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DURING APRIL, 1956

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REPORTS RELATED TO CIVILIAN APPLICATIONS
ISSUED DURING APRIL, 1956

- BMI-1078 "Solid-Phase-Reaction Studies of Control-Rod Materials", by Arnold F. Gerds and Manley W. Mallett.
- BMI-1080 "Progress Relating to Civilian Applications During March, 1956", by Russell W. Dayton and Clyde R. Tipton, Jr.

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A. DEVELOPMENT OF MATERIALS FOR HANFORD REACTORS

J. R. Keeler

The elevated-temperature properties of dilute uranium-aluminum and uranium-zirconium alloys are being studied. Hot-hardness measurements show that small amounts of either aluminum or zirconium increase the hardness of uranium at elevated temperatures.

Samples for additional solubility measurements in the thorium-uranium system are being prepared, and additional creep data on Zircaloy 2 are shown. Small zirconium-jacketed uranium samples were hydrostatically pressed at 2000 psi and 850 C. Good diffusion bonds were obtained, but the grain size of the uranium was large.

Studies on the radiation damage to graphite were continued. Considerable difficulty has been encountered in obtaining reproducible helium-density measurements of micropore content, and calibration of the equipment is continuing. Graphite samples prepared from Texas coke are being prepared for irradiation at Hanford.

Uranium Alloys for Slug-Type Fuel Elements

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

A number of dilute uranium alloys are being investigated in an attempt to develop a slug-type fuel element with improved properties. The alloying elements under consideration are aluminum and zirconium, which have little effect on the neutron-absorption characteristics of the slug.

Hardness, hot-hardness, and grain-size data have been obtained on specimens from 4-kg heats of the alloys under investigation. The data were obtained from samples hot rolled at 620 C, heated to 730 C for 30 min, water quenched, and annealed for 1 hr at 600 C. The results are given in Table A-1.

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TABLE A-1. HARDNESS AND GRAIN-SIZE DATA

Nominal Composition (Balance Uranium), a/o	Grain Size, mm	Hardness, DPH, at Indicated Temperature, C				
		25	400	500	600	700
1 aluminum	0.20	248	74	49	30	33
2 aluminum	0.04	273	102	54	32	38
2 zirconium	0.04	268	134	80	42	22
4 zirconium	0.01	317	153	78	28	4.1

These data, which agree closely with previously reported hot-hardness data for small arc-melted buttons, show that 2 a/o aluminum and 2 a/o zirconium are roughly equivalent in effect upon uranium. Aluminum has some advantage over zirconium at 700 C, but zirconium has the advantage at all temperatures up to 600 C. The hardnesses at 700 C show the effects of zirconium in restricting the beta-uranium phase. Some gamma uranium is undoubtedly present in the 4 a/o zirconium alloy at 700 C, and the heat treatment of this alloy may have to be modified in accordance with this finding.

Tensile tests designed to define the ductility-transition temperatures of the above alloys are in progress.

The Constitution of Thorium-Uranium Alloys

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

As part of a program for HAPO, an investigation to determine the solubility of uranium in thorium is being conducted.

Specimens are now being prepared for an electrical-resistivity study aimed at refining the approximate solubility limits determined by hardness, metallographic, and X-ray techniques. Alloys have been arc melted, and specimens are now being fabricated for this purpose.

Mechanical Properties of Zirconium and Zircaloy 2

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

The creep properties of Zircaloy 2 in the annealed and in the cold-worked condition are being investigated at temperatures up to 500 C. The results of several additional stress-rupture and 1000-hr creep tests are tabulated in Table A-2.

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TABLE A-2. CREEP PROPERTIES OF ANNEALED AND COLD-WORKED ZIRCALOY 2

Temperature, C	Stress, psi	Load On	Elongation, per cent				Time to Failure, hr	Test Time, hr	Creep Rate, per cent per hr
			100 Hr	500 Hr	1000 Hr	Total			
<u>Cold-Worked Longitudinal</u>									
230	59,000	0.70	--	--	--	12.0	37.6	--	0.021
425	15,000	0.10	0.52	0.90	1.27	1.345	--	1132.5	0.00076
500	2,000	0.06	0.215	0.355	--	0.485	--	1172.0	0.00008
<u>Annealed Longitudinal</u>									
345	15,000	0.45	0.565	0.61	0.637	0.64	--	1052.7	0.00004
425	17,500	0.05	--	--	--	42.00	80	--	0.147
500	8,000	0.00	1.1	6.4	15.5	16.6	--	1059.2	0.0093
500	5,000	0.025	0.11	0.30	0.46	0.46	--	1006.3	0.0003

