

MASTER

PROGRESS RELATING TO CIVILIAN APPLICATIONS
DURING OCTOBER, 1955

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by

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REPORTS RELATED TO CIVILIAN APPLICATIONS
ISSUED DURING OCTOBER, 1955

- BMI-1036 "The Mechanical Properties of Beta-Quenched Uranium at Elevated Temperatures", by Frederic R. Shober, Lyle L. Marsh, and George K. Manning.
- BMI-1037 "Fabrication and Welding of Arc-Cast Molybdenum", by Norman E. Weare, Robert E. Monroe, and George W. Rengstorff.
- BMI-1041 "Reaction of Nickel in Molten Sodium Hydroxide", by Robert S. Peoples, Paul D. Miller, and H. Dale Hannan.
- BMI-1043 "Progress Relating to Civilian Applications During September, 1955", by Russell W. Dayton and Clyde R. Tipton, Jr.
- BMI-1045 "Corrosion in 650 F Degassed Water of Uranium-Molybdenum Alloys Containing Impurity Additions", by Edward W. Cawthorne, Warren E. Berry, James E. Reynolds, Robert I. Jaffee, and Robert S. Peoples.

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**A. DEVELOPMENT OF PWR FUEL MATERIALS
AND FUEL ELEMENTS**

As noted in BMI-1043, the bulk of the PWR program was concluded in September. The remaining study "Modified UO_2 Fuel-Element Cores" is now included in Section F, with related AEC ceramic studies. Continuing corrosion testing of selected uranium-molybdenum alloys has been integrated with other AEC Reactor Development Division studies of uranium-alloy corrosion, also reported in Section F.

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B. DEVELOPMENT OF MATERIALS FOR REACTORS

J. R. Keeler

The program is directed primarily toward the development of uranium alloys having improved mechanical properties. Studies on the properties of cold-worked Zircaloy 2 and zirconium at elevated temperatures are also in progress, and the thorium-rich end of the thorium-uranium constitutional diagram is being investigated.

Uranium Alloys for Fuel Elements

H. A. Saller, F. A. Rough, and W. Chubb

A series of uranium alloys was prepared in an effort to produce alloys that have different physical and mechanical properties. It was hoped that these alloys could then be irradiated, and that a comparison of their irradiation behavior and their properties would lead to an understanding of the properties needed to resist damage. The alloys produced were arc-melted uranium which had low strength and moderate ductility, arc-melted uranium-0.5 a/o titanium which had low strength and low ductility, induction-melted uranium which had moderate strength and moderate ductility, arc-melted uranium-0.35 a/o chromium which had high strength and moderate ductility, and arc-melted uranium-1.5 a/o silicon which had high strength and low ductility. No differences have been detected in the thermal expansions of these alloys. The possibility of changing the properties of the alloys by means of heat treatments is now being investigated.

End-quench tests from 800 C produced no differences in grain size or hardness that could be attributed to the differences in quenching rate produced by this test. These tests have been repeated by quenching from 900 C. Hardness traverses on these bars show no hardness variations attributable to quenching rate for four of the alloys. The uranium-1.5 a/o silicon alloy shows a hardness of about 420 DPH at the quenched end, the hardness drops rapidly to about 320 DPH 1/2 in. from the quenched end, and then remains about the same through the remainder of the bar. Evaluation of this bar has not been completed, but the hardness change must be related in some way to the solubility of silicon in uranium.

Thermal-conductivity measurements on these alloys are almost complete and will be available next month.

A theoretical examination of the alloying nature of uranium shows that only chromium, molybdenum, niobium, titanium, vanadium, and

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zirconium have any appreciable solubility in alpha uranium. Cross-section considerations place a severe limitation on the amount of chromium, molybdenum, titanium, and vanadium that may be used. Larger amounts of niobium and zirconium may be used, so that these two elements appear most promising for the development of alloys having high strength and high ductility.

As a metallurgical assistance service, an attempt was made to fabricate 3/4-in. -diameter rod from an epsilon uranium-silicon alloy containing 3.8 w/o silicon. Several techniques for fabricating this alloy were investigated briefly. Castings, epsilonized 148 hr at 800 C, spalled at the edges and cracked badly when forged bare at 850 C, just below the peritectoid decomposition. Both forging and swaging tests were also made on specimens clad in steel pipe. The temperature of these operations was restricted to 1290 F by the iron-uranium eutectic. Both types of specimens cracked badly. Hot-hardness data indicated that the hardness dropped off rapidly at the peritectoid breakdown, which produced a higher silicide in a gamma-uranium matrix. However, forging tests on bare specimens at 950 C showed that the alloy was hot short in this phase region, and a zirconium-clad specimen swaged in this temperature range also was badly cracked after 30 per cent reduction.

Although satisfactory extrusions have been reported in the literature, the alloy appears to be unworkable by other fabricating processes.

The Constitution of Thorium-Uranium Alloys

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

An investigation to determine the constitution of thorium-rich thorium-uranium alloys is in progress. Alloys containing 0 to 20 w/o uranium have been prepared and are being heat treated at temperatures ranging from 500 to 1000 C for study. Preliminary metallographic examination has indicated a solubility of between 7 and 10 w/o uranium in thorium at 1000 C. The solubility apparently decreases with decreasing temperature. However, the differentiation of small amounts of uranium from other inclusions appearing in the alloys becomes increasingly difficult with decreasing temperature, and an attempt is being made to develop an etchant which will aid in such differentiation.

Lattice-parameter and hardness measurements of the heat-treated samples are planned.

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Mechanical Properties of Zirconium and Zircaloy 2

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

The mechanical properties of nominally 50 per cent cold-worked zirconium and Zircaloy 2 are being compared to those of the annealed materials at temperatures up to 500 C.

Elevated-Temperature Tensile Properties

No additional tensile tests on zirconium or Zircaloy 2 have been conducted this month. The data reported last month concerning the effect of annealing time at temperature on the mechanical properties at the same temperature for 50 per cent cold-worked Zircaloy 2 indicated that additional tests are needed at 932 F and 800 F. It is planned to determine the mechanical properties of Zircaloy 2 at 932 F after 100 hours at 932 F and at 800 F after 500 hours at 800 F. These tests should provide more information on shape of the softening curve at these temperatures.

Creep Properties

Additional stress-rupture tests were completed on the annealed Zircaloy 2 transverse sheet specimens. These results are tabulated in Table B-1. The results at 230 C, which show that the total elongation was reduced by approximately a factor of 2 when the stress was reduced from 29,000 psi to 24,500 psi indicate that strain aging is occurring during testing at this temperature.

In addition to stress-rupture tests, long-time creep tests are in progress, but no data from these tests are yet available.

Tube Bursting

Additional tube-bursting tests were conducted at room temperature on Zircaloy 2 process tubes in an effort to determine the best method of end closure.

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TABLE B-1. STRESS-RUPTURE DATA FROM ANNEALED ZIRCALOY 2 SHEET⁽¹⁾

Temperature, C	Stress, psi	Time to Failure, hr	Elongation, per cent
230	29,000	0.3	54.4
230	26,000	16.7	36.8
230	24,500	22.3	28.0
230	23,800	136.8	27.5
475	20,000	3.8	32.8
500	19,000	0.35	42.0
500	14,500	10.0	50.0
500	10,000	225.0	50.4

(1) Transverse direction.

Four Zircaloy 2 tubes, two welded and two seamless, were ruptured successfully. Two of these tubes had welded plates as end closures, and two were sealed by a combination of welding and externally supported stainless steel end caps. The results are given in Table B-2.

TABLE B-2. BURSTING PRESSURES FOR ZIRCALOY 2 TUBES AT ROOM TEMPERATURE

Type of Tube	Place of Failure	Bursting Pressure, psi
Cold formed, welded seam	At welded seam	5400
Cold formed, welded seam	At welded seam	6250
Extruded, seamless	In thin wall section	6800
Extruded, seamless	In thin wall section	7100

The combination welded and mechanical seal appeared to be the most satisfactory method for closing the tubes, and tests at elevated temperatures were started.

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C. FUEL-ELEMENT DEVELOPMENT

D. C. Martin

Various fuel-element development programs are being continued. Most of the work on the aluminum-uranium alloys has been completed. Liquidus temperatures have been determined for the 24.5 and 16.0 w/o uranium alloy. Further efforts are being directed toward obtaining additional points on the liquidus line at 15 and 19 w/o uranium. Work on internal cladding of tubes has been temporarily suspended. In the work on extrusion cladding of flat plates, the extrusion container was broken in the course of experimental work. A new extrusion container is being constructed.

Preparation of Aluminum-Uranium Alloys

H. A. Saller, R. F. Dickerson, and E. L. Foster, Jr.

Aluminum-uranium alloys containing 14 to 18 w/o uranium are being studied. The program of study has been concerned with the development of casting techniques that would produce sound, homogeneous, cylindrical extrusion blanks, and also the confirmation or correction of the existing phase diagram in the range of 14 to 20 w/o uranium. Since a casting technique has been developed that produces sound homogeneous castings, present efforts are being directed toward the confirmation of the phase diagram and the determination of the effect of cooling rate on segregation of the castings.

Liquidus temperatures of the 24.5 and 16.0 w/o uranium alloys were found to be 954 and 755 C, respectively. These points were determined by thermal analysis. The eutectic composition was confirmed by metallographic techniques to be approximately 13.2 w/o. The peritectic horizontal extends to approximately 16.2 w/o uranium. Further efforts are being directed toward obtaining additional points on the liquidus line at 15 and 19 w/o uranium by noting changes in resistivity as the temperature is varied.

Studies concerned with the determination of the effects of cooling rates on ingot segregation are being continued.

Internal Cladding of Tubes

R. J. Fiorentino, D. B. Roach, and C. J. Slunder

Work on this program has been temporarily suspended.

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Extrusion Cladding of Flat Plates

R. J. Fiorentino, D. B. Roach, and C. J. Slunder

In the cladding study, work with the extrusion equipment to clad a 3-in.-wide flat plate has been continued. The results of the initial test made last month indicated that the core was restrained and, thus, only an aluminum sheath was extruded. Examination of the core showed that the mandrel wall had compressed against the wide surfaces of the core. This deflection was caused by the high pressure developed during the extrusion. In the next test, a core, undersize by 0.010 in., was tried with the idea that the core might pass through the mandrel-tip opening, even though the latter would be narrowed by deflecting. In addition, a steel insert to fit into the die opening was pinned to the core. The purpose of the insert was to center the undersized core in the mandrel and die openings, and also to aid in starting movement of the core through the mandrel. During the test, the extruding aluminum exerted pressure on the insert, and started the core moving as expected. However, the core moved only about 1 in., and then was restrained as in the previous test. Shortly afterward, the extrusion container broke at a pressure of 63,000 psi. It is believed that the relatively low die temperature (about 600 F) contributed substantially to this high extrusion pressure.

The construction of a new extrusion container is under way. Provisions are being made to supply additional heat to the die so that a die temperature close to 1000 F can be maintained.

Undercutting Corrosion

W. E. Berry and R. S. Peoples

Variables affecting undercutting corrosion of fuel elements are being studied. Current investigations are concerned with effects on undercutting corrosion of outgassing the core and/or the entire fuel-element assembly prior to pressure bonding. Considerable effort has been spent on obtaining a reproducible test sample of the "half-dollar" type, i. e., aluminum picture frame, aluminum cover plate, nickel-plated core. Erratic undercutting behavior has been observed in boiling-water tests with samples bonded 5 min at 950 F at pressures up to 6000 psi. To date, the variables responsible for this erratic behavior have not been isolated. Rather than spend more effort on determining these variables, it has been decided that samples will be outgassed and pressed at several pressures until a minimum pressure is reached which produces a sample resistant to undercutting. With such a sample, it should be possible to vary conditions of plating, pressing,

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etc., until those variables which promote undercutting corrosion are isolated. A group of samples is being prepared by bonding at 6000 psi and 950 F for 5 min. The nickel-plated cores will be outgassed prior to bonding. These samples will be corrosion tested with an intentional defect in one face. The results of the corrosion test will determine whether pressure should be raised or lowered to obtain minimum conditions which resist undercutting.

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D. PLANT ASSISTANCE TO MCW

J. R. Keeler

A program of plant assistance to Mallinckrodt Chemical Works (MCW) is in progress. Studies on the methods of preparation and properties of UO_3 and UO_2 were continued, and corrosion problems related to the operation of the uranium refinery are being investigated.

Identification of Uranium Oxides

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

The reactivities of various modifications of UO_3 (uranium trioxide) are being investigated as an aid to the production of active UO_3 and UO_2 . Previous studies have indicated that the reactivity of UO_3 toward hydration may be related to the prior UO_3 structure. Early work had shown that the structure of UO_3 depended upon the method employed to decompose the nitrate. Thus, it appears that the activity of UO_3 is related to the production method. Also, the sinterability of UO_2 was found to be related to the structure of the UO_3 from which the UO_2 was made.

During the past month additional data were obtained on the reactivity toward hydration of UO_3 samples described in Table D-1. These data indicate the following conclusions: (1) the reactivity of amorphous UO_3 is decreased when it is converted to Type C UO_3 by hydration and dehydration and (2) the reactivities of Types H and C (the crystalline modifications of UO_3) are essentially unchanged by hydration and dehydration. Type C UO_3 containing some nitrate is very active by this test. However, this result may not be significant, since after hydration and dehydration the activity is approximately the same as normal Type C UO_3 .

In addition, data were obtained from Mallinckrodt tests on reactivity of amorphous UO_3 toward hydrogen reduction and hydrofluorination; these data indicate an even greater difference in activity between amorphous and Type C UO_3 than was indicated by the hydration test.

A preliminary investigation has been made of the amount of oxygen sorbed at room temperature by UO_2 preparations, as a measure of UO_2 reactivity. A comparison with sinterability data indicates that air-oxidation activity may be a measure of sinterability of UO_2 . Samples which pick up the largest amount of oxygen on exposure to air appear to attain the highest sinter density. However, insufficient data are available at present to establish a definite relationship.

TABLE D-1. DESCRIPTION OF UO_3 PREPARATIONS AND THEIR REACTIVITY TOWARD HYDRATION IN WATER-SATURATED AIR AT 30C.

Sample	Treatment Prior to Firing		Type Before Hydration	Initial Rate of Hydration, g of H_2O per g of UO_3 per hr	Equilibrium Water Content, per cent H_2O	Type After Hydration	Type After Dehydration at 300 C	Reactivity After Dehydration		
	Temp, C	Atmosphere						Initial Rate, g of H_2O per g of UO_3 per hr	Equilibrium Water Content, per cent H_2O	Type After Rehydration
374	175	Low-pressure argon	Amorphous	1.46(a)	13.3(a)	A	C	1.05	10.8	A
20	200	Atmospheric-pressure air	Amorphous	1.00	27.8	A	C	0.85	8.4	A
33	250	Low-pressure argon	Amorphous	1.20	19.8	A	C	0.87	9.9	A
196	450	In air	H	0.17	8.4	G	H + C	0.21	8.7	G
32	175	Low-pressure argon	C	0.89	10.3	A	C	0.86	10.5	A
281	400	In air	C	0.30	7.2	A	C	0.22	9.0	A
209	MCW-Pot (Stage 4)	Air	C + nitrate	0.80	40.0	--	--	--	--	--
210	MCW-Pot (Stage 5)	Air	C + nitrate	0.50	34.0	--	--	--	--	--
211	MCW-Pot (Stage 6)	Air	C	0.41	30.1	A	C	0.72	7.1	A
212	MCW-Pot (Stage 7)	Air	C	0.32	9.1	--	--	--	--	--
213	MCW-Pot (Stage 8)	Air	C	0.31	8.1	--	--	--	--	--

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TABLE D-1. (Continued)

Sample	Treatment Prior to Firing		Type Before Hydration	Initial Rate of Hydration, g of H ₂ O per g of UO ₃ per hr	Equilibrium Water Content, per cent H ₂ O	Type After Hydration	Type After Dehydration at 300 C	Reactivity After Dehydration		
	Temp. C	Atmosphere						Initial Rate, g of H ₂ O per g of UO ₃ per hr	Equilibrium Water Content, per cent H ₂ O	Type After Rehydration
214A ₁	MCW-Pot (Stage 9, final)	Air	C	0.26	7.5	A	C	0.35	5.4	A
214A ₂	MCW-Pot (Stage 9, final)	Air	C	0.30	7.5	--	--	--	--	--

(a) These results were obtained on 46 C hydration of Sample 374.

