PROGRESS RELATING TO CIVILIAN APPLICATIONS
DURING SEPTEMBER, 1955

Atomic Energy Commission
Contract No. W-7405-eng-92

by

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Photostat Price \$ 12.30

Microfilm Price \$ 4.50

Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

October 1, 1955

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REPORTS RELATED TO CIVILIAN APPLICATIONS

- BMI-1023 "Phase Relations in the Uranium-Zirconium-Oxygen Systems Involving Zirconium and Uranium Dioxide", by Henry A. Saller, Frank A. Rough, Joseph M. Fackelmann, Arthur A. Bauer, and J. Robert Doig.
- BMI-1026 "Heat Transfer from Parallel Rods in Axial Flow", by David A. Dingee, Wayne B. Bell, Joel W. Chastain, and Sherwood L. Fawcett.
- BMI-1028 "The Kinetics of the Zirconium-Uranium Dioxide Reaction", by Manley W. Mallett, Arnold F. Gerds, Alexis W. Lemmon, and Dan L. Chase.
- BMI-1030 "An Evaluation of the Data on Zirconium-Uranium Alloys", by Frank A. Rough.
- BMI-1031 "Eddy-Current Inspection of a Possible PWR Fuel Element", by David E. Stutz, Richard L. Gibbs, Ronald F. Dickerson, and Samuel A. Wenk.
- BMI-1033 "Analysis for Oxygen and Nitrogen in Uranium", by Cecil B. Griffith, William M. Albrecht, and Manley W. Mallett.
- BMI-1034 "Enamels for the Protection of Aluminum Cans for Uranium Slugs", by Harlan P. Tripp, John Schults, Burnham W. King, and Winston H. Duckworth.

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A. DEVELOPMENT OF PWR FUEL MATERIALS AND FUEL ELEMENTS

R. F. Dickerson

The major portion of the program of assistance to WAPD concerned with the development of PWR fuel materials and fuel elements has been concluded. Topical reports covering the effects of compositional variations on the corrosion behavior of uranium-molybdenum alloys, the bonding behavior of uranium-molybdenum alloys, and uranium dioxide fuel-element end closures are being prepared. The investigation aimed at developing bodies containing 80 volume per cent or more UO_2 and the corrosion testing of metallic fuel-element end closures will be continued.

Results to date of corrosion tests performed on additional uranium-molybdenum ternary alloys indicate that silicon in additions of 0.25 and 0.50 w/o, reduces corrosion life and zirconium additions of 2 and 4 w/o have a similar effect. Although alloys containing ternary additions of copper, nickel, platinum, or tungsten have been exposed only 21 to 28 days to 650 F water, the corrosion rates are low and the alloys appear promising. Tests show that the size of the corrosion specimen has a marked effect on the corrosion behavior of uranium-molybdenum alloys.

Experimental work on the study of the bonding behavior of uranium-molybdenum alloys has been completed and a report is being prepared. Corrosion tests are still in progress on a number of metallic fuel-element end closures. Twenty-seven of the 388 specimens originally put in test have failed in corrosion to date. Eight flash-welded and four of five upset-welded nonmetallic fuel-element end closures showed no weight change after 28 days of exposure to 750 F steam. All experimental work has been discontinued on this particular end-closure study.

Continued studies concerned with the preparation of a readily sinterable uranium dioxide powder have shown that the UO_3 must have some prior treatment before reduction, that ball milling with water for 1/2 to 1 hr is sufficient, and that drying the treated UO_3 at 180 to 250 F decreases the drying time without apparent change in the sinterability of the resulting UO_2 . As a part of the study of modified uranium dioxide fuel-element cores, work has been continued on the development of a reference material for comparison with UO_2 pellets made by WAPD. On the basis of bulk density and tensile strength, pellets pressed from oxide in the as-received condition will be used as the comparative standard for this investigation.

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Compositional Variables in Uranium-Molybdenum Alloys

W. E. Berry, J. E. Reynolds, R. I. Jaffee, and R. S. Peoples

Corrosion tests on additional cast uranium-molybdenum ternary alloys requested by WAPD are now in progress. Results obtained to date in 650 F degassed water are presented in Table A-1 and are summarized below.

Silicon. In general, additions of 0.25 or 0.50 w/o silicon reduce corrosion life of the 10.5 or 12.0 w/o molybdenum alloys. As reported in BMI-1025, an increase in corrosion life is obtained with 0.05 to 0.10 w/o silicon additions.

Zirconium. Optimum zirconium content for increased corrosion life appears to be approximately 0.5 to 1.0 w/o, since additions of 2.0 or 4.0 w/o zirconium to the 10.5 and 12.0 w/o molybdenum alloys reduced their corrosion life.

Copper, Nickel, Platinum, or Tungsten. Corrosion tests have not progressed far enough to definitely determine if additions of 0.05 or 0.10 w/o of each of the aforementioned elements to the 10.5 or 12.0 w/o molybdenum alloy improve corrosion life. However, these alloys appear promising. They exhibit low corrosion rates and are still intact after 21 to 28 days of exposure.

Corrosion results obtained in the additional heat-treatment studies proposed by WAPD are summarized below.

Effect of Specimen Size and Shape on Time to Failure. As reported in BMI-1025, wrought binary alloy samples 0.060 in. thick exhibited hydriding failure much sooner than similar cast alloys 0.250 in. thick. Forged and forged-and-rolled samples of the same thickness as the cast specimens are being corrosion tested to determine if specimen size is a factor in determining corrosion life. Homogenized specimens are exhibiting low corrosion rates and are still in test after 5 weeks of exposure. The thin, wrought alloy samples failed after 2 to 3 weeks of exposure and exhibited high corrosion rates. Thus, specimen size does appear to influence corrosion life. It is probable that increased life of thicker samples is due to the longer path hydrogen must traverse before complete grain-boundary hydriding can occur.

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TABLE A-1. TERNARY CAST URANIUM-MOLYBDENUM ALLOYS EXPOSED TO 650 F DEGASSED WATER

Nominal Composition, w/o		Corrosion Rate ^(a) , mg/(cm ²)(hr), and Life ^(b) , days, for Heat Treatments Indicated ^(c)					
		As Melted		Base		A	
		Rate	Life ^(d)	Rate	Life ^(d)	Rate	Life ^(d)
10.5		-0.15	56-63	-0.07	35-42	-0.07	7-14
12.0		-0.15	42-49	-0.09	21-28	-0.08	14-21
10.5	0.25Si	-0.32	7-14	--	0-3	-0.05	7-14
10.5	0.50Si	-0.32	7-14	-0.36	14-21	-0.11	7-14
12.0	0.25Si	-0.30	21-28	--	0-3	-0.08	3-7
12.0	0.50Si	-0.28	7-14	-0.32	21-28	-0.12	14-21
10.5	2.0Zr	-0.17	14-21	-0.93	7-14	--	0-3
10.5	4.0Zr	-0.22	7-14	--	0-3	--	0-3
12.0	2.0Zr	-0.14	>28	-0.65	14-21	--	0-3
12.0	4.0Zr	-0.22	3-7	--	0-3	--	0-3
12.0	0.05Cu	-0.14	>28	-0.08	>28	-0.05	>21
12.0	0.10Cu	-0.14	>28	-0.07	>28	-0.05	>21
12.0	0.05Ni	-0.20	>28	-0.08	>28	-0.11	>21
12.0	0.10Ni	-0.12	>28	-0.10	>28	-0.18	3-7
12.0	0.05Pt	-0.17	>28	-0.06	>28	-0.05	>21
12.0	0.10Pt	-0.16	>28	-0.06	>28	-0.06	>21
12.0	0.05W	-0.17	>28	-0.08	>28	-0.06	>21
12.0	0.10W	-0.16	>28	-0.10	>28	-0.07	>21

(a) Lowest observed rate.

(b) Time to cracking or disintegration (complete oxidation).

(c) Heat treatment: Base - 900 C/1 day/WQ

A - Base plus 400 C/7 days/WQ.

(d) Samples are still in test where corrosion life is indicated greater than a certain number of days.

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Effect of Various Homogenization Heat Treatments. Cast alloys homogenized 1, 2, or 7 days at 900 C and aged at 400 C exhibited about the same corrosion behavior as those homogenized 12 days at 900 C and aged at 400 C (heat treatment employed throughout these studies).

Effect of Longer Aging Treatments on Cast Silicon Containing Uranium-10.5 or 12.0 w/o Molybdenum Alloys. Longer aging of the 10.5 w/o molybdenum-0.01 or 0.10 w/o silicon ternary alloys drastically reduced their corrosion life. All samples aged 3 to 5 weeks at 400 C failed within 2 weeks in exposure in 650 F water. This compares with life in excess of 15 weeks for duplicate alloys (0.025 or 0.05 w/o silicon) which were aged only 1 week at 400 C. No failures were observed with 12.0 w/o molybdenum-silicon alloys after 2 weeks of exposure.

This concludes the compositional-variation study of PWR uranium-molybdenum alloys. A topical report covering all phases of the program is being prepared.

Bonding Behavior of Uranium-Molybdenum Alloys

H. A. Saller, S. J. Paprocki, and E. S. Hodge

One of the fuel elements once considered for use in the PWR was a Zircaloy 2-clad uranium-12 w/o molybdenum alloy. The nature of the bond interface between cladding and core and its corrosion behavior in high-temperature water was investigated and the effect of transition layers on the corrosion properties of the interface was studied.

In addition, an exploratory investigation was made of the effect of barrier layers on the diffusion rate between Zircaloy 2 and epsilonized uranium-3.8 w/o silicon. Reaction rates between core and barrier and cladding and barrier were determined for barrier layers of copper, molybdenum, niobium, platinum, and tantalum. Tantalum was the most effective barrier studied and platinum was the least effective.

A topical report summarizing the results of this work is being prepared.

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Metallic Fuel-Element End Closures

J. J. Vagi and D. C. Martin

Of 520 welded end-closure samples, 388 were originally placed in corrosion tests in 750 F, 1500-psi steam. During the past month, two of these samples failed, making a total of 27 failures so far. Data on the two most recent failures are given below.

<u>Sample Designation</u>	<u>Treatment</u>	<u>Time to Failure, hr</u>	<u>Remarks</u>
21-2	As welded	2016	No eddy-current indications of defects; no X-ray evidence of extruded fuel
36-6	Eddy-current tested, as welded	1344	Ditto

In addition, corrosion tests were continued on two samples welded early in the program using steel-backed glass sleeves. In BMI-1035 these samples were reported to be showing indications of severe failure. The samples are still being tested, and after 3392 hr in 750 F, 1500-psi steam the samples are covered with a tan corrosion product, but there are no other indications of severe failure.

Uranium Dioxide Fuel-Element End Closures

W. H. Kearns, H. E. Pattee, and R. M. Evans

The experimental work on the evaluation of resistance-welding methods for welding tube-to-end-cap joints in Zircaloy 2 fuel elements has been completed and a topical report of the study is being prepared.

Corrosion tests in 750 F steam of simulated fuel elements assembled by flash welding and upset welding were completed. Eight flash-welded elements and four of five upset-welded elements showed no significant weight change after 28 days of exposure (after 6 days, one upset-welded element had developed a fissure that appeared to be a defect in the weld). There were faint white lines at the welds which were not considered detrimental. Sectioned welds of both types showed no corrosion after 21 days of exposure to 750 F steam. These tests showed that flash- and upset-welded joints can be produced with good corrosion resistance.

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Preparation of Active Uranium Dioxide

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

This part of the WAPD-PWR fuel-element program is concerned with developing a readily sinterable UO_2 powder from MCW UO_3 for use in the production of fuel-element cores. Experiments have shown that such a powder can be produced simply by ball milling MCW UO_3 with water, drying, and then reducing it to UO_2 in water-saturated hydrogen. UO_2 , thus prepared, sintered to 90 per cent or more of theoretical density at 2800 F for 1 hr when compacted at 20,000 psi.

Last month, it was shown that the period for ball milling the MCW UO_3 in distilled water could be safely shortened from 4 hr to 1 hr in this process for making sinterable UO_2 .

This month, the study was extended to investigate shorter milling periods, dry ball milling, and substitute treatments for ball milling. Also, the effect of increased drying temperature and of variations in reduction time and temperature were investigated. The effect of these changes in processing was judged by microscopic examination of the treated UO_3 and by the sintered density of compacts made from the UO_2 powder under standard conditions. Table A-2 shows the results of these experiments.

The data in Table A-2 confirm previous indications that simple reduction of MCW UO_3 without prior treatment does not produce a readily sinterable UO_2 . Probably some hydration of the UO_3 prior to reduction is necessary.

Ball milling with water for shorter periods (1/2 to 1 hr) than the 2 or 4 hr used in earlier experiments gave satisfactory results. The data also show that ball milling can be replaced in the process by treating a water suspension of the UO_3 (100 g in 250 ml H_2O) with an Eppenbach Model L-1 Homo-Mixer or by subjecting it to ultrasonic treatment (20 kc at about a 4-mil amplitude) for as little as 6 min.

Heating the treated UO_3 at 180 or 250 F rather than the usual 100 F decreased the drying time without apparent change in the sinterability of the UO_2 formed by subsequent reduction.

Active UO_2 powder was also prepared by dry ball milling MCW UO_3 . The milled product was not optically homogeneous. The index of refraction ranged from 2.00 to 1.81, indicating varying degrees of hydration. However, this material reduced to readily sinterable UO_2 . It sintered to about 93 per cent of theoretical density at 3000 F for 1 hr when compacted at 20,000 psi.

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Eight trials were made in which wet ball-milled UO_3 was reduced to UO_2 by treatment with water-saturated (at 185 F) hydrogen at temperatures ranging from 930 to 1410 F for periods of from 1/2 hr to 4 hr. The bulk densities of compacts pressed at 20,000 psi and sintered at 2800 or 3000 F for 1 hr indicated that these variations in reduction conditions had little or no effect on the sinterability of the UO_2 product.

This concludes the present program for WAPD on the development of readily sinterable UO_2 powder. The work has demonstrated that such a powder can be made by simple treatment of MCW UO_3 prior to reduction to UO_2 , but has not been carried far enough to permit selection of the best combination, technically and economically, of processing variables. Also, prior to the use of this process for preparing UO_2 powder in the production of high-density fuel-element cores, information should be obtained on the effect of such process variables as forming pressure, sintering time, and temperature on pertinent properties of experimental cores.

Modified Uranium-Dioxide Fuel-Element Cores

D. J. Bowers, M. J. Snyder, and A. G. Allison

The objective of this research, a part of the PWR program, is to develop fuel-element cores containing 80 or more volume per cent of UO_2 which are less subject to "water logging" and thermal cracking and are better able to retain fission products than are the present pure UO_2 cores.

This month, laboratory work was continued on the development of a reference material for comparison with UO_2 pellets made by WAPD. In this work, compacts were made from MCW powder (1) as received, (2) sieved through 325 mesh, and (3) milled with uranium balls in a rubber-lined mill for 26 hr. Compacts were hydrostatically pressed at 100,000 psi and sintered in a hydrogen atmosphere at 3200 F for 2 hr. The bulk density and tensile strength of the sintered specimens and of pellets made by WAPD are given below:

<u>MCW Powder Used</u>		<u>Bulk Density^(a), per cent of theoretical</u>	<u>Tensile Strength, psi</u>
<u>Condition</u>	<u>Average Particle Size, μ</u>		
<u>Pellets Made at WAPD</u>			
--	--	89.8	4720
<u>Pellets Made at BMI</u>			
As received	25	83.3	5400
Sieved	9	85.1	6090
Milled	5	93.1	2320

(a) Theoretical density of UO_2 taken as 10.97 g per cm^3 .

