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PROGRESS RELATING TO CIVILIAN APPLICATIONS
DURING DECEMBER, 1956

by

Russell W. Dayton
Clyde R. Tipton, Jr.

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Classification cancelled (changed) per memo list in Sect. B1

by authority of dated 3-30-60

by J. C. Ridenour TISOR, date 4-7-60

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REPORTS RELATED TO CIVILIAN APPLICATIONS
ISSUED DURING DECEMBER, 1956

- BMI-1141 "Studies of Flow Distribution in the Core of a Quarter-Scale Flow Model of the PWR Reactor", by Herbert R. Hazard and John M. Allen.
- BMI-1147 "Fabrication of Integral Flat-Plate Zircaloy 2 Subassemblies by Roll Bonding", by Stan J. Paprocki and Rinaldo A. Paci.
- BMI-1149 "Progress Relating to Civilian Applications During November, 1956", by Russell W. Dayton and Clyde R. Tipton, Jr.

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A. DEVELOPMENT OF MATERIALS FOR HANFORD REACTORS

F. R. Shober

Thermal-conductivity measurements have been made on uranium, uranium-1.5 w/o zirconium, and Zircaloy 2 as part of a program to determine the feasibility of using clad specimens in this investigation. Results from these measurements indicate that the difference in thermal conductivity values between uranium and uranium-1.5 w/o zirconium is less than the anticipated 5 per cent.

The creep studies on Zircaloy 2 in the 149 to 343 C range are showing that its creep strength is apparently greatly dependent upon fabrication and heat treatment of the material. Seamless zirconium and Zircaloy 2 tubes are being evaluated by burst tests in the 28 to 343 C temperature range.

A hot hydrostatic pressing technique for cladding uranium with zirconium is being investigated. The bond area obtained between nickel-plated uranium cores and zirconium cans was increased from 90 per cent to approximately 95 per cent bonding by increasing the time at 1200 F and 10,000 psi from 2 to 4 hr. The creep testing of uranium has been concluded with tests at 730 C. The stress at this temperature necessary to produce 1 per cent total deformation in 100 hr was approximately 1200 psi.

A study of the radiation damage to graphite at elevated temperatures has been completed.

Thermal Conductivity of Uranium

H. W. Deem and C. F. Lucks

A study of the effect of irradiation on the thermal conductivity of uranium is being made. The purpose of the study is to make steady-heat-flow, thermal-conductivity measurements on irradiated uranium clad in Zircaloy 2 with NaK as the heat-transfer medium. HAPCO is fabricating the clad test specimens. A uranium-1.5 w/o zirconium alloy is being used in the exploratory measurements to represent irradiated uranium, as previous measurements have indicated it to have a thermal conductivity about 5 per cent lower than uranium and similar to that of irradiated uranium.

Some thermal-conductivity measurements have been made on unclad specimens of the three metals involved in the exploratory measurements: uranium, uranium-1.5 w/o zirconium, and Zircaloy 2. Table A-1 shows the observed thermal conductivities. The thermal conductivity of the

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uranium-1.5 w/o zirconium alloy was not the anticipated 5 per cent lower than uranium but the difference may be sufficient to establish the sensitivity of the proposed method of measuring clad specimens. An analysis of the alloy has not been made.

TABLE A-1. THERMAL CONDUCTIVITY OF URANIUM, URANIUM-1.5 PER CENT ZIRCONIUM ALLOY, AND ZIRCALOY 2

Temperature, C	Thermal Conductivity, $w(\text{cm}^2)(\text{C})$			Percentage by Which 1.5 w/o Zirconium Lowers the Thermal Conductivity of Uranium
	Uranium	Uranium-1.5 w/o Zirconium	Zircaloy 2	
20	0.23 ₁	0.22 ₃	0.11 ₇	3.5
100	0.25 ₀	0.24 ₁	0.12 ₀	3.6
200	0.27 ₂	0.26 ₄	0.12 ₃	2.9
300	0.29 ₇	0.28 ₉	0.12 ₈	2.7
400	0.32 ₃	0.31 ₅	0.13 ₀	2.5
500	0.35 ₁	0.34 ₃	0.13 ₅	2.3
600	0.38 ₃	0.37 ₄		2.4
700	0.42 ₁	0.40 ₈		3.1
800		0.44 ₀		
900		0.44 ₇		

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

The Constitution of Thorium-Uranium Alloys

R. F. Dickerson and A. A. Bauer

An investigation is being conducted to determine the solubility of uranium in thorium. On the basis of electrical-resistivity measurements of thorium alloys with varying uranium contents, the solubility of uranium in thorium is estimated to be about 1.5 w/o at 1000 C. This is in agreement with the solubility value estimated from X-ray data obtained previously. At 800 and 900 C the solubilities are estimated to be about 0.7 w/o uranium, both about the same within experimental accuracy. Resistivity data at

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600 and 700 C are inconclusive in establishing any consistent trend which can be attributed to solid solution of uranium in thorium. Previously obtained X-ray data had indicated a solid solubility of less than 1 w/o uranium at 710 C.

Earlier metallographic studies had been hampered by the general inability to identify small amounts of uranium in these alloys. However, present work with a new etchant appears promising in that it may be possible to identify small amounts of the uranium phase. Specimens previously studied are being re-examined.

Mechanical Properties of Zirconium and Zircaloy 2

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

The burst strengths of seamless zirconium and Zircaloy 2 tubes and the creep strength of Zircaloy 2 are being determined. The variations existing from lot to lot of Zircaloy 2 are to be evaluated and the creep rates obtained in 1000-hr tests are to be compared with creep rates from tests of longer duration.

Creep tests are in progress on a second lot of annealed Zircaloy 2 in the 149 to 343 C temperature range at stresses comparable to those used in an investigation of the first lot of material. The second lot of material was received from HAPO in the form of annealed sheet. The analyses of the two lots of Zircaloy 2 are listed below.

<u>Composition of Lot 1, w/o</u>	<u>Element</u>	<u>Composition of Lot 2, w/o</u>
1.61	Tin	1.56
0.11	Iron	0.137
0.049	Chromium	0.092
0.045	Nickel	0.052
Balance	Zirconium	Balance

The plates were fabricated and heat treated at HAPO as follows:

- (a) Rolled to give a 30 per cent reduction
- (b) Salt-bath annealed 5 min at 750 C, water quenched
- (c) Rolled to give a 30 per cent reduction

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- (d) Salt-bath annealed 5 min at 750 C, water quenched
- (e) Rolled to give a 25 per cent reduction
- (f) Vacuum annealed 1 hr at 750 C
- (g) Rolled to give a 35 per cent reduction
- (h) Part vacuum annealed 1 hr at 730 C; remainder retained in the cold-worked condition.

The annealed and cold-worked material had respective hardnesses of 74 to 77 R_G and 88 to 91 R_G. The results of creep tests in progress along with results from tests at comparable stresses on Lot 1 of Zircaloy 2 are given in Table A-2. The creep strength of Lot 2 based on deformation is less than that of Lot 1. Although there are compositional differences between the two lots, it does not seem probable that they are of the order to cause a twofold difference in creep strength. Determination of the grain size of the sheet material showed that Lot 1 grain size was 0.035 to 0.039 mm and Lot 2 was 0.022 to 0.026 mm. The differences in grain sizes of the material from the two lots is probably a factor contributing to the difference in their creep strengths. Chemical analysis for major alloying elements, spectrographic analysis for trace elements, and vacuum fusion gas analysis for gaseous elements will be made to further investigate the compositional mechanical-property differences observed between the two lots of material.

Seamless zirconium and Zircaloy 2 tubes are being evaluated by burst tests at 28, 149, 232, and 343 C to determine the effect of diameter and wall thickness on their burst strengths. The tubes were received in the annealed, 10 to 15 and 40 per cent cold-worked conditions. The results for tests at 28 and 149 C on 1.5-in. -diameter tubes are given in Table A-3. The internal pressure was applied at a constant rate of 1000 psi per min to standardize test conditions. The pressure required to burst the tube increased with wall thickness and with amount of cold work at each temperature. There was very slight difference in burst strengths of zirconium and Zircaloy 2 tubes having a wall thickness of 0.020 in.

The burst pressure decreased with temperature for comparable materials. An indication of the ductility of the tubes was obtained by measuring the greatest change in diameter at the point of rupture after test. Ductility increased with temperature for the fully annealed tubes, but changed very little for the cold worked material.

Tube burst tests will be continued at 232 C on the 1.5-in. Zircaloy 2 and zirconium tubes.

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TABLE A-2. CREEP PROPERTIES OF ANNEALED ZIRCALOY 2

Material Lot	Specimen	Temperature, C	Stress, psi	Time of Test, hr	Deformation at Indicated Time, per cent			
					Load on	50 Hr	100 Hr	500 Hr
1		300	23,000	1,000	0.385	0.90	0.97	1.09
2	31-1	300	23,000	650	0.175	1.80	1.96	2.29
1		300	25,000	1,000	0.385	1.50	1.65	2.17
2	31-2	300	25,000	635	0.23	2.90	3.15	3.60
2	31-4	550	17,500	125	0.48	1.335	1.345	
1		650	9,000	1,000	0.125	0.155	0.160	
2	3-2	650	9,000	150	0.06	0.09	0.1	
1		650	17,500	1,000	0.54	0.655	0.675	
2	3-4	650	17,500	200	0.945	1.615	1.642	
1		650	21,000	1,000	1.47	3.87	3.89	
2	3-5	650	21,000	360	3.30	4.43	4.47	
1		650	22,500	0.4	3.20	Ruptured		
2	3-6	650	22,500	425	4.50	9.45	9.52	

TABLE A-3. BURST STRENGTHS OF ZIRCALOY 2 AND ZIRCONIUM TUBES

Specimen	Material	Nominal OD, in.	Nominal Wall Thickness, in.	Measured OD, in.	Measured Wall Thickness, in.	Cold Work, per cent	Hardness, Rockwell	Burst Pressure, psi	Burst Stress(a), psi	Circumferential Elongation(c), per cent
<u>Test Temperature 28 C</u>										
244-1	Zirconium	1.5	0.020	1.499	0.020	0	15,3 30N	2,050	74,760	24.8
244-2		1.5	0.020	1.509	0.020	0	15,3 30N	2,050	75,030	23.2
250-1		1.5	0.020	1.506	0.020	40	29,8 30N	2,800	103,460	18.3
250-2		1.5	0.020	1.504	0.020	40	29,8 30N	2,800	102,340	16.5
256-1	Zircaloy 2	1.5	0.020	1.498	0.020	0	15,4 30N	2,150	78,800	34.3
256-2		1.5	0.020	1.500	0.020	0	15,4 30N	2,125	77,350	25.6
254-1		1.5	0.020	1.500	0.019	40	35,2 30N	2,800	102,200	15.3
254-2		1.5	0.020	1.502	0.019	40	35,2 30N	2,700	98,350	17.3
389-1		1.5	0.035	1.501	0.036	10-15	86,9 B	4,950	98,170	16.9
389-2		1.5	0.035	1.499	0.0355	10-15	86,9 B	4,950	99,280	23.2
400-1		1.5	0.060	1.501	0.061	0	81,5 B	7,250	83,375	30.3
400-2		1.5	0.060	1.500	0.060	0	81,5 B	7,250	83,315	31.7
404-1		1.5	0.060	1.501	0.060	40	93,8 B	10,100	(b)	--
404-2		1.5	0.060	1.499	0.061	40	93,8 B	9,900	113,685	17.0
<u>Test Temperature 149 C</u>										
244-3	Zirconium	1.5	0.020	1.496	0.020	0	15,3 30N	1,700	62,540	32.9
244-4		1.5	0.020	1.505	0.020	0	15,3 30N	1,800	65,250	43.0
250-3		1.5	0.020	1.509	0.020	40	29,8 30N	2,350	85,950	16.5
250-4		1.5	0.020	1.495	0.019	40	29,8 30N	2,350	85,630	14.2
256-3	Zircaloy 2	1.5	0.020	1.502	0.020	0	15,4 30N	1,850	67,760	43.5
256-4		1.5	0.020	1.493	0.020	0	15,4 30N	1,900	69,540	37.8
254-3		1.5	0.020	1.507	0.019	40	35,2 30N	2,250	86,430	21.3
254-4		1.5	0.020	1.491	0.019	40	35,2 30N	2,200	79,915	17.5
389-3		1.5	0.035	1.501	0.0355	10-15	86,9 B	3,650	73,360	29.3
389-4		1.5	0.035	1.499	0.036	10-15	86,9 B	3,700	74,312	29.9

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TABLE A-3. (Continued)

Specimen	Material	Nominal OD, in.	Nominal Wall Thickness, in.	Measured OD, in.	Measured Wall Thickness, in.	Cold Work, per cent	Hardness, Rockwell	Burst Pressure, psi	Burst Stress(a), psi	Circumferential Elongation(c), per cent
<u>Test Temperature 149 C (Continued)</u>										
400-3	Zircaloy 2	1.5	0.060	1.501	0.060	0	81.5 B	5,700	65,455	50.7
400-4		1.5	0.060	1.499	0.0605	0	81.5 B	5,650	64,927	38.2
404-3		1.5	0.060	1.500	0.060	40	93.8 B	7,900	90,718	16.5
404-4		1.5	0.060	1.502	0.0605	40	93.8 B	7,900	90,718	22.7

(a) Calculated by Barrow thin-tube formula: $S = \frac{Pd}{2t}$, where S = hoop stress, P = internal pressure, d = inside diameter, t = wall thickness.

(b) End failure.

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

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Zirconium Cladding

R. F. Dickerson and F. R. Shober

A hot hydrostatic pressing technique is being investigated as a method of bonding thin-wall zirconium cans to uranium cores. To prevent oxidation of the core during the canning process, nickel-plated uranium slugs have been substituted for the bare slugs. Three of the nickel-plated uranium cores canned in zirconium have been hydrostatically pressed. Two were pressurized at 10,000 psi at approximately 1200 F for 2 and 4 hr, respectively, and the other at 1350 F for 4 hr.

Metallographic examination of the bonded areas of the three specimens showed that 2 hr at 1200 F produced a thin metallurgical bond in approximately 90 per cent of the contact area. The 10 per cent unbonded area was in vicinities of small depressions and irregularities existing in the nickel plate. The specimen pressurized at 1200 F for 4 hr at 10,000 psi showed extensive diffusion in all areas except in the depressions and irregularities. In these areas, a thin diffusion zone was apparent, except at the bottom of the depression. It appeared that approximately 95 to 97 per cent of the area was bonded by a metallurgical bond. The specimen pressurized at approximately 1350 F for 4 hr at 10,000 psi exhibited extensive diffusion zones in both zirconium-nickel and the uranium-nickel interfaces. The grain size of the core was characteristic of beta-annealed uranium. A more detailed metallographic study of bonded specimens will be made to determine the extent of diffusion at both interfaces.

Three additional nickel-plated uranium cores have been canned and will be pressurized at 10,000 psi at 1200 F for 6 hr and at 1350 F for 2 and 6 hr. Several uranium cores without the nickel plate will be canned and tested upon completion of the nickel-plated series.

Miscellaneous Metallurgical Services

R. F. Dickerson and F. R. Shober

A program has been completed in which the creep properties of beta-quenched uranium have been determined at several elevated temperatures. Tests were run at 6,000 and 12,000 psi at 400 C and at 2500 and 1500 psi at 600 C. The stresses to produce 1 per cent total deformation in 100 hr at 730 and 800 C were determined. These data are summarized in Table A-4.