The creep properties of the 25 per cent cold-worked Zircaloy 2 are superior to the annealed material at all test temperatures for short times. At temperatures of 150, 230, and 345 C, the higher properties resulting from cold work persist for times up to 1000 hr, but at 425 and 500 C, the creep properties of the cold-worked material are inferior to the annealed material after test periods of 1000 and 500 hr, respectively.

Zirconium Cladding

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

Hydrostatic pressing at elevated temperatures using an inert gas as the fluid is being investigated as a method for preparing zirconium-clad uranium fuel slugs.

Four 3/4-in. -diameter by 1-in. -long specimens were hydrostatically pressed at 850 C and 2000 psi in order to evaluate the effect of surface preparation of the uranium and time at temperature. Metallographic examination of the specimens showed that a thin diffusion band had developed at the interface after 6 hr at temperature. After 24 hr at temperature, extensive diffusion was evident at local areas along the interface. The grain size of the uranium was large, and the effect of beta quenching on grain size and bond integrity is being investigated. No significant difference could be observed between electropolished and chemically pickled uranium surfaces.

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Additional samples are being prepared from 1-1/8 by 0.020-in. -wall zirconium tubing to further investigate the effect of pressing conditions on the quality of the bond and to provide samples for corrosion and thermal-cycling tests.

Radiation Damage to Graphite

L. D. Loch, A. E. Austin, and G. B. Engle

The cause of physical contraction of graphite during irradiation at high temperatures (300 to 450 C) is being investigated. Annealing studies have indicated that the contraction is not reversed by reheating to the irradiation temperature. Therefore, two possible contraction mechanisms are being considered: (1) elimination of micropores through radiation annealing, and (2) increased crystallinity of the graphite during high-temperature irradiation.

The first mechanism is being studied by helium-density measurements of micropore contents before and after irradiation. Progress on this phase has been delayed by difficulties in obtaining reproducible density values. Calibration measurements are being continued.

The possibility of crystal growth under the combined effects of neutron activation and high irradiation temperature is being examined by means of X-ray diffraction. Recent experiments showed that irradiation of CSF graphite at 100 C or below causes a 20 per cent decrease in crystallinity. Similar samples are being irradiated at 350 C for comparison.

In other work, extruded specimens were fabricated from Texas coke obtained from current production. After they have been baked and graphitized, the specimens will be irradiated at 350 C to determine their physical contractions. The results will show whether graphite made from current Texas coke is comparable to that now being used in the reactors at HAPO.

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B. DEVELOPMENTS FOR ALUMINUM-CLAD FUEL ELEMENTS

R. J. Carlson

Studies on extrusion cladding of flat plates are continuing. The dies and mandrel tips have been modified, and the effort has been redirected toward cladding of the leading end of the core.

Attempts will be made to internally clad six uranium tubes by the tube-expander technique as soon as the tubes have been nickel plated.

A series of small heats of aluminum-uranium alloys containing 30, 35, 40, and 45 w/o uranium is being made preliminary to developing techniques for large-scale castings of these alloys.

Work on the metallographic evaluation of dingot uranium has been directed toward determining the reason for the duplex structure observed in as-received dingot tube. It now appears that this is normal extruded-tube structure.

The hydraulically loaded ring-type test apparatus designed as part of the work on the mechanical properties of dingot uranium tubes has been tested and appears satisfactory.

Extrusion Cladding of Flat Plates

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

The work during April has been chiefly directed toward the preparation of materials and modification of the equipment so that a concerted effort can be applied to the problem of end cladding. Several ideas for cladding the leading and trailing ends of plates will be investigated and evaluated to determine the important factors which may influence the production of successful end closures by extrusion.

At the same time, dies, mandrels, and other tools are being reworked to provide better control of mandrel-tip-to-die distance and other variables which might contribute to the production of clad plates having the desired shape and dimensions. Some additional tools have also been ordered so that experimental work may be expedited.