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During the next period a number of samples of UO_3 are to be obtained from Mallinckrodt for hydration-reactivity studies. Additional data will be obtained on the sinterability and air-oxidation activity of various preparations of UO_2 .

Electrical and Magnetic Properties of UO_2

R. K. Willardson and H. L. Goering

The objective of this work is the correlation of the sintering characteristics of UO_2 with the electrical and magnetic properties both before and after sintering. An extensive study of the electrical conductivity and thermoelectric power has revealed a number of very interesting characteristics.

- (1) Specimens of MCW UO_2 which had been sintered at 2050 C had a very low electrical conductivity and conduction by electrons (n -type electrical conductivity).
- (2) An extrapolation of the electrical conductivity versus oxygen: uranium ratio indicates zero electrical conductivity at a ratio of about 2.01 rather than the stoichiometric ratio.
- (3) The energy-band separation in UO_2 as determined by the intrinsic conductivity data is about 3 ev.
- (4) The unusual changes in slope of curves relating the extrinsic electrical conductivity to reciprocal temperature occur in temperature regions where a change in phase might be expected according to the recent diagram of the equilibrium phases by Gronvald.
- (5) As the temperature is increased and the extrinsic electrical conductivity increases, the thermoelectric power also increases rather than decreasing as predicted by simple theory.

Specimens of MCW UO_2 which had been sintered at 2050 C have a very low electrical conductivity at room temperature and for Samples 1-1A-1 and 1-1A-4 conductivity is by electrons. Table D-2 summarizes these data. These results are surprising since the determinations of the oxygen:uranium ratio indicate about 2.5×10^{20} excess oxygen atoms per cm^3 , and interstitial oxygen atoms are associated with positive or hole conduction. The electrons which carry the electric current could be supplied either by an excess of uranium over the stoichiometric proportions or by impurities (with a valence

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TABLE D-2. ELECTRICAL PROPERTIES OF UO_2

Sample ^(a)	Oxygen: Uranium Ratio	Sinter Density, per cent of theoretical	Electrical Conductivity at 27 C, (ohm-cm) ⁻¹	Sign of Majority Carrier	Activation Energy ^(b) of Majority Carriers, b	Thermoelectric Power at 200 C, μ v per C
1-1A	2.011	86	300	Positive	0.40	--
1-1A-1	2.011	86	3.00	Negative	0.39	-110 ^(c)
1-1A-2	2.011	86	9.10	Positive	0.44	+325 ^(c)
1-1A-3	2.011	86	278	Positive	0.20	+700
1-1A-4	2.011	86	300	Negative	0.76	-500
1-1A-5	2.011	86	1.72	Positive	0.44	+350 ^(c)
1c-1A	2.036	79	1000	Positive	0.38	+215
1c-1B	2.072	--	3850	Positive	0.36	--
2c-1A	2.006	95	1460	Positive	0.28	+500
2c-1B	2.100	--	2630	Positive	0.42	--
3c-1A	2.024	84	1060	Positive	0.36	--
3c-1B	2.147	--	7400	Positive	0.38	--

(a) The details of the preparation of these samples of UO_2 , including crystallite size and lattice parameters, are given in the report 3MI-1043.

(b) The activation energy b is obtained from the relationship $\rho = Ae^{-b/2KT}$ and the temperature dependence of the electrical conductivity.

(c) Specimens believed to be heterogeneous containing both n- and p-type regions.

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greater than 4) replacing some of the uranium in the lattice. Thus, either the ignition method of determining the oxygen:uranium ratio could be in error, possibly due to the presence of impurities, or the effect of the excess oxygen could be compensated by the presence of an *n*-type impurity.

Previous experiments on the variation of the electrical conductivity of MCW UO_2 with oxygen:uranium ratio indicated that the conductivity (by positive carriers) increased linearly with oxygen content. However, the extrapolated point of zero conductivity occurred at a ratio of about 2.01 rather than at the expected stoichiometric ratio. On the other hand, Battelle "activated" Sample 2c-1A (ball milled) and Sample 4c-1A sinter to higher densities and become more nearly stoichiometric (according to the oxygen:uranium ratio), but retain the positive hole type of conduction which is characteristic of excess uncompensated oxygen. Thus it seems possible that one of the major differences between the "ordinary" and the "active" UO_2 is that a large portion of some impurity (probably not detectable by spectrographic techniques although the concentration should be 0.1 to 1 a/o) is removed from the latter by the activation process. However, any analysis of the electrical properties can be made much more complicated if phase changes occur. According to the recent diagram of the equilibrium phases by Gronvald, much of the excess oxygen could be taken up by a tetragonal second phase ($\text{UO}_{2.33}$) in the temperature region below 200 C, than by a U_4O_9 second phase at somewhat higher temperatures, but occurs in a single phase (apparently determined by the oxygen:uranium ratio) at still more elevated temperatures. Marked changes occur in the temperature dependence of the conductivity at temperatures which are in qualitative agreement with those expected. The tetragonal structure is merely an ordering of the interstitial oxygen in sites in planes perpendicular to the [001] direction of the fluorite cubic structure, while the U_4O_9 maintains the fluorite structure but presumably has an additional oxygen atom at the body center of the unit cell. Thus it seems probable that in all cases the excess oxygen over the ratio of 2.00 is available to furnish positive carriers for the extrinsic conductivity, but at a somewhat different activation energy.

The activation energy required to free a positive carrier from an excess oxygen atom appears to be: (1) about 0.3 ev if the oxygen is randomly distributed, (2) about 0.6 ev when the oxygen is in the U_4O_9 type arrangement, and (3) approximately 0.4 ev if the tetragonal structure is present. In Sample 2c-1A (ball milled), only the 0.3-ev conduction characteristics are observed.

The increase of the thermoelectric power with temperature poses a difficult problem. On the basis of the accepted model, a temperature-dependent population of current carriers (i. e., electrical conductivity) must necessarily lead to a thermoelectric power which decreases with increasing temperature.

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Battelle's results are not in agreement with such a model. Somewhat similar results have been reported for Cu_2O and SnS , but have not been satisfactorily explained.

Further studies of the electrical conductivity and thermoelectric power are planned.

The Corrosion Resistance of Selected Stainless Alloys

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

Some of the uranium-bearing materials now being digested in nitric acid at Mallinckrodt are of relatively high fluoride content. The fluoride-ion concentration of these liquors approaches 3 g per liter, which is sufficiently high to result in excessive corrosion of the Type 347 stainless steel digesters. Aluminum additions are being made to these solutions to help control this corrosion by complexing the fluoride ion. The aluminum addition also tends to increase the solubility of the uranium-containing materials. The fluoride-ion carry-over in the ether extraction phase of the refining is markedly reduced. Mallinckrodt has requested additional information concerning the amount of aluminum necessary to control the corrosiveness of these solutions to Type 347 stainless steel, particularly at welds.

In laboratory experiments, Type 347 stainless steel samples were exposed to boiling 45 per cent nitric acid containing 3 g per liter fluoride (see BMI-927). The addition of 3 g of aluminum per g of fluoride ion provided adequate corrosion protection for the unwelded samples.

Calculations were made of the corrosion rates of Type 347 stainless welds exposed to the above solution. Weld metal was found to corrode at rates up to five times those observed for sheet stock. Based on experimental results, an addition of 5 g of aluminum per g of fluoride resulted in adequate protection for the weld metal.

It had been suggested that beryllium might improve the corrosion resistance of copper to HF. Samples of beryllium copper and copper were exposed in boiling 38 and 48 per cent HF solutions. Laboratory results indicated that beryllium did not improve the corrosion resistance of copper to these solutions.

Tensile samples of ten stainless alloys are being evaluated in an atmosphere of cracked ammonia with sulfur present. In this new run, the exposure temperature has been increased from 1500 F to 1700 F. These additional tests are being undertaken as a result of recent information from Mallinckrodt indicating that higher local temperatures may occur in the reaction vessel than were originally anticipated.

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E. PROCESSING OF FEED MATERIALS

D. L. Keller

The improvement of uranium feed material and uranium feed-material processing methods are the objectives of current research studies for the National Lead Company of Ohio (NLO).

It has been demonstrated that, during the fabrication of uranium, hydrogen is picked up by the metal while the metal is submerged in heat-treating salt baths. The objectives of one program are to disclose the mechanism of hydrogen pickup as well as to develop salt-bath conditions which will lower this tendency.

Commercial ceramic refractories are being evaluated for their resistance to molten fluoride compounds as one step in demonstrating the feasibility of continuously reducing uranium fluoride to massive uranium metal. Seven different refractories have been heated in air in contact with sodium, aluminum, magnesium, and calcium fluorides at temperatures between 1000 and 1500 C.

In hopes of developing a more economical method for recovering metallic uranium from ingot croppings, the scavenging of carbon by zirconium is being investigated. Uranium melts with controlled additions of zirconium and carbon have been prepared and are presently being analyzed.

Studies concerned with the performance of plant solvent in the refinery have continued. Recent results indicate that a considerable decrease in DBP content occurred in the plant-solvent samples supplied by NLO representing a period of several months operation.

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 program is to develop salt-bath conditions which will lower the hydrogen pickup by uranium during heat treating.

In BMI-1043 it was reported that carbonates, chlorides, sulfates, phosphates, and silicates had been considered as possible components of a suitable salt bath. Of these, sulfates and phosphates were rejected on the basis of their affinity for water. Further study indicated that silicates do not appear suitable because of their high viscosity. This leaves carbonates, chlorides, or a mixture of the two to be investigated.

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A test program is being worked out which should provide a measure of the hydrogen pickup by uranium as a function of the water and hydroxyl-ion concentrations in the salt bath. Attempts will be made to correlate the water and hydroxyl-ion concentrations with the age of the salt bath and moisture in the atmosphere over the salt bath. These variables will be determined for various kinds of salt baths, namely, all carbonate, all chloride, and carbonate-chloride mixtures.

It is hoped that the test program will disclose the mechanism of hydrogen pickup by uranium. There seems to be some doubt as to whether water is physically dissolved in the salt bath and reacts with uranium directly, or whether the water reacts chemically with the salt bath to form hydroxides which in turn react with uranium to form hydrogen. Possibly, both reactions occur.

The salt mixtures (w/o) considered for the test program are 50-50 NaCl-KCl, 50-50 Na₂CO₃-KCl, and 46-54 Li₂CO₃-K₂CO₃.

It is clear that all of the salt systems studied may not be suitable for heat-treating baths, but a study of their performance should lead to information on the mechanism of hydrogen pick-up by uranium. Once that is understood, suitable remedial measures might be taken.

Refractories for Continuous Reduction of Uranium

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

In this portion of the NLO program, a study is being made of the suitability of commercial ceramic refractories for lining vessels used in the continuous reduction of uranium fluoride. Initially, slag resistance of the refractories is being assessed by a penetration test in which molten fluorides are heated in small containers made from the refractory specimens. After a predetermined heating time, the extent of fluoride penetration is observed by sectioning the container specimens.

Slag containers, made by drilling 3/4-in. -diameter holes, 2-1/2 in. deep, in 2-1/2 by 2-1/2 by 4-1/2-in. refractory blocks, were prepared last month from the commercial ceramics tabulated on the following page.

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<u>Brand</u>	<u>Supplier</u>
Monofrax H	Carborundum Company
Mullfrax	Carborundum Company
Alfrax K	Carborundum Company
Magnorite	Norton Company
Stabilized Zirconia	Norton Company
104	Corhart Refractories Company
Magnospall	Electro Refractories and Abrasives Corporation

This month, each of the refractory specimens was heated in air for 5 hr in contact with molten fluoride compounds at the following temperatures: NaF at 1000 C, AlF_3 at 1150 C, MgF_2 at 1450 C, and CaF_2 at 1500 C.

The cross sectioned specimens will be examined and those refractories that appear most resistant to slag attack will be similarly tested at 1650 C.

Metal-Recovery Studies

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

The ability of zirconium to scavenge carbon from uranium melts is being investigated as a possible means for recovering metallic uranium from ingot croppings.

Several heats were made with varying amounts of zirconium added. The zirconium addition, in the form of a uranium-20 w/o zirconium master alloy, was charged with the high-carbon (1200 ppm) uranium in an MgO-washed graphite crucible. All of the heats were held at 2550 for 30 min before pouring. The heats were bottom poured into 1-1/2-in. -diameter MgO-washed graphite molds. Sections from the top and bottom of the resulting ingots are being examined metallographically, and analyses for carbon and zirconium are in progress.

Degradation Products of Tributyl Phosphate

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

Phosphorus and uranium analyses have been completed on three samples of plant solvents supplied by NLO. On the basis of the phosphorus analyses of aqueous sodium carbonate extracts, the dibutyl phosphate contents of these solutions were 170, 40, and 2.4 mg per liter. These data indicate that a considerable decrease in DBP content had been effected during the several-month period covered by the samples.

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In uranium-containing solvents, DBP would be expected to combine with the uranium to form $\text{UO}_2(\text{DBP})_2$, with a molar ratio of 2:1. In all plant solutions, uranium in excess of this ratio is found, indicating that much of this uranium is tied up by diluent degradation products. The amount of this "excess uranium" appears to roughly correlate with the emulsion tendencies of the solvent. However, there appears to be no correlation with DBP content.

The solubility of $\text{UO}_2(\text{DBP})_2$ in 22-1/2 per cent TBP has been determined to be approximately 17 to 18 g per liter. With fresh solvent, some reduction to uranous dibutyl phosphate apparently occurs upon prolonged standing, based on the analysis of the green precipitate formed. The indicated solubility of $\text{U}(\text{DBP})_4$ in 22-1/2 per cent TBP is considerably below that of $\text{UO}_2(\text{DBP})_2$.

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F. GENERAL FUEL-ELEMENT DEVELOPMENT

H. A. Saller

The programs on general fuel-element development sponsored by the Reactor Division of the Atomic Energy Commission and studies for WAPD-PWR fall into three main classes: ceramics, metallurgy, and corrosion. Supplementing the corrosion research and reported for the first time in this section is the ORNL-supported study of the ignition limits in the hydrogen-oxygen-water system at elevated temperatures. Progress has been made on all phases.

In the ceramics programs, the study of methods for obtaining maximum strength in BeO is continuing. While MoSi₂ and graphite have adequate strength, uranium loss at high temperatures offers a problem. This is being investigated. Results of experiments on two materials, SiC and ruby glass, tend to confirm the validity of a theoretical relationship between thermal fracture and shape factor. Results from a third material are needed to make absolute confirmation of the validity of this equation. Studies on BeO to characterize sinterability are continuing.