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TABLE A-2. EFFECT OF TREATMENT OF MCW UO_3

Treatment of MCW UO_3			Optical Properties of UO_3			
Comminution	Time, hr	Drying Temperature, F	Major Phase		Minor Phase	
			Volume Per Cent	Refractive-Index Range	Volume Per Cent	Refractive-Index Range
None, as received	--	--	80.2	2.09-2.13	19.8	1.86-2.00
Ball milled ^(c) in distilled H_2O	1/2	100	99+	1.815-1.825	Trace	<1.80
Ditto	1	100	99+	1.815-1.820	Trace	<1.80
Ditto	2	100	93.6	1.820-1.830	6.4	1.63-1.66
Ditto	4	100	98.0	1.820-1.840	2.0	<1.80
Ditto	4	100	98.0	1.820-1.840	2.0	<1.80
Ditto	4	100	98.0	1.820-1.840	2.0	<1.80
Ditto	4	100	98.0	1.820-1.840	2.0	<1.80
Ditto	4	100	98.0	1.820-1.840	2.0	<1.80
Ditto	4	100	98.0	1.820-1.840	2.0	<1.80
Ditto	4	100	98.0	1.820-1.840	2.0	<1.80
Ditto	4	100	98.0	1.820-1.840	2.0	<1.80
Ditto	4	100	98.0	1.820-1.840	2.0	<1.80
Ditto	4	180	97.3	1.815-1.830	{2.2 0.5}	{1.64-1.66 >1.83}
Ditto	4	250	98.1	1.815-1.830	{0.9 1.0}	{<1.67 >1.84}
Eppenhach mixer ^(d)	1/4	100	98.5	1.815-1.830	{0.5 1.0}	{<1.80 >1.84}
Ditto	1/2	100	97.3	1.825-1.835	{0.2 2.0}	{<1.80 >1.84}
Ditto	1	100	97.8	1.815-1.825	{1.2 1.0}	{<1.80 >1.84}
Ultrasonic treatment ^(e)	1/10	100	81.5	1.815-1.830	{11.0 7.5}	{1.77 1.70}
Ball milled dry, first trial	4	--	{8 65 27}	{1.94-2.00 1.83-1.94 1.81-1.86}	--	--
Ball milled dry, second trial	4	--	{6 54 40}	{1.94-2.00 1.83-1.94 1.81-1.86}	--	--

(a) The theoretical density of UO_3 was taken as 10.97 g per cm^3 .

(b) Based on the diameter of the unsintered compact.

(c) Using a rubber-lined ball mill with Zircaloy balls. Unless otherwise specified, 100 g of UO_3 was milled in 250 ml H_2O .

(d) Eppenhach Homo-Mixer, Model L-1, Eppenhach, Inc., Long Island City, New York.

(e) 100 g of UO_3 in 250 ml of H_2O exposed for 6 min to vibration at 20 kc and about 4 mils of amplitude.CONFIDENTIAL

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FOR PRODUCTION OF SINTERABLE UO_2

Condition for the Reduction of UO_3 in Water-Saturated Hydrogen		Properties of UO_2 Compact Pressed at 20,000 psi and Sintered for 1 Hr at Indicated Temperature					
		2800 F			3000 F		
		Bulk Density		Linear Shrinkage ^(b) , per cent	Bulk Density		Linear Shrinkage ^(b) , per cent
Temperature, F	Time, hr	G per cm^3	Per Cent of Theoretical ^(a)		G per cm^3	Per Cent of Theoretical ^(a)	
1110	2	8.20	74.8	10.7	8.28	75.5	10.7
1110	2	10.25	93.5	21.4	10.42	95.1	21.8
1110	2	10.25	93.5	21.6	10.32	94.1	22.2
1110	2	10.32	94.1	21.6	10.46	95.3	22.0
1100	2	10.41	95.0	21.4	10.53	95.9	21.4
930	4	9.89	90.1	21.2	10.19	93.0	21.8
1110	1/2	9.90	90.3	19.5	10.40	94.9	20.6
1110	2	10.29	93.8	20.2	10.40	94.9	20.8
1110	4	9.90	90.3	19.7	10.46	95.5	21.2
1290	1/2	10.33	94.2	19.2	10.33	94.2	20.2
1290	2	10.12	92.4	19.7	10.43	95.2	20.0
1290	4	10.03	91.5	20.0	10.44	95.3	21.2
1470	1/2	9.96	90.9	20.2	10.37	94.6	21.2
1110	2	10.43	95.2	20.6	10.14	92.5	19.7
1110	2	10.51	96.0	19.7	10.07	91.9	18.1
--	--	--	--	--	--	--	--
--	--	--	--	--	--	--	--
1110	2	10.37	94.6	21.2	10.58	96.6	21.6
1110	2	10.25	93.5	20.2	10.41	95.0	20.6
1110	2	9.93	90.6	17.7	10.24	93.4	18.7
1110	2	9.72	88.8	17.1	10.14	92.5	18.1

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The low tensile strength of the compacts made from the milled powder probably resulted from grain growth observed in these specimens.

On the basis of these tests, as-received MCW UO_2 powder will be used in future studies. Also, at the suggestion of WAPD, the additives, polyvinyl alcohol and Sterotex (a powdered fat) will be used in all compacts. The experimental bodies to be investigated will be made of UO_2 in combination with beryllia, beryllium, ceria, silica, silicon, silicon nitride, titania, and zirconia.

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B. DEVELOPMENT OF MATERIALS FOR

REACTORS

J. R. Keeler

Investigations related to the development of improved materials for reactors are in progress. The physical and mechanical properties of several selected uranium alloys are being studied and the phase relationships in the thorium-rich region of the thorium-uranium diagram are being determined.

The mechanical properties of cold-worked zirconium and Zircaloy 2 at temperatures up to 500 C were measured and the effect of time at temperature on these properties investigated. Creep studies on these materials were continued and bursting tests on Zircaloy 2 process tubes were made.

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CONFIDENTIALThe Constitution of Thorium-Uranium Alloys

H. A. Saller, F. A. Rough, and A. A. Bauer

The constitution of thorium-rich thorium-uranium alloys is being determined.

Alloys of thorium containing 0 to 20 w/o uranium have been fabricated and are now undergoing heat treatment. Preliminary metallographic results have been obtained on a series of samples annealed at and quenched from 1000 C. A solubility between 7 and 10 w/o uranium in thorium at this temperature is indicated.

Additional data at lower temperatures are now being obtained.

Mechanical Properties of Zirconium and Zircaloy 2

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

The possible application of zirconium and Zircaloy 2 in reactor fuel assemblies has promoted an interest in the mechanical properties of these materials. The mechanical properties of nominally 50 per cent cold-worked zirconium and Zircaloy 2 are to be compared to those of the annealed

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materials at temperatures up to 500 C. Such a comparison should indicate whether the strength derived from cold working can be utilized for prolonged periods at elevated temperatures.

Short-Time Tensile Properties

Short-time tensile properties at a strain rate of approximately 0.006 per min have been determined at various temperatures. Room-temperature elastic-strain measurements were obtained with SR-4, Type A7 strain gages, while Bakelite SR-4 strain gages were used at 150 C. A supplementary clip-type extensometer was employed to measure both elastic and plastic strain. The samples were heated to the test temperature and held 1/2 hr prior to testing. At temperatures above 150 C, a flowing atmosphere of argon was used. The resulting data are summarized in Table B-1.

The effects of increasing the length of time at the test temperature prior to the application of the load are shown in Table B-2.

As reported in BMI-1035, available recrystallization data in the literature indicate that both 50 per cent cold-worked zirconium and Zircaloy 2 should recrystallize within 25 hr at 500 C and within 100 hr at 425 C. However, in the present study, neither the pure zirconium nor the Zircaloy 2 recrystallized appreciably in 100 hr at 425 C and only partially in 25 hr at 500 C. These observations imply that either the amount of cold work given the zirconium and Zircaloy 2 was somewhat less than 50 per cent or that compositional differences between the materials employed in this study and those used on the reported recrystallization study have resulted in differing recrystallization kinetics.

It is evident that cold work increases the short-time tensile properties of zirconium and Zircaloy 2 at temperatures up to 500 C. However, at 500 C, the strength of the cold-worked zirconium rapidly decreases with time at temperature so that after 10 hr at 500 C the ultimate strength is practically the same as that of the annealed sheet. With Zircaloy 2 at 500 C, the strength of the cold-worked sheet after 25 hr at temperature is still considerably higher than that of the annealed material.

At 425 C, the strength of the Zircaloy 2 decreased only slightly after 100 hr at temperature. The strength of the zirconium decreased somewhat more than did that of the Zircaloy 2, but a considerable portion of the increased strength resulting from the cold work was still evident after 100 hr at a temperature of 425 C.

Longer times at temperatures of 425 and 500 C are being investigated.

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TABLE B-1. MECHANICAL PROPERTIES OF ANNEALED AND COLD-WORKED ZIRCONIUM AND ZIRCALOY 2 SHEET AT ROOM AND ELEVATED TEMPERATURES

Properties	Temperature, C					
	28	150	230	345	425	500
<u>Annealed Zirconium</u>						
0.2 Per Cent Yield Strength, psi	31,700-32,700	16,800-17,500	10,700	7,800	7,500	5,200
Tensile Strength, psi	54,500-54,750	38,400-34,500	26,600	18,800	14,500	11,200
Elongation, per cent	42.0-38.0	47.7-55.5	55.3	55.5	59.1	88.5
Young's Modulus, psi	14.3-14.2 x 10 ⁶	13.0-12.7 x 10 ⁶	--	--	--	--
Poisson's Ratio	0.358	0.442-0.430	--	--	--	--
<u>Annealed Zircaloy 2</u>						
0.2 Per Cent Yield Strength, psi	43,000-41,000	27,200-27,500	19,700	17,500	16,200	13,800
Tensile Strength, psi	54,800-54,600	39,300-38,400	29,700	23,500	20,900	19,500
Elongation, per cent	32.0-28.7	46.5-42.0	46.5	40.4	37.4	42.1
Young's Modulus, psi	14.3-13.9 x 10 ⁶	13.3-13.8 x 10 ⁶	--	--	--	--
Poisson's Ratio	0.380-0.368	0.460-0.425	--	--	--	--
<u>50 Per Cent Cold-Worked Zirconium</u>						
0.2 Per Cent Yield Strength, psi	71,700-70,750	56,300-55,000	--	--	--	--
Tensile Strength, psi	80,000-79,300	62,000-61,750	--	--	--	--
Elongation, per cent	14.7-14.9	48.3-49.0	--	--	--	--
Young's Modulus, psi	13.8-14.0 x 10 ⁶	13.8-15.0 x 10 ⁶	--	--	--	--
Poisson's Ratio	0.370-0.377	0.390-0.383	--	--	--	--
<u>50 Per Cent Cold-Worked Zircaloy 2</u>						
0.2 Per Cent Yield Strength, psi	82,500-80,600	68,000	--	--	--	--
Tensile Strength, psi	90,500-90,000	74,700-74,150	--	--	--	--
Elongation, per cent	6.8-11.6	13.6	--	--	--	--
Young's Modulus, psi	14.5 x 10 ⁶	13.9-14.2 x 10 ⁶	--	--	--	--
Poisson's Ratio	0.382-0.406	0.432-0.392	--	--	--	--

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TABLE B-2. EFFECT OF TIME AT TEMPERATURE ON THE MECHANICAL PROPERTIES
OF COLD-WORKED ZIRCONIUM AND ZIRCALOY 2

Properties	Temperature, C	Time at Temperature(a), hr							
		1/2	1	2	5	10	25	50	100
<u>50 Per Cent Cold-Worked Zirconium</u>									
0.2 Per Cent Yield Strength, psi	230	--	--	--	--	--	--	--	45,400
Tensile Strength, psi	230	--	--	--	--	--	--	--	49,600
Elongation, per cent	230	--	--	--	--	--	--	--	17.2
Reduction in Area, per cent	230	--	--	--	--	--	--	--	51.6
0.2 Per Cent Yield Strength, psi	345	--	--	--	--	--	--	--	30,200
Tensile Strength, psi	345	--	--	--	--	--	--	--	36,100
Elongation, per cent	345	--	--	--	--	--	--	--	19.2
Reduction in Area, per cent	345	--	--	--	--	--	--	--	63.6
0.2 Per Cent Yield Strength, psi	425	18,900	22,600	--	--	20,000	--	17,200	15,700
Tensile Strength, psi	425	27,300	29,500	--	--	26,650	--	23,200	22,850
Elongation, per cent	425	25.9	21.5	--	--	26.1	--	33.1	33.6
Reduction in Area, per cent	425	68.5	73.5	--	--	64.6	--	74.0	74.1
0.2 Per Cent Yield Strength, psi	500	12,200	12,400	12,600	10,000	8,000	6,800	--	--
Tensile Strength, psi	500	18,400	17,000	17,100	14,600	10,800	10,800	--	--
Elongation, per cent	500	34.9	39.2	36.9	53.3	63.5	74.2	--	--
Reduction in Area, per cent	500	78.6	80.7	80.2	82.1	76.0	77.1	--	--
<u>* 50 Per Cent Cold-Worked Zircaloy 2</u>									
0.2 Per Cent Yield Strength, psi	230	--	--	--	--	--	--	--	61,000
Tensile Strength, psi	230	--	--	--	--	--	--	--	65,250
Elongation, per cent	230	--	--	--	--	--	--	--	13.6
Reduction in Area, per cent	230	--	--	--	--	--	--	--	54.8

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TABLE B-2. (Continued)

Properties	Temperature, C	Time at Temperature ^(a) , hr							
		1/2	1	2	5	10	25	50	100
50 Per Cent Cold-Worked Zircaloy 2									
0.2 Per Cent Yield Strength, psi	345	--	--	--	--	--	--		47,500
Tensile Strength, psi	345	--	--	--	--	--	--		52,400
Elongation, per cent	345	--	--	--	--	--	--		15.8
Reduction in Area, per cent	345	--	--	--	--	--	--		62.4
0.2 Per Cent Yield Strength, psi	425	35,700	39,200	--	--	38,700	--	37,500	37,700
Tensile Strength, psi	425	42,200	44,500	--	--	43,900	--	43,100	40,600
Elongation, per cent	425	19.2	19.5	--	--	18.2	--	19.1	20.0
Reduction in Area, per cent	425	68.2	67.3	--	--	67.3	--	67.2	66.8
0.2 Per Cent Yield Strength, psi	500	22,800	20,400	20,300	19,600	20,200	18,600	--	--
Tensile Strength, psi	500	32,900	32,800	32,800	29,000	31,000	28,500	--	--
Elongation, per cent	500	24.7	29.5	27.2	30.5	29.1	30.5	--	--
Reduction in Area, per cent	500	74.2	74.8	75.0	76.7	71.0	72.3	--	--

(a) Time at temperature before load was applied.

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Creep Properties

Creep studies on Zircaloy 2 were continued using sheet-type specimens. As reported in BMI-1035, initial stress-rupture tests on both rod and sheet material indicated a considerable difference between the two shapes. The time to failure for the rod was nearly 20 times greater than for the sheet under similar conditions, and the rod necked down nonuniformly. The creep tests on rod which had already been started were continued, but all new tests are to be made on sheet material. Both transverse and longitudinal sheet specimens will be investigated.

The results from rod specimens in test prior to the decision to change to sheet material are given in Table B-3. The test at 26,000 psi and 230 C had a comparatively low creep rate after quite rapid elongation in the first 75 hr of test. This may indicate that strain aging is occurring during the test.

TABLE B-3. CREEP PROPERTIES OF ANNEALED ZIRCALOY 2 ROD

Temperature, C	Stress, psi	Elongation, per cent		Minimum Creep Rate, per cent per hr	Time at Test, hr
		At 100 Hr	Total		
150	30,000	6.50	12.00	0.0048	1008
150	33,500	7.00	13.25	0.0060	900
230	26,000	5.40	5.95	0.0001	1003
345	20,000	3.00	2.38	0.00026	925
500	8,000	2.37	17.05	0.0167	900

Only a few stress-rupture tests have been completed on the annealed Zircaloy 2 transverse sheet specimens. These results are tabulated in Table B-4.