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Internal Cladding of Tubes

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

Six uranium tubes have been machined and are in the process of being nickel plated. Internal cladding of these tubes at three different temperatures by the tube-expander method will be tried when the tubes are ready.

Characterization of Inclusions and Metallographic
Evaluation of Dingot-Uranium Tubes

H. A. Saller, R. F. Dickerson, R. J. Carlson, and D. M. Cheney

A program is in progress that has as its objective the determination of the characteristics of the inclusions in dingot uranium. Metallographic examination of the extruded dingot tubing showed that it possessed a duplex-type structure consisting of clusters of relatively large grains, similar in appearance to the transformed-alpha structure after beta annealing. The balance of the structure was that which would be expected from any fabrication in the alpha region. As-reduced dingot metal was examined, and the results of this examination gave no clue as to the reason for the duplex structure.

The reported history of this tubing includes a beta-quench treatment after the extrusion step, but the duplex structure examined in no way resembles a beta-quench structure. In an attempt to determine if a fast beta quench would produce such a strained structure that subsequent annealing in the alpha region would result in a partially recrystallized structure similar to the observed duplex structure, thin sections of forged dingot metal were rapidly quenched from the beta region and examined. As would be expected, a typical beta-quenched structure was observed.

The specimens were then annealed in the alpha region for 2 hr and the resulting structures were examined. Although these structures were not the same as the structures in the dingot tubing, it is conceivable that the prior fabrication of the uranium might be responsible for this difference. A similar heat-treatment study on dingot-uranium tubing in the extruded condition would be helpful in establishing the effect of prior fabrication on the structure.

Metallographic analysis for hydrogen has been performed on as-reduced dingot uranium, forged dingot uranium, and extruded dingot tubing. The results of this analysis are tabulated on the following page.

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<u>Type of Uranium</u>	<u>Location of Sample</u>	<u>Estimated Hydrogen Content, ppm</u>
As-reduced dingot	Top	3 - 4
	Bottom	2 - 2.5
Forged dingot	Random sampling	1 - 1.5
Extruded dingot tube	Random sampling	4 - 5

Samples from each type of material have been submitted for chemical and vacuum-fusion analyses for carbon, hydrogen, nitrogen, and oxygen. When these results become available, an attempt will be made to correlate the metallographic examinations with the analyses.

Mechanical Properties of Dingot-Uranium Tubes

J. R. Keeler and F. R. Shober

Test methods for determining the mechanical properties of uranium tubes in the transverse direction and applicable to both irradiated and unirradiated uranium tubes are being investigated. The longitudinal and transverse mechanical properties of an extruded dingot-uranium tube are to be compared. A comparison of mechanical properties of extruded dingot- and ingot-uranium tubes will also be made.

Evaluation of the hydraulically loaded ring-type test has been started, with preliminary measurements on annealed 3S aluminum. Tensile properties of the aluminum were determined in the longitudinal and transverse directions at room temperature, using standard 0.505-in. -diameter tensile bars. These bars were cut from 2-in. -thick plate adjacent to material from which 2-1/2-in. -diameter by 2-in. -long ring specimens were machined. A direct comparison can thus be made between tensile properties obtained on the standard tensile bars and the properties obtained by the ring test.

Several aluminum rings were expanded elastically on the ring-test apparatus at room temperature to test the mechanical operation of the system. Strain gages, Types 9-A, 7-A, and 5-A, were mounted on the ring specimens, and strain measurements were made in the circumferential and axial directions. The test apparatus operated satisfactorily in the 0 to 300-psi range of pressures, and an elastic modulus of 10.5 to 11 by 10^6 psi was measured.

The use of miniature tensile specimens machined directly from the tube in the transverse direction is also being investigated. A specimen is being machined in the transverse direction from one of the aluminum rings,

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and adapters are being made to hold the specimen during testing. The data obtained from this specimen can be compared directly with values obtained on standard 0.505-in. -diameter tensile bars and with data from the ring test.

The tensile properties of extruded heat-treated dingot- and ingot-uranium tubes are to be compared at -75, 75, and 300 F. Sections of both dingot and ingot tubes were heated at 725 C for 15 min in a 50 per cent lithium carbonate-50 per cent potassium carbonate salt bath and air cooled.