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TABLE A-4. CREEP PROPERTIES OF BETA-QUENCHED URANIUM AT ELEVATED TEMPERATURES

Temperature, C	Stress, psi	Percentage Deformation at Time Indicated												
		Load on	1 Hr	5 Hr	10 Hr	20 Hr	30 Hr	40 Hr	50 Hr	60 Hr	70 Hr	80 Hr	90 Hr	100 Hr
400	6,000	0.05	0.07	0.1	0.11	0.14	0.17	0.2	0.22	0.24	0.26	0.28	0.30	0.32
400	12,000	0.47	--	0.57	0.64	0.76	0.91	1.06	1.23	1.42	1.60	1.80	2.07	2.33
600	2,500	0.05	0.52	1.65	2.5	3.9	5.8	8.4	11.3	14.1	17.4	--	--	--
600	1,500	0.01	0.07	0.09	0.11	0.15	0.19	0.22	0.28	0.36	0.44	0.51	0.59	0.82
730	1,000	0.035	--	0.036	0.055	0.085	0.12	0.15	0.19	0.22	0.30	0.35	0.43	0.50
730	700	0.05	--	--	0.07	0.11	0.13	0.15	0.16	0.175	0.180	0.185	0.205	0.23
730	575	0.035	--	0.039	0.044	0.053	0.062	0.072	0.078	0.085	--	--	--	--
800	100	0.15	--	--	Failed at 0.8 hr, 26.6 per cent deformation									
800	0	0	0.065	0.16	0.24	0.39	0.48	0.55	0.61	0.69	0.75	0.80	0.84	0.88

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The data show that approximately 1200 psi is necessary to produce the cited deformation in 100 hr at 730 C. At 800 C the weight of the specimen is sufficient to cause this amount of deformation in 100 hr.

Radiation Damage to Graphite

A. E. Austin and C. M. Schwartz

Irradiation of graphite at high temperatures (450 C) can produce physical contraction. A possible cause may be an increase in crystallinity of graphite or binder carbon during irradiation. Graphite made from Korite asphalt, which has shown physical contraction, has been used in experiments to determine possible changes in crystallinity and amount of graphite, in irradiations at low and high temperatures. The experiment on high temperature irradiation has been completed for comparison with earlier results at low temperatures.

Five identical specimens of graphite were irradiated at Hanford at about 500 C. There was no significant change in amount of crystalline graphite or in its crystallinity. The integrated intensity of X-ray diffraction lines was used as a measure of the amount of graphite. The degree of crystallinity was determined from diffraction-line contours and from the lattice constant c_0 . In comparison, the low-temperature experiment below 100 C had shown a 20 per cent loss in crystalline graphite. This loss was fully recovered by annealing at 2500 C without any net increase in amount of graphite or its crystallinity.

These results indicate that most of the carbon atoms displaced during irradiation at high temperature promptly return to normal graphite sites, and there is no appreciable crystal growth. Therefore, the cause of physical contraction is probably a change in physical macrostructure.

This concludes the current program, which had been reported recessed in BMI-1121.

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B. DEVELOPMENTS FOR ALUMINUM-CLAD FUEL ELEMENTS

R. J. Carlson

The high extrusion pressures recently encountered in extrusion-cladding work continue to be a problem. It has not been possible to relate these excessive pressures to surface roughness of the tools or to restraint of the core by the cracked mandrel. A new mandrel is being made, and its use may provide an indirect answer. By raising the temperature to 1100 F, it has been possible to completely clad uranium cores with attached M276 aluminum end plugs at speeds up to 36 in. per min.

The "ring-test" method of determining the transverse mechanical properties of uranium tubes has been developed, and a mechanical extensometer has been completed and calibrated. Additional tests will be made on beta-quenched tubes.

Extrusion billets of aluminum-uranium alloys containing 16, 30, 40, and 45 w/o uranium have been cast and shipped to Nuclear Metals, Inc., for fabrication studies. The 16 and 30 w/o uranium billets were sound and homogeneous; the 40 and 45 w/o uranium billets were homogeneous but porous. Future work will be directed toward decreasing the porosity of the high uranium content castings.

Extrusion Cladding of Flat Plates

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

The investigation to determine the cause of the high extrusion pressures that have been encountered within the past 2 months was continued. The increased pressure does not appear to be related to the surface roughness of the die or the mandrel. Attempts are being made to control other suspected factors in the operating techniques. It has not been possible to prove that the high pressures are caused by restraint of the core material due to compression of the cracked slot in the mandrel. However, a new mandrel is being made, and this may provide an indirect answer.

In the meanwhile, by raising the temperature to 1100 F, it has been possible to clad three uranium plates with M276 (12 per cent Al_2O_3) aluminum end plugs at speeds of 8, 20, and 36 in. per min. These will be tested and evaluated later at SRL.

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Mechanical Properties of Uranium Tubes

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

A "ring-test" method to determine the transverse mechanical properties of uranium tubes has been developed. The test method consists of internally pressurizing a section of tubing and measuring the subsequent tube expansion by means of a mechanical extensometer. The transverse properties of beta-quenched ingot uranium as determined by the ring test will be compared with the longitudinal properties obtained by standard sheet-tensile tests at -75, +75, and 300 F.

Modifications of the mechanical extensometer have been completed and the extensometer calibrated. Additional tests will be made on beta-quenched tubes.

Preparation of Aluminum-Uranium Alloys

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

Since aluminum-uranium alloys containing 30 w/o or more of uranium are of interest as possible reactor fuel, a program of research concerned with the development of suitable melting and casting techniques for these alloys is in progress. In addition to methods of preparation, the corrosion resistance and the relative fabricability of the alloys are being investigated.

As there is some carry-over of silicon during the processing of the aluminum-16 w/o uranium alloy, the effect of this silicon on the liquidus line of the aluminum-uranium phase diagram is being investigated. Alloys containing additions of 0.1, 0.2, 0.3, 0.5, and 1.0 w/o silicon have been prepared and fabricated. Conventional time-temperature curves, differential-cooling curves, and resistivity measurements are being obtained in order that the liquidus line may be established.

Extrusion billets of aluminum-uranium alloys containing 16, 30, 40, and 45 w/o uranium have been cast and shipped to Nuclear Metals, Inc., for fabrication studies. The billet containing 16 w/o uranium was prepared by the techniques outlined in BMI-1066. The aluminum-30 w/o uranium billet was vacuum melted at a pressure of less than 5 μ in a graphite crucible and bottom poured into a cored steel mold. The 40 and 45 w/o uranium billets were prepared in a manner very similar to the one used to produce the 16 w/o uranium billet. Only the quenching rate was significantly different. The high-uranium alloys were not quenched as drastically as was the 16 w/o uranium alloy. This was done so that the lower cooling rate would

B-3 and B-4

allow the escape of gases which might be evolved by the melt during solidification.

An examination of these billets reveals that while the 16 and 30 w/o uranium billets are sound and homogeneous, the 40 and 45 w/o uranium billets are porous, although they exhibit reasonable homogeneity. Although the major portion of this porosity is attributed to gas evolved during solidification, it is believed that some of the apparent porosity is due to shrinkage.

Future work will be concerned with vacuum melting and casting the high-uranium alloys by various melting techniques. Melts will be made under a dynamic vacuum of 5000 μ and poured into both the graphite and metal molds. Other melts will be made under a dynamic vacuum with helium gas flowing through the melt in an effort to remove the hydrogen gas that is thought responsible for much of the porosity encountered in these alloys. It is also hoped that the use of the graphite molds will retard the cooling of the melt, thereby allowing the escape of any gas evolved during solidification. After preliminary studies are completed, the most promising technique will be used to produce a full-size extrusion billet.

C-1

C. PLANT ASSISTANCE TO MCW

A. A. Bauer

The effect of the method of preparing UO_3 from uranyl nitrate upon the properties and type of UO_3 obtained is being studied. Hydrofluorination tests made on UO_3 preparations are reported as well as the results of phase studies on active UO_2 samples.

The observation has been made that water is absorbed by various oxide specimens and it is thought that variations in electrical properties may be traceable to the distribution of water present. The effect of absorbed water is therefore being investigated. However, tentative conclusions concerning phase relationships in the system may be drawn from the data obtained to date and are presented.

Corrosion tests of Type 304 ELC stainless steel in chloride- and fluoride-contaminated boiling nitric acid solutions have continued. Corrosion of specimens exposed to 18 and 30 per cent nitric acid solutions containing up to 0.10 per cent chloride has been found to be negligible after extended test periods. Specimens exposed to boiling 30 per cent nitric acid solutions indicate a significant decrease in corrosion resistance when the chloride contamination exceeds 0.5 per cent. Fluoride additions to chloride-containing nitric acid were found to increase the corrosion rate.

Measurements of hydrogen solubility in solid and molten magnesium fluoride slag, intended to trace the source of hydrogen in dingot uranium, have been completed. A solubility of less than 10 ppm hydrogen at temperatures up to 1350 C is indicated.

Investigation of Uranium Oxides

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

The preparation of UO_3 by the decomposition of uranyl nitrate hexahydrate is being continued. A quantity of "vacuum-amorphous" UO_3 and low-density Type III UO_3 was sent to Mallinckrodt for hydrofluorination tests. The nitrogen content of various forms of UO_3 was determined, and its effect upon the activity of UO_2 is being studied. A refinement in the preparation of vacuum-amorphous UO_3 (prepared by preliminary drying under reduced pressure, as distinguished from belt-denitrated amorphous) has been made, and further details of the activity of UO_2 made from this UO_3 have been studied.

C-2

Previously, amorphous UO_3 was made by heating to 125 C at reduced pressure, then slowly raising the temperature at atmospheric pressure. The UO_2 made from vacuum-amorphous UO_3 was considered to be of moderate activity because it oxidized rapidly to about $\text{UO}_{2.20}$ in air at room temperature. However, it continued to adsorb oxygen, slowly reaching $\text{UO}_{2.32}$ in approximately 3 weeks. A very active dioxide will oxidize immediately to $\text{UO}_{2.4}$ on exposure to air.

It has been found that if the preliminary vacuum drying is done at 150 C, the final heating may be done more quickly, no melting takes place, and a more homogeneous amorphous UO_3 is formed. The nitrogen content of vacuum-amorphous UO_3 is 0.76 w/o as compared with 0.36 w/o for the belt amorphous. It is not yet known whether the difference in nitrogen content or physical state of the amorphous UO_3 is the more determining factor affecting the reactivity of UO_2 .

Results have been received from Mallinckrodt for two materials previously submitted for hydrofluorination tests. Table C-1 shows the time for 90 w/o conversion to UF_4 , as determined for belt-amorphous and Type II UO_3 . Comparison is made with normal MCW Type III UO_3 .

TABLE C-1. HYDROFLUORINATION TEST ON UO_2 MADE FROM BATTELLE PREPARATIONS OF UO_3

Sample Description	UO_3 Type	Hydrofluorination Temperature, C	Time for 90 w/o Conversion, min
Belt denitrated UNH	Amorphous	450	6
Pot-denitrated UNH plus 1 w/o acetic acid	II	500	8
Normal MCW pot- denitrated UNH	III	500	70

High-temperature X-ray diffraction studies on samples of active UO_2 annealed at 450 C for 100 hr have been completed. The results indicate that the boundary between the single-phase-cubic region and the cubic-plus-orthorhombic region is between $\text{UO}_{2.30}$ and $\text{UO}_{2.35}$, up to 600 C.

The study of the effect of nitrogen content of UO_3 upon the reactivity of UO_2 will be continued during the next period.

C-3

The Electrical Properties of Uranium Dioxide

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

It has proven impossible to date to obtain reproducible electrical properties on specimens of uranium oxides prepared from active uranium dioxide. Specimens from the same ingot and presumably having identical oxygen contents display widely different electrical conductivities after being annealed. It was thought that the presence of water would account for some of the difficulties experienced since it was known that water was lost from the specimens during annealing. The weight of water lost under the annealing conditions by one sample was determined by weight changes. The specimen was annealed for 16 hr at 200 C in a small Vycor capsule under an argon pressure of about 1 atm. Originally the specimen was *p*-type and had a conductivity of $2.29 \times 10^{-3} \text{ ohm}^{-1}\text{-cm}^{-1}$. After quenching it was found that the specimen had lost water representing 0.95 per cent of its weight. The conductivity had increased to $1.00 \times 10^{-2} \text{ ohm}^{-1}\text{-cm}^{-1}$ and the specimen was *n*-type. The specimen was then exposed for 16 hr at room temperature to a stream of argon carrying water vapor and a gain in weight of 3.73 per cent was observed. However, the magnitude and type of conductivity remained unchanged. This water was lost when the specimen was again annealed at 200 C.

The above results indicate that water has little or no effect on the electrical properties of the oxides. However, it should be pointed out that the original water was probably taken up before the oxide powder was compressed and was probably distributed over all the grains. In this case, water is more likely to affect the bulk properties of the specimen than that taken up after the specimen had been compressed. Since it is felt that the absorption of water is related to both the electrical properties and the reactivity of the oxides, additional work along these lines is planned.

Even though it has proven difficult to obtain reproducible electrical properties of these specimens, conclusions about their character can now be drawn with some confidence. Above the oxygen-to-uranium ratio of about 2.30, the specimens, after annealing, are partly U_3O_8 in equilibrium with some lower oxide of uranium, possibly U_3O_7 or U_2O_5 . Below the ratio of 2.30 the specimens are U_3O_7 . These conclusions, drawn from the measured values of magnitude and type of electrical conductivity, are in qualitative agreement with X-ray data on the specimens.

Preliminary experiments with oxides prepared from "moderately" active uranium dioxide indicate the specimens to be U_3O_7 . However, the work has not proceeded far enough to draw definite conclusions and is being continued.

C-4

The Corrosion Resistance of Selected
Stainless Alloys

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

The investigations of the corrosion of Type 304 ELC stainless steel in boiling chloride- and fluoride-contaminated nitric acid solutions have been continued.

As reported in BMI-1149, duplicate tests with Type 304 ELC specimens exposed for prolonged periods to 18 per cent nitric acid boiling at 200 mm of mercury pressure and containing 0.00, 0.05, and 0.10 per cent chloride are under way. As of the last inspection, a 1000-hr exposure time had been completed and no severe corrosion has been observed on any of the specimens.

Seven 48-hr exposure periods were completed during the series of tests in which Type 304 ELC specimens were exposed to 30 per cent nitric acid boiling at 250 mm of mercury absolute pressure and containing chloride contaminations of 0.00, 0.025, 0.05, 0.10, 0.50, and 1.00 per cent. Severe corrosion was observed, at times, on all three of the specimens exposed at the different positions to 1.00 per cent chloride contamination. The only other case in which severe corrosion was observed involved the specimen exposed at the interface position of the solution containing 0.50 per cent chloride. This occurred during the second exposure period when the actual chloride contamination reached 0.67 per cent. No severe corrosion of this specimen was observed during the five subsequent periods. The corrosion of the specimens exposed to solutions containing lower values of chloride was insignificant.

Following the seven 48-hr exposure periods, the specimens from all of the tests mentioned in the preceding paragraph, except those from the nitric acid solution containing 1.00 per cent chloride, were replaced in fresh solutions of similar concentrations to those used in the 48-hr period test and are being exposed for prolonged periods to these solutions. At the same time, a sixth test with specimens exposed to 30 per cent nitric acid containing 0.30 per cent chloride was started. At the time of the last inspection of these specimens in December, a total of 1000 hr of exposure time had been completed on all of these specimens except those exposed to 0.30 per cent chloride, which had 666 hr. There has been a slight amount of corrosion occurring in the specimens exposed to solutions containing 0.30 and 0.50 per cent chloride, but at chloride concentrations of 0.10 per cent and lower the corrosion is insignificant.