Testing of a number of uranium alloys containing 3.5 to 15 w/o molybdenum or 3 to 20 w/o zirconium has continued. These studies are designed to obtain alloys suitable for high-temperature applications. The evaluation of low-melting alloys is still under way with no significant results available at this time. Preparation of fuel-element core mixtures of UC, U₂Ti, and UN in zirconium or stainless steel has continued. Some delays were encountered because of oxidation of the Zircaloy powder during crushing.

Corrosion tests on intentionally defected clad samples of pin-type and flat-plate fuel elements revealed much higher corrosion rates on the pin-type samples. This may indicate a lack of bond in these samples. The examination of the products formed on uranium exposed to hot water were continued. Results to date show that X-ray diffraction analysis alone will not explain obvious differences in the type of product obtained. Metallographic studies on both pure uranium and uranium alloys are still in progress.

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CERAMICSRefractory Fuel Elements

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

As an approach to attaining higher temperatures in power reactors, the refractory materials BeO, MoSi₂, and graphite are being developed as fuel-element matrices.

A study of the optimum calcining and sintering conditions for producing dense, strong BeO ceramics is nearing completion. Measurements of uranium losses from MoSi₂-UO₂ compacts in heated air were begun. Methods of controlling uranium losses from graphite elements are under study.

BeO

Previous work with ceramics made from readily sinterable BeO powders showed that strength and porosity were critically affected by the time and temperature used for powder calcination, as well as for compact sintering. A series of experiments is under way to determine the heat treatments that should be used to obtain optimum properties.

High-purity Be(OH)₂ supplied by the Brush Beryllium Company was calcined in air at temperatures from 1470 to 2190 F for 1 to 4 hr. Compacts were made from the resulting BeO powders by pressing in a rigid steel die at 20,000 psi using 3 w/o of camphor as a temporary binder. The compacts were sintered for 1 hr in flowing hydrogen at 2400 or 2600 F. The results of these tests are shown in Table F-1.

The data indicate that, within the range of the experiment, the sinterability of the BeO powder was more markedly dependent on temperature than on time of calcination. The powder prepared by calcination at 1830 F for 1, 2, or 4 hr appeared to be the most readily sinterable. However, the variation in density was so slight that the sintering trials will be repeated at lower temperatures in an attempt to determine more precisely which of the calcining conditions produce the most readily sinterable powder. From this, a calcination treatment will be selected for use in a study of the effect of sintering time and temperature on strength.

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TABLE F-1. EFFECT OF CALCINING CONDITIONS ON SINTERED DENSITY OF BeO COMPACTS

Calcing Conditions Temperature, F Time, hr		Bulk Density After Sintering 1 Hr at Indicated Temperature, F			
		2400		2600	
		G per Cm ³	Per Cent of Theoretical ^(a)	G per Cm ³	Per Cent of Theoretical ^(a)
1470	1	3.00	99.0	2.89	95.6
	2	2.98	98.5	2.95	97.5
	4	2.96	97.8	2.98	98.5
1650	1	2.99	98.7	2.98	98.5
	2	3.00	99.0	2.99	98.7
	4	2.97	98.1	3.00	99.0
1830	1	3.00	99.0	3.01	99.4
	2	3.00	99.0	3.01	99.4
	4	3.00	99.0	3.01	99.4
2010	1	2.87	94.8	2.98	98.5
	2	2.88	95.2	2.98	98.5
	4	2.85	94.2	2.98	98.5
2190	1	2.54	79.1	2.85	94.2
	2	2.46	81.3	2.78	92.0
	4	2.59	85.8	2.91	96.1

(a) Theoretical density of BeO taken at 3.025 g per cm³.CONFIDENTIAL
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Thermal Fracture of Ceramic Structures

A. K. Smalley and W. H. Duckworth

Research is being directed toward clarifying the problems arising from thermal stresses induced by nonuniform heating of ceramic structures. This program was undertaken with a view to evaluating the thermal-fracture properties of ceramic materials and shapes for potential use as reactor components.

In the past month, experiments were completed to check the reproducibility of fabrication and testing techniques used for obtaining recent shape-factor data on SiC-base specimens. In this work, a repeat series of SiC-base specimens was prepared and tested for resistance to thermal fracture. Each series consisted of about ten specimens of 2-in.-long tubes having circular inner boundaries and circular, square, or triangular outer boundaries. The results of these experiments indicated that there was a fair degree of reproducibility between the two series and that no statistically significant difference existed between the average Q_{\max} (power per unit length at fracture) of the two groups of circular shapes or between the average Q_{\max} of the two groups of triangles. A significant difference was observed between the Q_{\max} values for the two groups of square specimens, and determinations of the average specimen densities also showed a considerable difference in these values. The cause of this is unknown.

A comparison is made in the tabulation below of the values of Q_{\max} and relative shape-factors for the SiC-base specimens along with earlier data on sintered ruby specimens. The data shown for the SiC specimens were those considered most valid from the standpoint of average specimen density and average temperature at failure.

Outer-Boundary Configuration	SiC Specimens		Ruby Specimens	
	Average Power per Unit Length at Fracture, Q_{\max} , w per cm	Relative Shape Factor	Average Power per Unit Length at Fracture, Q_{\max} , w per cm	Relative Shape Factor
Circular	83.9 \pm 6.5(a)	1.00	39.8 \pm 0.45(a)	1.00
Square	74.9 \pm 3.5(a)	0.89	35.5 \pm 0.28(a)	0.89
Triangular	60.0 \pm 3.2(a)	0.72	29.9 \pm 0.89(a)	0.75

(a) 90 per cent confidence limits.

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These comparisons indicate the validity of the concept of separable shape and material factors for the three shapes and the two materials under study. Data on a third material are believed to be necessary for reasonably firm general conclusions.

In future work, investigations of UO_2 ceramics, as a third material, will be undertaken. Current effort consists of design and fabrication of forming equipment and development of forming techniques.

Characterization of Sinterable Oxide Powders

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

This research is directed toward the quantitative determination of factors affecting the sinterability of the refractory oxides of interest for nuclear reactor applications. In previous work, compacts of near theoretical density were made of BeO or MgO without resorting to compacting pressures or sintering temperatures higher than 20,000 psi or 3000 F, respectively. These results, obtained only on specially prepared oxide powders, indicated that both the preparation and calcination of the parent compound were significant factors controlling oxide sinterability.

Experiments are being conducted to determine the significance of the controllable factors involved in parent-compound preparation. Initial studies are concerned with $\text{Be}(\text{OH})_2$ precipitated from BeSO_4 solution, with special attention to the effect of precipitant compound, reactant concentration, and precipitate aging on the purity and sinterability of BeO made therefrom.

This month, preparations, by different methods, of 11 $\text{Be}(\text{OH})_2$ samples was completed. The hydroxides were decomposed by calcining in air at 1830 F for 2 hr, the residual BeO powders were compacted hydrostatically at 100,000 psi, and the compacts were sintered in hydrogen for 1 hr at 2400 F. The methods used for preparing the hydroxides and observations on the dried precipitate powders are given in Table F-2.

It was noted that the method of preparation had considerable effect on the bulk density of the precipitated $\text{Be}(\text{OH})_2$ powder. In general, boiling, or digesting the precipitate slurry near the boiling temperature, increased the density of the precipitate. The $\text{Be}(\text{OH})_2$ precipitated with gaseous NH_3 was somewhat denser than that precipitated with NaOH .

Some of the dried precipitates were examined spectrographically to determine the impurities. The results are given in Table F-3. The analyses showed that the $\text{Be}(\text{OH})_2$ precipitated with NH_3 was quite pure,

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TABLE F-2. PREPARATION AND PROPERTIES OF BERYLLIUM HYDROXIDES

Be(OH) ₂ Sample	Precipitant and Concentration, w/o	Concentration of BeSO ₄ ·4H ₂ O, w/o	Treatment Prior to Filtering	Powder Bulk Density, g per cm ³	
				Loose	Tapped
2 ^(a)	NaOH-25	40	Boiled 2 hr	0.73	0.93
3	NaOH-25	40	None	0.18	0.29
4	NaOH-1	2	None	0.25	0.36
5	NaOH-25	40	Digested 18 hr at 95 C	0.35	0.53
6	NaOH-1	2	Digested 18 hr at 95 C	0.32	0.50
7	NH ₃ -Gas	40	None	0.23	0.37
8	NH ₃ -Gas	2	None	0.24	0.32
9	NH ₃ -Gas	40	Digested 18 hr at 85 C	0.45	0.63
10	NH ₃ -Gas	2	Digested 18 hr at 85 C	0.63	0.90
11 ^(b)	NaOH-25	40	None	0.14	0.23
12 ^(b)	NH ₃ -Gas	40	None	0.28	0.37

(a) Precipitated Be(OH)₂ was dissolved in an excess of NaOH and reprecipitated by boiling.

(b) First precipitate of Be(OH)₂ was dissolved in H₂SO₄ and reprecipitated twice.

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and, except for sodium content, which was very high, that precipitated with NaOH was of equal purity. No significant increase in purity was attained by repeated solution and precipitation.

TABLE F-3. PURITY OF Be(OH)₂ PRECIPITATES^(a)

Sample	Precipitant	Times Precipitated	Impurities, ppm parts of BeO												Total
			Na	Al	S	Si	Ca	Mg	Fe	Ni	Mn	Pb	Su	Cu	
3	NaOH	1	>1000	100	5	80	75	20	50	<5	<1	5	<20	<1	>1360
7	NH ₃	1	100	50	5	80	75	50	100	10	10	5	<20	10	515
11	NaOH	3	>1000	100	5	80	50	20	50	20	5	5	<20	10	>1365
12	NH ₃	3	100	50	5	80	25	20	100	10	<1	5	<20	10	425

(a) Hydroxides were precipitated from a 40 w/o solution of BeSO₄·4H₂O.

Compacts of BeO made from the 11 specially prepared samples of Be(OH)₂ are being sintered in hydrogen at 2400, 2600, and 2800 F. Incomplete results of the sintering trials indicate that none of the specially prepared materials are as readily sinterable as BeO made from Brush high-purity Be(OH)₂. The compacts sintered at 2400 F had bulk densities lower than 70 per cent of theoretical.

Construction of gas-handling equipment for determination of surface areas and helium-displacement density of BeO powders was completed. One adsorption measurement, made by the BET method on a sample of active BeO, indicated a surface area for this powder of 7 m² per g. This is equivalent, for solid spheres, to an average particle diameter of about 0.3 μ.

Sintering trials, chemical analyses, and adsorption experiments will be continued in the effort to relate sinterability to surface areas and chemical purity of laboratory-prepared BeO powders.

Modified UO₂ Fuel-Element Cores

P. T. Woodberry, D. J. Bowers, and M. J. Snyder

This work in support of the WAPD-PWR program is a study of thermal cracking and water logging in UO₂ core containing additives. Cores containing 80 volume per cent or more of UO₂ in combination with various metals and ceramic materials are being studied.

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Work was continued on a reference material for comparison with WAPD pellets and the experimental core materials. Reference materials studied last month were made of UO_2 only. This month, the additives (Sterotex and polyvinyl alcohol) used by WAPD were added in fabricating the reference material. Compacts were made from as-received MCW UO_2 powder containing the additives; the compacts were hydrostatically pressed at 100,000 psi, and then sintered in a hydrogen atmosphere at 3200 F for 2 hr.

For the initial work on developing the modified fuel-element cores, bodies were made containing UO_2 in combination with 5, 10, or 20 volume per cent silicon or zirconia. The compacts were fabricated in the same manner as were the reference compacts except for the sintering temperature. The bulk densities and tensile strengths of sintered specimens, along with those of the reference compacts, are given in Table F-4.

The addition of silicon caused both a decrease in density and a reduction in tensile strength compared with the reference UO_2 compact. Although the addition of zirconia resulted in dense sintered compacts, additions above 5 volume per cent lowered tensile strength markedly.

The effect of varying sintering time and temperature on the physical characteristics of compacts of these compositions will be investigated further. The addition of other materials, as outlined previously, also will be studied.

METALLURGY

Uranium Alloys for High-Temperature Application

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

A study is in progress on selectively heat-treated binary uranium alloys containing 3.5 to 15 w/o molybdenum and 3 to 20 w/o zirconium. The objective of the program is to develop reactor fuels for operation above 700 C. Work is concerned with physical properties at elevated temperatures and with behavior of alloys under stress cycling.

Hot-hardness values of uranium-molybdenum alloys have been obtained on specimens containing both retained and transformed gamma structures. A general comparison of the two groups reveals the transformed 3.5 through 9 w/o molybdenum alloys are harder at room temperatures than are similar alloys quenched from 800 C. In addition, transformed uranium-12 and -15 w/o molybdenum alloys have greater hardnesses at 600 C and above. The

TABLE F-4. PHYSICAL PROPERTIES OF MODIFIED UO_2 COMPACTS

Composition, volume per cent			Sintering Temperature, F	Tensile Strength, psi	Bulk Density, per cent of theoretical	Theoretical Bulk Density ^(a) , g per cm ³
UO_2	Si	ZrO_2				
100 ^(b)	--	--	3200	5990	87.1	10.97
95	5	--	2500	4120	73.5	10.54
90	10	--	2500	3680	74.1	10.11
80	20	--	2500	3720	71.1	9.26
95	--	5	3050	6370	96.2	10.71
90	--	10	3050	3230	91.5	10.42
80	--	20	3050	2980	90.9	9.92

(a) Calculated on the following basis: density of UO_2 = 10.97 g per cm³; density of Si = 2.40 g per cm³; density of ZrO_2 = 5.73 g per cm³.

(b) Reference material.

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hardnesses of the balance of the retained and transformed gamma-phase alloys is in rough agreement with one exception. Transformed 3.5 w/o molybdenum has a greater hardness from 600 to 750 C than the same composition water quenched from 800 C.

Hot-hardness data are also available on uranium-3 through -20 w/o zirconium binary alloys. The data include results of four heat-treated conditions of each composition. Specifically the heat treatments are water quench from 800 C, furnace cool from 800 C, and two conditions of controlled cooling or transformation. The latter two groups of specimens were selected for hot-hardness measurements on the basis of microstructure and grain size.

For means of comparing hot-hardness of variously heat-treated uranium-zirconium alloys, a standard is necessary. The standard selected for this study is the hardness of uranium-zirconium alloys furnace cooled after 1 hr at 800 C (see BMI-1025). A general discussion of the remaining heat-treated alloys follows.

- (1) Alloys water quenched after 1 hr at 800 C have greater room-temperature hardnesses than the standard. Conversely, they are softer at 600 C.
- (2) Alloys heat treated by step or controlled cooling have lower room-temperature hardnesses than the standard. Step cooling uranium-3 w/o zirconium produces an increase in hardness over the standard in the range of 700 to 800 C. However, the uranium-10 w/o zirconium furnace-cooled specimens are harder than step-cooled specimens at 700 C and above.
- (3) Alloys isothermally transformed at 550 C have over-all hardnesses equivalent to those furnace cooled from 800 C. At 680 C, both 3 and 5 w/o zirconium isothermally transformed alloys are harder than the standard.

Dilation studies are in progress on alloys of both uranium-zirconium and uranium-molybdenum systems. In addition, specimens are being prepared for stress-cycling studies. After an evaluation of hot-hardness, dilation, and stress-cycling results, specimens of both systems will be considered for irradiation tests.

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Preparation and Properties of Low-Melting Alloys

H. A. Saller, R. F. Dickerson, and W. E. Murr

A program for the evaluation of low-melting uranium alloys for use as power-reactor fuel elements is in progress. The current phase of work is concerned with the construction and checking of equipment to be used for stress cycling specimens of selected alloys.