Longitudinal tensile specimens are being machined from the heat-treated tubes, and the tensile properties will be measured in the temperature range suggested by the Metal Quality Committee.

Preparation of Aluminum-Uranium Alloys

H. A. Saller, R. F. Dickerson, and N. E. Daniel

A program for the development of casting techniques for the production of aluminum-uranium alloys containing uranium in amounts of 30 w/o or higher has been initiated. Alloys that can be cast satisfactorily will be studied to determine their relative fabricability, corrosion resistance in both the as-cast and the fabricated condition, and the diffusion rate of uranium from the alloy into 2S aluminum.

A series of alloys containing 30, 35, 40, and 45 w/o uranium are being cast for preliminary investigations. Induction melting, both in vacuum and under a static helium atmosphere, is being studied. These relatively small castings — 1 in. in diameter by 5 in. long — will be analyzed for uranium content, and sections will be examined for porosity. Metallographic techniques will be used to determine the relationship between the compound particles and the matrix phase in the various alloys, and specimens of each composition will be corrosion tested in 100 C water in order to obtain preliminary information as to the relative corrosion resistance of the material.

Large-scale castings of alloys in this composition range will be attempted in the near future.

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C. PLANT ASSISTANCE TO MCW

J. R. Keeler

During the past month, the preparation of UO_3 was studied by means of differential thermal analysis. Three thermal arrests were observed. The significance of these arrests is being investigated further.

The electrical properties of UO_2 are being studied in an effort to correlate sinterability with these properties. The effect of annealing samples containing various amounts of excess oxygen at 400 C was measured. Marked changes in conductivity were observed which appear to be associated with the presence of U_4O_9 and U_3O_7 .

The corrosion studies on selected stainless steels and other corrosion-resistant metals in various plant liquors were continued. The effect of coupling titanium to Type 347 stainless steel in digest liquor was investigated, and the effect of chloride contamination on the corrosion rate of Type 347 stainless steel in refluxing 60 per cent nitric acid is being measured.

Investigation of Uranium Oxides

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

As assistance to Mallinckrodt Chemical Works, uranium oxides made by pyrolytic decomposition of uranyl nitrate are being studied. The objective is to characterize uranium trioxide in terms of reactivity, and dioxide in terms of reactivity and sinterability.

Previous reports have shown that there exists a relationship between the preparation method of the UO_3 and its structure type or reactivity toward hydration. These relationships are retained after hydrogen reduction. The reactivity of UO_2 toward air reoxidation and the sinterability of UO_2 are markedly affected by the structure and reactivity of the prior UO_3 .

During the past month, thermal activities (thermal arrest, by differential thermal analysis) of three preparations of UO_3 were determined in air and in hydrogen in order to understand better the process of reduction. The results, presented in Table C-1, show a marked effect of UO_3 preparation methods on the subsequent thermal activity in both air and hydrogen. Thermal arrests attributable to chemical reactivity occurred in three steps

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TABLE C-1. THERMAL ACTIVITIES OF THREE UO_3 PREPARATIONS DURING HEATING IN FLOWING AIR OR HYDROGEN

Sample	Method of Preparation ^(a)	Structure Type	Atmosphere ^(b)	Activity Measured by Differential Thermal Analysis ^(c)						Final Structure	Oxygen/Uranium Ratio After Exposure to Room-Temperature Air
				No. 1		No. 2		No. 3			
				Temperature, C	ΔT , C ^(d)	Temperature, C	ΔT , C ^(d)	Temperature, C	ΔT , C ^(d)		
203A	Continuous denitration of uranyl nitrate hexahydrate on moving belt at 450 C	Amorphous	Air	425	-3.0	595	-3.5	670	-3.5	U ₃ O ₈	2.68
			H ₂	330	+9.4	470	+29.5	535	+14.5	UO ₂	2.36
194A	50-g batch of uranyl nitrate hexahydrate denitrated for 24 hr at 250 C	III	Air	480	-1.5	595	-1.0	690	-31.0	U ₃ O ₈	2.67
			H ₂	480	+6.6	610	+33.0	670	+22.2	UO ₂	2.07
195A	50-g batch of uranyl nitrate hexahydrate denitrated for 24 hr at 400 C	III	Air	700	-24.5	--	--			U ₃ O ₈	2.67
			H ₂	580	+33.3	640	+20.6			UO ₂	2.13

(a) In the preparation, Samples 194A and 195A melted while Sample 203A decomposed without melting.