Seven 48-hr exposure periods have been completed in a series of tests in which Type 304 ELC specimens are being exposed to 18 per cent nitric

C-5 and C-6

acid solutions containing contaminations of fluorides, alone, and in combination with chlorides boiling at atmospheric pressure. The three concentrations studied were: (1) 0.05 per cent chloride, (2) 0.10 per cent fluoride, and (3) 0.50 per cent chloride plus 0.01 per cent fluoride. These results indicate that the addition of fluoride to these chloride-contaminated nitric acid solutions definitely increases the amount of corrosion which occurs. The corrosion rate of the specimens exposed to the liquid-phase of the solutions containing chloride and fluoride contaminations is reasonably high and seems to be increasing with continued exposure time.

During January, the effect of chloride contaminations in 5 per cent nitric acid solutions boiling at 200 mm of mercury absolute pressure, and the effect of combined fluoride and chloride contaminations in 5 and 30 per cent nitric acid solutions boiling at atmospheric pressure, will be studied.

Gas-Metal Studies

M. J. Trzeciak and M. W. Mallett

A study of relationships between magnesium fluoride slag and hydrogen is being made as part of Mallinckrodt Chemical Works' program to determine factors contributing to the hydrogen content of dingot uranium. Recent measurements have established the high-temperature solubility of hydrogen in the slag at less than 10 ppm. The new results show that some previously reported values, namely 72, 224, and 238 ppm for the solubility of hydrogen in slag are not reproducible and may be presumed to be in error.

Solubilities of hydrogen in slag under a 1-atm hydrogen pressure were made in five runs at temperatures 1150, 1260, and 1350 C. The sample, weighing 20.0 g, was contained in a molybdenum crucible heated by induction. In all cases, the hydrogen solubility was determined to be less than 10 ppm. This value represents the sensitivity limit of experimental measurements.

The reproducibility and consistency of these measurements along with those reported in BMI-1149 for samples heated in graphite crucibles point to the figure of less than 10 ppm as being the true solubility of hydrogen in magnesium fluoride slag at elevated temperatures.

It is planned to conclude the solubility measurements with an experiment using cp magnesium fluoride. Following this, a study of the diffusion and permeability of hydrogen in magnesium fluoride slag will be undertaken.

D-1 and D-2

D. STUDIES OF THE REACTION BETWEEN
ZIRCONIUM ALLOYS AND WATER

A. W. Lemmon, Jr.

A study was made of the probable extent of chemical reaction at high temperatures between Zircaloy 2 and water. All programs have now been concluded. The only activity this month was on the calculational program which was directed at predicting the probable maximum extent of chemical reaction which might occur in the PWR core after loss of coolant. As a result of the computations made, it had been concluded that the safety water-injection system would be effective in preventing all except a minor amount of chemical reaction and meltdown. For the "worst" case, less than 15 w/o of the Zircaloy 2 cladding in the reactor core would react. This includes additional reaction after melting, which would be appreciable.

Analysis of the Extent of Reaction and Efficacy of Cooling

L. E. Hulbert, A. W. Lemmon, Jr., and R. B. Filbert, Jr.

All selected cases have been computed in the program directed at the prediction of the probable maximum extent of chemical reaction which might occur in a loss-of-coolant situation in the PWR. All results of the computations have been studied and compared and conclusions have been reached.

Based on the calculations performed, the conclusion has been reached that the safety water-injection system would be effective in preventing all except a minor amount of chemical reaction in one of the blanket regions of the PWR core. No appreciable melting would occur. Delays of up to 2 min or more in the time of initial introduction of safety cooling water would not modify this result.

Even for safety-cooling-water rates of less than 1 per cent of that contemplated, less than 15 w/o of the Zircaloy 2 cladding in the PWR core would react. However, in this case, appreciable amounts of melting would occur.

This concludes the work to be done on this program. A topical report covering all phases of this computational program is being prepared.

E-1

E. GENERAL FUEL-ELEMENT DEVELOPMENT

F. A. Rough

This section includes studies in ceramics and metallurgy which are sponsored by the Reactor Development Division of the AEC.

Experiments designed to measure the diffusion of UO_2 through dense BeO were continued. A dense BeO disk with a coating of UO_2 was heated for 20 hr in a vacuum at 2300 F and the extent of UO_2 diffusion is being determined. The fabrication studies, concerned with rod- and sphere-shaped UO_2 -graphite fuel elements for possible use in gas-cooled power reactors, are in progress. After a 2300 F bake, the rod-shaped elements containing the matrix-type cores were straight and free of cracks, as were spherical elements with matrix-type cores.

The effect of specific contaminants on the sinterability of BeO calcines from $\text{Be}(\text{OH})_2$ is being investigated. The effect of moisture in the sintering furnace is also being studied.

The fabrication and encapsulation of the uranium-15 w/o zirconium and the uranium-10 and -20 w/o niobium alloys is in progress. These alloys are to be irradiated for evaluation as possible reactor fuels for high-temperature application. The low-melting castable uranium-5 w/o chromium-1 w/o molybdenum alloy is also being studied as a possible reactor fuel. Specimens for irradiation test were cast but the resulting structure was not considered representative. Additional specimens will be prepared.

Fabrication studies of UC , U_3Si , U_2Ti , and UN-Zircaloy 2 fuel elements and UC and UN-stainless steel fuel elements are being terminated. The work indicates that Zircaloy matrix materials may be fabricated by hot pressing powder frames, core, and cladding into one piece.

Oxide films formed at 650 C in low oxygen pressure provided a corrosion barrier for 21 hr in boiling water. Further work on oxide films is in progress. On the basis of research performed, it has been concluded that zone refining is an inefficient method of removing metallic impurities from uranium.

E-2

CERAMICSRefractory Fuel Elements

L. D. Loch, G. B. Engle, A. Roese, and A. G. Allison

In research on refractory fuel elements, experiments to measure the diffusion of UO_2 through dense BeO were continued, and the fabrication and design of graphite fuel elements were further investigated.

BeO

A dense BeO disk with a coating of UO_2 , produced by reduction of uranyl oxalate on one face, was heated at 2300 F for 20 hr in a vacuum furnace. Both faces then were exposed to an alpha-sensitive photographic plate. A 6-day exposure showed a heavy concentration of UO_2 at the outer edge of the treated face, but the concentration was much lower and uneven toward the center. There was no evidence that the UO_2 had diffused to the untreated face.

The treated face was polished to remove a 0.001-in. layer and re-exposed. The results of this exposure will indicate the extent of penetration of the UO_2 into the BeO .

Graphite

UO_2 -graphite fuel elements are being developed for a gas-cooled power reactor. Fabrication studies are concerned with rod- and sphere-shaped fuel elements. Measurements of uranium loss at 2300 F were continued.

In the fabrication work, spherical elements were made by cladding cores consisting of a mixture of minus 325-mesh UO_2 , graphite, and resin binder with unfueled graphite. Two types of cores were used: (1) green (as mixed), and (2) partially cured. These specimens were baked at 2300 F, along with the rod-shaped and spherical elements made last month.

After the 2300 F bake, the rod-shaped elements containing the matrix-type cores were straight and free of cracks. Transverse sections of the rods indicated that the fueled cores were well bonded and centered in the graphite sheaths. Radiographs confirmed these observations. No further fabrication experiments on rod elements are planned for the present.

E-3

Some of the spherical elements containing 0.4, 0.6, or 1.0 volume per cent UO_2 , in the form of sintered pellets, cracked during baking. All of the spheres made with the matrix-type UO_2 -graphite cores were free of cracks. Radiographs showed that the cores were well centered in all of the spherical elements except those that contained the green matrix-type cores.

Oxidation of the graphite remains the major obstacle to measuring uranium losses in flowing nitrogen at 2300 F. A vitrified alumina tube, tested this month, was not vacuum tight when heated to 2100 F.

The fabrication and testing of spherical fuel elements will be emphasized in future work. Experiments to measure uranium and fission-product losses will be continued. Further design studies, including preliminary estimates of power costs for a nitrogen-cooled reactor with graphite fuel elements will be made.

Characterization of Sinterable Oxide Powders

J. F. Quirk and N. Mosley

The relations between sinterability and the more basic properties of oxide powders are being studied. Current work is on BeO prepared by thermal decomposition of $\text{Be}(\text{OH})_2$. Impurity content of the starting material appeared in previous work to be one factor influencing the sinterability of BeO powder.

Last month, BeO powders of relatively high purity, prepared from $\text{Be}(\text{OH})_2$ by controlled calcination, were found to have poor sinterability when compacted and heated in moist hydrogen for 1 hr at 2600 F.

This month, effort was made to improve the sinterability by addition of specific contaminants. Magnesium ion contamination is being introduced by leaching four of the hydroxides with a 5 per cent solution of MgSO_4 . When the leachings are completed, chemical analyses and sinterability tests on BeO calcines made from the contaminated hydroxides will be made.

Also, experiments were made to assess the effect on sinterability of moisture in the sintering-furnace atmosphere. The bulk densities of BeO compacts sintered in a dry hydrogen-argon atmosphere at 2600 F for 1 hr are given in Table E-1. The densities of similar compacts previously sintered at 2600 F for 1 hr in moist hydrogen are shown for comparison. On the basis of these results, there was no consistent effect on sinterability from moisture in the sintering atmosphere.

TABLE E-1. EFFECT OF SINTERING ATMOSPHERE
ON DENSITY OF BeO COMPACTS

BeO Lot Number	Calcination Temperature, F	Bulk Density, g per cm ³	
		After Sintering in Indicated Atmosphere	
		Dry Hydrogen-Argon(a)	Moist Hydrogen(b)
28	750	2.15	2.12
28	1470	2.12	2.21
28A	750	1.52	1.25
28A	1470	2.33	1.97
29	750	2.49	2.75
29	1470	2.49	2.71
29A	750	1.56	1.35
29A	1470	2.54	2.11
C5659	1830	2.95	2.95

(a) Mixture of 90 volume per cent argon and 10 volume per cent hydrogen, with a dewpoint of about -40 F.

(b) Hydrogen with a dewpoint of about +70 F.

E-5

METALLURGYUranium Alloys for High-Temperature Application

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

This program is concerned with elevated-temperature properties of binary uranium alloys containing molybdenum, niobium, and zirconium. The alloys are of interest as possible power-reactor fuels. As part of the program, it is proposed to determine the effect of neutron damage on uranium-15 w/o zirconium and uranium-10 and -20 w/o niobium alloys after irradiation to a 1 a/o burnup.

Uranium-20 w/o niobium ingots (nominal composition) have been successfully fabricated. Arc-melted ring bars were prepared with high-purity niobium melting stock. The ingots were heated in a helium-atmosphere furnace for 30 min at temperatures of 1850, 2050, and 2150 F and rolled with the rolls set to give 8 to 10 per cent reduction per pass. The uranium-20 w/o niobium ingots were successfully reduced at the two higher temperatures but cracked when fabrication was attempted at 1850 F. It is believed that the improved fabricability of the uranium-20 w/o niobium alloy was due to the use of high-purity niobium melting stock.

The fabrication and encapsulation of alloy specimens containing enriched (19.85 w/o enrichment) uranium is continuing. Present plans are to begin irradiation of the first two capsules in February. Each capsule will contain one specimen each of uranium-15 w/o zirconium, uranium-10 w/o niobium, and uranium-20 w/o niobium. The specimens will receive three MTR cycles in temperature-controlled capsules, and will be returned to Battelle for postirradiation studies.

Preparation and Properties of Low-Melting AlloysC. F. Franklin, A. W. Hare, W. E. Murr, A. A. Bauer,
and R. F. Dickerson

Work is being continued on the development and the subsequent evaluation of low-melting castable uranium alloys for their possible use as a power-reactor fuel. The initial fuel which is presently under investigation is a uranium-5 w/o chromium-1 w/o molybdenum alloy.

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A program has been initiated to determine the effects of neutron irradiation on this alloy. Small pin-type specimens of the alloy will be irradiated in a temperature-controlled capsule at about 600 C and in a non-controlled capsule at about 300 C. The specimens will be irradiated to a total burnup of about 1 a/o. Each specimen will be sealed in a small individual capsule to permit the determination of the fission-product release.

Irradiation specimens were cast and examined metallographically. The structure obtained was found to be nonuniform and is not regarded as representative of the type structure that would be obtained under production conditions. It appears that the high cooling rate imposed in the casting of small pins may be responsible for the structures obtained. A brief study of the effect of variations in composition and cooling rate on the structure is being made, employing natural uranium alloys. Additional irradiation specimens will be prepared on the basis of the results of these studies.

Compartmentalized Fuel Elements

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

Fabrication studies are being terminated, and a program for the preparation of irradiation specimens is being initiated. Information which has been obtained in the first phase of the program is being compiled into a topical report covering fabrication of UC, U₃Si, U₂Ti, and UN-Zircaloy 2 fuel elements and UC and UN-stainless steel fuel elements.

Work currently in progress indicates that, in addition to the standard fabrication procedures of cladding either sintered or green cores with wrought frames and cover plates, Zircaloy 2 matrix materials may be fabricated by hot pressing powder frames, core, and cladding into one piece and either using the specimen in the hot-pressed shape or hot rolling the specimen into a more desirable plate shape. These Zircaloy 2 matrix elements may also be fabricated by sealing the green powder core, frame, and cladding components in an evacuated pack and hot rolling to the desired final size.

Elements fabricated by all these procedures are being corrosion tested.

E-7

CORROSIONMechanism of Uranium Corrosion

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

The mechanism of aqueous uranium corrosion is being studied to provide a basis for designing reactor fuel elements which would be corrosion resistant and, therefore, greatly reduce the hazard of a cladding failure.

Low-Temperature Corrosion

Thin oxide films formed at 650 C in low oxygen pressure provided a corrosion barrier for 21 hr in boiling water. From X-ray diffraction line broadening, it appeared that these oxide films were strained. During the past month, oxide films were prepared at 300 and 400 C in an attempt to reduce the amount of strain and thereby increase the useful life of the film. These films were thicker than those previously prepared and were not single phase. Diffractometer charts made of these films showed U_3O_8 and/or U_2O_5 to be present with the UO_2 . The corrosion rates for these samples were 3.65 and 3.71 mg/(cm²)(hr), respectively, showing that these films were not protective. These experiments are being repeated with thinner oxide films to determine whether a single-phase oxide produced at 300 and 400 C is protective.

The work on the ellipsometer is continuing. An error in the previous calibration has been found and corrected. The instrument is being used to determine the optical constants of a gold film as a final check before studying uranium oxide films.

Zone-Melting Studies

Work was continued on procedures for purifying dingot material by zone melting. A sample was subjected to 10 "floating zone" passes at 2 in. per hr. A metallographic examination showed that some elimination of nonmetallic impurities resulted. The rear section of the ingot contained about 1 ppm of hydride and the front section about 1-1/2 ppm. The original dingot material contained 3 to 4 ppm of hydride. The nitrides in the zone-melted bar were 1/4 the size of those in the dingot.

The following tabulation contains the results of a spectrographic analysis of the purified material.

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Specimen ^(a)	Content of Indicated Element, ppm										
	<u>Al</u>	<u>B</u>	<u>Ca</u>	<u>Co</u>	<u>Cu</u>	<u>Fe</u>	<u>Mg</u>	<u>Mn</u>	<u>Mo</u>	<u>Ni</u>	<u>Si</u>
A	10	1	5	30	4	20	1	4	2	10	30
B	20	1	5	20	6	30	1	8	2	20	30

(a) Specimen A was taken from portion of ingot first to freeze - front -; Specimen B from portion last to freeze.

On the basis of this analysis and previous work on the purification of uranium, it must be concluded that zone refining is an inefficient method of removing metallic impurities from uranium. Only slight segregation has been effected and many passes would be necessary, if at all possible, to reduce the total impurity content to less than 10 ppm.