Last month, five alloys were listed on the basis of their good thermal-cycling behavior. These alloys have since been induction melted and cast into warm graphite molds in the form of large hollow cylinders. These cylinders are being machined to tubes 3 in. long with a wall thickness of 0.32 in. and an inside diameter of 1.5 in. These tubes will be used as specimens in the stress-cycling tests.

After evaluation of stress-cycling behavior, the better behaved alloys will be given complete physical-property tests.

Compartmentalized Fuel Elements

H. A. Saller, D. L. Keller, and G. W. Cunningham

A development program for the improvement of cermet-type fuel elements is currently in progress. In an effort to obtain composite fuel-element cores with high-uranium loadings and possessing desirable physical properties, present emphasis is being placed on the following material combinations: UC and U_2Ti fuel dispersions in a Zircaloy 2 matrix and UN dispersions in a stainless steel matrix.

The UC and U_2Ti powders are being prepared by arc-melting techniques followed by crushing in an inert atmosphere, while the UN and Zircaloy 2 powders are produced by low-temperature, gas-metal reactions with intermediate crushing operations if needed. Each of the production steps will be checked as possible sources of material contamination.

The as-cast UC has analyzed 4.5 w/o carbon (less than 0.05 w/o free carbon), 0.02 to 0.05 w/o oxygen, 0.008 to 0.012 w/o hydrogen, and 0.003 to 0.006 w/o nitrogen. The gas analyses of the as-cast U_2Ti fall within these ranges, and the only phase reported by X-ray diffraction is the delta (U_2Ti) phase. These materials are presently being reduced to powder.

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Starting sheet material for the preparation of Zircaloy 2 powder contained 0.003 w/o nitrogen, 0.023 w/o hydrogen, and 0.11 w/o oxygen. After hydriding, there was no measurable increase in oxygen content. However, after crushing under an inert atmosphere and dehydriding, the oxygen content increased to approximately 0.71 w/o. Modifications are being made in these two operations in an effort to obtain a higher grade powder.

Picture-frame-type packs of Zircaloy 2 and stainless steel have been prepared, so hot-rolling studies with cold-pressed core compacts should be initiated next month.

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

D. R. Grieser and E. M. Simons

A study is being made of the effect of the cladding bond characteristics and core-alloy composition on the corrosion of fuel elements containing pinhole cladding flaws. The reaction of these elements when suddenly subjected to 600 F water is observed photographically by using a windowed autoclave. Also, the evolution of hydrogen from the reaction is measured by recording the pressure changes as the test progresses.

Table F-5 summarizes tests of two coin-shaped and two pin-type bonded specimens, all containing uranium-5 w/o zirconium alloy cores. Though all of the specimens were supposed to have bonded cladding, the pin-type cores were completely oxidized in less than an hour, which, as the table shows, would be approximately the expected time if they were unbonded. This might indicate that the bonds in the pin-type elements were considerably weaker than those in the coin-shaped specimens, even though all of the bonds appeared sound by radiographic examination.

The next tests will be repeat runs of unbonded and unclad pin specimens containing pure uranium cores to check the corrosion rates found previously.

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TABLE F-5. CORROSION OF CLAD URANIUM-5 w/o ZIRCONIUM ALLOY FUEL-ELEMENT CORES

Specimen Type	Bonding Conditions	Measured Time for Complete Oxidation of Core, hr	Calculated ^(a) Time for Complete Oxidation of Core, hr	
			Unbonded Specimen	Bonded Specimen
Coin	7.5 hr at 600 psi and 1700 F	(10) ^(b)	0.13	5.4
Coin	Ditto	5.0	0.13	5.4
Pin	36 hr at 2000 psi and 1500 F	0.67	0.79	4.5
Pin	Ditto	0.67	0.79	4.5

(a) Based on $R = 4400 \text{ mg}/(\text{cm}^2)(\text{hr})$ at 600 F.

(b) Estimated, since specimen was three-fourths consumed after a 7-hr exposure.

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Mechanism of Uranium Corrosion

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

Studies of the composition, structure, and mechanism of formation of hot-water corrosion products on uranium are in progress. Previous studies of the corrosion products on production-grade uranium in 60 C water have indicated (1) that the product adhering to the metal has the UO_2 structure but has a composition of U_3O_8 and (2) that the loose yellow corrosion product has the structure of a hydrated UO_3 .

During the past month additional corrosion products were obtained and analyzed for phase differences by X-ray diffraction, and for oxygen content by weight loss on ignition to U_3O_8 . Although by visual comparison the corrosion proceeded differently in this run, the corrosion products gave the same structures by X-ray diffraction. Weight loss on ignition indicated the composition of the corrosion product adhering to the surface to be $\text{UO}_2.88$. Part of this extra oxygen, implied in the formula, may be in the form of adsorbed water. However, in carrying out this experiment, an attempt was made to remove the physically adsorbed water by washing with 200-proof alcohol and drying by evaporation before igniting the sample at 750 C. Thus it appears that X-ray diffraction analysis cannot be used alone in the identification of these corrosion products.

The observed differences in appearance of the specimens, resulting from the two series of corrosion experiments, are unexplained. Pitting was observed after a 6-1/2-hr exposure in the first test but did not occur in 150 hr in the second test, at which time the surface corrosion product flaked off. On further exposure, the corroding surface appeared uniformly rough over the entire specimen. The average rate of corrosion in the first test was $0.271 \text{ mg}/(\text{cm}^2)(\text{hr})$; in the second test, $0.862 \text{ mg}/(\text{cm}^2)(\text{hr})$. The differences in the visual appearance of the corrosion process may be attributed to some unintentional variations in the surface preparation prior to corrosion. This possibility is being investigated.

Correlation of Microstructure With Corrosion
Behavior of Uranium Alloys

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

A study of the relationship between microstructure and corrosion behavior of uranium alloys is being made in connection with the general fuel-element development program.

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Metallographic studies are being conducted on binary uranium alloys exposed to 100 C water. Specimens represent unalloyed uranium and alloys containing up to 12 per cent of aluminum, iron, molybdenum, nickel, niobium, silicon, tantalum, or zirconium in both the alpha-annealed and gamma-quenched conditions. Studies to date have indicated some differences in grain size and the amount of nonmetallic inclusions present in the alloys. Cracking of the 12 w/o iron alloys (both alpha and gamma treatments) appears to be associated with corrosion of the alpha pools in the delta (U_6Fe) matrix. A build-up of corrosion products in these areas results in high stresses, which ultimately cause cracking of the hard brittle delta matrix.

Although some differences in structure have been observed for the other alloys, no definite correlation between microstructures and corrosion properties has been established. These studies are being continued and expanded.

Compositional Variations in Uranium-Molybdenum Alloys

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

The program was originally requested by WAPD in support of their PWR program, and was a study of the effects of compositional variations on the corrosion behavior in 650 F degassed water of uranium-molybdenum alloys. Results of the program as originally outlined have been reported in BMI-1045. Corrosion data are being obtained on a few additional materials that were not available for reporting in BMI-1045 and are discussed below and summarized in Table F-6.

Silicon. Silicon additions in the range of 0.05 to 0.10 w/o were found to increase corrosion resistance of uranium-10.5 or -12.0 w/o molybdenum alloys. However, additions of 0.25 to 0.5 w/o silicon to the above binaries resulted in decreased corrosion resistance. Thus, 0.05 to 0.10 w/o silicon additions appear to give optimum corrosion resistance.

Zirconium. Addition of 1 w/o zirconium to uranium-10.5 or -12.0 w/o molybdenum alloys resulted in increased corrosion resistance. Additions of 2.0 to 4.0 w/o zirconium destroyed corrosion resistance of the binaries. An exception was the as-cast uranium-12.0 w/o molybdenum-2.0 w/o zirconium alloy, whose corrosion life is in excess of 56 days with corrosion resistance at least equal to that of the 12 w/o molybdenum binary.

Copper, Nickel, Platinum, Tungsten. Additions of these elements in the range 0.05 to 0.10 w/o resulted in improved corrosion resistance of the homogenized and the homogenized and aged 1 week 10.5 and 12.0 w/o molybdenum binary alloys. This same beneficial effect may also be true

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TABLE F-6. 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	Rate	Life	Rate	Life
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	0.25 Si	-0.32	7-14	--	0-3	-0.05	7-14
10.5	0.50 Si	-0.32	7-14	-0.36	14-21	-0.11	7-14
12.0	0.25 Si	-0.30	21-28	--	0-3	-0.08	3-7
12.0	0.50 Si	-0.28	7-14	-0.32	21-28	-0.12	14-21
10.5	2.0 Zr	-0.17	14-21	-0.93	7-14	--	0-3
10.5	4.0 Zr	-0.22	7-14	--	0-3	--	0-3
12.0	2.0 Zr	-0.14	>56	-0.65	14-21	--	0-3
12.0	4.0 Zr	-0.22	3-7	--	0-3	--	0-3
12.0	0.05 Cu	-0.14	>56	-0.08	>56	-0.04	35-42
12.0	0.10 Cu	-0.13	>56	-0.06	35-42	-0.05	14-21
12.0	0.05 Ni	-0.20	49-56	-0.08	42-49	-0.11	14-21
12.0	0.10 Ni	-0.12	>56	-0.10	21-28	-0.18	0-3
12.0	0.05 Pt	-0.16	>56	-0.06	>56	-0.05	21-28
12.0	0.10 Pt	-0.15	>56	-0.06	>56	-0.06	28-35
12.0	0.05 W	-0.17	49-56	-0.08	>56	-0.05	42-49
12.0	0.10 W	-0.16	>56	-0.10	42-49	-0.07	28-35

(a) Lowest observed rate.

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

(c) Heat treatment: Base - 900 C, 1 day, water quenched.

A - base plus 400 C, 7 days, water quenched.

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for as-cast alloys, but tests were not of sufficient duration to definitely establish this fact. Platinum additions appeared most beneficial followed, in descending order, by tungsten, copper, and nickel.

Ignition Reaction Limits in the Hydrogen-Oxygen-Water
System at Elevated Temperatures

E. F. Stephan, N. S. Hatfield, and R. S. Peoples

Studies for ORNL of the reaction limits of a 2:1 hydrogen-oxygen mixture in saturated water vapor in the 3-in. -diameter autoclave and the effect of dilution with helium on the reaction limits of a 2:1 hydrogen-oxygen mixture in saturated water vapor in the microautoclave were continued.

The results of the tests so far in the microautoclave confirm previous results with the 1:1, 1:2, and 1:3 hydrogen-to-oxygen mixtures, namely, the addition of 200 psia of helium reduces the amount of the hydrogen-oxygen mixture required for reaction to take place. At 400 F, the amount is reduced from about 85 psia of the hydrogen-oxygen mixture with no helium to about 65 psia when 200 psia of helium were added. At 450 F, the reduction is from 145 psia to 85 psia and, at 475 F, both with and without helium, the limit is about 195 psia of the mixture. It appears that helium is not an effective diluent to inhibit the reaction at these temperatures.

In the 3-in-diameter autoclave at 505 F, the hydrogen-oxygen mixture, at a partial pressure of 8 psia, reacted. The limit at this temperature in the 2.5-in. -diameter autoclave was about 100 psia and over 200 psia in the microautoclave. At these temperatures and pressures, ignitions are difficult and tests are repeated several times to assure that reaction or failure to react is certain.

This work will continue and an attempt will be made to measure the peak reaction pressures of reactions as the partial pressures of the hydrogen-oxygen mixtures are gradually increased above the reaction limit.

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G. STUDIES OF ZIRCONIUM-URANIUM ALLOYS

H. A. Saller

The widespread interest in zirconium-uranium alloys has led to the sponsorship by the Reactor Development Division of the Atomic Energy Commission of a broad program to study zirconium-uranium alloys in the range up to 70 w/o uranium.

Based on examination of data available in the literature, a program was formulated and is well under way. The results, which so far are not definitive, are given in the sections that follow.

Constitution of Zirconium-Uranium Alloys

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

A quantitative study to determine the composition limits of the alpha-plus-beta-zirconium region of the zirconium-uranium system is planned with the intention of establishing the binary system by extrapolation.

A preliminary mathematical analysis of the experimental requirements has been made. However, the need for actual experimental data is indicated. Initial quantitative measurements are planned on heat-treated zirconium-22 and 40 w/o uranium samples in order to determine the precision with which the experimental measurements can be made. An analysis of the resulting data should provide a basis for the selection of additional alloy compositions.

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

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

The transformation kinetics of zirconium-uranium alloys containing up to 20 w/o uranium are being investigated in order to better interpret the heat-treating behavior and mechanical properties of such alloys. Currently, two alloy series are being studied; one contains 0.094 w/o oxygen and the other 0.27 w/o oxygen. High-purity alloys are currently being fabricated.

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The information obtained can conveniently be subdivided as outlined in the sections following.

Quenched Structures

Wafers, 1/16 in. thick by 1/2 in. in diameter, were heated in air for 30 min at 900 C and water quenched. The following hardness values were obtained on a series of alloys containing 0.094 w/o oxygen:

Nominal Composition, w/o uranium	Hardness, Rockwell A
7	63.5
10	67
15	70.5

Microstructures showed primary alpha phase surrounded by an acicular matrix for all three alloys. The amount of primary alpha as determined by lineal analysis decreased with increasing uranium content.

X-ray diffraction patterns (spectrometer-goniometer) revealed the presence of alpha-zirconium solid solution and epsilon phases and, possibly, alpha prime (martensite). The angle traversed during the X-ray analysis was not large enough to reveal definitely the presence of alpha prime, due to the coincidence of many of the lines of alpha and alpha prime. Furthermore, a preferred orientation of the rod shifted some lines noticeably. The presence of the primary alpha indicated undue oxygen contamination with a resultant increase of the alpha-plus-beta to beta transformation temperature. Consequently, the alloys were solution heat treated in the two-phase field, and an enriched-beta composition resulted from the partitioning of uranium and oxygen between the alpha and beta phases.

Subsequent heat treatments were performed on specimens which were solution treated in a neutral salt bath at 1000 C. This temperature was above that at which the alpha plus beta transforms to beta.

A 10 w/o sample quenched from 1000 C, after 30 min at temperature, gave a DPH hardness of 258. The microstructure showed former beta grain boundaries and a basket-weave acicular structure. An X-ray pattern revealed strong alpha and epsilon reflections.

A second 10 w/o wafer was held at 1000 C for 120 min and water quenched. The hardness was now 324 DPH, and the structure appeared to be retained beta with a finely dispersed phase not clearly resolved at 1000X. An X-ray pattern showed strong alpha reflections and very weak epsilon reflections. Once again, a small angle of scanning did not permit all lines to

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be recorded, and consequently, if a transition phase were present, the coincidence of reflections of the various phases did not permit an identification to be made. Future work will include X-ray analysis of silver samples by transmission techniques in order to establish the presence or absence of a transition phase.

The hardnesses of the 7 w/o and 15 w/o alloys quenched from 1000 C (60 min at temperature) are 274 and 433 DPH, respectively. A plot of hardness versus alloy content shows a sharp increase at 11.5 w/o uranium (actual composition of nominal 10 w/o alloy). The microstructures from 11.5 w/o uranium and higher show a pseudobeta structure. The increased hardness of this structure may possibly be attributed to a transition phase similar or analogous to the omega phase in titanium-base alloys.