(b) Flow rate of gas was 50 ml per min.

(c) Heating rate of the samples was 5.5 C per min.

(d) ΔT , the peak height is proportional to the heat of reaction.

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and at three distinct temperature levels in two samples (Samples 203A and 194A). The lower temperature arrests in these two samples may be attributed alone to the release of residual nitrate or water in the UO_3 . Hence, for comparison of activity in air one might consider the third arrest in Samples 203A with that in Sample 194A and with the one arrest of Sample 195A. It is evident that the difference in structure of the UO_3 results in a wide difference in activity (ΔT) of the final air reaction. In the case of a reducing atmosphere, there is a wider variation in the final reduction temperature than in the magnitude of the activity. The reactivity of the resulting UO_2 as determined by its oxygen/uranium ratio after reoxidation at room temperature increases as the final reaction temperature (DTA analysis) decreases.

In order to obtain data for equilibrium conditions at the temperature of each arrest shown in Table C-1, samples of these UO_3 preparations were heated in air at the temperatures specified in Table C-2 and the weight change determined. X-ray diffraction data were obtained at the beginning and end of each run to determine when a phase change occurred. The results given in Table C-2 show that the amorphous UO_3 (Sample 203A) is converted to U_3O_8 at a much lower temperature than either of the other two samples. The percentage weight loss from all of the samples is considerably in excess of the 1.86 w/o that would be expected in conversion of UO_3 to U_3O_8 . This would suggest a considerable retention of nitrate or water in the UO_3 used in this experiment. In the case of Sample 203A, the water content was evident by the presence of $\text{UO}_3 \cdot \text{H}_2\text{O}$ in the X-ray analysis.

The studies of the thermal activity of various preparations of UO_3 will be continued during the next period.

The Electrical Properties of Uranium Dioxide

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

The basic objective of this project is the correlation of the sintering characteristics with the electrical properties of uranium dioxide. Recently the work has been concerned with the effect of excess oxygen and heat treatment on the electrical conductivity of pressed specimens of the compound.

In the last monthly report, the effect of a series of anneals at 200 C on the room-temperature electrical conductivity of pressed specimens of UO_2 containing various amounts of excess oxygen was described. It will be recalled that after 100 hr of annealing, the room-temperature conductivity of all the specimens was nearly constant. It was suggested that these constant

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TABLE C-2. EQUILIBRIUM WEIGHT CHANGE AND STRUCTURE MODIFICATION
DURING THERMAL DECOMPOSITION OF UO_3 IN AIR

Sample	Type of UO_3	Reaction Temperature, C	Weight Loss, per cent	Final Structure
203A	Amorphous + $\text{UO}_3 \cdot \text{H}_2\text{O}^{(a)}$	430	3.2	Amorphous
		595	5.0	U_3O_8
		670	5.6	U_3O_8
194A	III	430	0.5	III
		595	0.8	III
		690	2.8	U_3O_8
195A	III	595	0.2	III
		700	2.1	U_3O_8

(a) Sample hydrated some prior to this run.

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values represented an equilibrium condition and they were related to the probable presence of the U_3O_7 and U_4O_9 phases.

During the past month the same specimens were subjected to a series of anneals at 400 C. The first effect of the higher annealing temperature was an enhanced conductivity in each case. After about 30 hr of annealing at 400 C, the conductivity of each specimen again approached a constant value. These constant values are summarized in Table C-3. For convenience, the results of the 200 C anneal are included in Table C-3.

To explain the data of Table C-3, it must be understood that oxygen atoms occupy certain preferred positions in the UO_2 , U_4O_9 , and U_3O_7 phases. In these preferred positions, the oxygen atoms contribute few charge carriers to the conduction process, and, hence, the electrical conductivity of these phases is extremely low. Now, the effect of heat treatment is to displace the oxygen atoms from their preferred positions to a more random distribution. In the random positions, denoted by UO_{2+x} , U_4O_{9-y} , etc., in Table C-3, the oxygen atoms do contribute carriers to the conduction process. The number of oxygen atoms displaced from their preferred positions is dependent upon the temperature of anneal: increasing the anneal temperature increases the conductivity of a particular specimen.