It is believed that part of the difficulty is due to the rapid diffusion of metallic impurities in the plasticlike state of uranium at temperatures near its melting point. If such is the case, then uranium would never yield to simple zone-refining techniques and refinements of the methods must be developed. One such refinement would be the application of an electric field to the ingot being zone melted. If metallic impurities are present as positive ions, then an electric field of the proper direction and strength might retard the back diffusion of impurities and increase the efficiency of segregation. Another refinement would be to cool the solid ingot (behind the molten zone) below the temperatures of its plasticlike state. This might be accomplished by placing a cooling coil directly behind the induction coil. However, since the thermal conductivity of uranium is relatively high, it might be necessary to operate at much higher input powers. Nevertheless, these new methods will be tried in the immediate future.

Another possible explanation of the poor segregation is that an optimum rate of zone travel has not been employed. All past work has shown some segregation of metallic impurities and slower rates of zone travel may improve the efficiency of the methods. Experiments designed to determine the effect of rate of zone travel are now under way.

High-temperature corrosion tests with this material are planned.

F-1

F. STUDIES OF ZIRCONIUM-URANIUM ALLOYS

F. A. Rough

The Reactor Development Division of the AEC supports several programs on zirconium alloys containing up to 70 w/o uranium.

The study of the constitution of the alpha-plus-beta region in zirconium-uranium alloys containing oxygen or nitrogen is essentially complete. Extrapolation of ternary data indicates that the beta boundary of the alpha-plus-beta region occurs at about 30 w/o uranium at 660 C.

The studies of transformation kinetics of zirconium-uranium alloys are largely completed, and emphasis is now being placed on the study of mechanical properties of 15, 22, and 30 w/o uranium.

The corrosion of alloys containing 7 through 70 w/o uranium additions to crystal-bar, sponge, and high-oxygen sponge zirconium have been evaluated in 500, 600, and 680 F water. Future studies will be directed toward an understanding of the effects of fabrication and heat treatment on the corrosion of clad samples. The evaluation of various ternary zirconium-uranium base alloys containing 70 w/o uranium is continuing.

Examination of various zirconium-22 w/o uranium samples which were irradiated at 400 and 675 C is in progress.

Constitution of Zirconium-Uranium Alloys

R. F. Dickerson and A. A. Bauer

A study to determine the solubility limits of the alpha-plus-beta zirconium region is being conducted by quantitatively studying oxygen- and nitrogen-containing alloys for the purpose of extrapolating the data obtained to the binary system.

Data obtained on zirconium-uranium alloys containing nitrogen have been re-evaluated and have been found to show the same trend as for oxygen-containing alloys. However, apparently less nitrogen is required to produce the same degree of beta-phase restriction than oxygen.

Plots of the beta-phase solubility curve as a function of both oxygen and nitrogen additions are found to extrapolate to a value of approximately 30 w/o uranium at 660 C in the binary system.

F-2

A final evaluation of the data is being made and a topical report will be written.

Transformation Kinetics and Hardening Reaction of Zirconium-Uranium Alloys Containing up to 20 w/o Uranium

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

Oxygen decreases the stability range of the intermediate phase, epsilon, in the zirconium-uranium system. The resultant effect on the transformation kinetics and on the type of structure obtained is being investigated in conjunction with the mechanical properties of these alloys.

Heat treatments (interrupted quench) are currently being conducted on alloys containing 0.3 w/o oxygen and up to 15 w/o uranium. The start of transformation is being determined at temperatures ranging from 300 to 750 C. Time-temperature-transformation curves are being drawn on the basis of metallographic examination of heat-treated samples and prior X-ray diffraction phase analysis of crystal-bar zirconium-uranium alloys.

Accompanying the kinetic study is an investigation concerned with a determination of the mechanical properties of zirconium-uranium alloys containing various microconstituents as formed on continuous cooling and other heat-treating conditions. The alloys to be studied contain 15, 22, and 30 w/o uranium.

Transformation Kinetics of Zirconium Alloys
Containing 20 to 70 w/o Uranium

R. F. Dickerson, F. A. Rough, A. A. Bauer,
and R. E. Maringer

Work has continued on the study of beta-decomposition kinetics in zirconium alloys containing 20 to 70 w/o uranium.

On the basis of experimental data obtained during this study, the reaction is found to be the same throughout the region of study, at least initially, beta decomposing to epsilon by a diffusion-controlled nucleation-and-growth process. In alloys which are either zirconium or uranium rich with respect to equilibrium epsilon, the epsilon formed from the beta phase is super-saturated; alpha zirconium and alpha uranium precipitate from the super-saturated phase on annealing.

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The rate of decomposition of beta to epsilon is slowest in the 50 w/o uranium alloy studied, the rate increasing as departures from this composition are made. Upon the basis of the postulated diffusion-controlled transformation, this observation is consistent with the minimum in diffusivity of atoms in the beta phase in the vicinity of 25 a/o uranium (approximately 47.5 w/o uranium) reported by Adda and Philibert.*

As a result of this increase in rate of decomposition of the beta phase, the ability to retain beta by quenching becomes increasingly difficult as uranium and zirconium are added to the epsilon-phase composition. The limit appears to be reached at a composition of approximately 22 w/o uranium in zirconium-rich alloys. This region was investigated this month and crystal-bar zirconium specimens containing 15, 20, and 22 w/o uranium were quenched from 925 C into iced brine in an attempt to determine this limit. Beta was retained in the 22 w/o alloy, while the 15 w/o alloy had transformed to strained, martensitic alpha zirconium, as identified by metallography and X-ray diffraction examination. The zirconium-20 w/o uranium alloy had transformed on quenching to epsilon (supersaturated), with alpha zirconium being rejected on quenching. Thus, apparently at some composition between 15 and 22 w/o uranium, the beta-to-epsilon decomposition is suppressed and beta decomposes by a martensitic process to alpha zirconium. The ability to retain zirconium in solution in the epsilon phase is apparently exceeded in the 20 w/o uranium alloy and alpha is rejected on quenching as epsilon forms.

This region of duplex transformation is extremely dependent on quenching rate. Thus, alpha zirconium is rejected from a 22 w/o uranium alloy when quenched under less ideal conditions than those described. Presumably the regions in which beta can be retained and in which beta transforms martensitically approach a limiting composition as the quench approaches ideality.

The kinetics of beta decomposition in alloys containing 22, 50, and 60 w/o uranium have been studied by means of dynamic-modulus measurements. The approach is based on the assumption that the modulus of a partially transformed specimen is equal to the sum of the fractional portion of the modulus of the two components (beta and epsilon) present. Specimens were quenched to retain the beta phase and were then transformed at temperatures ranging from 100 to 550 C and water quenched.

The 50 w/o uranium alloy was transformed for periods of 3 min and 1 and 16 hr. Resulting data were found to fit the following empirical equation:

*Adda, Y., and Philibert, J., "Etude de la Diffusion Uranium-Zirconium en Phase Gamma", *Comptes rendus*, 242, 3081-83 (1956).

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$$N = 1/2 \left[1 - \operatorname{erf} 0.118 \left(\frac{31,800}{RT} - \ln \frac{t}{\tau} \right) \right]$$

where N is the fraction of epsilon formed and τ is a constant equal to $e^{-23.65}$ when t is expressed in seconds. R is the universal gas constant and T the absolute temperature. The value of 31,800 cal per mole is in good agreement with the data of Adda and Philibert who report an activation energy for diffusion in the beta phase of about 31,000 cal per mole for a 50 w/o uranium alloy. The agreement suggests that transformation is controlled by diffusion in the beta phase.

Extension of this technique to the 22 and 60 w/o uranium alloys has not been particularly successful. While the same trends in change of modulus during transformation are observed, the results do not lend themselves to a ready mathematical interpretation. The measurements are apparently complicated by the rejection of the respective alpha phases. In the 22 w/o alloy, in addition, under the initial quenching conditions employed, it appeared obvious that beta was not retained and that the changes in modulus accompanying the transformation anneal represented only the completion of transformation rather than the complete beta-to-epsilon transformation.

An anomalous break occurs in the resistivity-versus-temperature curve of the 50 w/o uranium alloy at about 300 C. The break has been observed in specimens annealed at 500 C, water quenched, and then reheated slowly while measurements are made. The break near 300 C represents an increase in resistivity. On subsequent slow cooling to room temperature, the break is not observed and the room-temperature resistivity is higher than that obtained initially on quenching from 500 C. This phenomenon has not been investigated sufficiently to permit a complete understanding to be obtained. However, it might be occasioned by the freezing in of a nonequilibrium degree of order in the structure or of a nonequilibrium number of vacancies on quenching.

No further study is planned. A topical report will be written covering these studies.

Corrosion of Zirconium-Uranium Alloys

W. E. Berry and R. S. Peoples

Studies have been completed on the effect of water temperature and zirconium melting stock on the corrosion behavior of zirconium-uranium alloys. Alloy series containing 7 through 70 w/o uranium additions to

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crystal-bar, sponge, and high-oxygen sponge zirconium were evaluated in 500, 600, and 680 F degassed high-purity water. All samples were annealed 1 hr at 800 C and slowly cooled prior to corrosion testing.

A topical report is being prepared on the basis of results obtained after 3360 hr of exposure. Briefly summarized, the results indicated that corrosion rates increased with (1) increasing water temperature, (2) increasing oxygen content in the zirconium melting stock, and (3) increasing uranium content.

Future work will be directed toward a study of the effect of heat treatment on hardness and susceptibility to corrosive attack of diffusion layers in zirconium-clad zirconium-uranium alloys.

Development of Corrosion-Resistant 70 w/o
Uranium Alloys

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

A program has been undertaken with an aim of developing a corrosion-resistant zirconium-70 w/o uranium alloy. Heat treatment and ternary alloying are being investigated as means of achieving improved corrosion resistance.

Corrosion testing of specimens is in progress but complete data are not yet available. Zirconium-70 w/o uranium alloy specimens and zirconium-uranium alloy specimens containing ternary additions of molybdenum, silicon, and titanium are among those being tested.

Radiation Stability of Zirconium-Uranium Alloys

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

The program of study of the effects of radiation on uranium-zirconium alloys is being continued. The effects of radiation on zirconium-22 and 50 w/o uranium alloys are presently being investigated.

Nine specimens of zirconium-22 w/o uranium have been irradiated at the MTR to a calculated burnup of 1.95 total a/o (nominal flux of 0.8×10^{14} nv for 89.9 days). These specimens represent three different types of microstructures of the zirconium-22 w/o uranium alloy. Calculations show

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that during irradiation the specimen cores were at about 400 C. Also, three specimens of the zirconium-22 w/o uranium alloy of the same types of microstructure as above were irradiated in a temperature-controlled capsule at a temperature of 675 C to a calculated burnup of 0.43 total a/o.

The capsules are presently being opened and an evaluation of the specimens will begin immediately.

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G. CORROSION STUDIES OF ZIRCONIUM

R. S. Peoples

Research supported by the AEC Reactor Development Division pertaining to the study of the corrosion behavior of zirconium-base cladding materials in high-temperature water and steam is described in this section.

Long-term corrosion studies have been continued for samples representing Zircaloy 2 and modified Zircaloy 2 compositions exposed to 600 and 680 F degassed water and 750 F (1500 psi) steam.

Corrosion of Zirconium and Zirconium Alloys

W. K. Boyd and R. S. Peoples

Samples representing seven different melts of Zircaloy 2 have been exposed for 3-1/4 years to 600 F degassed water. To date, there is no indication of breakaway. However, weight gains are of the order of 50 mg per dm².

Results obtained for intentionally contaminated samples of Zircaloy 2 exposed 18 months in 680 F degassed water continue to indicate that: (1) hydrogen additions of from 500 to 1500 ppm do not affect corrosion properties; (2) oxygen levels in excess of 6000 ppm reduce corrosion resistance of Zircaloy 2; (3) nitrogen levels in excess of 200 ppm destroy corrosion resistance under the test conditions.

Zirconium Corrosion Committee Program

Long-term corrosion studies in support of the Zirconium Corrosion Committee's program to develop new corrosion-resistant zirconium alloys have been continued. Sponge-base alloys containing combinations of tin and iron, tin and nickel, and tin, iron, and nickel, with and without additions of nitrogen and aluminum, are being evaluated in 680 F degassed water and 750 F steam. Total-weight-gain data based on up to 504 days of exposure are summarized in Tables G-1 through G-3, inclusive. The following trends are indicated:

- (1) Increasing the nitrogen levels above 70 ppm to 300 ppm results in a progressive decrease in the corrosion resistance of 0.25 to 0.50 w/o tin-0.25 to 0.50 w/o iron alloys.

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TABLE G-1. CORROSION OF ZIRCONIUM-BASE ALLOYS, MELTED

Heat	Alloy Content					750 F Steam		Remarks ^(a)
	Sn, w/o	Fe, w/o	Ni, w/o	N, ppm	Al, ppm	Exposure Time, days	Weight Gain, mg per dm ²	
Vacuum Annealed 2 Hr at								
996	0.24	0.25	--	44	58	200	103	M, WP
974	0.25	0.25	--	48	63	200	102	M, WP
997	0.26	0.25	--	33	46	186	98	M, WP
984	0.26	0.25	--	47	68	212	109	M, WP
1001	0.26	0.27	--	55	62	181	145	M, WP
1003	0.48	0.41	--	219	43	135	120	M, WP
975	0.49	0.36	--	57	45	186	115	M, WP
1000	0.49	0.38	--	43	50	186	130	M, WP
983	0.50	0.39	--	53	70	194	118	M, WP
998	0.51	0.38	--	48	47	186	111	M, WP
990	0.48	0.25	0.23	47	56	186	111	M, WP
985	0.49	0.20	--	47	64	194	109	M, WP
1007	0.50	0.21	0.19	50	51	135	110	M, WP
999	0.53	0.20	0.18	64	46	186	123	M, WP
995	0.65	0.22	0.19	38	57	186	116	M, WP
1024	0.25	0.25	--	63	68	181	115	M, WP
1026	0.25	0.25	--	63	67	186	121	M, WP
1030	0.50	0.44	--	58	47	186	123	M, WP
1028	0.49	0.38	--	71	38	181	116	M, WP
1014	0.25	0.25	--	60	145	147	112	M, WP
1012	0.25	0.25	--	50	179	147	107	M, WP
1013	0.26	0.26	--	54	275	135	170	M, WP, S
1010	0.51	0.39	--	46	88	135	105	M, WP
1009	0.48	0.38	--	57	148	147	118	M, WP
1011	0.50	0.39	--	62	275	135	123	M, WP
1025	0.50	0.21	0.19	65	62	186	114	M, WP
1023	0.53	0.22	0.20	63	60	181	119	M, WP
1017	0.49	0.21	0.19	53	135	181	137	M, WP
1016	0.51	0.21	0.18	48	154	135	107	M, WP
1015	0.50	0.21	0.19	51	265	147	148	M, WP

(a) Key to remarks: G, WP - black tarnish with a white oxide pattern
M, WP - milky with a white oxide pattern
W - white oxide
F - flaking (heavy oxide)
S - segregated.