TABLE B-4. RESULTS OF STRESS-RUPTURE TESTS ON ANNEALED ZIRCALOY 2 SHEET IN THE TRANSVERSE DIRECTION

Temperature, C	Stress, psi	Time to Failure, hr	Elongation, per cent
150	37,000	0.4	42.8
150	35,000	1.2	38.0
345	22,500	0.4	34.8

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Tube Bursting

The bursting strength of seamless and of welded Zircaloy 2 process tubing at temperatures up to 500 C is being investigated.

Initial tests on tubing with welded end closures were unsatisfactory because failure occurred in the heat-affected zone adjacent to the weld. A threaded end cap of stainless steel gave good results at room temperature, and an internal pressure of 7400 psi was required to burst the "as-worked" seamless tube.

At 150 C, the threaded cap leaked, and the bursting strength could not be determined. Other types of end caps are being investigated for the elevated-temperature tests.

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D. PLANT ASSISTANCE TO MCW

J. R. Keeler

The work in progress for Mallinckrodt Chemical Works (MCW) is related to corrosion problems occurring in the refinery and to improvements in the processes for the production of orange oxide, UO_3 , and brown oxide, UO_2 .

Corrosion studies on various stainless steels in a cracked-ammonia atmosphere containing sulfur were concluded. Studies on the corrosiveness of NOK liquor and of the solution from the third stage of a triple-effect evaporator on stainless steel tubing is continuing.

The effect of the method of preparation on the activity of UO_3 toward hydration is being determined, and an effort to correlate the electrical and magnetic properties of UO_2 with the sinterability of this material is being made.

The Corrosion Resistance of Stainless Alloys

W. J. Braun, F. W. Fink, and R. S. Peoples

Hot cracked-ammonia gas is used by Mallinckrodt to reduce UO_3 to UO_2 . Water vapor is a product of this reduction. The effect of sulfur added to hot cracked ammonia on the corrosion resistance of selected stainless alloys is being evaluated. As reported in BMI-1035, samples of 13 stainless alloys were exposed at 1200 F to an atmosphere of cracked ammonia containing 54 grains of sulfur and 40 ft^3 of water vapor per 100 ft^3 of cracked ammonia. Little change in physical properties occurred to these alloys after exposure for 2000 hr.

For the present study, samples of 10 of the most resistant alloys were exposed at 1500 F with 97 grains of sulfur per 100 ft^3 of cracked ammonia present in the gas feed. See Table D-1 for the results of this test and a list of the alloys. Exposure for up to 1000 hr did not cause any changes in physical properties that could be attributed to the sulfur present for any of the exposed alloys. Weight gains resulting from scale formation were slightly higher than for samples exposed at 1200 F. No localized attack, such as pitting, was observed on the surface of the 10 alloys by examination at 20 diameters.

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TABLE D-1. EFFECT OF AN ATMOSPHERE OF CRACKED AMMONIA PLUS WATER VAPOR PLUS SULFUR AT 1500 F ON THE PHYSICAL PROPERTIES OF STAINLESS ALLOYS

Stainless Alloy	Exposure Time, hr	Sulfur, grains per 100 ft ³ of cracked ammonia	Tensile Data		Elongation, per cent	Hardness, Rockwell B	Weight Gain, mg per in. ²
			0.2 Per Cent Offset Yield Strength, psi	Ultimate Tensile Strength, psi			
Type 304	0	-	42,400	92,000	68	79	-
	500	97	33,700	88,800	67	80	1.3
	1000	97	35,100	87,700	63	81	1.7
Type 304 ELC	0	-	31,600	84,200	74	71	-
	500	97	25,200	79,600	68	72	1.4
	1000	97	27,200	80,000	72	75	1.8
Type 309	0	-	41,500	86,500	60	78	-
	500	97	35,100	86,000	49	80	1.6
	1000	97	35,200	87,400	43	82	2.1
Type 316	0	-	31,500	80,400	52	71	-
	500	97	26,900	79,600	41	70	1.6
	1000	97	27,200	80,000	45	73	2.1
Type 330	0	-	34,300	83,100	45	70	-
	500	97	37,900	86,500	34	83	1.3
	1000	97	38,000	84,400	28	83	2.4
Type 347	0	-	48,200	92,300	51	84	-
	500	97	35,900	90,200	50	87	1.2
	1000	97	36,400	91,500	48	83	1.7
Carpenter 20 + niobium	0	-	53,600	93,800	39	87	-
	500	97	44,700	95,700	30	94	1.1
	1000	97	45,800	100,000	27	95	1.9
Hastelloy C, quench annealed, lot 2	0	-	54,000	121,000	55	91	-
	500	97	80,700	146,000	6.0	110	1.2
	1000	97	80,000	142,000	4.5	110	1.8
Hastelloy F	0	-	59,000	107,000	44	91	-
	500	97	64,100	130,000	19	103	1.9
	1000	97	61,700	127,000	15	104	2.7
Inconel X	0	-	45,900	114,000	56	85	-
	500	97	88,200	156,000	23	108	3.8
	1000	97	77,700	148,000	21	106	2.6

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A study of the corrosiveness of NOK liquor and of solution from the third stage of a triple-effect evaporator on stainless steel tubing is continuing. The effect of fluoride added to these solutions is being evaluated.

Identification of Uranium Oxides

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

An investigation of the reactivity of various modifications of UO_3 prepared by decomposition of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (uranyl nitrate hexahydrate) is being carried out at Battelle as assistance to Mallinckrodt Chemical Works in the production of active UO_3 and UO_2 . Previous studies of the amount of hydration during exposure to a water-saturated air atmosphere at 46 C or 30 C indicated that the activity of UO_3 may be related to the prior UO_3 structure.

During the past month, work was continued to include hydration studies on several preparations of the various types of UO_3 . Also the structure and sinterability of UO_2 prepared from various types of UO_3 were determined.

UO_3 Reactivity

The results of the current investigation of hydration activity of several preparations of the various modifications of UO_3 , during exposure to a water-saturated air atmosphere at 30 C, are given in Table D-2. Amorphous UO_3 shows the highest activity toward hydration, both in initial rate and in equilibrium water content, the activity being two to three times that of the crystalline modifications, Type C or Type H.

Samples of Type C UO_3 , produced under pyrolytic conditions wherein melting had occurred (Samples Nos. 9, 35A, 268A, 214A, 281A) were less active than Type C UO_3 from preparations in which melting of the charge was not permitted. However, larger amounts of amorphous UO_3 , not detectable by X-ray diffraction, may have been present in the latter samples.

Structure of UO_2

A comparison of the unit-cell dimension, the crystalline size, and the oxygen uranium ratio with sinterability has been made for various preparations of UO_2 . The results are presented in Table D-3, from which the following conclusions are drawn:

TABLE D-2. DESCRIPTION OF UO_3 PREPARATIONS AND THEIR REACTIVITY TOWARD HYDRATION IN WATER-SATURATED AIR AT 30 C

Sample	Treatment Prior to Firing		UO_3 Type After Firing at 300 C	Initial Rate of Hydration, g H_2O per g UO_3 per hr	Equilibrium Water Content, per cent H_2O	Type Pattern After Hydration
	Temperature, C	Atmosphere				
35A	75	Low-pressure argon	C	0.51	8.4	A
9	110	Atmospheric-pressure air	C	0.66	9.8	A
10	150	Atmospheric-pressure air	Amorphous	1.00	26.7	A
10B	150	Low-pressure air	Amorphous + C	1.07	20.4	A
22C	150	Low-pressure air	Amorphous	1.20	22.3 ^(a)	A
31A	150	Low-pressure argon	C	1.1	16.0 ^(a)	A
11	175	Atmospheric-pressure air	C	0.8	10.6	A
32A	175	Low-pressure argon	C	0.89	10.3	A
12	200	Atmospheric-pressure air	Amorphous	1.0	27.6	A
13	250	Atmospheric-pressure air	Amorphous + C	1.0	18.6	A
356A	250	Low-pressure argon (amorphous)	-	1.05	18.0 ^(a)	A
33A	250	As 356A	Amorphous	1.20	19.8 ^(a)	A
268A	250	In air (Type C)	-	0.35	11.8	A
214A	MCW	In pot (Type C)	-	0.26	7.5	A
196A	450	In air (Type H)	-	0.17	8.4	G
265A	450	In air (Type H + C)	-	0.27	10.6	G
281A	400	In air (Type C)	-	0.30	7.2	A
275B	250	Type C hydrated in room air to G	-	0.11	2.0	A + faint G
34A		As 275 B	C	0.50	7.4	A

(a) Hydration carried out 57 hr; but equilibrium water content was not attained.

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TABLE D-3. COMPARISON OF UO_2 PREPARATION METHODS WITH STRUCTURE, COMPOSITION, AND SINTERABILITY

Sample	Description of UO_3 and Preparation of UO_2	Subsequent Treatment	O/U Ratio	Unit-Cell Dimension, Å	Crystallite Size, Å	Sintered Density, percentage of theoretical
1	MCW UO_2	As received	2.048	5.467 ₁	3000	-
1	MCW UO_2	As received	2.033	5.469 ₁	3000	-
1a	Minus 325-mesh MCW UO_2	As received	2.039	5.468 ₉	3000	-
1b	As 1a ball milled, 2 to 7- μ particle size	As ball milled	2.096	5.470 ₃	1200	-
1-1A	As 1	Sintered at 2050 C	Surface 2.036 Center 2.011	5.470 ₁ 5.472 ₂	3000 3000	86.3 83.0
1-2A	As 1	Sintered at 1760 C	Center 2.011	5.471 ₈	3000	83.0
1a-1A	As 1a	Sintered at 1760 C	Center 2.011	5.471 ₂	3000	86.0
1b-1A	As 1b	Sintered at 1760 C	Center 2.014	5.472 ₂	3000	92.0
1c-1A	1 pressed at 100,000 psi	Sintered at 1650 C	Surface 2.036	5.471 ₀	3000	79.3
1c-1B	1 pressed at 100,000 psi	Heat to 500 C in vacuum	2.072	5.467 ₁	1075	-
2a-1A	MCW UO_3 reduced at 600 C	Sintered at 1650 C	Surface 2.034 Center 2.027	5.470 ₈ 5.471 ₄	3000 3000	75.5
2b	MCW UO_3 , Battelle activated ^(a) and reduced at 600 C	As reduced	2.075	5.467 ₇	1080	-
2b-1A	2b pressed at 20,000 psi (camphor binder)	Sintered at 1650 C	Surface 2.010 Center 2.000	5.470 ₈ 5.474 ₄	3000 3000	- 95.0
2c-1B	2b pressed at 100,000 psi	Heated to 500 C in vacuum	2.100	5.466 ₅	730	-
2c-1A	2b pressed at 100,000 psi	Sintered at 1650 C	Surface 2.006	5.474 ₈	3000	95.5
3a	Battelle UO_3 (UNH decomposed at 250 C, heated at 450 C, reduced at 650 C)	As reduced, air oxidized	2.103	5.468 ₁		
3c-1A	3a pressed at 20,000 psi (camphor binder)	Sintered at 1650 C	Surface 2.024	5.472 ₄	3000	84.4
3c-1B	3a pressed at 100,000 psi	Heated at 500 C in vacuum	2.147	5.463 ₈	940	-
4	Battelle UO_3 (UNH dried at 150 C, decomposed at 300 C, reduced at 625 C)	As reduced	2.045	-	290	-
4a	Battelle UO_3 (UNH dried at 150 C, decomposed at 300 C, reduced at 625 C)	Air oxidized	2.444	5.439 ₇	180	-
4b-1A	4 pressed at 20,000 psi (camphor binder)	Sintered at 1650 C	Surface - Center -	5.469 ₃ 5.473 ₀	3000 3000	- 91.4
4c-1A	4a pressed at 20,000 psi (camphor binder)	Sintered at 1650 C	Surface 2.012	5.469 ₃	3000	
		Sintered at 1650 C	Center 2.004	5.471 ₆	3000	88.9

(a) Activated by ball milling in H_2O .

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- (1) The unit-cell dimension of UO_2 decreases linearly with increasing oxygen content.
- (2) The sinterability (percentage of theoretical density obtained on sintering) increases as the oxygen-to-uranium ratio approaches 2,000.
- (3) Small crystallite size (less than 1000 Å) appears to benefit sinterability. However, sinterability does not appear to increase linearly with crystallite size.
- (4) Ball milling UO_3 appears to have contaminated the oxide with a material which expands the sintered- UO_2 cell dimension.

During the next month additional studies of UO_2 structure, composition, and sinterability will be made.

Electrical and Magnetic Properties of Uranium Dioxide

R. K. Willardson and H. Goering

The objective of this work is the correlation of the sintering characteristics with the electrical and magnetic properties for specimens of pressed and sintered UO_2 . A careful study of the electrical properties of UO_2 as a function of temperature reveals a number of interesting observations.

- (1) The electrical conductivity is proportional to the O/U ratio (amount of excess oxygen) in both sintered and nonsintered specimens; sintered "active" UO_2 is an exception.
- (2) The closer the approach to the stoichiometric ratio of uranium to oxygen the higher the density.
- (3) The temperature dependence of the electrical conductivity from 27 to 200 C of both sintered and nonsintered specimens of UO_2 corresponds to an activation energy of 0.20 ± 0.02 ev; sintered active UO_2 is an exception.
- (4) The small magnitude of the Hall coefficient indicates a positive carrier concentration greater than 10^{17} per cm^3 in all samples studied.

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The electrical conductivity usually increases as the oxygen:uranium ratio is increased (see Table D-4). An exception to this statement is the high-density sintered specimen of active UO_2 . Since the concentration of free carriers should increase with an increase of impurity atoms (excess oxygen), one might suspect that the mobility of the carriers is responsible for the unusually large (i. e., large for the amount of excess oxygen present) conductivity in Sample 2c-1A. This suspicion is verified by the thermoelectric power which indicates that Sample 2c-1A has only about 4 per cent as many carriers as Sample 1c-1A. The reason the active sintered UO_2 has a carrier mobility more than an order of magnitude greater than the "ordinary" sintered UO_2 is not known at this time.

TABLE D-4. ELECTRICAL PROPERTIES OF URANIUM DIOXIDE

Sample ^(a)	O/U Ratio	Sintered Density, percentage of theoretical	Electrical Conductivity at 27 C., ohm-cm ⁻¹	Activation Energy ^(b) , b	Thermoelectric Power at 200 C., $\mu\text{V per C}$
1-1A	2.011	86	0.00030	0.20	--
1c-1A	2.036	79	0.00100	0.19	215
1c-1B	2.072	--	0.00363	0.18	--
2c-1A	2.006	95	0.00146	0.14	800
2c-1B	2.100	--	0.00263	0.21	--
3c-1A	2.024	84	0.00106	0.18	--
3c-1B	2.147	--	0.00740	0.19	--

(a) The details of the preparation of these samples of UO_2 , including crystallite size and lattice parameters, is given in the previous subsection of this report, "Identification of Uranium Oxides".

(b) The activation energy b is obtained from the relationship $\sigma = A e^{-b/KT}$ and the temperature dependence of the electrical conductivity.

From Table D-4 it is noted that the O/U ratio decreases as the sintered density increases. This is apparently contrary to the usual conception that the transport of matter during sintering is roughly proportional to the deviation from stoichiometry. However, it is well to remember that the excess oxygen in UO_2 does not create metal vacancies to aid diffusion, but rather goes into the lattice interstitially. In fact, the contraction of the lattice due to the excess oxygen probably hampers the diffusion process taking place in the small equilibrium concentration of metal vacancies.