It would appear from Table C-3 that the order of stability of the phases is: UO_2 , U_3O_7 , and U_4O_9 . Thus, at higher temperatures U_4O_9 tends to disappear according to the reaction:

This was particularly evident in the specimen having an oxygen/uranium ratio of 2.160. Stabilizing the specimen at 200 C resulted in n -type conductivity. Annealing at 400 C changed the specimen to p -type, with a much higher conductivity.

Some evidence of the reversibility of the above processes was obtained last month. After the 400 C anneal the specimens were allowed to age at room temperature for 2 weeks. They were then given a 16-hr anneal at 400 C. In each case the resulting conductivity was lower than previously measured and compared to the values obtained at 200 C. Since it is felt that the reversibility of the reactions involve a long and complicated time-temperature relationship, it will not be studied further.

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TABLE C-3. OXYGEN/URANIUM RATIO AND CONDUCTIVITY OF UO_2
BROUGHT TO EQUILIBRIUM AT 200 AND 400 C

Oxygen/ Uranium Ratio	Conductivity, 10^3 ohm-cm	Type	Probable Phases Present
<u>200 C</u>			
2.032	4.6	P	UO_{2+x}
2.074	6.5	P	$a\text{UO}_{2+x}+b\text{U}_4\text{O}_9$, $a>b$
2.132	4.8	P	$a\text{UO}_{2+x}+b\text{U}_4\text{O}_9$, $a\sim b$
2.160	8.0	N	U_4O_9-y
2.208	6.5	N	$b\text{U}_4\text{O}_9-y+c\text{U}_3\text{O}_7$, $b\sim c$
2.264	5.5	N	U_3O_{7-z}
2.317	1.3	N	U_3O_{7-z}
<u>400 C</u>			
2.032	7.5	P	UO_{2+x}
2.074	13.0	P	$a\text{UO}_{2+x}+b\text{U}_4\text{O}_9$, $a>>b$
2.132	9.1	P	$a\text{UO}_{2+x}+b\text{U}_4\text{O}_9$, $a>b$
2.160	15.0	P	$a\text{UO}_{2+x}+b\text{U}_4\text{O}_9$, $a\sim b$
2.208	18.5	N	$b\text{UO}_{9-y}+c\text{U}_3\text{O}_7$, $c>b$
2.264	12.7	N	U_3O_{7-z}
2.317	4.0	N	U_3O_{7-z}

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It is believed that the results discussed in the last several monthly reports have an important bearing on the sintering characteristics of uranium dioxide. The past work has demonstrated the following facts:

- (1) The linear increase of conductivity of UO_2 with increasing oxygen/uranium content up to about an oxygen/uranium ratio of 2.08
- (2) The existence of U_3O_7 and U_4O_9 phases in UO_2 of an oxygen/uranium ratio greater than 2.08
- (3) The instability of U_4O_9 at elevated temperatures
- (4) The enhancement of the conductivity of UO_2 by proper heat treatment.

Since it is felt that the presence of the U_3O_7 and U_4O_9 phases would hinder the proper sintering of UO_2 , it would appear that heat treatment of UO_2 having an oxygen/uranium ratio of about 2.07 to 2.09 would result in material with desirable sintering properties as well as maximum electrical conductivity.

It is planned to test these possibilities during the next month by determining the effect of preheat treatment on the sintering characteristics of regular MCW UO_2 .

Corrosion Studies of Titanium and Type 347 Stainless Steel

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

The corrosion of selected stainless alloys and other corrosion-resistant metals in various plant liquors from the process at the Mallinckrodt Uranium Refining Center is being studied. This month the galvanic action of titanium, coupled with Type 347 stainless steel in digest liquor, and the effect of chloride contamination on the corrosion rate of Type 347 stainless steel exposed to boiling nitric acid were investigated.

Titanium, as a construction material for process equipment, is known to perform well corrosionwise. Considering the high cost of titanium, it would be advantageous if it could be used only at critical points in equipment fabricated from Type 347 stainless steel. This necessitates studying the galvanic action of these two metals in several liquors representative of stages in the uranium-refining process.