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AT THE BUREAU OF MINES FOR ZIRCALOY 3 EVALUATION

680 F Water			750 F Steam			680 F Water		
Exposure Time, days	Weight Gain, mg per dm ²	Remarks(a)	Exposure Time, days	Weight Gain, mg per dm ²	Remarks(a)	Exposure Time, days	Weight Gain, mg per dm ²	Remarks(a)
775 C and Furnace Cooled			Heated 2 Hr at 900 C in Vacuum and Water Quenched					
462	93	M, WP	170	118	M, WP	448	65	G, WP
406	178	M, WP	170	106	M, WP	448	69	G, WP
434	105	M, WP	182	111	M, WP	448	62	G, WP
406	106	M, WP	170	102	M, WP	448	68	G, WP
378	21	M, WP, F	182	111	M, WP	448	70	G, WP
294	125	M, WP	135	136	M, WP, S	420	100	M, WP
434	102	M, WP	170	110	M, WP	448	67	G, WP
434	109	M, WP	170	135	M, WP	448	81	G, WP
406	102	M, WP	170	107	M, WP	448	67	G, WP
434	106	M, WP	170	132	M, WP	448	66	G, WP
462	105	M, WP	170	111	M, WP	448	79	G, WP
462	101	M, WP	170	107	M, WP	448	80	G, WP
294	160	M, WP	135	113	M, WP	364	106	M, WP
406	101	M, WP	170	134	M, WP	448	92	M, WP
462	94	M, WP	170	106	M, WP	448	78	G, WP
378	109	M, WP	158	134	M, WP, S	448	95	M, WP
406	106	M, WP	170	127	M, WP, S	448	78	G, WP
462	87	M, WP	158	127	M, WP	448	85	G, WP
406	100	M, WP	158	125	M, WP	448	88	G, WP
322	116	M, WP	158	128	M, WP	448	92	M, WP
322	Lost weight	W, F	123	112	M, WP	420	103	M, WP
182	118	M, WP	105	108	M, WP	364	122	M, WP
266	110	M, WP	105	107	M, WP	420	117	M, WP
294	120	M, WP	105	112	M, WP	420	105	M, WP
266	97	M, WP	93	115	M, WP	364	111	M, WP
378	97	M, WP	158	132	M, WP	448	83	G, WP
378	104	M, WP	158	142	M, WP	420	100	M, WP
378	121	M, WP	105	105	M, WP	420	104	M, WP
322	114	M, WP	93	98	M, WP	392	107	M, WP
266	125	M, WP	93	108	M, WP	364	141	M, WP

TABLE G-2. CORROSION OF SPONGE-BASE ZIRCONIUM ALLOYS IN 750 F STEAM AND 680 F DEGASSED WATER

Alloys Vacuum Annealed 1 Hr at 775 C and Furnace Cooled

Heat	Alloy Composition (Balance Zirconium), w/o	750 F Steam			680 F Water		
		Exposure Time, days	Weight Gain, mg per dm ²	Remarks ^(a)	Exposure Time, days	Weight Gain, mg per dm ²	Remarks ^(a)
556	0.05Fe-0.002Ni-0.007N	105	Lost weight	W, F	333	105	M
585	0.05Fe-0.002Ni-0.007N	105	Lost weight	W, F	305	193	W, F
557	0.05Fe-0.15Ni-0.007N	207	99	M	361	68	G
558	0.05Fe-0.15Ni-0.015N	172	111	M	305	107	M
559	0.05Fe-0.15Ni-0.0225N	159	114	M	277	114	M
560	0.05Fe-0.15Ni-0.030N	118	137	M	221	140	M
563	0.05Fe-0.15Ni-0.007N-0.5Sn	166	104	M	361	70	G
564	0.05Fe-0.15Ni-0.015N-0.5Sn	159	103	M	361	103	M
565	0.05Fe-0.15Ni-0.0225N-0.5Sn	159	113	M	305	103	M
566	0.05Fe-0.15Ni-0.030N-0.5Sn	136	119	M	305	130	M
567	0.25Fe-0.25Sn-0.007N	207	89	M	361	53	G
568	0.25Fe-0.25Sn-0.015N	172	109	M	361	83	LM
569	0.25Fe-0.25Sn-0.0225N	172	127	M	305	101	M
570	0.25Fe-0.25Sn-0.030N	159	114	M	277	115	M
573	0.40Fe-0.50Sn-0.007N	172	110	M	361	62	G
574	0.40Fe-0.50Sn-0.015N	172	119	M	361	79	G
575	0.40Fe-0.50Sn-0.0225N	136	104	M	361	105	M
576	0.40Fe-0.50Sn-0.030N	124	116	M	305	109	M
579	0.20Fe-0.20Ni-0.50Sn-0.007N	159	110	M	361	70	G
580	0.20Fe-0.20Ni-0.50Sn-0.015N	159	132	M	361	90	M
581	0.20Fe-0.20Ni-0.50Sn-0.0225N	118	120	M	305	119	M
582	0.20Fe-0.20Ni-0.50Sn-0.030N	118	108	M	305	104	M
561	0.05Fe-0.15Ni-0.007N-0.02Al	159	132	M	221	126	M
571	0.25Fe-0.25Sn-0.007N-0.02Al	136	112	M	249	121	M
577	0.40Fe-0.50Sn-0.007N-0.02Al	124	114	M	305	119	M
583	0.20Fe-0.20Ni-0.50Sn-0.007N- 0.02Al	136	112	M	361	93	M
562	0.05Fe-0.15Ni-0.007N-0.01Ti	159	105	M	305	113	M
572	0.25Fe-0.25Sn-0.007N-0.01Ti	118	115	M	277	112	M
578	0.40Fe-0.50Sn-0.007N-0.01Ti	159	119	M	361	78	G
584	0.20Fe-0.20Ni-0.50Sn-0.007N- 0.01Ti	136	108	M	361	91	M

(a) Key to remarks: G - black tarnish film (good material)

M - milky

W - white oxide

F - flaking (heavy oxide)

LM - light milky.

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- (2) Aluminum contents of 200 ppm increase the corrosion rates of the modified Zircaloy 2 compositions.
- (3) Tin-nickel alloys (0.2 to 0.5 w/o tin-0.03 to 0.5 w/o nickel) are somewhat more resistant to 750 F steam than are tin-iron alloys of similar compositions; however, the reverse is true in 680 F degassed water.
- (4) Heat treatments consisting of a slow cool from 775 C or a water quench from 900 C do not affect corrosion behavior of the tin-iron and tin-nickel alloys.

Corrosion tests are being continued; however, as weight gains exceed 100 mg per dm² in the 750 F steam test, samples are being removed.

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TABLE G-3. CORROSION OF ARC-MELTED (ROCKING-HEARTH METHOD)

Alloy Melted

Heat	Alloy Composition (Balance Zirconium), w/o	750 F Steam			680 F	
		Exposure Time, days	Weight Gain, mg per dm ²	Remarks(a)	Exposure Time, days	Weight Gain, mg per dm ²
Heated 1 Hr at 775 C in Vacuum and Furnace Cooled						
						<u>Tin and</u>
462	Unalloyed	1-1/2	768	W	210	211
463	Unalloyed	1-1/2	839	W	210	210
464	0.22Sn-0.28Fe	106	108	M	490	68
465	0.23Sn-0.30Fe	106	105	M	490	54
466	0.22Sn-0.38Fe	136	100	M	490	62
467	0.22Sn-0.39Fe	136	100	M	490	64
469	0.25Sn-0.27Fe	112	102	M	490	47
468	0.25Sn-0.28Fe	112	105	M	490	61
470	0.25Sn-0.33Fe	136	102	M	490	58
471	0.25Sn-0.34Fe	112	107	M	490	48
473	0.27Sn-0.25Fe	106	105	M	490	36
472	0.29Sn-0.25Fe	106	115	M	490	40
475	0.27Sn-0.28Fe	148	109	M	490	43
474	0.28Sn-0.34Fe	106	104	M	490	56
477	0.47Sn-0.44Fe	112	112	M	490	54
478	0.51Sn-0.47Fe	142	109	M	490	55
481	0.52Sn-0.47Fe	136	106	M	490	44
479	0.50Sn-0.50Fe	136	95	M	490	56
476	0.49Sn-0.51Fe	124	100	M	490	51
480	0.51Sn-0.53Fe	124	102	M	490	50
						<u>Tin and</u>
488	Unalloyed	1-1/2	680	W	126	136
489	Unalloyed	1-1/2	570	W	154	111
491	0.17Sn-0.03Ni	249	114	M	434	109
490	0.18Sn-0.04Ni	231	103	M	434	102
492	0.13Sn-0.08Ni	249	109	M	490	61
493	0.18Sn-0.08Ni	189	112	M	490	64
495	0.17Sn-0.19Ni	249	107	M	490	84
494	0.19Sn-0.19Ni	249	115	M	490	95
496	0.21Sn-0.04Ni	267	78	W, F	490	88
497	0.22Sn-0.04Ni	249	117	M	462	102
498	0.22Sn-0.07Ni	213	102	M	490	71
499	0.22Sn-0.08Ni	207	115	M	490	70
501	0.21Sn-0.20Ni	213	100	M	490	76
500	0.22Sn-0.41Ni	249	113	M	490	61
502	0.27Sn-0.03Ni	213	108	M	462	102

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SPONGE ZIRCONIUM IN 750 F STEAM AND 680 F DEGASSED WATER

at Battelle

Water	750 F Steam			680 F Water		
	Exposure Time, days	Weight Gain, mg per dm ²	Remarks(a)	Exposure Time, days	Weight Gain, mg per dm ²	Remarks(a)

Heated 1 Hr at 900 C in Vacuum and Water Quenched

Iron

M, F	10	1680	W	28	Lost weight	W, F
M, F	10	1325	W	28	66	W, F
G	136	109	M	504	46	M
G	136	109	M	504	49	M
G	136	104	M	504	82	M
G	136	100	M	504	67	G
G	184	105	M	504	56	M
G	136	100	M	504	44	G
G	147	100	M	504	72	M
G	136	105	M	504	59	M
G	184	108	M	504	64	G
G	147	96	M	504	61	G
G	147	102	M	504	57	G
G	136	100	M	504	78	M
G	147	111	M	504	85	M
G	136	113	M	504	59	M
G	136	105	M	504	78	M
G	136	110	M	504	88	M
G	147	106	M	504	81	M
G	136	104	M	504	85	M

Nickel

M	26	Lost weight	W, F	42	251	W
W	26	Lost weight	W, F	42	231	W
M	206	105	M	392	134	W, S
M	242	117	M	364	150	W, S
G	158	Lost weight	S, F	476	73	G
G	242	113	M	476	71	G
G	242	116	M	476	69	G
M	206	102	M	476	64	G
M	261	Lost weight	W, F	476	68	G
M	261	Lost weight	W, F	476	63	G
G	166	Lost weight	S, F	476	84	G, S
G	242	106	M	476	57	G
G	201	111	M, S	476	59	G
S	206	107	M	476	67	G, S
M	140	Lost weight	W, F	476	66	G

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TABLE G-3.

Heat	Alloy Composition (Balance Zirconium), w/o	750 F Steam			680 F	
		Exposure Time, days	Weight Gain, mg per dm ²	Remarks ^(a)	Exposure Time, days	Weight Gain, mg per dm ²
<u>Tin and Nickel</u>						
503	0.27Sn-0.04Ni	213	108	M	462	106
505	0.27Sn-0.08Ni	213	100	M	490	83
504	0.28Sn-0.08Ni	213	100	M	490	71
506	0.26Sn-0.19Ni	213	103	M	490	83
507	0.25Sn-0.20Ni	207	146	M	490	75
508	0.56Sn-0.04Ni	249	106	M	434	102
509	0.56Sn-0.04Ni	213	102	M	490	91
510	0.54Sn-0.07Ni	213	103	M	490	88
511	0.56Sn-0.07Ni	207	117	M	490	75
513	0.51Sn-0.18Ni	207	120	M	462	101
512	0.54Sn-0.20Ni	207	118	M	462	97
<u>Tin, Iron, and</u>						
483	0.51Sn-0.16Fe- 0.090Ni	124	104	M	490	110
482	0.49Sn-0.23Fe- 0.097Ni	148	110	M	490	78
485	0.47Sn-0.27Fe- 0.13Ni	136	102	M	490	93
484	0.48Sn-0.31Fe- 0.13Ni	136	102	M	490	65
486	0.48Sn-0.38Fe- 0.18Ni	148	106	M	490	78
487	0.48Sn-0.44Fe- 0.18Ni	148	116	M	490	83

(a) Key to remarks: G - black tarnish film (good material)

M - milky

W - white oxide

F - flaking (heavy oxide)

S - segregated (areas of good and poor material).

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(Continued)

<u>Water</u>		<u>750 F Steam</u>		<u>680 F Water</u>		
Remarks ^(a)	Exposure	Weight	Remarks ^(a)	Exposure	Weight	Remarks ^(a)
	Time, days	Gain, mg per dm ²		Time, days	Gain, mg per dm ²	

(Continued)

M	206	Lost weight	S, F	476	78	G
M	261	Lost weight	W, F	476	86	G, S
G	242	110	M	476	66	G
G	206	103	M	476	78	M
G	206	117	M	476	87	M
M	206	108	M	476	77	M
M	206	139	M	476	90	M
G	206	131	M	448	109	M
G	206	141	M	476	87	M
M	201	126	M	476	90	M
M	206	133	M	476	92	M

Nickel

M	136	148	M	420	154	M
G	136	105	M	504	75	G
M	136	107	M	504	113	M
G	136	104	M	504	73	G
G	130	107	M	504	78	M
G	130	107	M	504	93	M

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H. REACTOR-MATERIALS DEVELOPMENT

F. A. Rough

General reactor-development programs sponsored by the AEC Reactor Development Division and a program of assistance to ANL are reported in this section.

Phosphate enamel coatings with and without mill additions of Vycor (silica glass) are being evaluated for uranium.

The study of the kinetics of the reaction between zirconium and UO_2 is essentially complete. Extensive data are presented for reaction experiments at 1100 and 1525 F.

The effects of water vapor on the oxidation of niobium at 600, 800, and 1000 C have been determined. The oxidation resistance and properties of various niobium alloys are being determined.

The study of uranium-rich uranium-titanium alloys is continuing.

Study of the vapor deposition of molybdenum from a mixture of hydrogen and MoCl_5 vapor on the inside of small-diameter stainless steel tubes is continuing. The most recent experiments, performed at atmospheric pressure, were not successful. Therefore, additional experiments are now being performed at reduced pressures.

Enameling of Special Metals

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

Current work is emphasizing the development of enamel coatings for uranium.

Crazing during the cooling of coatings applied to uranium has been a major problem. One approach to the solution of this problem being investigated is the use of relatively thin, partially devitrified coatings. Another recent approach is to use mill additions of Vycor (silica glass) powder in an aluminum phosphate enamel which is subject to minor crazing when applied on uranium.

With coatings having a high Vycor addition, it was found necessary to use a ground coat containing little or no Vycor in order to obtain

H-2

satisfactory wetting of the uranium. Several of the coatings so produced were crazed less than the phosphate enamel alone.

However, somewhat better results were obtained with a phosphate enamel containing iron oxide, lead oxide, and sodium oxide. Minor variations in composition and changes in the firing schedules resulted in a reduction of the undesirably high bubble population reported previously, and in a further slight reduction in crazing.

The results of preliminary trials on the effect of annealing upon crazing were inconclusive.

Future work will include additional variations of the compositions under study and of other compositions which can be applied as thin coatings on uranium. The effect of annealing upon crazing will be studied further.

Kinetics of the Zirconium-Uranium Dioxide Reaction

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

Zirconium-clad UO_2 fuel elements are being considered for some reactor applications. This study of the interaction kinetics in the temperature range of 950 to 1600 F is being made to estimate the useful life of such elements in reactor service. Sandwich-type elements, containing a plane surface of high-fired UO_2 in intimate contact with a plane surface of zirconium, are being used for the study.

Analyses for uranium and oxygen on thin layers machined in the zirconium beginning at the UO_2 interface have been completed for a large element heated at 1525 F for 227 hr. These analyses are shown graphically in Figure H-1. The data are quite similar to those previously reported for the reaction at 1600 F for 95 hr. The oxygen concentration descends sharply from a high initial value near the interface to a minimum value at about 4.5 mils from the interface. At this position the uranium concentration, which increased from a lower value near the interface, is at its maximum value. This region of maximum uranium and minimum oxygen corresponds to a dark-etching uranium-rich region in the microstructure. After reaching its peak value, the uranium content decreases sharply and levels off at about 0.002 w/o at 16 to 17 mils from the interface.