Isothermal Transformation

Four wafers of 10 w/o alloy were solution treated at 1000 C for 60 min, quenched into a salt bath at 525 C, held for 50, 100, 200, and 400 min, respectively, and quenched into water at room temperature. X-ray patterns revealed the existence of alpha and epsilon in both the 50- and 400-min samples. Microstructures of these two specimens contained small bars of proeutectoid alpha (more present in the 400-min alloy) dispersed throughout the matrix. The beta grain boundaries contained a light-etching, fanlike constituent (acicular) that grew into the beta grains. The remainder of the matrix was a dark-etching acicular phase. It is thought that the grain-boundary phase was the transformation product, alpha plus epsilon, and that the dark, acicular matrix was martensite formed from the untransformed beta. Microautoradiographs will be made to determine the relative uranium contents and, possibly, to thus identify the phases.

Dilatometry

An improvised, quenching dilatometer was used to measure the dilatation of a 10 w/o uranium-alloy solution heat treated at 900 C and isothermally transformed at 525 C. The alloy showed a very slight expansion (almost negligible) for 100 min followed by a contraction of about 3.5 per cent over about 420 min, and finally a rapid expansion greater than 6 per cent over a period of about 200 min. The sample microstructure showed primary alpha, an alpha grain-boundary network, and what appeared to be a lamellar matrix. This specimen, also, never reached the beta region and, consequently, underwent an enrichment of the beta phase. The dilatometric curve seemingly indicates a secondary reaction with a rate greater than that of the primary reaction. This behavior suggests the possibility of an intermediate phase or complications arising from the enriched-beta

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decomposition. Electron microscopy showed that the matrix was neither lamellar nor acicular but a random dispersion of rounded plates and bars. This structure does not represent that of a true eutectoid decomposition.

Future Work

The construction of a quenching, recording dilatometer is nearing completion. It will be used for isothermal-transformation studies and adapted for high-speed dilation versus temperature service for M_s determinations.

Metallographic and automicroradiographic techniques will be used to identify the phases formed and to determine the solid-state reactions. X-ray work will be continued in order to clarify the transition-phase hypothesis.

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

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

A study of the transformation kinetics of the beta-zirconium-to-epsilon decomposition in alloys containing 20 to 70 w/o uranium is planned. The last of the alloys in this series are now being fabricated and experimental work aimed at achieving a description of the decomposition will begin shortly.

Meanwhile, specimens of the 50 w/o uranium alloy have been prepared and heat treated for study. These specimens have been annealed 1 hr at 800 C, water quenched, and then transformed at 500 C for various periods of time. Microstructural and hardness changes are to be correlated with resistance changes of specimens similarly treated. A set of specimens of this alloy has also been isothermally transformed at 500 C after 1 hr at 800 C for a comparative study.

Equipment is now available for the study of resistance changes during transformation of the retained beta and measurements are to begin shortly.

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Heat Treatment of Zirconium-Uranium Alloys

H. A. Saller, F. A. Rough, and W. Chubb

Because zirconium-uranium alloys are potentially very promising as fuel-element materials for nuclear reactors, a program has been undertaken to further clarify the heat-treatment behavior of these alloys. Alloys of interest to the present program may contain up to 70 w/o uranium. The effect of contamination on heat treatment is also being investigated. For this purpose, zirconium containing 300 to 3000 ppm of oxygen is being used as the base for different alloys.

End-quench tests are being performed as a preliminary to other heat-treatment studies. The results to date show that alloys containing 7, 10, and 15 w/o uranium transform by a martensite-type reaction when water quenched from 900 C. At slower cooling rates, transformation starts at the beta grain boundaries and results in the typical "acicular alpha" structure. The etching characteristics of this acicular alpha structure indicate that it is a two-phase structure, probably alpha plus epsilon at room temperature. Because the formation of acicular alpha begins at grain boundaries, the original beta grain boundaries are quite distinct in this structure. The martensite structure, because of its uniform chemical composition, is much more difficult to etch and beta boundaries are virtually invisible.

End-quench tests on a series of alloys containing 22 w/o uranium and varying amounts of oxygen show that beta is retained at the fastest quenching rates. This retained beta is quite hard, indicating that transformation has begun. The alloy containing the least oxygen showed a hardness peak of about 500 DPH at 0.02 in. from the quenched end of the bar. Additional oxygen caused the hardness peak to become broader so that the hardness remained virtually constant in the first 0.02 in. of a bar containing about 2500 ppm oxygen. This effect may have been caused by the presence of alpha zirconium in the bars at 900 C.

End-quench tests on zirconium alloys containing 40 to 60 w/o uranium and various amounts of oxygen produced almost identical results regardless of composition. In each case the retained beta on the quenched end had a hardness between 200 and 270 DPH; and a hardness peak of 430 to 450 DPH was observed within 1/2 in. of the quenched end. The hardness peak occurred at 1/8 in. from the quenched end for the 40 w/o uranium alloys and at about 1/4 in. from the quenched end for the 45, 50, 55, and 60 w/o uranium alloys. This indicates that the beta-decomposition process occurs at a slightly slower rate in the 45 to 60 w/o uranium alloys than in the 40 w/o uranium alloys. This observation is in agreement also with the theory that beta decomposition occurs to a limited extent during water quenching of the 22 w/o alloy.

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The structures of the end-quench bars containing 40 to 60 w/o uranium are clearly retained beta for half the distance to the hardness peak. Before the hardness peak is reached, subgrain boundaries begin to appear within the beta grains. Since subgrains are undoubtedly present in beta grains before transformation begins, it is not necessary to postulate a nucleation and growth process for the appearance of these subgrain boundaries; in fact, no very small subgrains were observed. It would appear that the strains involved in the process of transformation cause the migration of dislocations to subgrain boundaries, thereby increasing their angular relations. As a result, the subgrain boundaries appear more and more pronounced as transformation proceeds. No change in size of the subgrains was observed in the end-quench bars. Acicular alpha zirconium appeared in the subgrain boundaries of the 40 w/o uranium alloys at about 1-1/2 in. from the quenched end.

Alpha zirconium was present at 900 C in a 50 w/o uranium alloy containing about 1500 ppm oxygen, but no acicular alpha was observed in the bar after quenching. This amount of oxygen produced no change in the hardness in the first inch of the end-quenched bar, but the second and third inches of the bar were noticeably harder than the corresponding regions of a bar containing nominally 150 ppm oxygen.

A longitudinal slice from an end-quenched bar containing 50 w/o uranium has been submitted for corrosion testing. This test may show whether retained beta or transformed beta is more desirable for corrosion resistance.

Future work will include end-quench tests on alloys that are now in process of fabrication. Attempts to develop processes for surrounding grains of epsilon with alpha zirconium are continuing.

Corrosion of Zirconium-Uranium Alloys

W. E. Berry and R. S. Peoples

The corrosion behavior of zirconium-uranium alloys is being studied as part of the over-all AEC program to investigate the properties of zirconium-uranium alloys. Corrosion tests are being conducted in 680 F degassed water.

Testing of zirconium-22 w/o uranium alloys heat treated to produce a variety of microstructures is continuing. A summary of results obtained to date is presented in Table G-1. Samples from four of the six heat treatments under study continue to lose weight and corrode at a constant rate, as

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

Heat Treatment	Total Exposure, hr	Total Wt Change, mg per cm ²	Corrosion Rate ^(a) , mg/(cm ²)(hr)
(1) 1550 F, 36 hr, furnace cooled	2016	158.0	-0.07
(2) Rolled at 1000 F; alternately cold swaged and annealed at 1000 F; 1000 F, 1 hr; furnace cooled	840 ^(b)	-48.0	-0.05
(3) 1550 F, 36 hr, furnace cooled to 1200 F at 0.5 F per min; furnace cooled to room temperature	1680	-89.0	-0.04
(4) 1550 F, 36 hr, water quenched; reheated to 1020 F, held 22 days, furnace cooled	1680	-134.0	-0.09
(5) 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	1680	-51.0	-0.01
(6) 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	1680	-165.0	-0.10

(a) Corrosion rate calculated at maximum exposure.

(b) Samples alternately gained and lost weight with each 168-hr exposure after 840 hr.

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reported in BMI-1043. Samples given the fifth heat treatment developed an adherent film and steadily gained weight through a 1176-hr exposure. However, at a 1344-hr exposure, the film began to break up and the samples lost weight. At a 1680-hr exposure, the rate of weight loss began to decrease and has not yet become constant. The heat treatment employed was: 1550 F, 36 hr, furnace cooled; reheated to 1550 F, quenched to 1020 F, held 0.5 hr; and reheated to 1300 F, held 10 hr, quenched to 1020 F, held 1 hr, and water quenched. As reported in BMI-1043, samples which were alternately cold swaged and annealed at 1000 F lost weight at a constant rate through a 840-hr exposure and then alternately began to gain and lose weight with each successive exposure (168 hr). An attempt will be made to correlate microstructure with this erratic behavior. The following samples will be examined: (1) one which is gaining weight, (2) one which is losing weight, and (3) an untested sample.

Radiation Stability of Zirconium-Uranium Alloys

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

The study of the radiation stability of zirconium-uranium alloys is continuing. Zirconium-uranium alloys (22 and 40 w/o uranium) which were irradiated will be investigated in the first phase of this work.

Specimens of both the 22 and 40 w/o uranium alloys which were irradiated below the transformation temperatures will be thermally cycled through the transformation temperature in an attempt to correlate the effects of inpile cycling with postirradiation cycling. Specimens of zirconium-40 w/o uranium which had 1.65 and 4.5 total a/o burnup will be thermally cycled in NaK-filled capsules. The rate of fission-gas release and the amount of fission-product release will be measured. The details of this initial phase of the program are now being worked out.

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H. CORROSION STUDIES OF ZIRCONIUM

R. S. Peoples

The research described in this section covers the AEC Reactor Development Division's studies on the corrosion behavior of zirconium-base cladding materials for high-temperature water-cooled reactors. Also included are ORNL-supported studies of zirconium oxide films and electrocladding zirconium for improved corrosion resistance. Extended-exposure data continue to show that Zircaloy 2 is an excellent cladding material which can tolerate considerable amounts of hydrogen, oxygen, or nitrogen before corrosion resistance is destroyed. Investigations are also in progress which support the Zirconium Corrosion Committee's program to develop new zirconium-base alloys. Principal effort has been directed toward a study of zirconium alloys containing tin, iron, and/or nickel.

Fundamental studies are being initiated to study the reaction of zirconium with water vapor at subatmospheric pressures.

In other investigations, the role of hydrogen in breakaway in corrosion rates is being studied. Data indicate that the role of hydrogen is to damage the surface layer rather than to cause lowered resistance due to the presence of a hydride phase.

A phase-identification study also is being made of the oxide films formed on zirconium alloys during exposure to high-temperature water.

Corrosion of Zirconium and Zirconium Alloys

W. K. Boyd and R. S. Peoples

Corrosion studies to determine the effect of impurity and alloy additions on the corrosion behavior of sponge zirconium and sponge-base alloys are being continued. Tests are being conducted in 600 and 680 F degassed water and 750 F steam (1500 psi).

Zircaloy 2 samples representing seven different melts continue to exhibit a tarnish film and low weight gains (55 to 65 mg per dm²) after approximately 30 months of exposure to 600 F degassed water.

In addition, the effect of hydrogen, nitrogen, and oxygen on the corrosion behavior of Zircaloy 2 is being studied.

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The extended-exposure data described below (total 182 days in 680 F degassed water) for gas-impregnated samples continue to support earlier observations.

- (1) Zircaloy 2 can tolerate up to 390 ppm nitrogen before corrosion resistance is impaired. Samples containing more than 390 ppm exhibited early failure.
- (2) Oxygen additions up through 6000 ppm do not affect corrosion resistance of Zircaloy 2. However, failure occurred at the 8000-ppm level.
- (3) No effect of hydrogen in the range of 500 to 1500 ppm was observed. Higher levels were not investigated.

Zircaloy 2 samples containing oxygen and nitrogen added as master alloys during melting are showing similar corrosion behavior after up to 196 days of exposure to 600 and 680 F degassed water.

Zirconium Corrosion
Committee Program

In connection with the Committee's program to develop new zirconium-base alloys, the corrosion behavior of zirconium-0.25 to 0.50 w/o tin alloys containing from 0.04 to 0.45 w/o iron and/or nickel is being studied in 750 F steam (1500 psi) and 680 F degassed water. Specimens representing each alloy composition were evaluated in two heat-treated conditions, namely, (1) vacuum annealed 1 hr at 775 C and furnace cooled, and (2) water quenched after a 1-hr soak at 900 C in vacuum.

Corrosion data summarized in Table H-1 indicate no significant effect of heat treatment on the corrosion behavior of either the tin-iron or tin-nickel alloys. In general, the tin-nickel alloys are showing better resistance to 750 F steam than are the tin-iron alloys after similar exposure times. However, both alloy series are equally resistant to 680 F degassed water.

In addition, samples of 30 ingots prepared at the BuMines for Zircaloy 3 evaluation are being exposed to 680 F degassed water and 750 F steam (1500 psi). These ingots represent ternary and quaternary combinations of 0.25 and 0.50 w/o tin and 0.2 to 0.3 w/o iron plus either 0.2 w/o nickel or 100 to 150 ppm nitrogen or 50 through 200 ppm of aluminum. Each alloy was studied in both the vacuum-annealed and water-quenched conditions. Corrosion data based on up to 105 days of exposure in 750 F steam and 126 days of exposure in 680 F water are presented in Table H-2. The vacuum-annealed samples show a light oxide pattern after exposure in both 750 F steam and 680 F water, as do quenched samples exposed to 750 F steam.