The slope of the curve obtained by plotting extrinsic conductivity versus the reciprocal of the absolute temperature curve of sintered active UO_2 is constant from 27 C to about 700 C; at 700 C the intrinsic conductivity predominates. Similar curves for the nonsintered materials and the ordinary sintered UO_2 have a slope about 30 per cent greater in the 27 to 200 C

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region. In the temperature region between 200 and 500 C the slope is about 100 per cent greater for the ordinary UO_2 than for the sintered active material. Then, in the 500 to 700 C region, the ordinary sintered UO_2 samples have a very unusual negative dependence of the conductivity on temperature. Thus, the active materials have distinctly different electrical conductivities than the other samples of UO_2 .

Attempts to measure the Hall effect were not successful because the value of the Hall coefficient is rather small. However, its absence at the highest level of sensitivity of the measuring equipment indicates a concentration of greater than 10^{17} free carriers per cm^3 for all samples listed in Table D-4. Thus, for Sample 2c-1A, the carrier mobility is less than 0.1 cm^2 per v-sec, and use of the thermoelectric power data shows that the carrier mobility in Sample 1c-1A is less than 0.01 cm^2 per v-sec. Measurements on Sample 2c-1A showed a Hall voltage which did not reverse when the magnetic field was reversed. Although dissymmetry in the Hall voltage has been observed in a number of different materials (bismuth, tellurium, antimony, bismuth sulfide, cadmium sulfide, and UO_2), a satisfactory explanation for this effect has never been given. This dissymmetry seems to be dependent on the crystalline structure of the material, being larger when the crystalline structure is very uniform. It has also been noted that the dissymmetry decreases rapidly with a rise in temperature. The dissymmetry in the Hall voltage may be several orders of magnitude greater than the actual Hall voltage. In some cases it has been possible to attribute the dissymmetry in the Hall effect to a change in the electrical conductivity due to the magnetic field. However, measurements on the change of the electrical conductivity with magnetic field on Sample 2c-1A seem to indicate that such changes are several orders of magnitude too low to account for the dissymmetry observed in the Hall effect.

Measurements of resistivity and thermoelectric power as a function of temperature will be made on additional samples of both sintered and non-sintered, active and ordinary UO_2 specimens. Hydrogen atmospheres as well as vacuum will be used.

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E. PROCESSING OF FEED MATERIALS

D. L. Keller

Research programs for National Lead Company of Ohio (NLCO) concerned with improving uranium-metal processing methods were continued this month.

Thermodynamic calculations have shown that sulfate and phosphate salt systems would be unsatisfactory for heat treating uranium because of their high affinity for water. Carbonate, chloride, and possibly silicate systems will be subjected to more extensive testing in which the rate of moisture pickup is measured and correlated with the hydrogen content of uranium metal submerged in the baths.

In the continuous reduction program, samples of nine commercial refractories have been received for testing in contact with molten fluoride slags at temperatures ranging from 1830 to 2730 F.

High-carbon ingots and zirconium-uranium master alloys have been prepared in order to study the effectiveness of zirconium on scavenging carbon from uranium.

Recent tests in which samples of plant solvent containing uranyl dibutyl phosphate were equilibrated with aqueous phases have indicated uranium distribution coefficients of 15 to 20 (O/A). This accounts for much of the discrepancy in uranium analyses of DBP-spiked solvents which have been equilibrated with aqueous uranium sulfate.

Salts for Use in Uranium Heat-Treating Salt Baths

K. A. Sense, M. J. Snyder, and R. B. Filbert, Jr.

The general objective of this project is to develop improved salt mixtures for use in the heat treating of uranium metal. The primary improvement sought is a reduction in the hydrogen content of the heat-treated metal below that obtained at present.

The past month was devoted to the acquisition of background information and to a survey of salt systems which could possibly be used.

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It is clear that the hydrogen which contaminates the uranium could originate from only two sources. One of these is the moisture in the atmosphere above the salt bath; the other is hydrogen-containing impurities initially present in the salt bath. Hydrates or, possibly, bicarbonates which react with uranium are possible impurities. If the problem is moisture pickup from the atmosphere, a slight amount of moisture could be troublesome. The problem could be solved by either finding a salt bath which is nonhygroscopic or by providing for a moisture-free atmosphere above the salt bath. On the other hand, if the problem is the presence of hydrogen-containing impurities in the salt bath initially, these impurities could be neutralized by a suitable scavenger. Once this has been accomplished, care would have to be taken to prevent atmospheric moisture from entering into the salt bath. If the salt bath is completely nonhygroscopic, the problem would be solved. If it were hygroscopic, a moisture-free atmosphere would have to be provided over the salt bath.

On the basis of this line of reasoning, efforts were made to find a salt system which would not pick up moisture at 1340 F. Considered were carbonates, chlorides, sulfates, phosphates, and silicates. Thermodynamic calculations showed the sulfates to be very unsatisfactory from the standpoint of moisture pickup. Phosphates are also eliminated because of their affinity for water. Carbonates showed up very favorably as far as reaction with water is concerned. This, of course, does not exclude the possibility of water physically dissolving in a carbonate bath or of the formation of hydrates. No calculations were made on chlorides or silicates, since, with a few notable exceptions, they should be virtually free from moisture pickup.

A test program will be initiated in which the rate of moisture pickup for various salt baths at 1340 F will be measured. These data will be correlated with the amount of hydrogen picked up by uranium metal submerged in the salt bath. Attempts will also be made to provide a moisture-free atmosphere over a salt bath and to determine the hydrogen pickup (if any) by uranium under that condition. Carbonates, chlorides, and silicates will be considered in this experimental program.

Refractories for Continuous Reduction of Uranium

C. Hyde, J. F. Quirk, and A. G. Allison

This portion of the NLO research program is concerned with the selection of commercial refractories for use in the continuous production of metallic uranium from the fluoride.

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Samples of nine commercial refractories have been received and slag-test pockets are being prepared. Preliminary testing will be done in air with NaF at 1000 C, AlF_3 at 1150 C, MgF_2 at 1450 C, and CaF_2 at 1500 C.

Those refractories that appear most resistant to slag attack under these test conditions will be tested at 3000 F (1650 C) as originally planned.

Metal-Recovery Studies

H. A. Saller, J. R. Keeler, and L. J. Cuddy

The effectiveness of zirconium in scavenging carbon from uranium is being investigated as a method of recovering metallic uranium from ingot croppings.

High-carbon starting material and a zirconium-uranium master alloy have been prepared and are being analysed. Two unalloyed melts were made for standards. These heats were melted in MgO-washed graphite crucibles and were poured at 2550 and 2650 F, respectively, after holding 30 min at temperature. Zirconium-containing heats are in preparation.

Degradation Products of Tributyl Phosphate

A. E. Bearse, R. A. Ewing, and S. J. Kiehl, Jr.

Uranium analyses of DBP-spiked solvents which have been equilibrated with aqueous uranium sulfate solutions have generally been lower than stoichiometric for uranyl dibutyl phosphate. Recent tests, in which uranyl dibutyl phosphate-containing samples of plant solvent were equilibrated with aqueous phases, appropriately acidified, have indicated uranium distribution coefficients of 15 to 20 (O:A), which would account for much of the discrepancy. Phosphorus analyses are in progress to determine whether the dibutyl phosphate is accompanying the uranium, or whether the $\text{UO}_2(\text{DBP})_2$ is undergoing metathesis. The latter possibility has been suggested by the results of one recent test in which a rather large concentration of DBP (2.25 per cent) was added to plant solvent before equilibration with aqueous uranyl sulfate solution. Preliminary analyses of the organic phase indicate that although 97 to 98 per cent of the phosphorus was present, only the usual 90 per cent of the uranium was found.

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Previous tests have shown that plant solvent, or solvent prepared from nitrated kerosene, extracts some uranium from uranyl sulfate solutions, even in the absence of dibutyl phosphate. Equilibration of two samples of typical plant solvent with 0.005 M UO_2SO_4 gave a uranium concentration in the organic phase of 23 mg per liter for each. In another test, on a sample of plant solvent which appears to be less completely oxidized, the uranium concentration was only 1.5 mg per liter. Neither filtration nor water-scrubbing reduced the uranium concentration, although the uranium is removed by scrubbing with Na_2CO_3 . This behavior of blanks indicates that a correction factor may be necessary when uranium analyses are made the basis of DBP determinations.

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F. GENERAL FUEL-ELEMENT DEVELOPMENT

H. A. Saller

Efforts on the general fuel-element development programs for the Reactor Development Division of the AEC have continued.

The development of ceramic fuel elements for high-temperature operation has stressed the determination of optimum calcining and sintering conditions to obtain maximum strength in BeO bodies. Similar attention is being given to the problem of uranium loss at high temperatures in molybdenum disilicide- and graphite-matrix elements. Experimental results obtained from the thermal fracture of a number of silicide-carbide-base specimens have been obtained. Additional data are needed before a firm conclusion as to the validity of the theory proposed can be reached. Previous work on the sinterability of ceramic bodies has been reviewed and a series of experiments based on BeO prepared from $\text{Be}(\text{OH})_2$ have been initiated. These experiments are expected to determine, quantitatively, the factors affecting sinterability of refractory oxide powders.

In the metallurgy programs, the study of alloys for operation at elevated temperatures has included the study of the effect of heat treatment on the hot hardness of uranium alloys containing from 3 to 20 w/o zirconium. Additional tests on this series of alloys are under way. The evaluation of low-melting uranium alloys by means of thermal cycling is continuing. Quantities of UC, U_2Ti , and UN have been prepared and will be incorporated into various matrix materials.

Corrosion studies are continuing. The first coin-shaped clad sample tested in the windowed autoclave was not well bonded and gave erratic results. Well-bonded samples will be used in future tests. Examination by X-ray diffraction of the corrosion product formed on pure uranium exposed to hot water indicated that the major phase was UO_2 with a minor amount of hydrated uranium trioxide.

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CERAMICSRefractory Fuel Elements

L. D. Loch, C. Hyde, J. R. Gambino, H. D. Sheets,
C. Cline, and J. F. Quirk

Fuel elements based on the refractory matrix materials BeO, MoSi₂, and graphite are under development for use in reactors operating at very high temperatures. Within the next few months, prototype elements using one or more of these materials are expected to be ready for advanced testing.

Current research on the BeO matrix is concerned with the calcining and sintering conditions required for developing maximum strength in ceramics made from "active" BeO powder. Attention is being given to the problem of uranium loss at high temperatures from MoSi₂- and graphite-matrix elements.

BeO

The strength and porosity of BeO shapes made from active powder are very sensitive to the temperature and time used in preparing the powder and in sintering the compacts. A series of experiments is under way to determine precisely the heat treatments that should be used to obtain optimum properties.

Most of the necessary calcinations, made by heating in air at 1470 to 2190 F for 1/2 to 4 hr, have been completed. Compacts made from the calcined powders will be sintered in hydrogen at 2250 to 2600 F for 1 to 16 hr. Bend strengths and bulk density will be determined on the sintered compacts.

MoSi₂

Experiments were begun to measure uranium losses from sintered MoSi₂-UO₂ compacts during exposure in air at 2500 F. These data are needed to assess the potentialities of MoSi₂-UO₂ fuel elements for high-temperature air-cycle reactors. Also, similar compacts were corrosion tested in hot water and in steam.

To measure uranium losses, sintered MoSi₂-UO₂ compacts will be placed in a quartz tube and heated to 2500 F while dry air passes around the

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compacts and bubbles through a nitric acid solution at the tube exit. Volatile uranium collected in the acid solution, or removed from the tube walls, will be determined by chemical analysis. For calibration purposes, a trial was made with this apparatus using U_3O_8 pellets which are expected to show rapid loss. Chemical analyses to determine volatilized uranium are being made.

Sintered compacts of $MoSi_2$ and of $MoSi_2-30$ w/o UO_2 were exposed to degassed water (650 F) or steam (750 F) at a pressure of 1500 psi. The changes in weight and in visual appearance after 24-hr and 168-hr exposures are given in Table F-1. The specimens tested at 650 F in water changed color from metallic gray to blue black. The discoloration also was evident in specimens tested in 750 F steam, but these also had a spotty gray coating. The results indicated that $MoSi_2$ had moderate resistance to water corrosion at high temperature. Further tests of $MoSi_2-UO_2$ compositions are needed to verify these preliminary results. Steam appeared to be much more corrosive than water in these tests, possibly because the steam might have contained oxygen.

TABLE F-1. CORROSION OF $MoSi_2$ AND $MoSi_2-30$ w/o UO_2 CERAMICS BY STEAM AND HOT WATER

Specimen Type	Test Conditions ^(a)	Weight Change ^(b) , mg per cm ² , After Indicate Exposure		Appearance
		24 hr	168 hr	
$MoSi_2$	Degassed water at 650 F	0	-0.21	Tan after 24 hr; dark blue black after 168 hr
$MoSi_2-30$ w/o UO_2	Degassed water at 650 F	-1.51	-0.34	Tan after 24 hr; dark blue black after 168 hr
$MoSi_2$	Steam at 750 F	-0.18 ^(c)	(d)	Dark blue black with some gray patches
$MoSi_2-30$ w/o UO_2	Steam at 750 F	+0.59	(d)	Dark blue black with some gray patches

(a) A single specimen was tested in water or steam at 1500 psi.

(b) Sample weight was about 3 g, sample area was 4 to 6 cm².

(c) Weight loss probably was due to flaking of gray coating.

(d) No determination made because of the severity of attack after 24 hr.

Measurements of uranium loss in hot air, both dry and humid, will be made on $MoSi_2-UO_2$ ceramics. Corrosion tests in hot water and steam will not be repeated unless a specific need arises for such data.

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Graphite

Because of the appreciable porosity of graphite shapes, losses of fuel and fission products are expected to be major problems at high operating temperatures. Previous experiments have shown that refractory coatings applied to the graphite surface effectively reduce fuel losses at 3000 F.

Losses should be further reduced by enclosure of the fuel mass in a relatively thick-walled graphite sheath. This approach is being explored, using uranium wire to form an axial concentration of UC in a graphite cylinder.

During the month, 0.080-in. -diameter uranium wire of low oxygen content was pickled in nitric acid, inserted in a graphite tube, and heated at 3100 F for 1/2 hr in a vacuum induction furnace. Examination of the heated composite showed nearly complete conversion of the uranium to UC. Use of the low-oxygen uranium eliminated the gas pockets formed in previous trials and resulted in a uniform, dense fuel mass.

In future work, the insertion of UO_2 rods in graphite will be investigated. After a method of inserting UO_2 is developed, experiments will be made to determine whether UC or UO_2 is more satisfactory for the high-temperature core.

Thermal Fracture of Ceramic Structures

A. K. Smalley and W. H. Duckworth

The behavior of ceramic structures under conditions of thermal stress is being investigated. This work is directed toward determining the extent of validity of the concept of separable shape and material factors for defining the resistance of ceramic structures to fracture from thermal stresses.

During the past month, a series of experiments designed to evaluate the shape factors of tubular SiC-base specimens was completed. In this work, silicon nitride-bonded SiC specimens were broken in the usual manner by the radial, steady flow of heat from a resistor rod aligned at the tube axis. These specimens had either circular, square, or triangular outer peripheries and the same circular inner peripheries. The ID was 0.86 in. and all specimens were 2 in. long. The circular specimens had an OD:ID ratio of about 1.6:1. The outer dimensions of the square and triangular specimens were such that they had the same solidity as the circular specimens. The results of these tests are shown on the following page.

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Series Number	Outer-Boundary Configuration	Number of Specimens Tested	Average Power Per Unit Length at Fracture (Q_{max}), w per cm	Relative Shape Factor
10041-46	Circular	10	82.7 $\pm$ 3.1 ^(a)	1.00
10041-48	Square	12	65.9 $\pm$ 4.0 ^(a)	0.80
10041-50	Triangular	12	60.0 $\pm$ 3.2 ^(a)	0.73

(a) 90 per cent confidence limits.