The oxygen content increases from its minimum value in the uranium-rich region and reaches a peak value at 7 to 8 mils from the interface. The microstructure in this region consists of light-etching metallic zirconium with oxygen in solid solution. Some spikes of the uranium-rich phase appear to lie in grain boundaries in the zirconium. The oxygen content

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FIGURE H-1. COMPOSITION OF ZIRCONIUM SAMPLE AFTER HEATING IN CONTACT WITH UO_2 AT 1525 F FOR 227 HR

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decreases smoothly but slowly and appears to level off at about 0.130 w/o at a distance of about 25 mils from the interface.

Analyses for uranium and oxygen also were obtained on thin layers machined in the zirconium from an element heated at 1100 F for 394 days under a 5000-psi helium pressure in an autoclave. These analyses are shown graphically in Figure H-2. The microstructure in the reaction zone of this element differs from that obtained at higher temperatures in that the dark-etching band of uranium-rich material, present in elements heated at higher temperatures, is absent in this element. This is also reflected in the analytical data and is shown on the graph in that the maximum in the uranium content and the minimum in the oxygen content near the interface are absent.

Both the uranium and the oxygen contents decrease sharply from their maximum values at the interface. The microstructure shows the two phases, alpha uranium and alpha zirconium, adjacent to the UO_2 . No doubt, the alpha zirconium contains the oxygen in solid solution. The uranium appears to reach a constant value of about 0.015 w/o at a distance of about 4 mils from the interface. The minimum oxygen value is reached at about 10 mils from the interface. All of these distances of penetration are much less than those observed for the reactions at higher temperatures.

The experiment at 1450 F in which a uranium foil, 1 to 2 mils thick, was placed at the zirconium- UO_2 interface, has been completed. Many less voids appeared at the interface at which the uranium foil had been placed. The phases found in the reaction zone were the same as those produced without the foil. The two-phase region (alpha uranium plus alpha zirconium), adjacent to the UO_2 , was somewhat thinner, while the dark-etching uranium-rich phase in grain boundaries was somewhat thicker and more continuous than that produced in the absence of foil. Penetration of oxygen was greater probably because there were fewer voids at the interface to interfere with diffusion.

Correlation of the analytical data from the machined specimens is continuing. The apparent diffusion constant for oxygen in zirconium, based on the data from elements heated at 1300, 1450, 1525, and 1600 F, can be expressed by the equation $D = 0.00168 \exp - 33,800/RT$ where D is expressed cm^2 per sec and T is in deg K. Because of the complexity of the process, however, the equation probably does not yield reliable values for the true diffusion constant for oxygen in zirconium.

The amount of UO_2 reacting at these four temperatures is expressed by the equation $\log_{10} (Wt^{-1/2}) = 1.823 - 4.787 T^{-1}$ where W is expressed in g of UO_2 per cm^2 , t is in hr and T is in deg K.

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FIGURE H-2. COMPOSITION OF ZIRCONIUM SAMPLE AFTER HEATING IN CONTACT WITH UO_2 AT 1100 F FOR 394 DAYS (9456 HR)

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Work is continuing on the preparation of the topical report summarizing the information obtained in this investigation.

Oxidation-Resistant Niobium Alloys

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

The present program is an investigation of the oxidation behavior of pure niobium and the effects of alloying elements on oxidation. Fabrication and mechanical properties of attractive alloys are also being studied.

The effects of known amounts of moisture in the air on the oxidation of pure niobium have been further investigated in 2-hr continuous-weighting oxidation tests on 20-mil niobium strips. The data from these runs were treated in the same manner as the data reported last month; i. e., the data were correlated by the general oxidation equation:

$$W = Kt^n,$$

where

W = weight gain, mg per cm²

K = oxidation rate constant, mg/(cm²)(minⁿ)

t = time, min

n = slope of a log-log plot of the data.

Ideally, the exponent n is 1.0 for linear oxidation and 0.5 for parabolic oxidation.

Values of the constants K and n, along with 1- and 2-hr weight gains, are given in Table H-1 for four tests on pure niobium. Comparison of the data for two tests at 600 C given in Table H-1 with the data reported in BMI-1149 indicates that moisture accelerates oxidation and decreases the protectiveness of the scale, i. e., raises the value of n. The value of n increased sharply from 0.70 in dry air to 0.92 in air in which the water-vapor pressure was 6.1 mm and less rapidly to 1.0 in air in which the water-vapor pressure was 17.3 mm. The 1-hr weight gains under these conditions were 2.15, 6.4, and 8.5 mg per cm², respectively. Thus, at 600 C, small amounts of water vapor increase the oxidation rate sharply, while larger amounts of water increase oxidation still further but at a lessened rate.

At 800 C, it was shown previously that a 6.1-mm water-vapor pressure decreased the oxidation weight gain from 29.9 mg per cm² in dry air to 10.3 mg per cm². The data in Table H-1 indicate that a further increase in water content to a 13.3-mm vapor pressure increased the 1-hr weight gain to 17.3 mg per cm², which is still much less than in dry air. The presence of water vapor also increased the linearity of the oxidation curve,

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raising the value of n from 0.635 for dry air to 0.988 for air with a water-vapor pressure of 13.3 mm. Thus, at 800 C, water vapor decreases the oxidation rate and promotes more linear oxidation.

TABLE H-1. AIR-OXIDATION RATES FOR NIOBIUM AND NIOBIUM-TITANIUM ALLOYS

Alloy Composition, a/o	Temperature, C	Water-Vapor Pressure, mm Hg	Values of Constants		Weight Gain, mg per cm ²	
			K, mg/(cm ²)(min ⁿ)	n	1 Hr	2 Hr
100Nb	600	13.3 ^(a)	0.117	0.958	6.0	11.7
	800	13.3	0.284	0.988	17.3	32.2
	1000	13.3	2.13	0.726	40.8	67.6
	600	17.3 ^(b)	0.141	1.00	8.5	17.1
Nb-10Ti	1000	0	0.49	0.778	12.2	20.7
Nb-20Ti	1000	0	0.352	0.651	5.5	8.7
Nb-30Ti	1000	0	0.179	0.826	5.2	9.4

(a) 76 per cent relative humidity at 20 C.

(b) 100 per cent relative humidity at 20 C.

At 1000 C, water vapor had little effect on the oxidation rate. Weight gains were similar for oxidation in air with a water vapor pressure of 0, 6.1, or 13.3 mm. The value of n increased from 0.573 to 0.726, indicating that the oxidation curve tended more toward linearity as the concentration of water vapor increased.

A spectrographic analysis on the niobium sheet used for these tests showed the material to contain 0.6 w/o zirconium, 0.01 w/o silicon, and 0.06 w/o or less of other individual metallic impurities. The effects of these amounts of zirconium and silicon on the oxidation behavior of niobium are not known.

Continuous-weighing oxidation tests have been conducted on three niobium-titanium alloys in dry air at 1000 C. These samples were obtained from arc-melted ingots which were hot and cold rolled to 30-mil strip, as reported previously. The data, as reported in Table H-1, confirm the earlier data obtained in intermittent-weighing tests which showed titanium to be beneficial in reducing the oxidation rate of niobium. The 1-hr weight-gain data indicate that oxidation weight gains decrease with increasing titanium contents up to 30 a/o titanium. However, the 2-hr data show that, of the three alloys tested, the niobium-20 a/o titanium had the lowest

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weight gain. This alloy had also the lowest n value, indicating that the oxide was most protective of the three alloys evaluated. Previous oxidation tests on cast alloys in undried air showed a minimum in oxidation rate at 25 a/o titanium.

Oxidation tests could not be performed on the rolled niobium-vanadium alloy strip because of the poor surface and severe edge cracking. Work is continuing to prepare defect-free strip suitable for oxidation testing.

Vacuum heat treatments have been performed on samples from the wrought niobium, niobium-titanium, and niobium-vanadium strips to determine recrystallization behavior. The samples were heated for 1 hr at 1100, 1200, 1300, and 1400 C. Hardness values have been obtained and are given in Table H-2. These data indicate that pure niobium is softened by annealing at 1100 C, but complete softening does not occur until 1400 C. The niobium-titanium alloys are fully softened after 1 hr at 1100 C, but the niobium-20 a/o titanium and niobium-30 a/o titanium alloys are hardened by heating at 1200 C and higher. The niobium-vanadium alloys were softened by annealing at 1100 C, and further softening was obtained by annealing at 1200 C. These samples will be examined microscopically.

TABLE H-2. HARDNESS VALUES OF WROUGHT AND ANNEALED NIOBIUM AND NIOBIUM-BASE ALLOYS

Alloy Composition, a/o	Vickers Hardness Number					
	As Cast	As Rolled ^(a)	Annealed 1 Hr at Indicated Temperature			
			1100 C	1200 C	1300 C	1400 C
100Nb	125	195	160	162	158	125
Nb-10Ti	172	223	147	133	133	131
Nb-20Ti	179	236	165	172	172	181
Nb-30Ti	187	249	188	197	209	238
Nb-5V	186	257	206	191	192	193
Nb-10V	228	296	228	203	196	189
Nb-15V	260	329	249	228	225	222

(a) Cold rolled 61 to 68 per cent.

Future work includes:

- (1) Continued melting and cold rolling of niobium-titanium, niobium-vanadium, niobium-molybdenum, and niobium-chromium alloys for oxidation and mechanical-properties tests

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- (2) Additional oxidation tests in wet air on thicker samples of pure niobium to insure that an appreciable thickness of unreacted metal remains at the conclusion of the tests.

Uranium-Titanium Alloy Studies

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

The redetermination of the uranium-rich end of the uranium-titanium alloy system is proceeding by thermal analysis (inverse-rate method) and by quantitative metallography. A subsequent study of the $\gamma_{\text{U-Ti}} \rightarrow \alpha'$ reaction and a study of the $\beta_{\text{U-Ti}}$ decomposition will be performed.

Inverse-rate cooling curves of alloys containing up to 6 a/o titanium have been made in a vacuum furnace. All alloys were solution treated 1 hr at 800 C and cooled in the furnace at the rate of about 7 C per min. Thermal arrests have been detected for some alloys, but other alloys exhibited anomalous arrests. Additional tests must be performed, and several reruns are necessary.

Equilibration of all alloys at several temperatures is in progress. Quantitative metallography (lineal analysis) of the equilibrated structures will establish the amounts of second phase and matrix present. Subsequent correlation with the thermally determined $\gamma/\gamma + \beta$ transus will fix the solubility of titanium in β -uranium by application of the lever rule.

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 outside and inside of small-diameter Type 304 stainless steel tubes.

During previous work, uniform, adherent coatings were applied to the outside of 20-in. lengths of tubing by hydrogen reduction of MoCl_5 vapor at a total pressure of 20 to 50 mm of mercury. Adherent, nonuniform molybdenum coatings were applied on the inside of short lengths of tubing, but the attempt to coat internally a 20-in. length of tubing resulted in the plugging of the tube with lower chlorides of molybdenum, and the formation of a nonadherent, powdery deposit.

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During the past month, the modified internal tube coater was operated at atmospheric pressure.

Molybdenum deposition in the modified internal tube coater is accomplished by mixing separate streams of MoCl_5 vapor (carried in argon) and hydrogen inside of the heated tube to be coated. The region of mixing is moved through the tube from end to end to obtain a uniform coating throughout the length of tubing.

When operated at atmospheric pressure and at a specimen temperature of 920 C a thin coating was obtained, but a large part of the molybdenum was deposited as a tube which built up on the end of the nozzle which injected the mixture of argon and MoCl_5 vapor into the specimen tube. Molybdenum metal powder was also formed and blown out of the tube with the waste gases. At a specimen temperature of 800 to 840 C there was no buildup of metal on the end of the injection nozzle, and the amount of metal powder formed was smaller. Metallographic examination of the tube coated at atmospheric pressure showed a thin (0.1 mil or less), spotty coating. The coating was uniform in coverage with respect to the area covered by the coating nozzle, however, the irregularity in thickness being on a semimicro scale. This irregularity in coating thickness and the formation of molybdenum powder are believed to be caused by operation of the coating unit at atmospheric pressure. Consequently, the operation of the coater at reduced pressure will be studied during the coming month.

I-1

I. PHYSICAL METALLURGY

F. A. Rough

Basic programs in ceramics and metallurgy which are supported by the Research Division of the AEC are reported in this section.

Various binary uranium compounds with silicon, aluminum, or boron have been prepared for a study of basic physical and thermodynamic properties.

Experimental details for study of the tensile properties of uranium at strain rates of 0.1 to 0.0001 in. per in. per sec are being arranged as part of the investigation of the tensile transition in alpha uranium.

Routine progress is reported on the study of the constitution of uranium-molybdenum-zirconium alloys. A transformation is reported for UC_2 at about 1800 C. No transformation has been observed in UC present in two-phase samples.

Additional experiments are reported which are intended to provide the necessary data for evaluation of the fundamentals of bonding.

In the study of the niobium-hydrogen reaction, emphasis is being placed on the obtaining of equilibrium data which are essential to the interpretation of kinetic-data experiments.

PROPERTIES OF URANIUM COMPOUNDS

This program is aimed at determining basic physical and chemical properties of selected refractory binary compounds of uranium.

Preparation, Fabrication, and Physical Properties

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

In this phase of the research, specific-heat measurements on three uranium silicides were continued, compacts of four compounds were examined metallographically, and the compound UB_4 was prepared.

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Enthalpy measurements on USi, USi₂, and USi₃ up to a temperature of 300 C were completed. The data are being programmed for computer calculations of the specific heats.

Metallographic examination of polished sections showed that the sintered compacts of U₃Si₂, USi, USi₃, and UAl₂ made last month were essentially one-phase materials. The U₃Si₂ appeared to be well sintered, with a grain size of 0.1 to 0.2 mm, and little intergranular porosity. A few isolated pores and numerous cracks were observed.

The other three compounds had very porous structures and much smaller grains than the U₃Si₂. Higher sintering temperatures than those used previously will be required to densify these materials.

The compound UB₄ was prepared from a powder compact of high-purity boron and UH₃, made by reacting uranium with pure hydrogen derived from decomposition of other UH₃. The mixture was reacted at 1000 C for 16 hr in a vacuum furnace and then heated to 1500 C in the same furnace to insure complete reaction. X-ray diffraction and metallographic analyses showed that the product was predominantly UB₄, with less than 5 per cent of extraneous phases. The compact was very porous and no incipient melting was observed, showing that this compound has a melting point well above 1500 C.

In future work, USi, USi₂, USi₃, and UAl₂ will be sintered at higher temperatures to obtain denser compacts. An attempt will be made to prepare a dense compact of UB₄. Thermal-expansion measurements will be resumed and metallizing the ends of silicide samples for thermal-diffusivity measurements will be attempted.

Reaction With Gases

W. M. Albrecht and M. W. Mallett

Reaction of uranium compounds with common gases are being investigated.

Samples of sintered compacts of U₃Si₂, USi, USi₃, and UAl₂ on hand are being prepared for reacting with oxygen and nitrogen, using a micro-balance to obtain semiquantitative weight-gain data.

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Heat-of-Formation Measurements

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

Methods for the measurement of the heat of formation of uranium compounds are being investigated. The search is continuing for a suitable reaction of USi_2 and UAl_2 with acids at room temperature. Consideration is being given to the possibility of measuring the heat of formation directly from a reaction of the elements. Samples of UC and UN have been prepared for use in determination of solubilities in acids.

INVESTIGATION OF THE TENSILE TRANSITION
IN ALPHA URANIUM

L. L. Marsh and G. K. Manning

An investigation is being made which is concerned with a better understanding of the tensile transition in uranium. The experimental approach has been to study the temperature variation of mechanical properties and modes of plastic deformation through the transition region. Uranium has been observed to deform by twinning and slip, with the former becoming predominant in the critical-temperature range.

