-mil sheet were free of porosity. Since the thicker sheet was not sound, it was suspected that starting-material quality played an important role in this situation. During February, these results were explored further. Additional gas-shielding and welding-procedure studies indicated that these particular factors had little effect on the porosity condition. Analytical data now on hand shed little light on the question. For example, as-polished samples of weld joints in the 40-mil sheet gave no evidence of intermetallic inclusions. In addition, analyses for carbon, hydrogen, nitrogen, and oxygen in the 30-mil (weldable) and 40-mil (unweldable) material indicated that these elements were not responsible for the behavior since the amounts found in the former material were actually greater than in the latter. A summary of these analyses is listed below:

Material	Chemical Analysis, ppm			
	Carbon	Nitrogen	Oxygen	Hydrogen
30-mil tantalum	110	160	208	1.0
40-mil tantalum	20	40	40(a)	0.6

(a) The low oxygen value was substantiated in part by an average low hardness of 100 VHN (2-1/2-kg load).

Several simulated tube-to-header assemblies were made during February with a special welding fixture designed to aid in the welding of tantalum tubes to a tantalum header. The material used in this work was the 30- and 40-mil tantalum sheet mentioned above and sections of sintered tubing (3/16 in. in ID, 15-mil wall). Metallographic studies of sections through the tube-to-header joints indicated gross porosity in specimens made with the 40-mil sheet. Minor porosity existed in the assemblies made with the 30-mil material; however, this porosity is believed to stem from the tubing used. In fact, a section through a bead weld made on this tubing showed porosity similar to that found in the welds in the 40-mil material.

Future work will consist of making additional simulated tube-to-header assemblies. The 30-mil sintered tantalum which is readily weldable will be used along with tubing fabricated from arc-cast material (if delivered on schedule). Meanwhile, it is planned to check small samples of arc-cast tantalum to determine whether this material can consistently yield porosity-free joints. Future work will consist also of changing the spacing distance of the tubes in the header. At present, the closest distance of approach of the tubes is 3/64 in. Changes which will be made will be to increase and decrease the tubing separation to 1/16 and 1/32 in., respectively. This represents an attempt to improve the weld penetration on the back side of the tube-to-header joint.

Determination of Oxygen in Sodium

P. H. Goble, W. M. Albrecht, and M. W. Mallett

A new analytical method for the determination of oxygen in sodium with a sensitivity of 0.0001 w/o is being appraised. It is based on the gettering of oxygen from sodium by a metal which in turn may be analyzed for oxygen pickup.

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L-4

The first analytical run with the new getter apparatus was made in late February. Clean analytical-reagent-grade sodium and a getter of 10-mil sheet titanium were used. The sodium was heated in contact with the titanium for 4 hr at 525 C with constant stirring. According to the subsequent analyses made on it, the titanium picked up an amount of oxygen equivalent to 0.0014 w/o in the sodium. This value is quite low and it is believed that the getter reaction was incomplete under the experimental conditions. The next run will be made in the range 800 to 900 C. This increase in temperature does not materially affect the thermodynamics of the reaction but should considerably improve the kinetics.

A supply of filtered sodium has been obtained. An apparatus which will deliver a metered charge of this sodium directly into the gettering chamber is nearing completion. This same supply of sodium is also being used for check-out runs with an amalgamation apparatus that has been constructed for service-analysis work.

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M-1

M. PROCESSING OF FEED MATERIALS

E. L. Foster, Jr.

Hydrogen is undesirable in uranium-slug feed material. Because of this a program of direct interest to the Feed Metals Processing Center (FMPC) is in progress. This program is concerned with the role of salt-bath heat treatment in the pickup of hydrogen by uranium slugs. From previous studies, it was determined that a significant increase in hydrogen content could be attributed to the salt bath now in use. In addition, further results gave indication that uranium heat treated in baths of two salt systems contained less than the expected quantity of hydrogen. The salt baths selected for further study were NuSal (50 w/o sodium chloride-50 w/o potassium chloride) and K-2 (50 w/o potassium chloride-50 w/o sodium carbonate). The present program is to continue and confirm on a pilot-plant scale, the results of the initial work.

Within the present program, and in addition to the hydrogen-pickup phase, data on the weight loss of the uranium slugs and the relative corrosion attack by the salt bath on both uranium slugs and salt-bath container materials are being gathered. However, these observations are contributory in that the hydrogen content is presently the critical variable of interest.

Results to date are not conclusive because only a few hydrogen analyses have been reported. Uranium slug weight losses continue to be low in the baths being tested and corrosive attack is slight. Corrosion of the mild steel containers appear to be greater in the pot containing K-2 salt mixture than in the pot with the NuSal salt bath.

Salt-Bath Development

L. L. Lortscher, K. A. Sense, and R. B. Filbert, Jr.

Studies of the hydrogen pickup by uranium rods heat treated in pilot-plant-scale salt baths is the object of a program in progress at Battelle. Previous laboratory-scale work indicated that two particular salt mixtures might reduce hydrogen pickup below that obtained with the salt mixture now in use at Fernald. These salt mixtures are (1) 50 w/o sodium chloride-50 w/o potassium chloride, and (2) 50 w/o potassium chloride-50 w/o sodium carbonate. In the present program, uranium specimens are heated at weekly intervals during each salt-bath test, each of which is run continuously for 3 weeks. Treatment of uranium specimens in three of the five salt-bath tests originally planned has been completed. Hydrogen analyses (conducted by NLO at Fernald) have been obtained for 4 of the 20 uranium specimens treated so far.