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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 per dm ²	Remarks ^(a)	Exposure Time, days	Weight Gain, mg per dm ²	Remarks ^(a)	Exposure Time, days	Weight Gain, mg per dm ²	Remarks ^(a)	Exposure Time, days	Weight Gain, mg per dm ²	Remarks ^(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	154	83	M	10	1680	W	28	Lost weight	W, F
463	Unalloyed	1-1/2	839	W	154	69	M	10	1325	W	28	66	W, F
464	0.22Sn-0.28Fe	106	108	M	154	31	G	136	109	M	168	37	G
465	0.23Sn-0.30Fe	106	103	M	154	33	G	136	109	M	168	33	G
466	0.22Sn-0.38Fe	130	100	M	154	33	G	136	104	M	168	37	G
467	0.22Sn-0.39Fe	130	100	M	154	29	G	136	100	M	168	33	G
469	0.25Sn-0.27Fe	112	102	M	154	26	G	142	90	M	168	39	G
468	0.25Sn-0.28Fe	112	105	M	154	26	G	136	100	M	168	31	G
470	0.25Sn-0.33Fe	130	98	M	154	28	G	142	104	M	168	38	G
471	0.25Sn-0.34Fe	112	107	M	154	32	G	136	105	M	168	40	G
473	0.27Sn-0.25Fe	106	105	M	154	31	G	142	89	M	168	34	G
472	0.29Sn-0.25Fe	106	115	M	154	26	G	142	102	M	168	37	G
475	0.27Sn-0.28Fe	130	91	M	154	33	G	142	93	M	168	40	G
474	0.28Sn-0.34Fe	106	104	M	154	28	G	136	100	M	168	39	G
477	0.47Sn-0.44Fe	112	112	M	154	32	G	142	102	M	168	42	G
478	0.51Sn-0.47Fe	130	108	M	154	34	G	136	113	M	168	32	G
481	0.52Sn-0.47Fe	130	106	M	154	32	G	136	105	M	168	42	G
479	0.50Sn-0.50Fe	130	96	M	154	34	G	136	110	M	168	46	LM
476	0.49Sn-0.51Fe	124	100	M	154	32	G	142	100	M	168	44	G
480	0.51Sn-0.53Fe	124	102	M	154	32	G	136	104	M	168	46	LM
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	154	111	W	26	Lost weight	W, F	42	231	W

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TABLE H-1. (Continued)

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Heat	Alloy Content, w/o	750 F Steam			680 F Water			750 F Steam			680 F Water		
		Exposure Time, days	Weight Gain, mg per dm ²	Remarks ^(a)	Exposure Time, days	Weight Gain, mg per dm ²	Remarks ^(a)	Exposure Time, days	Weight Gain, mg per dm ²	Remarks ^(a)	Exposure Time, days	Weight Gain, mg per dm ²	Remarks ^(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 (Continued)													
491	0.17Sn-0.03Ni	142	80	M, S, F	154	47	G	140	70	M	140	42	G
490	0.18Sn-0.04Ni	142	85	M	154	42	G	140	61	M	140	32	G
492	0.13Sn-0.08Ni	142	74	M	154	33	G	140	Lost weight	S, F	140	35	G
493	0.18Sn-0.06Ni	142	69	M	154	38	G	140	63	M	140	35	G
495	0.17Sn-0.19Ni	142	75	M	154	37	G	140	65	M	140	39	G
494	0.19Sn-0.19Ni	142	77	M	154	36	G	140	71	M	140	34	G
496	0.21Sn-0.04Ni	142	66	M	154	48	G	140	56	M	140	36	G
497	0.22Sn-0.04Ni	142	90	M	154	48	G	140	68	M	140	34	G
498	0.22Sn-0.07Ni	142	79	M	154	37	G	140	Lost weight	S, F	140	36	G
499	0.22Sn-0.08Ni	142	81	M	154	48	G	140	70	M	140	32	G
501	0.21Sn-0.20Ni	142	86	M	154	37	G	140	90	M	140	38	G
500	0.22Sn-0.41Ni	142	79	M	154	37	G	140	86	M	140	35	G
502	0.27Sn-0.03Ni	142	86	M	154	48	G	140	Lost weight	S, F	140	32	G
503	0.27Sn-0.04Ni	142	87	M	154	46	G	140	33	S, F	140	35	G
505	0.27Sn-0.08Ni	142	83	M	154	39	G	140	39	S, F	140	36	G
504	0.28Sn-0.08Ni	142	88	M	154	37	G	140	72	M	140	36	G
506	0.26Sn-0.19Ni	142	93	M	154	38	G	140	75	M	140	34	G
507	0.25Sn-0.20Ni	142	119	M	154	38	G	140	81	M	140	40	G
508	0.56Sn-0.04Ni	142	72	M	154	46	G	140	87	M	140	35	G
509	0.56Sn-0.04Ni	142	86	M	154	32	G	140	80	M	140	33	G
510	0.54Sn-0.07Ni	142	89	M	154	36	G	140	84	M	140	37	G
511	0.56Sn-0.07Ni	142	93	M	154	36	G	140	80	M	140	33	G
513	0.51Sn-0.18Ni	142	100	M	154	38	G	140	94	M	140	34	G
512	0.54Sn-0.20Ni	142	100	M	154	37	G	140	91	M	140	35	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 per dm ²	Remarks ^(a)	Exposure Time, days	Weight Gain, mg per dm ²	Remarks ^(a)	Exposure Time, days	Weight Gain, mg per dm ²	Remarks ^(a)	Exposure Time, days	Weight Gain, mg per dm ²	Remarks ^(a)		
Heated 1 Hr at 775 C in Vacuum and Furnace Cooled						Heated 1 Hr at 900 C in Vacuum and Water Quenched									
						<u>Tin, Iron, and Nickel</u>									
483	0.51Sn-0.16Fe- 0.090Ni	124	104	M	154	37	G	136	148	M	168	64	G		
482	0.49Sn-0.23Fe- 0.097Ni	130	83	M	154	34	G	136	105	M	168	39	G		
485	0.47Sn-0.27Fe- 0.13Ni	130	108	M	154	31	G	136	107	M	168	50	G		
484	0.46Sn-0.31Fe- 0.13Ni	130	102	M	154	31	G	136	104	M	168	42	G		
486	0.48Sn-0.38Fe- 0.18Ni	130	88	M	154	33	G	124	107	M	168	46	G		
487	0.48Sn-0.44Fe- 0.18Ni	130	97	M	154	32	G	124	107	M	168	50	G		

(a) Key to remarks:

G - Black tarnish film (good material)

M - Milky

LM - Light milky

W - White oxide

F - Flaking (heavy oxide).

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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 per dm ²	Remarks(a)	Exposure Time, days	Weight Gain, mg per dm ²	Remarks(a)	Exposure Time, days	Weight Gain, mg per dm ²	Remarks(a)	Exposure Time, days	Weight Gain, mg per dm ²	Remarks(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	105	52	M, WP	126	38	G, WP	99	65	M, WP	112	28	G
984	0.25Sn-0.25Fe	105	52	M, WP	126	39	G, WP	99	59	M, WP	112	32	G
996	0.25Sn-0.25Fe	105	52	M, WP	126	38	G, WP	99	67	M, WP	112	29	G
997	0.25Sn-0.25Fe	105	51	M, WP	126	37	WP	99	54	M, WP	112	28	G
1001	0.25Sn-0.25Fe	105	76	M, WP	126	53	G, WP	99	57	M, WP	112	33	G
975	0.50Sn-0.40Fe	105	53	M, WP	126	40	G, WP	99	66	M, WP	112	37	G
983	0.50Sn-0.40Fe	105	55	M, WP	126	40	G, WP	99	62	M, WP	112	28	G
1000	0.50Sn-0.40Fe	105	63	M, WP	126	41	G, WP	99	73	M, WP	112	30	G
998	0.50Sn-0.40Fe	105	57	M, WP	126	40	G, WP	99	61	M, WP	112	28	G
1003	0.50Sn-0.40Fe	105	96	M, WP	126	56	M, WP	99	99	M, WP, S	112	39	G
990	0.50Sn-0.20Fe- 0.20Ni	105	55	M, WP	126	38	G, WP	99	62	M, WP	112	31	G
985	0.50Sn-0.20Fe- 0.20Ni	105	49	M, WP	126	33	G, WP	99	58	M, WP	112	33	G
995	0.50Sn-0.20Fe- 0.20Ni	105	59	M, WP	126	41	G, WP	99	62	M, WP	112	32	G
999	0.50Sn-0.20Fe- 0.20Ni	105	62	M, WP	126	40	G, WP	99	71	M, WP	112	33	G
1007	0.50Sn-0.20Fe- 0.20Ni	105	87	M, WP	126	67	M, WP	99	81	M, WP	112	34	G
1024	0.25Sn-0.25Fe- 100N(b)	105	71	M, WP	126	43	M, WP	99	88	M, WP, S	112	39	G
1026	0.25Sn-0.25Fe- 150N(b)	105	64	M, WP	126	41	M, WP	99	73	M, WP, S	112	33	G
1030	0.50Sn-0.40Fe- 100N(b)	105	61	M, WP	126	43	M, WP	99	77	M, WP	112	37	S
1028	0.50Sn-0.40Fe- 150N(b)	105	73	M, WP	126	41	M, WP	99	81	M, WP	112	32	G
1014	0.25Sn-0.25Fe- 50Al(b)	105	79	M, WP	126	48	G, WP	99	81	M, WP	112	32	G

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 per dm ²	Remarks ^(a)	Exposure Time, days	Weight Gain, mg per dm ²	Remarks ^(a)	Exposure Time, days	Weight Gain, mg per dm ²	Remarks ^(a)	Exposure Time, days	Weight Gain, mg per dm ²	Remarks ^(a)
Vacuum Annealed 2 Hr at 775 C and Furnace Cooled							Heated 2 Hr at 900 C in Vacuum and Water Quenched						
1012	0.25Sn-0.25Fe- 100Al ^(b)	105	78	M, WP	126	51	G, WP	99	86	M, WP	112	31	G
1013	0.25Sn-0.25Fe- 200Al ^(b)	105	130	M, WP, S	126	Lost weight	W, F	99	105	M, WP	112	36	G
1009	0.50Sn-0.40Fe- 50Al ^(b)	105	83	M, WP	126	51	M, WP	99	99	M, WP	112	30	G
1010	0.50Sn-0.40Fe- 100Al ^(b)	105	82	M, WP	126	61	M, WP	99	102	M, WP	112	34	G
1011	0.50Sn-0.40Fe- 200Al ^(b)	105	100	M, WP	126	60	M, WP	93	115	M, WP	112	34	G
1025	0.50Sn-0.20Fe- 0.20Ni-100N ^(b)	105	58	M, WP	126	42	G, WP	99	92	M, WP	112	33	G
1023	0.50Sn-0.20Fe- 0.20Ni-150N ^(b)	105	71	M, WP	126	41	G, WP	99	91	M, WP	112	35	G
1017	0.50Sn-0.20Fe- 0.20Ni-50Al ^(b)	105	74	M, WP	126	42	G, WP	99	102	M, WP	112	33	G
1016	0.50Sn-0.20Fe- 0.20Ni-100 Al ^(b)	105	83	M, WP	126	46	G, WP	93	98	M, WP	112	35	G
1015	0.50Sn-0.20Fe- 0.20Ni-200Al ^(b)	105	104	M, WP	126	60	M, WP	93	108	M, WP	112	37	G

(a) Key to remarks:

- G - Black tarnish film (good material)
- WP - Light to moderate white oxide pattern
- M - Milky
- S - Slight segregation.

(b) In ppm.

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Duplicate quenched samples are still exhibiting a tarnish film after 112 days of exposure to 680 F water. Alloys containing 100 to 150 ppm aluminum are not so resistant as alloys containing lesser amounts of aluminum. In general, these alloys have a milky appearance and/or high weight gains. These studies are being continued.

Zirconium-Boron Alloys

Results of corrosion tests conducted in 600 and 680 F degassed water indicate that boron additions in the range of 0.45 to 0.50 w/o destroys corrosion resistance of both sponge zirconium and Zircaloy 2. The alloys evince a moderate to heavy powdery oxide pattern similar to that noted for the zirconium-carbon alloys.

Compositional Factors Affecting Corrosion Properties of Zirconium

W. K. Boyd and D. J. Maykuth

This program is concerned with investigating variations in composition which affect corrosion behavior of zirconium alloys. Alloys prepared in the rocking-hearth furnace represented both sponge and crystal-bar melts containing additions of carbon, chromium, germanium, gold, iridium, iron, nickel, niobium, nitrogen, oxygen, palladium, platinum, silver, or ruthenium. After from 2-1/2 to 17 months of exposure to 600 and 680 F degassed water and 750 F steam (1500 psi), only iron and nickel additions proved to be effective in improving corrosion behavior.

In other investigations, zirconium-tin-iron-nickel alloys containing additions of from 70 to 300 ppm nitrogen or 200 ppm aluminum or 100 titanium are being evaluated in 680 F degassed water and 750 F steam (1500 psi). No failures have been noted after 28 days of exposure. These tests are being continued.

Effect of Heat Treatment

Extended-exposure data (total 131 days in 750 F steam) continue to indicate that the size and distribution of the intermetallic compound particles affect the corrosion resistance of zirconium-iron and zirconium-nickel alloys. Structures containing large colonies of particles separated by platelets of alpha zirconium have less resistance than those containing a fine dispersion of compound particles in the alpha matrix. The heat treatments employed are described in detail in BMI-1012.

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Zirconium-Gas Reactions

M. W. Mallett and W. M. Albrecht

Zirconium Water Vapor

In conjunction with a program on the water corrosion of zirconium, a study is being initiated on the reaction of zirconium with water vapor at sub-atmospheric pressures. A microbalance technique will be employed to obtain continuous rate data. Receipt of a microbalance for use in the study is expected during the month of November.

Mechanism of Zirconium Corrosion

C. M. Schwartz and D. A. Vaughan

The role of hydrogen in the mechanism of high-temperature-water corrosion of zirconium is being investigated. Previous studies have shown that the corrosion resistance of the surface of hydrogen-impregnated zirconium or Zircaloy 2 is less than that of machined and pickled surfaces of these samples, with either low or high hydrogen contents.

During the past month additional corrosion tests were carried out on hydrogen-impregnated and impregnated and degassed specimens of Zircaloy 2. The results confirmed the previous observation that hydrogen impregnation destroys the corrosion resistance of Zircaloy 2. Also, it was found that removal of the hydrogen by vacuum degassing does not restore the corrosion resistance of this surface layer. Thus, it appears that the role of hydrogen is to damage the surface layer rather than to cause lowered corrosion resistance due to the hydride phase produced at the metal surface. Hydrogen analyses of the impregnated and the degassed samples will be completed during the next month.

Identification of Corrosion Products on Various
Zirconium Alloys

C. M. Schwartz and D. A. Vaughan

As assistance to ORNL, a phase-identification study is being made of oxide films produced on a series of zirconium-base alloys during exposure to high-temperature water. The purpose of this work is to survey a number of alloys to determine which alloy additions tend to form and stabilize the tetragonal modification of ZrO_2 . Previous results on corrosion films

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produced in uranyl sulfate solution indicated that a 15 w/o niobium alloy did form and retain some tetragonal ZrO_2 in a 50-hr test at 250 C. However, a 3 w/o cerium alloy produced the monoclinic ZrO_2 and CeO_2 in a similar test.

During the past month, the samples described in Table H-3 were examined by X-ray and electron diffraction. Of particular interest in this series of alloys are the 10 w/o molybdenum and the 6, 8, and 10 w/o niobium alloys, which show a definite tendency to form and stabilize the tetragonal modification of ZrO_2 . It would be of interest to resurface these alloys and corrode them in uranyl sulfate solution to determine which oxide phase will be produced.

During the next period, the remaining alloys corroded in high-temperature water will be examined.

Electrocladding of Zirconium With
Platinum Metals

A. B. Tripler, Jr., J. G. Beach, and C. L. Faust

Zirconium and Zircaloy 2 are materials being studied for construction of spherical shells in a homogeneous reactor at ORNL. In uranyl sulfate solutions at a pH of 1.7 to 2.5 and at temperatures of 250 to 350 C, these metals corroded rather slowly, generally at a rate less than 2 mils per year. However, under radiation, the corrosion rate increased to about 9 mils per year.

Zirconium or Zircaloy 2 clad with a protective layer of one or more of the platinum-group metals was proposed because platinum, in comparable out-of-pile tests, showed corrosion rates between 0.03 and 0.81 mil per year. Since electrocladding of zirconium with a platinum-group metal appears to offer a better chance of success than does mechanical cladding, a study of electrocladding was initiated for ORNL.

A satisfactory platinum-group metal electrocladding must be adequately bonded to the zirconium, must be continuous and impervious, must resist corrosion in uranyl sulfate solutions under irradiation, and should not exceed the thermal-neutron-absorption cross section equivalent to 250 mils of zirconium. The equivalent thicknesses of various metals being considered are tabulated on page H-12.