The current program is concerned with the effect of grain size and strain rate on the modes of plastic deformation and the resulting mechanical properties. In order to obtain a significant variation in strain rate, a subpress used in conjunction with a hydraulic press has been modified to suit the present tensile-specimen design. The load will be measured by means of a calibrated load cell; the strain will be measured by means of a Brush strain analyzer and recorder. The range of strain rates which can be obtained is 0.1 to 0.0001 in. per in. per sec.

CONSTITUTION OF URANIUM ALLOYSUranium-Base Ternary Alloys

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

A study of the phase relationships which occur between the delta phases of the uranium-zirconium and uranium-molybdenum systems is being conducted.

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Metallographic examination of heat-treated specimens is almost completed. Alloys quenched from 900 and 700 C indicate the existence of a two-phase region at intermediate compositions. Alloys quenched from 625 C show an apparent three-phase region in a range of compositions near the molybdenum-rich end of the ternary cut. Specimens have been selected for X-ray diffraction studies in the regions of interest.

Additional alloys prepared for the determination of the extent of the terminal solid solutions and for pinpointing critical regions of the original series of alloys have been fabricated and are being heat treated in preparation for metallographic examination.

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

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

The uranium-carbon system is being studied to determine phase fields between UC and UC₂. Last month it was found that UC₂ transformed at 1800 C to a face-centered-cubic phase. It had also been suggested that there might be a second intermediate transformation.

Continued studies of the UC₂ composition at intermediate temperatures have shown that a single structure exists to its transformation at 1800 C. Tentative results, based on the structure proposed by Litz* for UC₂, have shown peculiar expansion characteristics. Parameter calculations based on the proposed structure have shown the a-axis expansion to be much greater than the c-axis expansion with the c dimension apparently reversing above 1200 C and contracting, so that at 1600 C it has a value only slightly larger than at room temperature. This anomalous behavior is supported by a plot of volume expansion which shows a uniform increase with temperature.

Several additional samples have been examined; it was found that heat treating must be performed in the camera to obtain a homogeneous phase distribution. Samples containing UC plus UC₂ have shown no transformation for UC, and the usual transformation was observed for UC₂. Estimates of the amount of UC₂ present in some samples indicates increasing solubility with temperature of UC₂ in UC.

The U₂C₃ phase has not as yet been detected, although it is not believed to exist above the UC₂ transformation temperature. Current work

*Litz, L. M., Garrett, A. B., Croxton, F. C., J. Am. Chem. Soc., 70, 1718 (1948).

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will investigate its formation and temperature-existence region, which is believed to occur below the transformation.

The plasticity of UC at elevated temperatures appears remarkable. One sample became spot welded to the tantalum heating element while being rotated at 1900 C with the result that it simply "wound up" without fracture. Apparently, its elevated-temperature strength is low and its behavior is metal-like.

Samples are currently being prepared for study of U_2C_3 .

STUDY OF BONDING FUNDAMENTALS

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

In December, work was continued in the investigation of solid-state bonding fundamentals. Experiments were intended to determine the effect of diffusion and creep, both time-dependent processes, on the growth of the contact area formed under an applied load between a gold needle point and a plane gold surface. Strength tests of these simulated single-asperity junctions were conducted at 400 and 500 C after applying a 400-mg. bonding load for periods ranging from several sec to 60 min. The plane bonding surfaces were in the annealed state. Data indicate no diffusion or creep effect at 400 C, since breaking strengths of the contact areas showed no time dependence. At 500 C, a slight increase in bond strength with time was observed.

Data reported in BMI-1149 had established a time dependence of bond strength under similar conditions when the plane bonding surface was cold worked. Previously, it was postulated that the strength of the bond was the sum of two terms: $S = S_0 + C_2(T)Dt^{0.4}$. The present effort is being directed toward a study of the factors that influence the initial, or zero-time, bond strength.

It is expected that temperature and load will be the dominant factors in establishing the value of the S_0 term. Also, the effects of temperatures on the second term of the expression will be more thoroughly investigated.

NIOBIUM-GAS REACTIONS

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

The kinetics and mechanisms of the reactions of niobium with hydrogen and nitrogen are being investigated. Certain apparent anomalies appear in current kinetic experiments and published data of others who have made exploratory studies of the hydrogen-niobium system. Because of this, the basic premises of kinetic studies were reviewed. In the simplest and most often encountered case of the oxidation of metals, the kinetics of formation of a saturated phase on the metal surface is determined. Characteristic of this phase is its very low dissociation pressure, often less than 10^{-6} mm of mercury. In manometric systems where the limit of measurement is of the order of 0.1 mm of mercury, such pressures are undetectable. Under these circumstances, the composition of the reaction product (if only one is formed) is constant under all experimental conditions of pressure.

In contrast with this, there are the metal hydrides which have comparatively high dissociation pressures of several mm or atmospheres, depending on the hydride and the temperature. Thus, unless the system pressure equals or exceeds the dissociation pressure, the desired (saturated) reaction product is not formed. An additional complication is that many of the metal-hydride systems show wide solid-solubility regions of metal dissolved in a terminal hydride phase. In such systems, reactions carried out at constant system pressures yield products which vary in composition with temperature. Therefore, the kinetic data show no recognizable relationship. However, orderly data should result if first the composition of the surface product (solid solution) is fixed. Then the experiments are carried out at system pressures corresponding to the dissociation pressures of the selected product at the experimental temperatures. If experiments are carried out in this manner for several product compositions, the effect of the composition variable may be evaluated.

It is apparent that, if meaningful kinetic data are to be obtained for hydride systems of this type, experimental conditions must be selected on the basis of accurate and detailed knowledge of the pressure-temperature-composition equilibria of the system. Therefore, in the study of the hydrogen-niobium reaction, emphasis is being placed on obtaining of the essential equilibrium data needed for interpretation of kinetic experiments.

J-1

J. DEVELOPMENTAL STUDIES FOR THE PWR

R. W. Dayton

Studies of flow in a model of the PWR pressure vessel have continued, with further study of velocities and flow directions in the upper plenum space. Flow patterns were examined with smoke. Further studies of flow distribution in the core have continued, and will be completed next month.

Feasibility studies of X-ray photometry as a method for detecting voids in end closures have shown that a 0.012-in. -spherical void can be detected.

Air-Flow Studies on PWR Pressure Vessel

L. J. Flanigan and H. R. Hazard

Air-flow studies in a quarter-scale flow model are being conducted at Battelle to provide design data for the Westinghouse PWR reactor. Work previously completed includes a study of flow distribution in the reactor core, studies of coolant flow in the thermal-shield passages, a study of mixing in the lower plenum, and a study of flow patterns throughout the upper plenum space involving the original hold-down barrel.

Flow studies in the upper plenum space involving the revised hold-down barrel were continued in December. Velocities and direction of flow in the annular space between the hold-down barrel and the outer shell and along the surfaces of the upper dome were determined for all loop configurations. Also, velocities and pressure differentials were measured for determination of forces acting on control-rod guides and general flow patterns throughout the upper plenum space were determined using TiCl_4 smoke as a tracer.

The extended studies of flow distribution in the reactor core were continued during the month. The large sponge-rubber gasket between the orifice retaining plate and the core-tube plate leaked slightly, resulting in a data spread of about ± 1.5 per cent, compared with a comparable spread of ± 3 per cent of earlier core studies. Replacement of the sponge-rubber gasket with a gasket of soft gum rubber increased the leakage. In a final attempt to eliminate leakage, a closed-cell sponge-rubber gasket will be used early in January. To further study the effect of inlet configuration on flow distribution, the flow baffle and the orifice-retaining plate were removed. A calibration was made on the measuring orifice of each simulated fuel cluster, including the effect of inlet configuration. Flow distribution

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was determined for two-, three-, and four-loop configurations with the flow baffle and restricting orifices removed, but analysis of the data for these tests has not been completed.

The second topical report, describing the lower plenum mixing studies, was submitted to Bettis for coordination on December 17.

The current contract ends January 31, 1957. In January, the extended studies of flow distribution in the core will be completed, three remaining topical reports will be completed and sent to Westinghouse for coordination, and the second topical report will be reproduced and distributed.

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

J. B. Schroeder and C. M. Schwartz

The experimental work has been completed on a study aimed at determining the feasibility of using X-ray photometry to detect weld porosity in fuel-pin end closures.

The data obtained during the feasibility study indicate that spherical voids 0.012 in. in diameter can be positively identified in welded Zircaloy 2 fuel pins 0.420 in. in diameter. Based on considerations of available means of increasing the X-ray intensity and detector efficiency, a test instrument with this sensitivity could be built which would examine 0.080 in. (i. e., about one-half) of the width of the weld zone in 1 min. By providing interchangeable collimating heads, the same instrument would also be able to measure the uranium content of alloy fuel elements to plus or minus 0.02 g per cm², and to locate the core in clad fuel elements.

K-1

K. EVALUATION OF A REFLECTOR-CONTROLLED
HETEROGENEOUS BOILING REACTOR

J. W. Chastain

Attention is directed toward the development of a reactor system which will operate unmanned for long periods of time. To obtain satisfactory operation of such a reactor requires built-in safety and control systems. Such a system is being investigated for a boiling heterogeneous reactor.

Control of the boiling heterogeneous reactor is obtained by varying the height of the reflector in an annular tank surrounding the reactor core. The annular reflector tank is connected to a pressurized surge tank; the flow of water between the tanks depends on which is at the higher pressure. For instance, if the reactor power increases, the steam pressure will increase and force water out of the reflector tank. This lowers the height of the reflector and permits more neutron leakage, which reduces the power.

Two experiments are being performed to check the feasibility of this means of control. One of these is a critical experiment to determine the reactivity worth of the reflector. The critical assembly started operation during the month and the first loading has been completed. This loading was not sufficient to obtain criticality but criticality probably will occur in the next loading.

The other experiment is a duplication or simulation of the reactor system. Part of this is a full-scale mock-up of the hydraulic system including the reflector tank and surge tank. Both pressure and water level are measured. An electrical signal representing the liquid level is fed to an analog computer. The computer sends a signal to the pressure recorder-controller unit, which adjusts the pressure in the tanks. The reactivity worth of the reflector as a function of height must be known to adjust the pressure properly. This will be provided by the critical-assembly experiments.

All wiring is complete and final calibration has been started. During January, the entire system will begin operation.

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Critical Experiment

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

The results of this experiment will be an evaluation of the worth and effectiveness of the reflector system of control, and will be used as input data to the reactor simulator to evaluate the transient behavior of the reactor system.

The reflector has been installed and the table operation checked. The first core loading, consisting of 3059.40 g of uranium-235, has been completed without reaching criticality. This loading was achieved in six successive runs of 1203.26, 1691.16, 2150.11, 2555.76, 2933.32, and 3059.40 g of uranium-235, respectively.

From the data obtained during the above loading an estimate was made for a second loading containing 3.75 kg of uranium-235. This new loading is now being done in successive steps as before in an attempt to achieve criticality.

It is anticipated that the critical mass will be attained shortly after the first of the year.

Simulator Studies

B. B. Gordon and J. J. Stone

During December the pressure controller and the associated control valves were received and were installed. The pneumatic signal connections from the controller to the control valves, the pressure connection from the simulated reflector tank to the controller, and the electrical wiring from the computer to the controller were installed. The final calibration of all instruments in the system was started.

During January, time has been reserved on the analog computer for operation of the entire control system. Prior to this operation, the calibration of the instrumentation will be completed.

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L-1

L. STUDIES OF SODIUM-TANTALUM COMPATIBILITY
AT ELEVATED TEMPERATURES

J. H. Stang

Work is under way at Battelle on several problems associated with a fast reactor (LAMPRE I) featuring an all-tantalum core cooled by high-temperature flowing sodium. Fluid temperatures in the 1000 to 1500 F range are of current interest.

Components are being fabricated for five flow loops which will be used in sodium-tantalum corrosion studies.

High-temperature mechanical-property data for tantalum are being sought. A first lot of test material was annealed in a newly constructed furnace rig. It was found to have unusually high hardnesses following the annealing procedure. The probability that this stemmed from high oxygen and nitrogen content is being checked.

Initial tantalum welding studies started using the inert-gas-shielded tungsten-arc process. The welds that were made were somewhat oxidized and embrittled. It is obvious that the shielding requirements to eliminate these effects are stringent.

An analytical procedure for very low concentrations of oxygen in sodium, based on a gettering technique, is being explored. Equipment for gettering experiments is in the final design stage. Meantime, an amalgamation apparatus for routine service analyses has been built and initial runs with it are starting.

Tantalum-Sodium Compatibility Studies

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

The tantalum-sodium compatibility studies discussed here have two broad objectives. The first is to investigate the corrosion and mass-transfer behavior of tantalum which is exposed to sodium in the temperature range from 1000 to 1500 F. The second is to secure information about the effect of such exposures on high-temperature mechanical properties of the test material. Since it is believed that the oxygen content of the sodium that is used will have an important bearing on experimental results in each of these phases, it is imperative that this parameter be accurately controlled and measured in the test rigs.

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As was pointed out in BMI-1149, polythermal pumping loops (constructed of Type 316 stainless steel with tantalum test inserts) have been selected as the basic test systems because of simplicity and flexibility. Oxygen levels in the sodium will be regulated by the use of cold traps or getters. During December, the fabrication of components for five test loops was started and orders were placed for the instrumentation that will be required for their operation. It now appears that one of these loops can be assembled during January and be ready for trial runs near the end of the month.

The High-Temperature Mechanical Properties of Tantalum

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

An investigation to determine the mechanical properties of tantalum at temperatures between 1000 and 2000 F is being made to provide information for use in design of LAMPRE I. The primary objective is to determine the effect of oxygen contamination on hardness, tensile, and stress-rupture properties of tantalum. The oxygen content of test specimens will be varied by adding oxygen to a vacuum system in which the tantalum is heated. If necessary, very low concentrations will be obtained by degassing under high vacuum at temperatures above 3600 F. Construction of apparatus for the gas-addition experiments is about to start.

Construction of the vacuum-annealing apparatus (which is an adjunct to the equipment discussed above) has been completed, and preliminary test-annealing operations were carried out. The annealed room-temperature hardnesses (VHN 10 kg, 168 to 170) obtained in these test runs were considerably higher than expected. This condition requires further study especially with respect to the oxygen and nitrogen content in the tantalum before and after annealing.

A preliminary stress-rupture test with a tantalum specimen has been started at 1600 F in a vacuum system with a dry helium "bleed in" to maintain a pressure of 5 μ of mercury. This system is intended to limit gas contamination of the sample during testing. The chief purpose of the test now running is to check out the reliability of the system from this viewpoint.

L-3 and L-4

Weldability of Tantalum for High-Temperature Systems

S. M. Silverstein and R. P. Sopher

The major portion of this research is concerned with a method of welding thin-wall (3/16-in. OD with 15-mil wall) tantalum tubes to a thin tantalum header. During December, the inert-gas-shielded tungsten-arc welding process was used in preliminary studies involving simple butt joints and beads on tantalum plate. This method appears to be the most satisfactory of the standard arc welding processes for this application. However, it is apparent from the preliminary studies that extremely good inert-gas shielding is required if the welds are to remain unoxidized and unembrittled.

Some difficulty was encountered in this initial work with tantalum in making weld beads of uniform width on plate. In addition, porosity was noted in most of the welds that were made. It may have stemmed from the fact that the base material was fabricated from sintered stock; it is known that a powder metallurgy product, when welded, is likely to give a somewhat porous weld. If weld porosity persists, it might be overcome by remelting the weld deposit with the welding arc. This technique may permit some of the gases to be evolved prior to freezing.

During the month, a small amount of tantalum tubing and sheet was received. These samples were machined to give the first set of test joints. These will be welded when the fixture, which has been designed for this purpose, is completed.