A first comparison is made in the tabulation below of the above Q_{max} and relative-shape-factor values with similar values obtained earlier on these shapes of a sintered-ruby material.

Outer-Boundary Configuration	SiC Specimens		Ruby Specimens	
	Average Power Per Unit Length at Fracture, w per cm	Relative Shape Factor	Average Power Per Unit Length at Fracture, w per cm	Relative Shape Factor
Circular	82.7	1.00	39.8	1.00
Square	65.9	0.80	35.5	0.89
Triangular	60.0	0.73	29.9	0.75

The relative shape factors of the square and triangular shapes appear to be in reasonably close agreement for the materials, indicating that the concept of separable shape and material factors can be safely extended to these shapes. However, careful analysis of the experimental control and of the data are needed before accepting these results, and data from specimens of a third material are considered necessary for a firm conclusion. Work during the immediate future will be directed along these lines.

Characterization of Sinterable Oxide Powders

J. F. Quirk, G. B. Engle, and C. Hyde

This research is directed toward determining, quantitatively, the factors affecting the sinterability of refractory oxide powders. Current studies are concerned with BeO prepared from Be(OH)₂. In previous work, BeO prepared by calcining NaOH-precipitated Be(OH)₂ was sintered to essentially theoretical density by heating in hydrogen at temperatures as

low as 2400 F. However, BeO prepared in a similar manner from NH_3 -precipitated $\text{Be}(\text{OH})_2$ did not approach theoretical density even when sintered at 3200 F. This wide variation in the sintering behavior of BeO is being studied initially as an approach to the more general problem of oxide sinterability and characterization.

Previous experience and examination of the literature indicates that the fabrication of densely sintered pure oxide ceramics may be regarded as a heat treatment of the parent compound (in this case $\text{Be}(\text{OH})_2$) which is interrupted at the proper stage for compaction to the desired shape. Experiments with BeO (and with MgO) indicated that the severity of heat treatment before compaction was one critical factor controlling the sinterability. The later studies on BeO made by calcination of different hydroxides indicated that the preparation of the parent compound was also an important factor. To determine the significant characteristics of sinterable oxide powders and the manner in which they can be controlled is the purpose of this investigation.

A continuing survey of the literature indicates that the major material characteristics affecting the sinterability of a given ceramic oxide are thought to be:

- (1) Ultimate particle, or crystallite size.
- (2) Aggregation of crystallites as the result of heat treatment and of compaction.
- (3) The amount and distribution of chemical impurities capable of reducing the melting point of the oxide.
- (4) Crystal imperfection, including disorder and lattice vacancies at the surfaces or throughout the crystallites. This includes the effect of nonstoichiometric minor impurities.

BeO powders are being prepared from $\text{Be}(\text{OH})_2$ in ways which are expected to give large differences in sinterability. Measurement of the listed properties for these powders, and the compacts made therefrom, should lead to a better understanding of the factors controlling sinterability. For this experiment, the criterion of sinterability will be the relation between sintering treatment and bulk density of the powder compact. Structural characteristics, including surface areas of powders and compacts, will be determined by inert-gas adsorption and displacement, by light and electron microscopy, and X-ray diffraction. Surface activities will be investigated by adsorption-desorption experiments with different gases. Chemical impurities will be determined by conventional methods, mainly spectroscopy.

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Work on the preparation of beryllium hydroxides from BeSO_4 solution is about half completed. Six samples of NaOH -precipitated $\text{Be}(\text{OH})_2$ have been made, with variations in solution concentration, aging of precipitate, and number of precipitations. Additional samples of $\text{Be}(\text{OH})_2$, precipitated with NH_3 , are being prepared for calcination and sintering trials. Apparatus for gas adsorption and displacement experiments has been constructed and is being calibrated. The possibility of relating dielectric properties with crystal or surface imperfection and sinterability of oxide powders is being studied.

METALLURGYUranium Alloys for High-Temperature Application

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

Uranium alloys containing 3.5 to 15 w/o molybdenum and 3 to 20 w/o zirconium are being studied as part of a program to develop reactor fuels for operation above 700 C. Evaluation is being accomplished by means of the hot-hardness and dilation values on selectively heat-treated specimens and the behavior of the alloys under stress cycling.

Previously, hot-hardness values of uranium-3 to 20 w/o zirconium alloys, water quenched (BMI-1012) and furnace cooled (BMI-1025) from 800 C, were reported. This report lists hot-hardness data on the alloys that were heat treated by controlled or step cooling from 800 C. The results are listed in Table F-2.

TABLE F-2. HOT HARDNESS OF URANIUM-ZIRCONIUM ALLOYS

Alloy, w/o Zirconium	Hardness, DPH, kg/mm^2 , at Indicated Temperature, C							
	RT	600	650	680	700	725	750	800
3(a)	266	48.9	27.6	9.3	15.7	13.1	10.9	--
5(a)	295	37.2	35.3	19.5	7.7	6.0	5.2	--
7(a)	306	--	--	12.8	10.8	8.5	7.7	5.9
10(a)	312	39.7	30.7	27.3	4.3	2.5	2.3	1.8
15(a)	317	63.9	30.9	15.5	19.5	15.4	13.6	9.6
20(b)	353	74.9	31.7	19.0	18.0	13.6	12.6	--

(a) 3, 5, 7, 10, and 15 w/o zirconium-uranium treated 1 hr at 800 C, furnace cooled to 670 C, held 24 hr, and furnace cooled.

(b) 20 w/o zirconium treated 1 hr at 800 C, furnace cooled to 750 C, furnace cooled from 750 C to 570 C at 1/2 C per min.

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The most noticeable change between alloys receiving controlled or step cooling and those water quenched or furnace cooled are their lower hardnesses at room temperature, and their generally greater hardnesses about 650 C.

The uranium-3 w/o zirconium alloy decreases rapidly in hardness from 650 to 680 C and increases in hardness from 680 to 700 C. The uranium-10 w/o zirconium alloy decreases rapidly in hardness from 680 to 700 C and from 700 to 800 C at a more gradual rate.

Hot-hardness data on uranium-zirconium and uranium-molybdenum alloys having other heat treatments is being obtained. In addition, dilation studies have begun on alloys of both systems.

Preparation and Properties of Low-Melting Alloys

R. F. Dickerson and W. E. Murr

A program aimed at the development of low-melting alloys for possible use as power-reactor fuel elements is in progress. During the past month, the work has been chiefly concerned with construction of thermal-stress-cycling equipment.

On the basis of recently completed thermal-cycling studies, a number of low-melting alloys were selected for further study. The alloys listed in the tabulation below will be thermally stressed and examined.

<u>Composition, w/o</u>	<u>Approximate Melting Point, F</u>
Uranium-5.9% chromium-2.69 thorium	1840
Uranium-5.0 chromium-1.0 molybdenum	1680
Uranium-4.82 chromium-0.72 silicon	1650
Uranium-2.56 chromium-2.26 vanadium	1785
Uranium-5.0 chromium-1.0 germanium	1650

The objective in thermally stressing the alloys is to reproduce, in model specimens, stress patterns similar to those present in a reactor fuel element. To do this, it is necessary to duplicate the geometry, temperature pattern, and linear power-generation rate in a scale-size model.

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Linear power generation can be simulated by the use of surface induction-heating effects. The temperature pattern in the fuel can be reproduced by introducing a coolant flow through the interior of the heated cylindrical model. For handling ease and in order to avoid corrosion problems, helium under pressure appears to fulfill the coolant requirements.

The specimens will be in the form of hollow cylinders 3.00 in. long, 1.50 in. in ID, and 0.32 in. thick. Requirements of the testing equipment are that a temperature gradient of approximately 40 F be established between inside and outside cylinder walls at the mean outside wall temperature of 840 F. The gradient is produced by combined surface heating and internal gas cooling of the test specimens.

After screening of alloys by stress cycling, those appearing stable will have physical properties determined. The ultimate goal of the project is to produce one or more promising alloys for irradiation-damage studies.

Compartmentalized Fuel Elements

D. L. Keller and G. W. Cunningham

A fuel-element fabrication program concerned primarily with developing improved cermet-type cores is in progress at Battelle. In this program, fuel-particle dispersions other than uranium dioxide are being investigated for use in zirconium-base and iron-base alloy matrices. Among the important considerations will be the effect the fuel particles have on the corrosion resistance, the fabricability, and the physical properties of the composite fuel-element cores.

A screening program for selecting the most promising uranium compounds for use as fuel dispersions has been completed. Among the materials investigated were UC, UC₂, UAl₃, UFe, U₂Ti, UNi₅, UN, and UCu₅. During this program, compacts prepared from each of these fuel materials dispersed in matrices of titanium, zirconium, Zircaloy 2, and stainless steel were cold pressed, sintered at 2280 F, and hot rolled in protective steel jackets at 1475 F (the stainless steel compacts were rolled at 2200 F). In practically all cases, a reaction occurred between the fuel and matrix materials during sintering, one exception being the UN-stainless steel system. However, hot rolling at the lower temperature was generally successful.

From these studies, the most promising material combinations, UC and U₂Ti in Zircaloy 2 and UN in stainless steel, have been selected for more detailed investigation. In order to minimize reactions between the components of the Zircaloy 2 systems, fabrication temperatures will be reduced substantially from 2280 F.

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One basis for the selection of these materials is their high density and high uranium concentration. Approximately 35, 40, and 45 w/o more uranium can be loaded as UC, UN, and U_2Ti , respectively, into the same volume occupied by UO_2 .

This month 500-g buttons of UC and U_2Ti were prepared by arc-melting techniques. A tungsten electrode was used for preparing the U_2Ti but proved unsatisfactory for melting the UC because of contamination. Instead, a carbon electrode was used and weight losses were noted. Complete analyses of these materials are not available as yet.

The UN has been produced by an established procedure in a gas-tight glass system using high-purity uranium and nitrogen. Zircaloy 2 has been hydrided and is being powdered.

Fabrication studies with these materials will be initiated as soon as the powders are available in sufficient quantity.

CORROSION

The Reaction of Fuel-Element Cores With Elevated-Temperature Water

D. R. Grieser and E. M. Simons

Continued use is being made of the windowed autoclave to study the corrosion behavior of uranium-alloy fuel elements containing cladding flaws.

A coin-shaped specimen with a Zircaloy 2 cladding pressure bonded to the 5 w/o zirconium-uranium core was subjected to 600 F water. From the nature of the resulting failure, it was concluded that the bond between the frame and the cover plate had been imperfect. This caused the core attack to be initiated at the bond face rather than at the 10-mil drilled hole in the center of the top cover plate.

The bonding procedure has been modified to overcome this difficulty and new specimens will be tested.

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Mechanism of Uranium Corrosion

C. M. Schwartz, D. A. Vaughan, and G. D. McDowell.

A study of the composition, structure, and mechanism of formation of corrosion products on uranium during exposure to hot water is in progress. Previous work described the visual progress of corrosion of a sample of production-grade uranium. The major phase in the corrosion product was identified as UO_2 by X-ray diffraction. However, a small quantity of hydrated uranium trioxide was detected.

During the past month, an attempt to obtain a gravimetric analysis of the loose portion of the corrosion product showed no change in weight on ignition to U_3O_8 . Thus it would appear that the corrosion product has the composition $\text{UO}_2 \cdot 6\text{H}_2\text{O}$, but has the structure of UO_2 . However, it is possible that a loss of moisture from the corrosion product during ignition balanced the weight gain on conversion of UO_2 to U_3O_8 . The sample has been re-surfaced and is being recorroded in 60 C water. The rate of attack is considerably less than was previously observed. The initial oxide film accentuates the grain structure rather than producing a uniformly colored film. Only a few pits have formed in a 150-hr exposure. It is possible that the differences in corrosion rate are due to differences in the amount of deformation in the corroding surface.

Corrosion studies of production-grade uranium will be continued during the next period and work on the higher purity uranium will be started.

Correlation of Microstructure With Corrosion

W. K. Boyd, W. E. Berry, and R. S. Peoples

As a part of the general fuel-element development program, the relationship between corrosion properties and microstructure of uranium alloys is being investigated.

Preliminary metallographic studies are being continued on binary alloys which were exposed to 100 C water. Both alpha-annealed and gamma-quenched specimens of alloys containing up to 12 w/o of aluminum, iron, molybdenum, nickel, niobium, silicon, tantalum, or zirconium are being examined. No data are available at this time.

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G. STUDIES OF ZIRCONIUM-URANIUM ALLOYS

H. A. Saller

A broad program to study uranium-zirconium alloys in the range up to 70 w/o uranium is in progress under the sponsorship of the Reactor Development Division of the Atomic Energy Commission.

Experimental work on various phases of the program is just getting under way. The programs were based on results of a complete literature survey which was issued as BMI-1030.

Constitution of Zirconium-Uranium Alloys

F. A. Rough and A. A. Bauer

In order to determine the composition limits of the alpha-plus-beta zirconium phase region, a quantitative study of the phases present in zirconium-rich zirconium-uranium alloys as a function of oxygen and nitrogen content is planned.

A preliminary mathematical analysis of experimental requirements for the study is being made. Upon the basis of this analysis alloys will be prepared and heat treated for quantitative measurements.

Transformation Kinetics and Mechanical Properties of Zirconium Alloys Containing Up to 20 w/o Uranium

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

The transformation kinetics and the hardening reaction in zirconium-uranium alloys containing up to 20 w/o uranium are being studied to permit a correlation between mechanical properties and the various microstructures obtained by heat treatment. The composition intervals are 7, 10, 15, and 20 w/o uranium.

Two series of alloys prepared from sponge zirconium and containing 0.094 and 0.27 w/o oxygen have been prepared. These alloys were forged at 800 C and rolled to final shape at 700 C. The series of alloys being prepared from iodide crystal-bar zirconium is not as yet finished.

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To augment the metallographic phase of the program, a dilatometer is being modified to a quenching, recording dilatometer. If the lineal changes which result during beta-phase decomposition are of sufficient magnitude to permit quantitative evaluation of the extent of transformation, the equipment will be completely converted.

The experimental phase of the program is being initiated with a determination of the martensite-start (M_s) temperature as a function of uranium content. Because an etchant is not presently known that will distinguish the martensitic phase from a tempered martensitic phase in this system, X-ray diffraction techniques are being investigated. Standard samples are being prepared with different amounts of the martensite phase as determined by lineal analysis. It is hoped that a correlation can be obtained between the intensity of diffraction lines from the martensite phase and the volume per cent of the phase. As a further means for interpreting the X-ray diffraction patterns, samples of the 7, 10, and 15 w/o uranium alloys have been solution treated at 900 C for 100 hr and are being cooled at a rate of 3 C per hr. This cooling rate should provide an equilibrium microstructure of alpha and epsilon phases and provide a standard for lattice-parameter determinations.

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

F. A. Rough and A. A. Bauer

Alloys containing 20 to 70 w/o uranium are being prepared for an investigation of the kinetics of the beta zirconium-to-epsilon decomposition. Experimental work, aimed at achieving a description of this decomposition, will begin when the complete series of alloys is available. The alloys are being consumable-electrode arc melted from biscuit uranium and crystal-bar zirconium.

A study of the 50 w/o uranium alloy to correlate resistance and microstructure has begun. A resistivity specimen has been machined from a 50 w/o uranium-alloy rod after it was annealed at 800 C and water quenched. The isothermal transformation of retained beta to epsilon is to be followed by resistance measurements. Equipment is being set up for this purpose.

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Heat Treatment of Zirconium-Uranium Alloys

F. A. Rough and W. Chubb

A series of zirconium-uranium alloys containing from 7 to 70 w/o uranium is being prepared for heat-treatment studies. The effect of oxygen on the heat-treatment behavior of these alloys is also being examined. Oxygen contents will be varied from 300 to 3000 ppm. Alloys containing 7 to 15 w/o uranium and 900 to 3000 ppm oxygen are now available for study.