The test of Salt Bath 2, consisting of 93.0 w/o K-2 (50 w/o KCL-50 w/o Na_2CO_3) plus 3.1 w/o Li_2CO_3 and 3.9 w/o K_2CO_3 , has been completed. Three groups of two specimens each were treated (one group at each of the three weekly intervals) by the previously established procedure, which consists of immersing a pair of uranium specimens in the salt bath at 1350 F for 13.5 min, quenching in water for 2 min, and rinsing for 10 sec in a second tank of water.

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M-2

TABLE M-1. HYDROGEN CONTENT OF URANIUM SPECIMENS TREATED
THE FIRST AND SECOND WEEKS IN SALT BATH 1
(93.5 w/o NuSal, 6.5 w/o K-2)

Specimens	Hydrogen Content, ppm
1-1-a	0.51
1-1-b	0.21
1-2-a	0.40
1-2-b	0.37

TABLE M-2. WEIGHTS OF URANIUM SPECIMENS TREATED
THE THIRD WEEK IN SALT BATH 2 (93.0 w/o
K-2, 3.1 w/o Li_2CO_3 , 3.9 w/o K_2CO_3)

	Specimen 2-3-a	Specimen 2-3-b
Weight Before Treatment ^(a) , g	943.37	949.64
Weight After Treatment, g	941.00	947.74
Weight Loss Due to Treatment, g	2.37	1.90
Weight Loss, per cent	0.25	0.20

(a) Treatment refers to operations of heating, quenching, rinsing, and drying the specimens.

TABLE M-3. WEIGHT LOSS OF URANIUM SPECIMENS TREATED THE FIRST, SECOND,
AND THIRD WEEKS IN SALT BATH 3 (93.5 w/o K-2, 1.6 w/o Li_2CO_3 ,
4.9 w/o K_2CO_3)

Specimens ^(a)	Weight Loss	
	G	Per Cent
3-1-a	1.85	0.19
3-1-b	2.70	0.28
3-2-a	2.25	0.23
3-2-b	1.70	0.19
3-3-a	2.05	0.21
3-3-b	1.95	0.20
3-3-c ^(b)	7.60	0.82
3-3-d ^(b)	7.35	0.78

(a) These specimens treated as noted in Footnote (a) of Table M-2.

(b) These specimens were treated for 135 min instead of 13.5 min.

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M-3 and M-4

Work with Salt Bath 3, which consisted of 93.5 w/o K-2, 1.6 w/o Li_2CO_3 , and 4.9 w/o K_2CO_3 , has also been completed. The same mild steel pot and mild steel electrodes used for the previous K-2 test (Salt Bath 2) were retained for this salt-bath test. During this test the heat-treating procedure was modified by adding a second rinse of 5 min in duration in separate 140-ml samples of distilled water for each uranium specimen. The pair of specimens treated when the salt bath was 1 week old was treated by the old procedure. The two pairs of specimens treated when the salt bath was 2 and 3 weeks old were treated by the modified procedure. A fourth pair of specimens was treated for 135 min instead of 13.5 min when the bath was 3 weeks old.

Hydrogen analyses were received for four of the six uranium specimens treated in Salt Bath 1 (described in Report BMI-1161) which consisted primarily of NuSal. The hydrogen contained in these specimens ranged from 0.21 to 0.51 ppm. The difference between specimens treated the first week and specimens treated the second week of the test were not significant. The individual results are recorded in Table M-1.

No uranium specimens treated in Salt Baths 2 and 3 showed a visible salt coating after quenching. Rinse samples obtained from the modified procedure were analyzed for chloride content to determine whether there is any salt coating retained that is not seen by visual inspection. Results from the rinse samples obtained when Salt Bath 3 was 2 weeks old showed less than 8.35×10^{-6} g per cm^2 of specimen surface. Visible surface corrosion was negligible and weight losses were between 0.2 and 0.3 per cent, except for the two specimens treated in Salt Bath 3 for 135 min. The latter specimens showed some visible surface corrosion and greater weight losses. This long-term heat treatment was carried out to obtain an estimate of the amount of continued weight loss and hydrogen pickup that would occur with increased time. The actual weight losses are recorded in Tables M-2 and M-3.

Quantitative comparison between corrosion specimens suspended in the three salt-bath tests completed to date are not yet available. Qualitatively, the corrosion that took place on the mild steel pot and mild steel electrodes was greater with the K-2 salt baths than with the NuSal salt bath. Visual inspection indicates that the Type 330 stainless steel corrosion specimen corroded much less in the K-2 salt baths than did the mild steel and the Type 304, Type 416, and Type 446 stainless steel corrosion specimens. Metallographic examinations now in progress should provide more exact estimates of the relative corrosion rates of these corrosion specimens.

The planned work consists of initiating and completing the treatment of specimens in another NuSal salt-bath test.

RWD:CRT/all