Determination of Oxygen in Sodium

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

An attempt is being made to develop a new and more sensitive method for the determination of oxygen in sodium. The principle being currently investigated is that of gettering the oxygen from a large amount of sodium by a small quantity of a metal having an oxide more stable than sodium monoxide. The getter is then analyzed for oxygen by the vacuum-fusion technique. Construction of a stainless steel reaction chamber to carry out the gettering reaction (using titanium initially) is now nearing completion. It is hoped to start experimental runs during January.

Construction of an amalgamation apparatus which will be used for service analyses of sodium with oxygen levels above 0.001 w/o is now completed and exploratory runs with the equipment have started.

M-1

M. PROCESSING OF FEED MATERIALS

E. L. Foster, Jr.

The evaluation of salt baths for the heat treatment of uranium rods is under study for National Lead Company of Ohio (NLO). Two binary salt bath systems, 50 w/o sodium chloride-50 w/o potassium chloride and 50 w/o potassium chloride-50 w/o sodium carbonate, are currently being investigated. These baths, containing various additions of salt from baths now in use at NLO, are being studied to determine the amount of hydrogen picked up by uranium heat treated in them.

Work has progressed and tests are now in progress. Uranium specimens have been heat treated for 13.5 min at 1350 F in a week-old salt bath of 50 w/o sodium chloride-50 w/o potassium chloride containing 6.7 w/o of K₂, (50 w/o Na₂ CO₃-50 w/o KCl). The specimens were quenched in water and sent to NLO for total hydrogen analysis. Specimen weight loss was very small and corrosion negligible. Qualitative corrosion information on the salt bath container materials and proposed container materials is being gathered concurrently.

Salt-Bath Development

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

The evaluation of salt baths, on a pilot-plant scale, to determine their effect on the quantity of hydrogen picked up by uranium rods heat treated in them is under study. This program is concerned primarily with two salt baths. These are the 50 w/o sodium chloride-50 w/o potassium chloride and the 50 w/o potassium chloride-50 w/o sodium carbonate salt baths. Qualitative information on the corrosion of materials in contact with the salt baths is also being gathered.

A salt bath consisting of 93.6 lb of NuSal*, with 6.7 lb of K₂** added to approximate carry-over contamination, was started up in a modified Ajax-Hultgren immersed-electrode salt-bath furnace. The furnace was modified by installing a mild-steel pot liner (3/8 in. wall thickness, 12.2 in. inside diameter, and 19.6 in. inside depth), and replacing the nickel-chromium electrodes with mild steel. The temperatures of the salt bath were controlled at 1350 F by a radiation pyrometer; a platinum versus

* NuSal contains 50 w/o NaCl and 50 w/o KCl.

** K₂ contains 50 w/o Na₂CO₃ and 50 w/o KCl.

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platinum-rhodium thermocouple within a ceramic protection tube was installed as a secondary temperature controller.

Two uranium specimens, each approximately 1.5 in. in diameter and 2 in. long, were treated for 13.5 min in this week-old salt bath and quenched in water. The uranium specimens showed weight losses during the heat treatment and quenching of 0.1 and 0.2 per cent (the actual weight losses for each specimen are recorded in Table M-1). The specimens upon removal from the water quench seemed to be completely free from any visible salt coating. Visual inspection of the surfaces of the specimens seemed to indicate that the corrosion of the uranium was negligible. These uranium specimens have been shipped to NLO for an analysis of hydrogen pickup.

At the beginning of this first salt bath run, four mild-steel (two cold-rolled and two hot-rolled) and two stainless steel (Type 304) corrosion specimens were suspended in the salt bath. Quantitative corrosion information will be obtained from an examination of these specimens as well as the pot liner and electrodes at the end of the salt-bath run.

The work schedule for January consists of completing the first run and starting a second run with a new salt-bath composition. The first run will be completed by aging the salt bath at the operating temperature another 2 weeks. Uranium specimens will be heat treated at weekly intervals to test the effect of salt-bath age on hydrogen pickup. The second run will also be operated for 3 weeks with three heat treatments made at weekly intervals.

TABLE M-1. WEIGHTS OF URANIUM SPECIMENS FOR THE FIRST HEAT TREATMENT
OF THE FIRST SALT-BATH RUN

	Specimen 1-1-a	Specimen 1-1-b
Weight before heat treatment, g	928.00	982.52
Weight after heat treatment, quenching, and drying, g	926.19	981.26
Weight loss due to heat treatment and quenching, g	1.81	1.26
Weight loss, per cent	0.20	0.13

N-1

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

Charles L. Peterson, Paul D. Miller, Robert S. Peoples,
Earl L. White, E. Burt Friedl, and Oliver M. Stewart

The investigations concerning the corrosion problems associated with the reprocessing of spent reactor fuel elements have been continued during the month of December as part of a program of assistance to ORNL.

Four 7-day exposure periods have been completed with tantalum, titanium, and Type S-816 specimens in the nitric acid elimination-type tests connected with the Zircex process. An arbitrary value of 3 mils per month has been established as the value above which corrosion is too great for the metal to be considered for further testing. By this means metals such as Illium R, AISI Type 304 ELC stainless steel, Hastelloy B, "A"-Nickel, Inconel, and Monel have been eliminated from further testing in most of these solutions either by a short-term exposure in the regular type of test or by test-tube-size tests of a preliminary nature.

The results of these tests are given in Tables N-1 to N-4. The solutions for the tests in 3 M and 5 M H^+ were made using uranyl nitrate hexahydrate, hydrochloric acid, nitric acid, and distilled water so that the final concentrations are equivalent to the desired values for H^+ and for UCl_3 . The solutions for the tests in 0.5 M H^+ were made using nitric acid, distilled water and some UCl_3 whose purity was only approximately known. Since the chloride ion is unstable in 15 M HNO_3 , the solutions used in the tests in 15 M H^+ were made up with nitric acid and uranyl nitrate hexahydrate to be 15.0 M HNO_3 , 0.4 M $UO_2(NO_3)_2$, and anhydrous hydrogen chloride gas was bubbled through the solution at a low rate throughout the test.

The results with tantalum, titanium, and Type S-816 specimens have been quite encouraging in the nitric acid elimination-type tests, with the exception of those tests in 15 M HNO_3 . The tantalum specimens survived the 4 weeks' exposure to this solution but, during the fourth week, the titanium and Type S-816 specimens which had been relatively unattacked were suddenly attacked quite severely in some cases. This attack was most pronounced in the case of the specimens exposed in the vapor of these solutions, where there is a large amount of hydrochloric acid fumes with a low concentration of nitric acid. Similar experiences have been encountered with titanium specimens exposed to hydrogen chloride in the vapor-phase elimination-type tests. These experiments will be repeated but, at present, caution is indicated in any contemplated use of titanium for fabricating a vessel in which a chloride-stripping reaction is likely to occur.

N-2

At present, similar elimination-type tests are under way with Type S-590, Haynes 25, Carpenter 20, Carpenter 20 stabilized, Hastelloy C, and Vitallium alloys in certain of the nitric acid concentrations. Vitallium, Haynes 25, and Type S-590 appear to be the most promising of these materials, while failures have been encountered with Hastelloy C. These data will be reported when the full 4 weeks of exposure have been completed.

Six more runs have been completed in the vapor-phase elimination-type tests. These have indicated that, in the temperature range from 400 to 600 C, neither tantalum nor titanium can be expected to withstand the attack of hydrogen and anhydrous hydrogen chloride gas. The conditions and observations of these runs are summarized in Table N-5.

Calculations of the equilibrium constants for various reactions involving the hydrochlorination of titanium have been made at Battelle and these show that, thermodynamically, the tendency for titanium to hydrochlorinate is very great from room temperature up to 1200 C.

Investigations designed to select a suitable material of construction for the dissolver vessel in the Darex system have been begun. In this system, fuel elements, either clad or alloyed with stainless steel, are dissolved in a dilute mixture of nitric and hydrochloric acids referred to as dilute aqua regia. The starting acid will probably be 5 M HNO_3 -2 M HCl . This is consumed by the fuel-element dissolution until an acid concentration of about 1 M H^+ is reached. By this time, the solution is nearly saturated with uranium and the various ions arising from the dissolution of stainless steel.

The tests which have been devised for this system are of the boiling acid reflux type in which three sets of duplicate specimens are exposed to the liquid, the interface, and the vapor. Since fission products have been observed to promote corrosion in certain cases, half of the first group of tests are being made with 50-ppm additions of ruthenium, selected as a possible fission-product corrosion promoter. The first series of these tests is under way. The midpoint concentrations of acid and stainless steel ions have been selected for these tests. Only tantalum, titanium, and Type S-816 are under consideration, at present, as possible materials of construction. The results look encouraging thus far and no corrosion promotion can be attributed to the presence of ruthenium as yet. Two more series will be started soon, testing the beginning and final solution concentrations which can be expected in the dissolver. These results will be reported in tabular form when four 7-day exposure periods have been completed.

RWD:CRT/all

TABLE N-1. ZIRCEX BOILING NITRIC ACID ELIMINATION-TYPE TESTS

(ca 0.5 M H⁺, ca 0.4 M UCl₃)

Specimen	Specimen Position	165.5 Hr		331.5 Hr		491.5 Hr		658.5 Hr	
		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
Tantalum	Vapor	+1.2	Weight gain	+2.8	Weight gain	+0.5	Weight gain	+3.4	Weight gain
	Interface	+4.1	Ditto	+5.4	Ditto	5.1	0.01	2.1	0.00
	Liquid	+1.0	Ditto	+1.6	Ditto	+3.7	Weight gain	+1.3	Weight gain
Titanium	Vapor	0.0	0.00	+1.3	Weight gain	+2.5	Weight gain	+3.9	Weight gain
	Interface	+0.4	Weight gain	+1.0	Ditto	+0.7	Ditto	+1.0	Ditto
	Liquid	0.0	0.00	+4.8	Ditto	+0.4	Ditto	+0.4	Ditto
Type S-816	Vapor	50.8	0.38	51.3	0.19	54.0	0.14	54.0	0.10
	Interface	57.0	0.43	60.3	0.23	65.6	0.17	67.6	0.13
	Liquid	39.8	0.30	47.2	0.18	48.3	0.12	53.2	0.10

Note: Specimens of Illium R, Monel, Hastelloy B, and "A"-Nickel failed in a short time in this solution.

TABLE N-2. ZIRCEX BOILING NITRIC ACID ELIMINATION-TYPE TESTS

(3.0 M H⁺, 0.4 M UCl₃, 2.8 M NO₃⁻)

Specimen	Specimen Position	156 Hr		318 Hr		506 Hr		674 Hr	
		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
Tantalum	Vapor	+3.8	Weight gain	+3.6	Weight gain	+0.2	Weight gain	+5.5	Weight gain
	Interface	+1.2	Ditto	+1.9	Ditto	+1.9	Ditto	+2.4	Ditto
	Liquid	+0.2	Ditto	+0.5	Ditto	+0.1	Ditto	+0.1	Ditto
Titanium	Vapor	+1.4	Weight gain	1.3	0.01	2.3	0.01	3.8	0.01
	Interface	1.9	0.03	3.1	0.02	3.4	0.02	4.8	0.02
	Liquid	0.9	0.01	0.6	0.00	1.8	0.01	2.0	0.01
Type S-816	Vapor	34.8	0.30	43.7	0.19	58.6	0.16	66.9	0.13
	Interface	63.4	0.52	86.7	0.35	117.6	0.30	146.6	0.28
	Liquid	73.1	0.56	102.5	0.39	146.9	0.35	192.7	0.34

Note: Specimens of AISI Type 304 ELC, Illium R, Hastelloy B, "A"-Nickel, Inconel, and Monel failed in a short time in this solution.

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TABLE N-3. ZIRCEX BOILING NITRIC ACID ELIMINATION-TYPE TESTS

(5.0 M H⁺, 0.4 M UCl₃, 4.6 M NO₃⁻)

Specimen	Specimen Position	162 Hr		328 Hr		502 Hr		663 Hr	
		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
Tantalum	Vapor	+6.0	Weight gain	+6.1	Weight gain	+6.0	Weight gain	+4.7	Weight gain
	Interface	+1.6	Ditto	+0.2	Ditto	+0.6	Ditto	+0.5	Ditto
	Liquid	+0.5	Ditto	0.0	0.00	+0.1	Ditto	+1.2	Ditto
Titanium	Vapor	11.3	0.16	20.3	0.15	35.3	0.17	44.8	0.16
	Interface	2.7	0.04	3.9	0.03	4.2	0.02	3.2	0.01
	Liquid	2.5	0.03	1.4	0.01	1.9	0.01	1.0	0.00
Type S-816	Vapor	187.8	1.40	268.0	0.99	340.7	0.82	463.6	0.85
	Interface	235.1	1.76	398.9	1.48	561.6	1.36	839.0	1.54
	Liquid	289.4	2.15	474.0	1.74	739.7	1.77	1003.9	1.82

Note: Specimens of AISI Type 304 ELC, Illium R, Hastelloy B, "A"-Nickel, and Monel failed in a short time in this solution.

TABLE N-4. ZIRCEX BOILING NITRIC ACID ELIMINATION-TYPE TESTS

(15 M HNO₃, 0.4 M UO₂(NO₃)₂, HCl bubbled through)

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
		<u>168 Hr</u>		<u>330.5 Hr</u>		<u>493 Hr</u>		<u>656 Hr</u>	
Tantalum	Vapor	+2.9	Weight gain	+5.3	Weight gain	+2.4	Weight gain	+2.1	Weight gain
	Interface	+2.5	Ditto	+2.8	Ditto	+2.9	Ditto	+2.5	Ditto
	Liquid	+2.2	Ditto	+2.5	Ditto	0.5	0.00	+2.4	Ditto
		<u>168 Hr</u>		<u>330.5 Hr</u>		<u>493 Hr</u>		<u>543 Hr</u>	
Titanium	Vapor	+3.5	Weight gain	9.1	0.06	15.3	0.07	6285.3	27.01 ^(a)
	Interface	1.1	0.02	26.2	0.18	35.6	0.16	+23.7	Weight gain
	Liquid	2.5	0.03	76.3	0.54	101.3	0.48	76.8	0.33
		<u>162.5 Hr</u>		<u>325 Hr</u>		<u>486 Hr</u>		<u>534 Hr^(b)</u>	
Type S-816	Vapor	220.7	1.64	474.8	1.76	677.5	1.68	7816.8	17.67 ^(c)
	Interface	260.1	2.01	615.0	2.37	971.8	2.51	6574.2	15.44 ^(d)
	Liquid	236.1	1.83	705.1	2.73	1208.4	3.13	1723.0	4.07

(a) Specimens nearly dissolved.

(b) These specimens were accidentally exposed during the fourth period to the solution left over from the fourth-period exposure of the tantalum specimens.

(c) Top corner of specimen completely dissolved.

(d) Vapor-phase area of specimen completely dissolved.

Note: Specimens of AISI Type 304 ELC, Illium R, and "A" -Nickel failed in a short time in this solution.

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TABLE N-5. ZIRCEX VAPOR-PHASE ELIMINATION-TYPE TESTS

Run	Specimen	Temperature, C	Time, hr	Atmosphere	Observations at End of Run	
					Specimen	Furnace Exit Product
B-3	Tantalum	600	28	HCl + H ₂	Disappeared	White deposit
B-4	Tantalum	400	24	HCl + H ₂	Brittle, scaled	No deposit
B-5	Titanium	400	17	HCl + H ₂	Disintegrated	White and yellow deposit
B-6	Tantalum Titanium	400	24	HCl	Brittle, scaled Half gone, scaled	White and yellow deposit plus yellow liquid
B-7	Titanium	400	25	HCl	Disintegrated	White deposit plus yellow liquid
B-8	Tantalum	400	24	HCl	Brittle, scaled	White deposit

N-7 and N-8

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