Initial attempts to vary the structure of alloys containing 7 to 15 w/o uranium and 900 to 3000 ppm oxygen have been unsuccessful, the familiar Widmanstätten structure being produced in every case. A preliminary examination of end-quenched bars shows that these alloys contain equilibrium alpha zirconium at 900 C. This effect is caused by the oxygen present. Hardness traverses on these bars indicate that hardening effects due to quenching are negligible at 7 w/o uranium, but increase to an appreciable extent in the 15 w/o uranium alloy. A hardness increase of 20 DPH was observed near the quenched end of a 7 w/o uranium alloy; a hardness increase of over 70 DPH was observed near the quenched end of a 15 w/o uranium alloy.

The structures observed in the end-quenched bars will be used as a guide in future attempts to vary the structure of these alloys.

Corrosion of Zirconium-Uranium Alloys

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

A study is being made of the corrosion behavior of zirconium-0 through 60 w/o uranium alloys as part of the over-all AEC program to investigate the properties of zirconium-uranium alloys. Tests are being conducted in 680 F degassed water.

Corrosion tests are continuing on extruded zirconium-22 w/o uranium alloys heat treated to produce a range of microstructures. In general, samples are corroding at a linear rate, with corrosion rates ranging from +0.02 to -0.10 mg/(cm²)(hr). Heat treatment and corrosion rates after 5 to 8 weeks of exposure are presented in Table G-1. Alloy samples which were rolled at 1000 F then alternately cold swaged and annealed at 1000 F, then held 1 hr at 1000 F and furnace cooled lost weight at a constant rate up to 840 hr of exposure. However, with succeeding 168-hr exposures, the alloy samples alternately gained and lost weight. Apparently, the oxide film grew to a certain thickness and then spalled off. The reason for this behavior is not yet known, but could be due to a surface layer different in structure or alloy and impurity

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content from the bulk of the sample. Of the several heat treatments investigated, only one resulted in an adherent corrosion film on the zirconium-22 w/o uranium alloy. In this treatment the alloy was heated to 1550 F, held 36 hr, and furnace cooled; reheated to 1550 F, quenched to 1020 F, and held 0.5 hr; reheated to 1300 F, held 10 hr, quenched to 1020 F, held 1 hr, and water quenched. While the relationship between microstructure and corrosion behavior is not clear at this time, it should be pointed out that the above-mentioned heat treatment apparently results in a nonequilibrium condition in the alloy. The final treatment is insufficient to produce an equilibrium epsilon phase, whereas the other treatments should have produced essentially equilibrium structures. Studies on correlation of microstructure with corrosion behavior will be continued.

TABLE G-1. CORROSION DATA OBTAINED ON ZIRCONIUM-22 w/o URANIUM ALLOY SAMPLES EXPOSED TO 680 F DEGASSED WATER

Heat Treatment	Total Exposure, hr	Total Weight Change, mg/cm ²	Corrosion Rate ^(a) , mg/(cm ²)(hr)
1550 F, 36 hr, furnace cooled	1344	-122.0	-0.07
Rollled at 1000 F; alternately cold swaged and annealed at 1000 F; 1000 F, 1 hr, furnace cooled	840 ^(b)	-48.0	-0.05
1550 F, 36 hr, furnace cooled; reheated to 1550 F, quenched to 1020 F, held 0.5 hr; reheated to 1300 F, held 10 hr, then quenched to 1020 F, held 1 hr, water quenched	1008	+16.0	+0.02
1550 F, 36 hr, furnace cooled to 1200 F at 0.5 F per min; furnace cooled to room temperature	1008	-52.0	-0.04
1550 F, 36 hr, water quenched; reheated to 1020 F, held 22 days, furnace cooled	1008	-91.0	-0.09
1550 F, 36 hr, water quenched; reheated to 1020 F, held 0.5 hr, water quenched; reheated to 1400 F, held 10 hr, furnace cooled	1008	-120.0	-0.10

(a) Corrosion rate calculated at maximum exposure time.

(b) Alloy alternately gained and lost weight after each successive 168-hr exposure between 840 and 1344 hr.

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Radiation Stability of Zirconium-Uranium Alloys

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

As a part of the over-all program concerned with the study of zirconium-uranium alloys in assistance to the AEC, an investigation of the radiation stability of these alloys has been initiated. The first step in this investigation will consist of postirradiation studies on specimens of both 22 and 40 w/o zirconium-uranium alloys that have been irradiated by KAPL.

It is planned to use these specimens in an attempt to determine the effect of postirradiation heat treatment on the release of fission products and on other properties such as microstructure, hardness, and density. In addition to these experiments, normal postirradiation examinations will be performed on the alloys as they are received from KAPL.

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H. CORROSION STUDIES OF ZIRCONIUM ALLOYS

R. S. Peoples

Investigations concerned with the development of zirconium-base alloys for use as cladding materials in high-temperature water-cooled reactors are described in this section. Data continue to show that Zircaloy 2 is an excellent cladding material. Studies which support the Zirconium Corrosion Committee's program to develop new zirconium-base alloys are being continued. Sponge-base ternary and quaternary zirconium-tin-iron and zirconium-tin-nickel alloys are being studied in 600 and 680 F degassed water and 750 F steam.

Other investigations are concerned with (1) the role of hydrogen in breakaway in corrosion rate, (2) a study of the reaction of zirconium with water vapor at subatmospheric pressures in an effort to determine some of the mechanisms involved in the growth of the reaction product film, and (3) the identification of corrosion products on various zirconium alloys. The last-named studies have been initiated as an aid to ORNL. A large number and variety of zirconium alloys, previously exposed to high-temperature water, are being examined to determine if the cubic tetragonal modification of ZrO_2 is formed.

Corrosion of Zirconium and Zirconium Alloys

W. K. Boyd and R. S. Peoples

Investigations to determine the effect of impurity and alloy additions on the corrosion properties of sponge zirconium, zirconium-tin alloys, and Zircaloy 2 are being continued. Alloys are being evaluated in 600 and 680 F degassed water and 750 F steam (1500 psi).

Zircaloy 2

The samples representing seven melts of Zircaloy 2 continue to evince excellent corrosion resistance to 600 F degassed water. After more than 2-1/2 years of exposure, the samples possess a dark tarnish film and corrosion rates of the order of 2 mg/(dm²) (month).

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The effect of contaminants - hydrogen, nitrogen, and oxygen - on the corrosion behavior of Zircaloy 2 is also being investigated. Corrosion data for gas-impregnated samples, based on 154 days of exposure in 680 F degassed water, indicate the following trends:

- (1) Zircaloy 2 samples containing 500 to 1500 ppm hydrogen exhibit corrosion rates comparable to unimpregnated specimens.
- (2) Corrosion behavior of Zircaloy 2 is not affected by nitrogen additions up to 390 ppm. Specimens containing 390 to 500 ppm have a light, white oxide coating, while nitrogen levels above 500 ppm destroyed corrosion resistance.
- (3) Oxygen additions through 6000 ppm do not affect corrosion behavior. However, an oxygen content of 8000 ppm resulted in early failures.

Similar corrosion properties have been observed for Zircaloy 2 samples containing nitrogen and oxygen added as a master alloy during melting. These studies are being continued.

Zirconium Corrosion Committee
Program

Ternary and quaternary sponge-base alloys in the composition range 0.25 to 0.50 w/o tin plus 0.04 to 0.45 w/o iron and/or nickel are being studied in connection with the Committee's program to develop alloys with properties superior to those of Zircaloy 2. Each alloy composition is being studied in 680 F degassed water and 750 F steam (1500 psi) in two conditions of heat treatment: (1) vacuum annealed 1 hr at 775 C and furnace cooled, and (2) soaked 1 hr at 900 C in a vacuum and water quenched.

On the basis of up to 124 days of exposure in 750 F steam and 140 days in 680 F water, the following statements can be made concerning the data summarized in Table H-1:

- (1) No significant effect of heat treatment on corrosion behavior of either tin-iron or tin-nickel alloys is seen.
- (2) The tin-nickel alloys are showing better resistance than the tin-iron alloys to 750 F steam (1500 psi). Both are equally resistant to 680 F degassed water.

In other investigations, corrosion studies have been continued on the series of alloys melted at the BuMines for Zircaloy 3 evaluation. These alloys contain 0.25 to 0.50 w/o tin and 0.2 to 0.3 w/o iron plus either 0.2 w/o

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TABLE H-1. CORROSION OF ARC-MELTED (ROCKING-HEARTH METHOD) SPONGE ZIRCONIUM IN 750 F STEAM AND 680 F DEGASSED WATER

Heat	Alloy Content, w/o	750 F Steam			680 F Water			750 F Steam			680 F Water		
		Exposure Time, days	Weight Gain, mg/dm ²	Re-marks ^(a)	Exposure Time, days	Weight Gain, mg/dm ²	Re-marks ^(a)	Exposure Time, days	Weight Gain, mg/dm ²	Re-marks ^(a)	Exposure Time, days	Weight Gain, mg/dm ²	Re-marks ^(a)
		Heated 1 Hr at 775 C in Vacuum and Furnace Cooled						Heated 1 Hr at 900 C in Vacuum and Water Quenched					
					Tin and Iron								
462	Unalloyed	1-1/2	768	W	126	52	M	10	1680	W	28	Lost weight	W, F
463	Unalloyed	1-1/2	839	W	126	45	M	10	1325	W	28	66	W, F
464	0.22Sn-0.28Fe	106	108	M	126	31	G	124	100	M	140	39	G
465	0.23Sn-0.30Fe	106	103	M	126	33	G	124	93	M	140	35	G
466	0.22Sn-0.38Fe	112	93	M	126	33	G	124	95	M	140	37	G
467	0.22Sn-0.39Fe	112	89	M	126	25	G	124	91	M	140	33	G
469	0.25Sn-0.27Fe	112	102	M	126	23	G	124	75	M	140	39	G
468	0.25Sn-0.28Fe	112	105	M	126	24	G	124	87	M	140	31	G
470	0.25Sn-0.33Fe	112	98	M	126	27	G	124	92	M	140	35	G
471	0.25Sn-0.34Fe	112	107	M	126	30	G	124	98	M	140	40	G
473	0.27Sn-0.25Fe	106	105	M	126	31	G	124	77	M	140	37	G
472	0.29Sn-0.25Fe	106	115	M	126	28	G	124	85	M	140	38	G
475	0.27Sn-0.28Fe	112	95	M	126	33	G	124	84	M	140	45	G
474	0.28Sn-0.34Fe	106	104	M	126	28	G	124	100	M	140	39	G
477	0.47Sn-0.44Fe	112	112	M	126	32	G	124	91	M	140	42	G
478	0.51Sn-0.47Fe	112	94	M	126	33	G	124	100	M	140	30	G
481	0.52Sn-0.47Fe	112	93	M	126	34	G	124	97	M	140	43	G
479	0.50Sn-0.50Fe	112	93	M	126	34	G	124	102	M	140	42	LM
476	0.49Sn-0.51Fe	112	100	M	126	32	G	124	89	M	140	43	G
480	0.51Sn-0.53Fe	112	102	M	126	32	G	124	98	M	140	46	LM

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TABLE H-1. (Continued)

Heat	Alloy Content, w/o	750 F Steam			680 F Water			750 F Steam			680 F Water		
		Exposure Time, days	Weight Gain, mg/dm ²	Re-marks ^(a)	Exposure Time, days	Weight Gain, mg/dm ²	Re-marks ^(a)	Exposure Time, days	Weight Gain, mg/dm ²	Re-marks ^(a)	Exposure Time, days	Weight Gain, mg/dm ²	Re-marks ^(a)
		Heated 1 Hr at 775 C in Vacuum and Furnace Cooled						Heated 1 Hr at 900 C in Vacuum and Water Quenched					
Tin and Nickel													
488	Unalloyed	1-1/2	680	W	126	136	M	26	Lost weight	W, F	42	251	W
489	Unalloyed	1-1/2	570	W	126	51	M	26	Lost weight	W, F	42	231	W
491	0.17Sn-0.03Ni	118	63	LM, S	126	39	G	116	50	G	112	34	G
490	0.18Sn-0.04Ni	118	60	LM	126	37	G	116	47	G	112	25	G
492	0.13Sn-0.08Ni	118	54	LM	126	28	G	116	75	M, S	112	33	G
493	0.18Sn-0.08Ni	118	50	LM	126	31	G	116	50	M	112	34	G
495	0.17Sn-0.19Ni	118	56	LM	126	32	G	116	63	M	112	38	G
494	0.19Sn-C, 19Ni	118	58	LM	126	32	G	116	68	M	112	34	G
496	0.21Sn-0.04Ni	118	51	LM	126	40	G	116	51	G	112	37	G
497	0.22Sn-0.04Ni	118	63	LM	126	41	G	116	53	G	112	34	G
498	0.22Sn-0.07Ni	118	62	LM	126	34	G	116	84	M, S	112	38	G
499	0.22Sn-0.08Ni	118	60	LM	126	35	G	116	59	M	112	36	G
501	0.21Sn-0.20Ni	118	60	LM	126	40	G	116	74	M	112	38	G
500	0.22Sn-0.41Ni	118	59	LM	126	37	G	116	66	M	112	35	G
502	0.27Sn-0.03Ni	118	70	LM	126	48	G	116	49	G	112	32	G
503	0.27Sn-0.04Ni	118	71	LM	126	43	G	116	46	G	112	34	G
505	0.27Sn-0.08Ni	118	65	LM	126	42	G	116	60	M, S	112	36	G
504	0.28Sn-0.08Ni	118	62	LM	126	41	G	116	50	M	112	36	G
506	0.26Sn-0.19Ni	118	65	LM	126	41	G	116	49	M	112	34	G
507	0.25Sn-0.20Ni	118	85	LM	126	42	G	116	54	M	112	40	G
508	0.56Sn-0.04Ni	118	62	LM	126	43	G	116	63	M	112	37	G
509	0.56Sn-0.04Ni	118	73	LM	126	35	G	116	63	M	112	33	G
510	0.54Sn-0.07Ni	118	74	LM	126	38	G	116	66	M	112	39	G

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TABLE H-1. (Continued)

Heat	Alloy Content, w/o	750 F Steam			680 F Water			750 F Steam			680 F Water		
		Exposure Time, days	Weight Gain, mg/dm ²	Re-marks ^(a)	Exposure Time, days	Weight Gain, mg/dm ²	Re-marks ^(a)	Exposure Time, days	Weight Gain, mg/dm ²	Re-marks ^(a)	Exposure Time, days	Weight Gain, mg/dm ²	Re-marks ^(a)
		Heated 1 Hr at 775 C in Vacuum and Furnace Cooled						Heated 1 Hr at 900 C in Vacuum and Water Quenched					
511	0.56Sn-0.07Ni	118	68	LM	126	40	G	116	58	M	112	33	G
513	0.51Sn-0.18Ni	118	68	LM	126	40	G	116	71	M, S	112	38	G
512	0.54Sn-0.20Ni	118	66	LM	126	41	G	116	55	M	112	36	G
<u>Tin, Iron, and Nickel</u>													
483	0.51Sn-0.16Fe-0.090Ni	112	96	M	126	41	G	124	135	M	140	64	G
482	0.49Sn-0.23Fe-0.097Ni	112	83	M	126	34	G	124	99	M	140	39	G
485	0.47Sn-0.27Fe-0.13Ni	112	96	M	126	34	G	124	98	M	140	46	G
484	0.48Sn-0.31Fe-0.13Ni	112	90	M	126	37	G	124	96	M	140	44	G
486	0.48Sn-0.38Fe-0.18Ni	112	83	M	126	35	G	124	107	M	140	51	G
487	0.48Sn-0.44Fe-0.18Ni	112	81	M	126	36	G	124	107	M	140	50	G

(a) Key to remarks:

G-black tarnish film (good material)

LM-light milky

M-milky

W-white oxide

F-flaking (heavy oxide)

S-slight segregation (areas of good and poor material).