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TABLE H-3. DESCRIPTION OF ZIRCONIUM ALLOYS AND RESULTS OF X-RAY AND ELECTRON DIFFRACTION EXAMINATION OF WATER-CORROSION PRODUCTS

Sample	Alloy Content, w/o	Appearance of Corrosion Film	Corrosion Test		Phases Identified ^(a)	
			Time, hr	Temperature, F	By X-Ray Diffraction	By Electron Diffraction
5	2 Mo	Thick gray	500	650	ZrO ₂	ZrO ₂
6	3 Mo	Thick gray	500	650	ZrO ₂	ZrO ₂
7	4 Mo	Thick gray	500	650	ZrO ₂	ZrO ₂
8	5.5 Mo	Thin black ^(b)	350	650	ZrO ₂ ^(b)	Unidentified
9	10 Mo	Thin black	700	650	ZrO ₂ plus tet. ZrO ₂	ZrO ₂
10	0.25 Nb	Silver gray	9408	680	ZrO ₂	ZrO ₂ ^(c)
11	0.5 Nb	Silver gray	9408	680	ZrO ₂	ZrO ₂ ^(c)
12	1 Nb	Silver gray	3696	680	ZrO ₂	ZrO ₂
13	3 Nb	Thin black	8032	650	ZrO ₂	ZrO ₂ ^(c)
14	4 Nb	Thick gray	400	650	ZrO ₂	-
15	6 Nb	Thin gray	350	650	ZrO ₂ plus tet. ZrO ₂ ^(c)	Tet. ZrO ₂ plus ZrO ₂
16	8 Nb	Black ^(b)	150	650	ZrO ₂ plus tet. ZrO ₂ plus NbO	ZrO ₂
17	10 Nb	Thin black	2352	680	ZrO ₂ plus tet. ZrO ₂ ^(c)	Tet. ZrO ₂ plus ZrO ₂ plus NbO
18	0.5 Ni	Thin gray	7596	750	ZrO ₂ ^(c)	ZrO ₂ ^(c)
19	2 Ni	Gray-black	5032	680	ZrO ₂	ZrO ₂
20	2 V	Thick green-white	150	650	ZrO ₂	ZrO ₂
21	4 V	Thick green-white	150	650	ZrO ₂	ZrO ₂
22	0.2 Y	Thick white	50	650	ZrO ₂	ZrO ₂
23	1 Y	Thick white	18	650	ZrO ₂ plus cubic Y ₂ O ₃	ZrO ₂
24	0.5 Nb plus 2 Mo	Thick gray	350	650	ZrO ₂	ZrO ₂
25	1 Nb plus 1 Mo	Thick gray-white	400	650	ZrO ₂	ZrO ₂
26	1 Nb plus 2 Mo	Thick gray	400	650	ZrO ₂	ZrO ₂
27	2 Nb plus 2 Mo	Thin gray	400	650	ZrO ₂	ZrO ₂
28	1 Nb plus 3 Mo	Thick gray	400	650	ZrO ₂	ZrO ₂
29	2 Nb plus 3 Mo	Thick gray	400	650	ZrO ₂ plus tet. ZrO ₂	ZrO ₂
30	2 Nb plus 4 Mo	Gray-black	350	650	ZrO ₂ plus tet. ZrO ₂	ZrO ₂
31	2 Nb plus 3 Sn	Thin gray-brown	5368	650	ZrO ₂ ^(c)	ZrO ₂
32	3 Nb plus 3 Sn	Gray-black	4024	650	ZrO ₂ ^(c)	ZrO ₂
33	3 Nb plus 4 Sn	Gray-black ^(b)	4024	650	ZrO ₂ ^(c)	ZrO ₂

(a) All ZrO₂ monoclinic unless identified as tetragonal (tet.).

(b) Segregated with gray-white streaks.

(c) These ZrO₂ films are very hard and appear to have a preferred orientation, but may be two phase.

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<u>Metal</u>	<u>Thickness, mils</u>
Zirconium	250
Platinum	3.5
Palladium	3.5
Rhodium	0.2
Nickel	5.0
Iron	9.5

Zirconium rods 0.150 in. in diameter and about 4 in. long are being processed for test samples. Arc-melted crystal-bar zirconium was rolled and swaged to about 1/4 in. in diameter. Centerless grinding to 0.150 in. removed the seams and stringers in the as-fabricated rod. Chemical polishing to remove 3 1/2 mils of the as-ground surface metal apparently provides a sound zirconium surface for subsequent electroplating studies.

Methods are known from past work for electrodepositing nickel and iron on zirconium with good bonding. Accordingly, nickel will be studied as a bonding layer between the platinum-metal electrocladding and the zirconium. However, for the preliminary tests, 0.150-in.-diameter nickel rod has been used.

Of the known platinum-plating baths, the diammino nitrite bath is perhaps the most widely used, and for this reason is obtainable in ready-to-plate form from numerous suppliers. Its chief disadvantages are its low cathode-current efficiency (10 per cent) and the fact that if thick deposits (1 mil or more) are desired, plating must be done at a current density of about 5 amp per ft². Even under these conditions the deposits are somewhat rough.

Tests here have revealed that if the plating current is periodically reversed with the proper cycling, relatively heavy deposits are feasible at 50 to 60 amp per ft². At the present time, the periodic reverse (PR) operates cathodically for 5 sec and anodically for 2 sec. There is no difference in appearance between a 0.2-mil-thick coating and a 0.8-mil-thick coating; both have a smooth, mat surface. This indicates that any desired thickness of sound plate can now be built up. The latter conclusion was substantiated with the production of a 1.6-mil-thick deposit.

When the current was not reversed but merely interrupted (e. g., current for 5 sec, no current for 2 sec, etc.), an acceptable deposit was not produced. The anodic cycle appears to be necessary.

Thus far, no difficulty has been experienced with adhesion of the electroplates on nickel. Some corrosion testing has been done. The 0.8-mil platinum coating on nickel is impervious to 70 F 1:1 hydrochloric acid after 4 days. More severe corrosion tests are planned.

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A literature survey has disclosed details for an alkaline platinum-plating bath for which 100 per cent cathode efficiency is claimed. The platinum compound used in the bath, $\text{Na}_2\text{Pt}(\text{OH})_6 \cdot 2\text{H}_2\text{O}$ is not available commercially. It is being prepared. For heavy deposits, the recommended current density is 2 to 3 amp per ft^2 . It is quite possible that a high current density with a periodic reverse will give satisfactory heavy platinum coatings in a shorter time than that required with the diammino nitrite bath.

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I. REACTOR MATERIALS DEVELOPMENT

H. A. Saller

The Reactor Development Division of the Atomic Energy Commission supports several programs which are designed to develop materials for general reactor application.

It is now believed that hydrogen contamination has been an important factor in the relatively low ductility obtained in zirconium alloys. This is being investigated.

Efforts on the enameling of zirconium were suspended to produce samples of enameled uranium for testing by Argonne. The zirconium program will be reactivated.

Studies of the kinetics of the reaction between zirconium and UO_2 are in progress.

Studies of Zirconium Heat Treatment

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

The present objective of this research program is to study the response to heat treatment and transformation kinetics of zirconium-base alloys. Strengths up to 200,000 psi have now been obtained in certain alloys by solution treating, quenching, and aging. The ductility of the alloys at this strength level is not yet satisfactory. Elongation values have varied with the alloy composition; thus, a niobium-tin alloy has shown better ductility than a molybdenum-tin alloy at a comparable strength level. However, it is believed that other factors, e. g., hydrogen contamination, have prevented the alloys studied to date from developing their best properties. Additional work to determine the cause of these variations in ductility is in progress. Some delay was experienced in October in the second melting operation of a 20-lb heat of a zirconium-5 w/o molybdenum alloy. This material is to be used in the ductility study and in a more extensive investigation of aging kinetics and heat treatments.

While awaiting the new alloy stock, the age-hardening characteristics of the zirconium-5.5 w/o molybdenum alloy studied earlier were correlated with X-ray diffraction data. Vickers hardness data and X-ray diffraction-pattern intensities are shown in Figure I-1 as a function of aging time at 480 C. The specimens were ice-brine quenched from the beta field (830 C) and aged for times up to 200 hr at 480 C.

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The transformation kinetics of this alloy closely duplicated the sequence observed in certain titanium alloys. In the quenched condition, the alloy consisted largely of retained beta, having a composition of about 5.5 w/o molybdenum, which formed at the solution temperature, 830 C. The hardness, as expected, was low. During the quench, part of the beta transformed to omega, the presence of which was detected in the as-quenched sample. After 15 min at 480 C, the hardness reached a maximum (475 VHN) as the quantity of omega phase increased. As omega formed, the molybdenum content of some of the beta was increased, which suggests that the omega, like that in titanium, has a relatively low solubility limit for beta-stabilizing elements. The enriched beta is distinguishable by X-ray diffraction from the beta of original molybdenum content. With increasing time (2 hr), the omega pattern became more intense, while beta of original composition, enriched beta, and a more highly enriched beta existed at the same time.

Hardness remained high (over 400 VHN) for about 30 hr. After 50 hr, the omega pattern was still intense although the alloy had overaged to a hardness level of 375 VHN. At this stage in the transformation process, alpha had begun to form. After a 100-hr aging time, a strong alpha pattern was obtained, the omega had almost disappeared, and the only beta remaining was highly enriched. The hardness had decreased to about 300 VHN. After 200 hr, the hardness remained at about the same level; however, the compound $ZrMo_2$ had begun to appear, the omega had completely disappeared, and alpha was present. It is expected that, with further aging, only compound and alpha would remain as equilibrium products.

It is believed that omega is responsible for the extreme hardening and embrittlement that occurs in beta-stabilized zirconium and titanium alloys. The aging behavior shown in Figure I-1 is very similar to that of beta-stabilized titanium alloys. It will be noted from the figure that the peak hardness does not coincide exactly with the time at which the omega pattern was the strongest. This is believed to result from the fact that those omega particles which effect maximum hardness are not necessarily detectable by X-ray diffraction. Extreme overaging or softening after about 100 hr of aging appears to correlate with the decreasing intensity of omega. At intermediate aging times, e. g., 24 to 50 hr, the omega reflections are strong but hardness is decreasing. This may be attributable to loss of coherency between the well-developed omega phase and the beta matrix.

These studies will be continued as soon as material from the 20-lb ingots of the zirconium-5 w/o molybdenum-2 w/o tin and zirconium-5 w/o niobium-2 w/o tin alloys is available.

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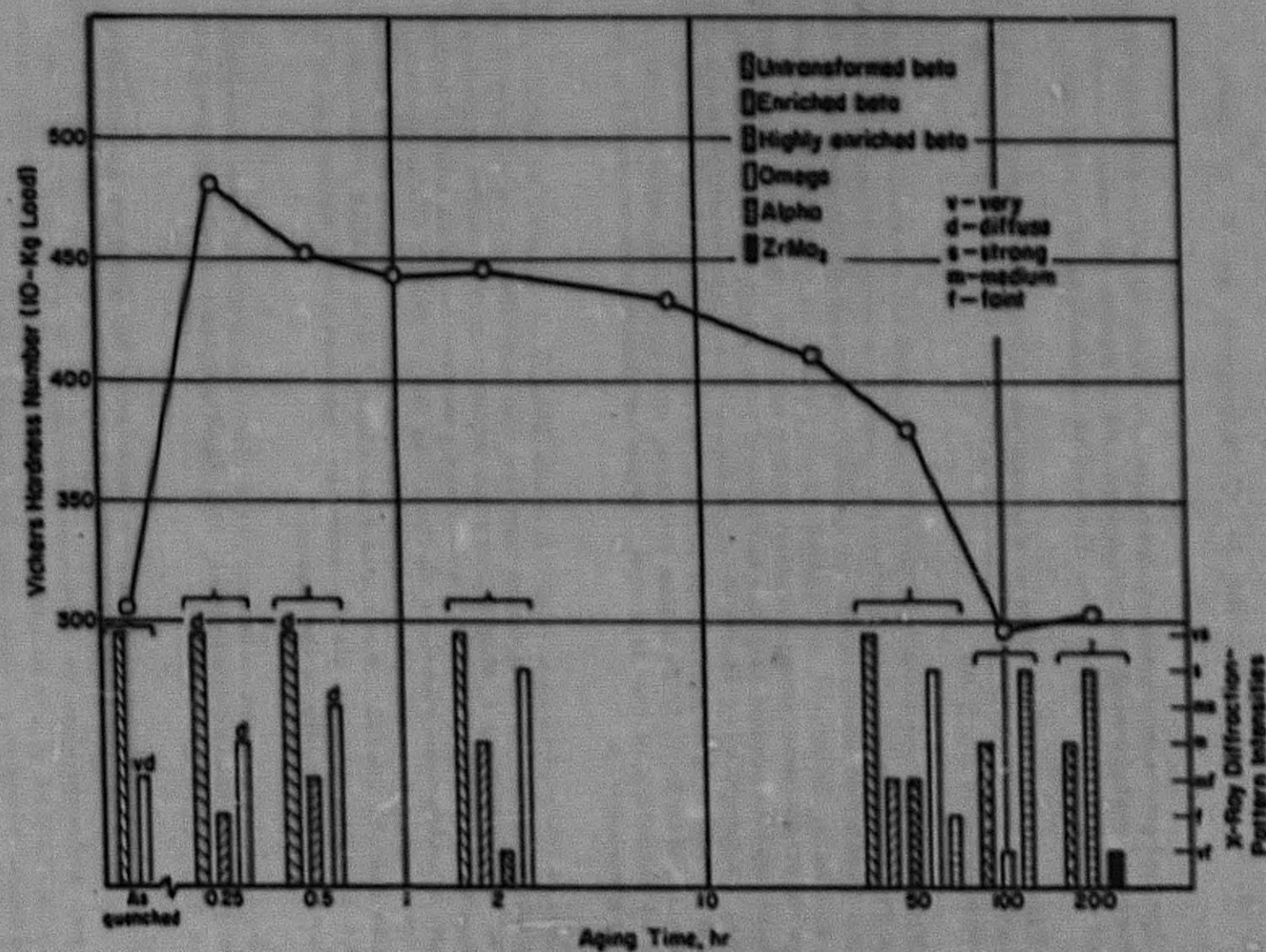


FIGURE I-1. EFFECT OF AGING AT 480 C ON THE HARDNESS AND X-RAY DIFFRACTION-PATTERN INTENSITIES OF A ZIRCONIUM-5.5 w/o MOLYBDENUM ALLOY QUENCHED FROM 830 C

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Enameling of Special Metals

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

Special porcelain-enamel coatings are being developed to increase the usefulness of metals such as zirconium and uranium for reactor service. Most of the work in the past was devoted to enameling of zirconium.

This month, the work on zirconium was temporarily recessed in favor of the enameling of uranium, following a request from Argonne for specimens of enameled uranium.

Enamels for uranium had been investigated on a separate program and the results published in BMI-1024. Alkali-alumina-phosphate enamels had been developed which could be applied successfully to uranium. The better enamels, however, contained Li_2O , which is undesirable because of its high thermal-neutron-absorption cross section. An enamel containing no lithium was reported and had been used with success. This enamel, however, required very strict firing-temperature and heating-rate control for good results. The factors of fusion, wetting, adherence, and thermal expansion had to be held in a fine balance, and these all varied with the degree of oxidation of the uranium. Some oxidation was necessary, but too much was disastrous.

It was attempted to produce a more practical enamel by minor changes in the composition. It was found that the CuO content could be reduced from 8 w/o to 4 w/o without losing adherence while minimizing the tendency of the glass to devitrify. About 7 w/o Fe_3O_4 proved to be an effective flux. Uranium trioxide was effective in reducing the tendency of the glass to crack on cooling because of the difference in thermal expansion between the glass and the metal. Not more than about 6 w/o of this refractory oxide could be smelted into the glass, however, and even this amount greatly decreased the fusibility of the enamel.

Beta quenching the uranium plate eliminated directional cracking. Grit-blasting improved adherence, but good adherence was attained without blasting with some enamels.

Rapid firing of the enamel was necessary for good wetting when firing in air. It also eliminated the need for phosphate treating the metal. Rapid firing was accomplished by induction heating or by setting the uranium directly on a piece of preheated graphite while firing. No benefits were derived from firing in a controlled atmosphere when a 1/8-in. uranium plate was being enameled.