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nickel or 100 to 150 ppm of nitrogen or 50, 100, and 200 ppm of aluminum. Specimens representing each of the 30 ingots are being studied in the alpha-annealed (2 hr at 775 C in a vacuum and furnace cooled) and water-quenched (2 hr at 900 C in vacuum and water quenched) conditions. Corrosion data reported in BMI-1035, based on 57 to 69 days of exposure in 750 F steam and 70 days of exposure in 680 F water, indicated that the alpha-annealed samples had a faint oxide pattern, while the water-quenched samples possessed a shiny black tarnish film. An additional month of exposure (total 75 to 81 days in 750 F steam and 84 to 98 days in 680 F water) has resulted in no change for the annealed samples (see Table H-2). However, the quenched samples exposed to 750 F steam are now showing a faint oxide pattern. Duplicate samples exposed to 680 F water still show a shiny black tarnish film. Alloys containing 200 ppm of aluminum are not so resistant as those containing lesser amounts of aluminum. These tests are being continued.

Zirconium Boron Alloys

Arc-melted sponge-base alloys containing 0.45 w/o boron and Zircaloy 2 melts containing 0.5 w/o boron are being studied in 600 F and 680 F degassed water. Data obtained to date indicate that boron additions in the above range impair corrosion resistance of both sponge and Zircaloy 2 melts. Duplicate samples of sponge exposed up to 98 days in 600 F water and 84 days in 680 F water evince oxide films ranging from light to heavy, with weight gains of up to 61 mg/dm². Samples of Zircaloy 2 were covered with a gray oxide film after 28 days of exposure. Weight gains range from 52 to 98 mg/dm².

The Composition Factors Affecting Corrosion
Properties of Zirconium

W. K. Boyd and D. J. Maykuth

This program is concerned with determining compositional factors which affect the corrosion resistance of zirconium-base alloys. Sponge- and crystal-bar-base melts containing additions of chromium, germanium, gold, iridium, iron, nickel, niobium, nitrogen, oxygen, palladium, platinum, silver, or ruthenium are being evaluated in 600 and 680 F degassed water and 750 F steam (1500 psi).

Extended-exposure data (70 days to 16 months) continue to support the observations summarized in BMI-1035. In general, only iron and nickel additions are effective in improving corrosion resistance.

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TABLE H-2. CORROSION OF ZIRCONIUM-BASE ALLOYS MELTED AT THE BUREAU OF MINES FOR ZIRCALOY 3 EVALUATION

Heat	Alloy Content. w/o	750 F Steam			680 F Water			750 F Steam			680 F Water		
		Exposure Time, days	Weight Gain, mg/dm ²	Re-marks ^(a)	Exposure Time, days	Weight Gain, mg/dm ²	Re-marks ^(a)	Exposure Time, days	Weight Gain, mg/dm ²	Re-marks ^(a)	Exposure Time, days	Weight Gain, mg/dm ²	Re-marks ^(a)
		Vacuum Annealed 2 Hr at 775 C and Furnace Cooled						Heated 2 Hr at 900 C in Vacuum and Water Quenched					
974	0.25Sn-0.25Fe	81	45	G,FP	98	35	G-FP	75	52	G,FP	84	28	G
984	0.25Sn-0.25Fe	81	44	G,FP	98	39	G-FP	75	49	G,FP	84	32	G
990	0.25Sn-0.25Fe	81	45	G,FP	98	38	G-FP	75	56	G,FP	84	28	G
997	0.25Sn-0.25Fe	81	49	G,FP	98	39	G-FP	75	47	G,FP	84	28	G
1001	0.25Sn-0.25Fe	81	65	LM,FP	98	53	W	75	48	G,FP	84	31	G
975	0.50Sn-0.40Fe	81	44	G,FP	98	40	G-FP	75	46	G,FP	84	29	G
983	0.50Sn-0.40Fe	81	47	G,FP	98	39	G-FP	75	49	G,FP	84	27	G
1000	0.50Sn-0.40Fe	81	54	G,FP	98	42	G-FP	75	58	G,FP	84	27	G
998	0.50Sn-0.40Fe	81	50	G,FP	98	40	G-FP	75	47	G,FP	84	27	G
1003	0.50Sn-0.40Fe	81	78	LM,FP	98	49	LM-FP	75	92	G, S,FP	84	37	G
990	0.50Sn-0.20Fe-0.20Ni	81	48	G,FP	98	38	G-FP	75	56	G,FP	84	31	G
985	0.50Sn-0.20Fe-0.20Ni	81	41	G,FP	98	38	G-FP	75	52	G,FP	84	31	G
995	0.50Sn-0.20Fe-0.20Ni	81	52	G,FP	98	41	G-FP	75	55	G,FP	84	29	G
999	0.50Sn-0.20Fe-0.20Ni	81	55	G,FP	98	39	G-FP	75	57	G,FP	84	34	G
1007	0.50Sn-0.20Fe-0.20Ni	81	77	G,FP	98	57	LM-FP	75	68	G, S,FP	84	32	G
1024	0.25Sn-0.25Fe-100N ^(b)	81	59	G,FP	98	41	LM-FP	75	67	G, S,FP	84	36	G
1026	0.25Sn-0.25Fe-150N ^(b)	81	57	G,FP	98	40	LM-FP	75	53	G,FP	84	30	G
1030	0.50Sn-0.40Fe-100N ^(b)	81	53	G,FP	98	43	G-FP	75	67	G,FP	84	36	G, S
1028	0.50Sn-0.40Fe-150N ^(b)	81	61	G,FP	98	41	G-FP	75	66	G,FP	84	33	G

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TABLE H-2. (Continued)

Heat	Alloy Content, w/o	750 F Steam			680 F Water			750 F Steam			680 F Water		
		Exposure Time, days	Weight Gain, mg/dm ²	Re-marks ^(a)	Exposure Time, days	Weight Gain, mg/dm ²	Re-marks ^(a)	Exposure Time, days	Weight Gain, mg/dm ²	Re-marks ^(a)	Exposure Time, days	Weight Gain, mg/dm ²	Re-marks ^(a)
		Vacuum Annealed 2 Hr at 775 C and Furnace Cooled						Heated 2 Hr at 900 C in Vacuum and Water Quenched					
1014	0.25Sn-0.25Fe-50Al ^(b)	81	71	G,FP	98	42	G-FP	75	70	LM, S, FP	84	28	G
1012	0.25Sn-0.25Fe-100Al ^(b)	81	69	G,FP	98	40	G-FP	75	75	M,FP	84	32	G
1013	0.25Sn-0.25Fe-200Al ^(b)	81	99	M, S, FP	98	44	W	75	87	M,FP	84	33	G
1009	0.50Sn-0.40Fe-50Al ^(b)	81	72	G,FP	98	42	LM-FP	75	80	M,FP	84	30	G
1010	0.50Sn-0.40Fe-100Al ^(b)	81	73	G,FP	98	56	LM-FP	75	83	M,FP	84	35	G
1011	0.50Sn-0.40Fe-200Al ^(b)	81	82	G,FP	98	56	LM-FP	75	103	M,FP	84	32	G
1025	0.50Sn-0.20Fe-0.20Ni-100Al ^(b)	81	52	G,FP	98	42	G-FP	75	80	M,FP	84	33	G
1023	0.50Sn-0.20Fe-0.20Ni-150Al ^(b)	81	62	G,FP	98	41	G-FP	75	82	M,FP	84	34	G
1017	0.50Sn-0.20Fe-0.20Ni-50Al ^(b)	81	65	G,FP	98	44	G-FP	75	90	M,FP	84	30	G
1016	0.50Sn-0.20Fe-0.20Ni-100Al ^(b)	81	78	G,FP	98	44	G-FP	75	92	M,FP	84	35	G
1015	0.50Sn-0.20Fe-0.20Ni-200Al ^(b)	81	81	G,FP	98	50	G-FP	75	98	M,FP	84	34	G

(a) Key to remarks:

G-black tarnish film (good material)

W-white oxide pattern

FP-faint white oxide pattern

LM-light milky

M-milky

S-slight segregation (areas of good and poor material).

(b) in ppm.

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In other studies, zirconium-base tin-nickel-iron alloys containing additions of aluminum, nitrogen, or titanium are being studied in 750 F steam and 680 F degassed water. After up to 2 weeks of exposure, all alloy compositions are showing a tarnish film and low-weight gains (15 to 36 mg/dm²).

Effect of Heat Treatment

Research is being continued to determine the effect of size and distribution of compound particles on the corrosion properties of sponge-base alloys containing 0.25, 0.5, and 1.0 w/o iron or 0.01, 0.025, 0.05, 0.10, 0.25, and 0.5 w/o nickel. Corrosion tests are being conducted in 750 F steam.

After up to 113 days of exposure, the data continue to indicate that a fine dispersion of compound particles in an alpha matrix results in the best corrosion properties. Structures containing large colonies of compound separated by platelets of alpha zirconium have poor corrosion resistance. Under these conditions, increasing the iron or nickel content results in an increased rate of attack. In general, the iron alloys appear to be less affected by the heat treatments than do the nickel alloys. The heat treatments employed were described in detail in BMI-1012.

Zirconium-Gas Reactions

M. W. Mallett and W. M. Albrecht

Zirconium-Oxygen

As part of the program on the water corrosion of zirconium, fundamental studies are being made of the reactions of oxygen with zirconium. Preliminary experiments were made for a study of the diffusion of oxygen in alpha and beta zirconium. The results obtained from an oxygen gradient prepared in a zirconium cylinder at 1100 C for 30 min gave a diffusion coefficient of 5.2×10^{-6} cm²/sec. No further diffusion gradients will be prepared. The diffusion study is being discontinued for the present.

Zirconium-Water Vapor

It is planned to initiate a study of the reaction of zirconium with water vapor at subatmospheric pressures and to determine some of the mechanisms involved in the growth and breakaway of the reaction-product film. Included in this study will be work on:

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- (1) The kinetics of the reaction
- (2) The macrostructure and microstructure of the reaction film
- (3) Mechanical stability of the films
- (4) The effect of the interstitials O_2 , N_2 , and H_2 on the reaction
- (5) The composition of gaseous products
- (6) A comparison of the films with those obtained in high-temperature high-pressure water corrosion tests.

A microbalance technique (weight-gain measurements) will be used to obtain the kinetic data. Thus, it will be possible to obtain continuous rate data at a constant temperature. This is in contrast to the data obtained during present autoclave corrosion tests where it is necessary to interrupt the reaction each time a weight-gain measurement is made.

Mechanism of Zirconium Corrosion

C. M. Schwartz and D. A. Vaughan

Battelle is investigating the mechanism of zirconium corrosion during exposure to high-temperature water. Previous studies have indicated that hydrogen absorbed during corrosion damages the surface of zirconium and Zircaloy 2 and thus reduces the resistance to corrosion in 750 F steam.

During the past month, additional corrosion tests were made on hydrogen-impregnated and impregnated and degassed Zircaloy 2 specimens. The results did not confirm previous observations, in that the weight gain was much less than previously observed. However, this duplicate set of samples had a thin tarnish film on the surface following hydrogen impregnation. The tarnish film was apparently caused by accidental surface oxidation and was not present on the first set. A new set of hydrogen impregnated alloys is being prepared, using precautions to avoid surface oxidation.

Identification of Corrosion Products on Various
Zirconium Alloys

C. M. Schwartz and D. A. Vaughan

To assist ORNL, an investigation of the oxides formed on a series of zirconium-base alloys during exposure to high-temperature water has been

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initiated to determine if, in any case, the cubic or the tetragonal modification of ZrO_2 is formed. Tests at ORNL have indicated that monoclinic ZrO_2 transforms to the cubic or tetragonal modification in a high neutron flux. This transformation may be the cause of poor corrosion resistance of Zircaloy 2 on exposure to uranyl sulfate solution at 250 C in a high neutron flux. Stabilization of the cubic form may be effected by certain metallic additions. The objective of the current investigation is to see whether the stabilized phase may be produced as a tarnish film on suitable zirconium alloys.

During the past month, a set of alloys selected from a large number and variety of compositions, available at Battelle from earlier corrosion testing, has been collected. X-ray and electron-diffraction studies have been started, but the analyses have not been completed as yet. In addition, four samples (arc melts of zirconium, Zircaloy 2, zirconium-15 w/o niobium, and zirconium-3 w/o cerium) were prepared and corroded at ORNL in 300 C uranyl sulfate solution for diffraction analysis. Preliminary results on these samples indicate an increased amount of tetragonal (cubic) ZrO_2 on the zirconium-niobium alloy over the amount of that phase detected on the zirconium or Zircaloy 2 specimens. The cerium alloy gave only the monoclinic modification of ZrO_2 plus one line which can be attributed to the strongest diffraction line of CeO_2 . This study will be continued.

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I-1

I. REACTOR MATERIALS DEVELOPMENT

H. A. Saller

Several programs on the development and utilization of materials for general reactor application are included in this section of the report. These programs are in the interest of the Reactor Development Division of the AEC.

The X-ray analysis of heat-treated zirconium alloys failed to explain why an alloy containing niobium has better ductility than a molybdenum-containing alloy. Both alloys did reveal the presence of a hydride phase. Further efforts to remove the hydrogen are planned.

The study of enamels as coatings for reactor materials has continued. Corrosion tests of two enameled zirconium samples in a 99 w/o bismuth-uranium liquid were not conclusive. Enamels have been successfully applied to Zircaloy 2, as well as to pure zirconium.

The study of the kinetics of the zirconium-uranium dioxide reaction is under way. Some preliminary experiments using sandwich-type diffusion samples have been conducted with no conclusive results available so far.

Studies of Zirconium Heat Treatment

H. A. Robinson, M. W. Mote, and P. D. Frost

The heat treatability of zirconium alloys has been demonstrated for alloys containing about 5 w/o of a beta stabilizer with or without an alpha-stabilizing element. Strengths of up to 200,000 psi have been obtained through the beta $\rightarrow$ omega $\rightarrow$ alpha transformation. A niobium-bearing alloy appeared to have much better ductility than a molybdenum-bearing alloy at the same strength levels. Preliminary X-ray analyses did not indicate conclusively the reasons for this, and the investigation to correlate phases present in the alloys with properties is being continued. For the purposes of this investigation, one 20-lb ingot of zirconium-5 w/o molybdenum-2 w/o tin and of zirconium-5 w/o niobium-2 w/o tin was single melted and forged in preparation for the second melting operation.

Metallographic observations revealed the hydride phase in these and in earlier heats. Steps will be taken to remove hydrogen more completely than has been done in the heats made to date.

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In addition to the work planned for these two alloys, an exploratory study has been begun to evaluate the effects of various elements, individually and in combination with each other, on the heat treatability of zirconium.

Enameling of Special Metals

B. W. King, J. Schultz, and E. D. Dietz

Porcelain-enamel coatings for special metals of interest to the AEC are being developed on this program. Coatings for zirconium are being studied at present.

During the past month, it was attempted to test the resistance of two zirconium coatings to an LMFR type of fuel. A 99 w/o bismuth 1 w/o uranium mixture was placed in contact with each of the coatings and maintained at 600 C for 100 hr in an argon atmosphere. One of the coatings tested was a lead silicate enamel. The other was a frit-refractory coating containing 35 w/o Al_2O_3 .

The test results were inconclusive; the atmosphere was not pure enough to prevent oxidation of the molten alloy. An oxide coating formed on the surface, and there may have been some oxide in contact with the enamel. Under these conditions, the coatings showed a slight degree of attack. Bare zirconium was badly attacked under the same conditions.

Samples of Zircaloy 2 were enameled successfully with the same type of enamels used to coat zirconium. There was little apparent difference in the enameling properties of this alloy and pure zirconium.

Specimens of niobium have been obtained and an attempt will be made to develop enamels for coating this metal. In addition, experiments will be made to obtain more specific data on the stability of coated zirconium in the presence of a bismuth-uranium alloy.

Kinetics of the Zirconium-Uranium Dioxide Reaction

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

The solid-phase reaction between zirconium and uranium dioxide is being studied as part of a basic AEC program. Information obtained will aid in predicting the compatibility of zirconium metal and its alloys in contact with uranium dioxide in atomic reactors.

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During the past month, a number of preliminary experiments were performed. Portions of a sandwich-type zirconium- UO_2 element, previously heated at 1300 F and slowly cooled, were reheated in evacuated Vycor capsules at 1325 F for times up to 69 hr and water quenched. The previously observed phases in the reaction zone failed to change appreciably after the reheat and water-quench treatment. This may indicate either that the phases observed in the slowly cooled element were the phases in equilibrium at 1300 F or that 69 hr reheating at 1325 F was not sufficiently long to redissolve the precipitated phases. Another specimen will be quenched after heating for at least 150 hr.

A means was developed for more rapidly cooling from operating temperature the autoclaves in which the sandwich-type diffusion elements will be heated. By the technique developed, an autoclave can be cooled from 1300 F to 500 F in about 35 min. Previously, cooling through the same temperature range required more than 4 hr.

Several inert materials will be tested as markers for the original metal-oxide interface. The preparation of experimental specimens is nearing completion and it is expected that sandwich-type elements soon will be placed on test at the lower temperatures, 900 and 1050 F.

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J. PHYSICAL RESEARCH

H. A. Saller

This section covers programs in ceramics, metallurgy, and gas-metal studies of interest to the Research Division of the AEC.

A literature search on uranium compounds has been completed. In general, there is little information on the various compounds. Preparation of two of the more promising materials, UN and U_3Si , is under way.

In the study of internal friction of uranium, it was observed that internal friction increased with temperature and heating rate. This has been observed consistently on samples in a variety of states of heat treatment.

Alloys in the range from uranium-31.5 a/o molybdenum to uranium-34 a/o titanium have been investigated by means of differential thermal analysis. In these alloys, there is evidence of a transformation which increases in temperature with increasing titanium content from about 590 to 650 C.

In the study of bonding fundamentals, results obtained on closed-die pressed-silver cylinders showed bond strength to be dependent on both temperature and pressure, as would be expected.

The fundamental study of embrittlement in zirconium was continued. In samples broken by tensile impact, the presence of hydride needles had little effect on breaking strength. The sample containing hydride needles did have a much lower reduction of area than that obtained in the sample free of hydrides.

Oxidation studies on a series of niobium-1 to 25 a/o titanium alloys showed no evidence of the formation of an adherent protective oxide film. The rate of oxidation did decrease considerably with increasing titanium content.

In the study of uranium-hydrogen reactions, an equation defining reaction rates as a function of temperature and pressure has been established. Data obtained from several test runs fit the equation well. Preliminary results on a uranium-5 w/o zirconium alloy indicate a reaction rate lower than that obtained for pure uranium.

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Properties of Uranium Compounds

L. D. Loch, J. R. Gambino, and G. B. Engle

Some of the less-familiar uranium compounds are being investigated as possible nuclear fuels. The basic requirements of a good fuel material are high uranium content, relatively high melting point, and low neutron absorption cross section. These considerations have narrowed the field to the monatomic compounds of uranium with carbon, nitrogen, oxygen, and sulfur and the intermetallic compounds with aluminum, nickel, silicon, and titanium. A survey of the literature on these materials was completed during the month, and preparation of two of the compounds was begun.

The literature survey disclosed very little data on any of the compounds that would help to evaluate them as fuel materials. UN, US, and U_3Si are reported to be corrosion resistant in hot water. USi_2 is said to be resistant to high-temperature oxidation. However, these are casual observations that need confirmation.

The first compounds to be studied will be UN and U_3Si because of their reported chemical stability and ease of preparation in pure form. Samples of these materials were prepared during the month. When their exact compositions have been determined, preliminary measurements of thermal and chemical stability will be made.

The Development of Uranium-Titanium Alloys

L. L. Marsh and G. K. Manning

A research program has been started to survey and evaluate several uranium-rich binary alloys of titanium with regard to potential usefulness in reactors. The alloys have been prepared by consumable-electrode arc melting. Final forging and rolling has not yet been completed on these alloys.

Investigation of the Tensile Transition in Alpha Uranium

L. L. Marsh and G. K. Manning

A research program has been initiated on the tensile transition in alpha uranium. The program is based upon a study of the variation in mechanical properties through the transition. Particular emphasis will be placed on following any changes in the plastic portion of the stress-strain

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curve. Coordinated with such a study will be a visual examination of microstructure. Both optical and electron microscopy will be used in order to determine any change in the dominant plastic deformation process.

Biscuit uranium has been rolled at 600 C and at 300 C in order to provide tensile specimens with two fabrication histories (two degrees of preferred orientation). Tensile specimens have been machined from these materials and testing will start immediately.

Since it would be desirable to make metallographic examinations directly on the surface of the tensile specimens, an electropolishing technique has been developed using the CrO_3 -glacial acetic acid bath in standard proportions. (One hundred g of CrO_3 are dissolved in 118 g of water; one part of this solution is mixed with four parts glacial acetic acid.) Tensile specimens will be prestrained various plastic strains along the stress-strain curve and the resulting microstructure studied to determine the role of twinning in the tensile transition.

Internal Friction of Uranium

R. E. Maringer, L. L. Marsh, and G. K. Manning

The internal friction of uranium is being investigated in order to learn more about the behavior of twins in uranium. It has been observed previously that the internal friction of uranium increases as the heating rate increases. During the past month, effort has been expended to further develop the relation between internal friction and heating rate.

Internal friction versus temperature tests between 30 C and 200 C have been performed at two approximately linear heating rates, 3.78 C per min and 1.79 C per min, on uranium wire in the following conditions:

- (1) As-rolled at 600 C
- (2) Alpha annealed (10 hr at 600 C), furnace cooled
- (3) Same as (2), but water quenched
- (4) Beta treated (1/2 hr at 725 C), furnace cooled
- (5) Same as (4), but water quenched.

Two additional tests have been performed on the beta-treated and furnace-cooled specimen at heating rates of 1.26 C per min and 0.85 C per min.

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In all cases, these tests show that the internal friction increased with temperature and heating rate. During the time interval at 200 C required to start the cooling cycle, the internal friction decreases, presumably due to relaxation of stresses. On cooling, the internal friction again increases at approximately the same rate as on heating. Further, it has been observed that the internal friction at a particular temperature decays at a rate depending on the heating rate to that temperature; i. e., the faster the heating rate, the faster the rate of initial decrease in internal friction. However, the total time required to reach equilibrium at temperature seems to be the same in both cases.

Intermediate or Delta-Phase Alloys

H. A. Saller, F. A. Rough, and A. A. Bauer

The investigation of the phase relationships between the delta phases of the uranium-molybdenum and uranium-titanium systems has continued.

Alloys prepared for this investigation range in composition from uranium-31.5 a/o molybdenum to uranium-34 a/o titanium. Differential thermal data indicate a transformation in these alloys. The transformation temperature increases with increasing titanium content from about 590 to 650 C. Molybdenum-rich alloys containing less than 2 a/o titanium showed no thermal arrest on heating, the stabilized gamma phase evidently never having transformed during the previous homogenization and furnace-cooling treatment. Molybdenum additions to the uranium-titanium delta phase, which transforms to gamma at about 900 C, cause a gradual decrease in the gamma transformation temperature.

A series of samples annealed at 850 C is now being prepared for metallographic examination and additional samples are being prepared for both metallographic and X-ray studies.

Study of Bonding Fundamentals

J. E. Reynolds, H. R. Ogden, and R. L. Jaffee

The two points of attack on the problem of solid-state bonding are being continued. The bonding of needle points to flat surfaces for the purpose of eliminating the microscopic mating variable has not yet been put on an experimental basis which yields consistent results. Nucleation-and-growth studies on silver have been continued.

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Building vibrations are believed to be seriously affecting bonding of the needles in the parallel sheet-metal spring device, and dashpots with vacuum oil or magnetic dampers have not eliminated this effect. The torsional balance for needle bonding is almost completed, and a small cylindrical platinum-wound furnace has been built to use in connection with it. The apparatus should be ready for bonding tests in the next 30 days. The vibrations appear to be less serious with the torsional balance than with the sheet-metal spring device.

It now seems unlikely that a rigorous mathematical treatment can be applied to the nucleation and growth of solid-state bonds, because nucleation is very dependent upon mechanical phenomena. This does not rule out the possibility of obtaining useful information, and studies with silver are being continued because of the general importance of the bond interface. The present method of evaluating a metallurgical bond by metallographic studies is far from adequate. Conditions are now being established under which a partial bonding of two cylindrical specimens is obtained. When this condition is found, microstructure will be studied, using the electron microscope, to attempt identification of bonded and unbonded regions.

Data shown in Table J-1 have been determined in closed-die pressing for 1/4-in. -diameter silver rods, using a universal testing machine for loading and testing.

TABLE J-1. BOND-STRENGTH TEST DATA

Run	Temperature, C	Time, min	Load, psi	Bond Strength, psi
1-T	300	1	15,000	421
2-T	300	10	15,000	294
4-T	300	1	30,000	1263
3-T1	300	10	30,000	4631
3-T2	300	10	30,000	4316
5-T1	300	10	45,000	1364
5-T2	300	10	45,000	3593

These data show that the amount of bonding as measured by the bond strength is both temperature and pressure dependent, as would be expected.

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A Fundamental Investigation of Embrittlement in Zirconium

C. M. Schwartz and A. P. Young

The objective of this investigation is to study the slip-line and twinning structure of deformed zirconium to determine why hydrogen lowers the impact strength of slow-cooled samples, as compared with quenched samples. Last month, quenched and slow-cooled samples of arc-melted crystal-bar zirconium, deformed at slow strain rates, showed little difference in either tensile behavior or slip-line structure. Tensile impact studies have been made this month.

A slow-cooled and a quenched sample of arc-melted crystal-bar zirconium were tested in tensile impact. The impact energy was nearly the same for both samples. However, there was a marked difference in reduction in area in the two samples. Based on reduction in area as a criterion, the quenched sample was more ductile. This is in agreement with some recent work at Battelle⁽¹⁾, in which it was found that alpha titanium containing hydride needles is embrittled at room temperature in an unnotched impact tensile test.

The most noticeable difference in the deformation structure of samples strained at impact and low strain rates is the much greater incidence of twinning in the impact samples. There was visual evidence of twinning in about 15 per cent of the grains in the impact samples. In low-strain samples less than 1 per cent of the grains had twins. In the slow-cooled impact sample, twins appeared to terminate at hydride needles. In some cases two sets of twins terminated on opposite sides of a hydride needle. This would make the hydride needle a region of high stress which could originate a crack. Cahn⁽²⁾ has noted cracks starting in the region of approach of two or more twin in molybdenum crystals after compressive impact.

Because of the low hydrogen content (30 to 40 ppm) in the zirconium used in this examination, not very many grains have both twins and hydride needles. In the future this study will be repeated, using zirconium with a higher hydrogen content.

(1) Lenning, G. A., Craighead, C. M., and Jaffee, R. L., "The Effect of Hydrogen on the Mechanical Properties of Titanium and Titanium Alloys", Summary Report, Contract No. DA-33-019-ORD-938 (July 31, 1964).

(2) Cahn, R. W., "Mechanical Twinning in Molybdenum", *Jour. Inst. Metals*, 53, 493 (1955).

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Solid-State Studies of Thorium and Uranium Alloys

A. E. Austin and C. M. Schwartz

The dependence of the thorium transformation upon oxygen content is to be studied by means of high-temperature X-ray diffraction. Iodide thorium containing initially 0.04 w/o oxygen has had additional oxygen added for a total of 0.12 w/o oxygen. However, tarnish of the surface indicated that not all of the additional oxygen diffused into the metal. These two specimens are being swaged and machined for X-ray diffraction study. Oxygen analysis will be obtained after the high-temperature studies are completed.

Alloys of 1, 2, and 5 w/o uranium are being fabricated for study of the phase diagram.

Oxidation-Resistant Niobium Alloys

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

Niobium and its alloys have considerable potential for use as structural materials at elevated temperatures. Pure niobium, however, suffers from excessive oxidation and contamination when exposed to air at temperatures of 400 C and higher. The present investigation was undertaken to evaluate the effects of alloying additions on the resistance of niobium to air oxidation at elevated temperatures.

Ingots of pure niobium and binary niobium-base alloys are being prepared by arc melting. The hardnesses of the niobium ingots are about 115 VHN. The first alloys investigated were in the niobium-titanium system. Rectangular specimens measuring 0.1 by 0.2 by 0.5 in. were cut from the alloy ingots and exposed to air for 1, 5, and 10 hr at 600, 800, and 1000 C. Oxidation rates for each of the niobium-titanium samples varied linearly with exposure time, indicating that none of the alloys formed protective films. Compositions, hardnesses, and oxidation rates are tabulated below:

Alloy	Hardness, VHN	Oxidation Rate, mg/(cm ²)(hr)		
		600 C	800 C	1000 C
Niobium-1 a/o titanium	108	5.8	21.6	26.0
Niobium-5 a/o titanium	115	6.7	21.0	13.7
Niobium-10 a/o titanium	135	0.15	7.5	7.7
Niobium-25 a/o titanium	156	0.05	0.6	1.9

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Titanium additions to niobium markedly decrease the rate of air oxidation from 600 to 1000 C. The niobium-1 a/o titanium and niobium-5 a/o titanium samples formed white, powdery, free-scaling oxides at all temperatures. The scales formed on the other alloys were gray and more adherent, although not protective.

It is planned to make hardness traverses on these alloys to determine the depths of contamination at each temperature. Other alloys of niobium will also be studied. In addition, oxidation rates of pure niobium will be measured in a modified Sieverts apparatus at 600, 800, 1000, 1200, and 1400 C in oxygen and in air to secure baseline oxidation data. Tests will be conducted in nitrogen if significant differences in the oxidation rates are noted between oxygen and air.

Uranium-Hydrogen Reactions

M. W. Mallett and W. M. Albrecht

As part of the AEC Research Division program, fundamental studies are being made of the reactions of uranium and uranium alloys with hydrogen.

Further consideration was given to the variation of the reaction rates with temperature and pressure. It appears that the dissociation pressure of the product hydride as well as the system pressure is important in determining the pressure dependency of the reaction. This is normally the case in dealing with the kinetics of a reaction at nearly equilibrium conditions. A good fit of the data was obtained with the equation

$$r = k \left(\frac{p - p_0}{p_0} \right),$$

where

r = reaction rate

k = reaction rate constant

p = system pressure

p_0 = dissociation pressure of uranium hydride.

However, this equation is empirical and further considerations must be made before the mechanism of the reaction can be established.

Reaction-rate runs were made with uranium and hydrogen at 114 and 224 C at $p - p_0$ of 740 mm of mercury. Linear rates were obtained which agreed with previous data when interpreted according to the above equation.

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Preliminary rate runs were made with a uranium-5 w/o zirconium alloy and hydrogen at 250 C at $p-p_0$ of 430 mm of mercury and at 100 and 200 C at $p-p_0$ of 150 mm of mercury. After initial deviations, the reactions followed a linear rate. The rates appeared to be slower than those for the reaction of unalloyed uranium with hydrogen at corresponding temperatures and pressures. However, more data must be obtained to establish the true kinetic behavior.

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