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Improved results were obtained by forming an enamel from two frits - one a soft, fusible glass and the other a high- UO_3 -bearing frit. Further work will be done along this line and with UO_3 powder admixed with a soft frit.

A few attempts were made at enameling niobium with enamels on hand. A lead-silicate glass was dusted on specimens and fired at 1550 F in air, argon, or argon-2 per cent oxygen. In all cases, adherence was poor. Firing in air at that temperature caused excessive oxidation of the metal.

An alkali-alumina-phosphate enamel was applied to niobium and fired at 1700 F in air. Excellent adherence was obtained. However, crazing occurred because of the high thermal expansion of the glass compared with that of niobium. The enamel fused rapidly enough at the firing temperature to prevent excessive oxidation.

Specific enamels for application to niobium will be developed in the future. More refractory enamels, in particular, will be sought.

The work on enameled zirconium will continue with further study of the effect of bismuth-uranium alloy on the coating at elevated temperature.

Kinetics of the Zirconium-Uranium Dioxide Reaction

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

A study is being made of the solid-solid reaction between zirconium and UO_2 . The data obtained will be useful in estimating the extent of reaction that may occur when zirconium or its alloys are used in contact with UO_2 .

A portion of a zirconium- UO_2 sandwich-type element, previously heated at 1300 F for 37 days and cooled to room temperature in about 20 hr, was reheated in an evacuated Vycor capsule at 1325 F for 285 hr and water quenched. The phases noted in the reaction zone of the slow-cooled specimen apparently were unchanged by further heating and quenching. This seems to indicate that the observed phases are the equilibrium phases formed at the reaction temperature.

Tests using several inert materials to mark the original metal-oxide interface were inconclusive because the contact between the zirconium and

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the UO_2 in the experimental specimen was not sufficiently good. Further marker experiments will be made.

Zirconium- UO_2 sandwich-type elements have been placed on test at 950, 1100, and 1200 F in autoclaves at 5000-psi inert-gas pressure. Specimens will be removed from test and analyzed for transfer of uranium and oxygen into the zirconium after the reaction has proceeded for a suitable time. Another type of equipment is being assembled to perform experiments at 1450 and 1600 F.

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J. PHYSICAL METALLURGY

H. A. Saller

The Research Division of the Atomic Energy Commission is sponsoring a variety of research programs in the broad fields of ceramics, metallurgy, and gas-metal studies.

Actual determination of properties of uranium compounds was started. Some tests have been made on U_3Si and UNi_2 . Samples of UN , U_2Ti , and U_6Ni are ready for evaluation.

Determination of internal friction on a quenched sample of uranium after various aging times at room temperature showed a decrease in internal friction with time. This probably indicates a relaxation of internal stresses.

Preliminary metallographic studies on ternary alloys ranging from uranium-31.5 a/o molybdenum to uranium-34 a/o titanium indicate that two delta phases exist in equilibrium at temperatures below 575 C. Additions of titanium to the uranium-molybdenum alloy tend to destabilize the sluggish gamma-uranium phase.

A torsional-balance device for bonding needle points to flat pieces has been set up and tested. Approximately 100 samples of gold have been bonded and are being evaluated.

In the development of oxidation-resistant niobium alloys, testing of a series of niobium-zirconium alloys was completed. In general, zirconium was much less effective than titanium in reducing the rate of oxidation. Neither alloying element brought about the formation of an adherent oxide layer.

Studies of hydrides of zirconium and zirconium alloys containing 2.3 a/o of molybdenum, magnesium, nickel, or titanium are in progress. N_H values are being determined at temperatures from 1000 to 2000 F.

Properties of Uranium Compounds

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

A study is being made of some of the lesser known uranium compounds to aid in evaluating these compounds as potential nuclear fuels. The field of

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interest has been narrowed to about 13 compounds which have high uranium contents and high melting points.

U_3Si and UNi_2 samples were prepared by arc melting in helium. The X-ray diffraction patterns of these compounds corresponded to those found in the literature.

Both compounds reacted with concentrated HCl , HNO_3 , and H_2SO_4 , but not with a 0.1 N solution of $NaOH$. Both reacted with air at 500 C, gaining about 18 per cent in weight after 1 hr. Massive samples of each appeared unchanged and had no weight loss after 1 hr in boiling water. However, some darkening of the surface was observed with granular samples after 1 hr.

Preliminary tests on U_3Si and UNi_2 will be completed next month. The UN that was made last month was contaminated with oxygen and will be re-prepared along with U_2Ti and U_6Ni . After the exact composition of these compounds is determined, preliminary thermal and chemical tests will be begun.

Development of Uranium-Titanium Alloys

L. L. Marsh and G. K. Manning

The objective of this program is the determination of selected mechanical and physical properties in an alloy system to provide background data for designers and engineers on the potential utility of the system. In the present study uranium-rich binary alloys with titanium are being evaluated.

The compositions being studied are 5, 15, 25, and 50 a/o titanium. The 25 and 50 a/o titanium alloys have been cast and rolled to sheet at 1800 F. Some difficulty was experienced in casting and fabricating these alloys. On cooling from the casting temperature, both ingots shattered. In an effort to salvage a portion of the 25 a/o titanium alloy, part of the ingot was placed in a furnace at 1800 F for forging. During reheating, the alloy again shattered with considerable force. It was subsequently observed that slow heating the 25 a/o titanium alloy to the forging temperature (1800 F) yielded satisfactory material which could be rolled to sheet with little edge cracking. Using this technique, the 50 a/o titanium alloy was fabricated to sheet at 1800 F. The surface finish was very good and the amount of surface oxidation after hot rolling appeared less than a uranium-zirconium alloy of similar composition. Tensile and heat-treating specimens are being prepared from these alloys.

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Investigation of the Tensile Transition in Alpha Uranium

L. L. Marsh and G. K. Manning

A research program concerned with the tensile transition in uranium is in progress. Biscuit uranium having two types of fabrication history, i.e., rolled at 300 C and at 600 C, is being used as the base material.

At present, the temperature range of the tensile transition is being located for both materials in the as-rolled condition. Similar tests are in progress to locate the transition in material with both fabrication histories and alpha annealed 10 hours at 600 C in vacuum. Preliminary evaluation indicates that the tensile transition occurs at a lower temperature for 300 C rolled material than for 600 C rolled material. Annealing for 10 hr at 600 C does not appear to eliminate the difference in behavior.

Internal Friction of Uranium

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

The internal friction of uranium is being studied in an effort to learn more about the deformation process in uranium; particularly the behavior of twins during deformation and during thermal changes. It has been observed that the internal friction increases as the rate of temperature change increases and that the internal friction at a particular temperature decays with time at a rate influenced by the heating rate to that temperature.

The internal friction of a specimen of uranium heat treated for 16 hr at 600 C and water quenched has been observed during room-temperature aging after quenching. Damping measurements commenced from about 20 min after quenching. The internal friction was observed to decrease linearly with the logarithm of time, and is still decreasing after about 25 days of aging. This is interpreted as a relaxation of internal stresses set up by quenching. This relaxation may be occurring by twin boundary motion as previously proposed. This type of time-dependent internal friction draws attention to the difficulties which would be encountered in using single internal-friction values to compare specimens with unknown histories.

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Intermediate or Delta-Phase Alloys

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

The phase relationships between the delta phases of the uranium-molybdenum and uranium-titanium systems are being studied in a series of alloys ranging in composition from uranium-31.5 a/o molybdenum to uranium-34 a/o titanium.

Preliminary metallographic studies made on heat-treated samples of these alloys indicate that the two delta phases exist in equilibrium below about 575 C. It is also indicated that the addition of titanium to the uranium-molybdenum alloy destabilized the sluggish gamma-uranium phase.

X-ray studies of the heat-treated specimens are planned with the aim of confirming metallographic interpretation of the phase present and determining the solubility limits of the ternary addition to the delta phases.

Study of Bonding Fundamentals

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

One objective of this study is to examine the bonding variables, such as time, temperature, and contamination, in the absence of the usual macroscopic mating variable. To do this, it is necessary to develop a device for bonding needle points to flat surfaces. The second main objective in this work concerns the nucleation and growth occurring at the bond interface.

The torsional-balance device for bonding needle points to flat surfaces has been tested, using gold specimens. The results are encouraging. Approximately 100 gold-to-gold bonding tests have now been made in air, using 14 gold needles and test temperatures of 200 to 500 C. Measurable bonds were obtained in about 98 per cent of the specimens. The scatter in the results is less than in tests using the parallel sheet-metal spring device. Work is now being directed toward control and standardization of test specimens and test conditions in order to obtain reproducibility.

Specimens are being prepared for electron-microscope studies to attempt differentiation between bonded and unbonded areas at the bond interface.

No progress was made this month on the nucleation-and-growth experiments in silver.

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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, in order to determine why hydrogen lowers the impact strength of slow-cooled samples, as compared with quenched samples. Last month some evidence was found that the embrittlement is related to the initiation of cracks at the intersection of twins and hydride platelets. To test this theory further, samples with higher hydrogen content are being prepared. To facilitate the measurement of elongation and reduction in area in tensile-impact tests, the new samples have a longer gage length than those previously used.

Some work has been done the last month in developing an electropolish suitable for electron-microscope examination of slip in zirconium. The slip and twinning structure in deformed samples with higher hydrogen content will be investigated by both light and electron microscopy.

Solid State Studies of Thorium and Uranium Alloys

A. E. Austin and C. M. Schwartz

The influence of oxygen upon the thorium transformation is being studied. Specimens of iodide thorium with varying oxygen contents have been prepared. They will be studied at temperature by means of X-ray diffraction when the high-temperature camera becomes available from other work in progress.

Analyses of the thorium-uranium alloys are being obtained. Compositions of nominal 1, 2, and 5 w/o uranium have been prepared and will be machined into specimens for X-ray diffraction.

Oxidation-Resistant Niobium Alloys

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

Although pure niobium is free scaling at elevated temperatures, the oxide is not volatile. The present investigation is being conducted to evaluate the effect of alloying on the contamination and oxidation (scaling) rate of niobium at elevated temperatures, with an objective of developing protective heterogeneous oxides.

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Air-oxidation rates have been measured on samples of niobium-zirconium alloys exposed for 1 and 5 hr at 600, 800, and 1000 C. Like the niobium-titanium alloy reported previously, these alloys were all free scaling, and oxidized linearly with exposure time. However, the rates of oxidation, as given below, are much higher than for the corresponding niobium-titanium alloys. Small zirconium additions caused an increase in the oxidation rate, as compared with the pure niobium controls. A maximum oxidation rate appears to occur at about 1 to 5 per cent zirconium; further additions of zirconium decrease the rate slightly. Oxidation rates are tabulated below:

Alloy Composition, a/o	VHN	Oxidation Rate, mg/(cm ²)(hr), at Indicated Temperature, C		
		600	800	1000
100 niobium	147	7.0	31.9	25.8 ^(a)
Niobium-1 zirconium	176	7.1	64.8	71.0
Niobium-5 zirconium	167	3.8	41.2	135
Niobium-10 zirconium	209	0.9	25.2	101
Niobium-20 zirconium	272	4.7	17.7	49.5

(a) This value is in doubt; further tests are planned.

Hardness traverses are being obtained on cross sections of the oxidized niobium, niobium-titanium, and niobium-zirconium samples to determine the depths of contamination. These data will be used to calculate the diffusion coefficients for air for each of the experimental alloys.

Binary alloys of niobium containing chromium, molybdenum, and tungsten have been prepared by arc melting. Air-oxidation specimens are being prepared from these ingots.

Oxidation-rate studies in a modified Sieverts apparatus have been completed on pure niobium in a pure oxygen atmosphere at 600, 800, 1000, and 1200 C. Oxidation rates are being calculated from the test data, and hardness traverses also will be obtained on these samples. Similar air-oxidation studies will commence shortly. If the data for air and pure oxygen do not agree, the effect of nitrogen will be investigated.

Uranium-Hydrogen Reactions

M. W. Mallett and W. M. Albrecht

The reactions of uranium and uranium alloys with hydrogen are being investigated. These studies are being made under the conditions that $p-p_0$ is a constant, where p is the system pressure and p_0 is the dissociation pressure of uranium hydride.

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Equilibrium studies were made of a uranium-5 w/o zirconium alloy with hydrogen in the range 330 to 420 C to determine the dissociation pressure, p_0 , of the hydride of this alloy. These data can be expressed by the equation:

$$\log p_0 \text{ mm} = - \frac{5280}{T} + 10.37.$$

This equation will be used to extrapolate values of p_0 for lower temperatures where equilibrium is reached very slowly, as well as to calculate p_0 values at higher temperatures.

Reaction-rate runs were made with the alloy and hydrogen at 100 and 248 C at $p-p_0$ of 430 mm of mercury, at 335 C at $p-p_0$ of 150 mm, and at 100 and 195 C at $p-p_0$ of 70 mm. As reported previously, the reactions followed a linear rate after initial deviations. From the data obtained thus far, the linear reaction rates are about one-half of those obtained for the reaction of hydrogen with unalloyed uranium at the same condition of temperature and pressure.

Further rate data will be obtained.

Study of Hydrides

M. W. Mallett and M. J. Trzeciak

A fundamental study is being made of factors affecting the thermal stability of hydrides which find applications as moderators and shielding materials. High temperature N_H (N_H = number of atoms of hydrogen per $\text{cm}^3 \times 10^{-22}$) values are being determined for hydrides of various zirconium alloys. Table J-1 gives N_H values of four zirconium-alloy hydrides at several temperatures in the range 1000 to 1700 F where resistance heating is used. Measurements in the range 1700 to 2200 F using induction heating will be made subsequently.

For purposes of comparison, N_H values for pure zirconium hydride determined previously are included in Table J-1. The data of Table J-1 show that the alloy hydrides behave similarly to pure zirconium hydride, with the exception of the zirconium-2.3 at/o molybdenum alloy hydride. This hydride exhibits comparatively low N_H values at the lower temperatures. However, at 1650 F its N_H is 4.3, compared with 3.8 for pure zirconium hydride. The nature of this trend will be made evident when the 1700 to 2200 F experiments are conducted.

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TABLE J-1. ELEVATED-TEMPERATURE N_H VALUES FOR ZIRCONIUM AND ZIRCONIUM ALLOYS

Temperature, F	N_H Values				
	Iodide Zr	Zr-2.3 a/o Nb	Zr-2.3 a/o Mn	Zr-2.3 a/o Mo	Zr-2.3 a/o Ti
1000	6.9	7.4	7.1	5.7	7.0
1200	6.5	6.9	6.7	5.5	6.5
1400	6.0	6.4	6.1	5.0	6.0
1500	5.7	6.0	5.4	4.8	5.5
1600	4.6	4.3	5.0	4.4	4.4
1650	3.8	--	4.0	4.3	4.2
1700	3.8	--	--	--	3.9

It was observed experimentally, although it is not evident from the data in Table J-1, that the zirconium-2.3 a/o manganese hydride transformed at 1620 F. The presence of manganese tends to increase the transformation temperature, which is 1550 F for pure zirconium hydride. The nature of this transformation is a structural change from tetragonal hydride below 1550 F, to a solid solution of hydrogen in the body-centered-cubic structure (beta-zirconium phase) above this temperature. The beta-solid-solution structure represents a lattice contraction of 15 per cent from that of the tetragonal hydride phase.

The measurement of high-temperature N_H values will continue. A second apparatus is being constructed to facilitate production of data.

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