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Both galvanic couples of Type 347 stainless steel with RC-55 titanium (commercially pure titanium) and uncoupled specimens were exposed separately for 96 hr to refluxing Reference 80 digest liquor (plant digest liquor containing 157 g per liter uranium adjusted to 80 g per liter uranium and 6 N free nitric acid).

Titanium, whether coupled or not, was not attacked by this exposure. Uncoupled Type 347 stainless steel corroded at a rate of 1.90 mils per month. Coupled to a small piece of titanium, the corrosion rate of the steel was of the same order, viz., 1.93 mils per month. However, Type 347 stainless steel, coupled to a titanium specimen of approximately equal area, corroded at a rate of 2.34 mils per month. These data indicate that relatively small areas of titanium could be attached to large areas of Type 347 stainless steel for use in a digest liquor without serious consequences. The use of large areas of titanium in contact with small areas of steel may prove to be unsafe from a corrosion standpoint. Further exposure of titanium-Type 347 stainless steel couples of various size relationships to digest liquors and other plant liquors will be made.

Type 347 stainless steel is used extensively throughout the nitric acid recovery system. Chloride contamination of the nitric acid is suspected, and studies are in progress to see how such contamination will affect the corrosion resistance of the equipment.

A series of twelve Huey-type corrosion tests has been completed. Type 347 stainless steel specimens were exposed for five 48-hr periods in the vapor, at the interface, and in the liquid phase of refluxing 60.0 per cent nitric acid containing chloride contamination. These contaminations ranged from 0.1 to 10.0 g per liter chlorides.

In this particular apparatus, the chloride concentration had little effect on the corrosion rates of the specimens in the liquid phase and only moderately affected those exposed at the interface. Specimens exposed in the vapor phase corroded excessively and erratically. There was a minimum amount of attack in the range of 0.5 to 2.5 per liter chlorides, with higher attacks occurring at chloride concentrations above and below this range. Presently, this is not completely understood. It is known that the chlorides do not persist, as such, for very long in boiling 60 per cent nitric acid. Further work will be directed toward improvising equipment which will allow a more constant chloride concentration to be maintained and which will give more reproducible corrosion rates.

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D-1

D. PROCESSING OF FEED MATERIALS

E. L. Foster, Jr.

A part of the research studies for National Lead of Ohio (NLO) is concerned with the evaluation of various salt-bath systems for use in the uranium production process. A reduction in the hydrogen picked up by the uranium during heat treating is the major improvement sought. Recent improvements in the testing apparatus have resulted in a definite correlation between atmospheric moisture content over the molten salt and the hydrogen content of the uranium treated in the salt.

Difficulties are being encountered in preparing dry ammonium diuranate in a form suitable for determining its heat capacity and heat of formation. Air drying the precipitated compound has reduced the ammonia-to-uranium ratio from the theoretical 1 to 1 to about 0.4 to 1.

Equipment for determining the melting point of UF_4 - UO_2 - UO_2F_2 mixtures has been assembled and tested.

Salts for Use in Uranium-Heat-Treating Salt Baths

R. A. Gilbert, K. A. Sense, and R. B. Filbert, Jr.

It is desired to develop a salt bath for processing uranium which provides for a minimum hydrogen pickup by uranium. Since a heat-treating bath is desired which will yield uranium with a minimum hydrogen content, the effect of moisture content of the atmosphere on hydrogen pickup is being investigated quantitatively for various salt mixtures.

As reported previously, the humidity control originally employed was not satisfactory. Following the installation of nickel liners in the furnaces, and flowmeters to measure air input, atmosphere checks indicated that much better control of the moisture content is being obtained.

It has also been determined that only platinum crucibles satisfactorily prevent "creeping" of the salts in a closed furnace such as is now being used.

The following procedure has been adopted for the tests: Two salt samples are tested at one time. Three samples of each salt are placed in each of two furnaces. The furnace temperatures are maintained at 600 F overnight to dry the salts, and then increased to 1350 F. In one furnace the partial pressure of water in the atmosphere is held at 70 mm mercury, while

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D-2

in the other furnace it is maintained at 0.5 mm mercury. At the end of a 5-day period, uranium samples are dropped into two of the three samples of each salt in each furnace and left for 1 hr. These samples are then removed, quenched in water, examined, and analyzed for hydrogen content.

The results obtained with this procedure are shown in Table D-1.

TABLE D-1. HYDROGEN CONCENTRATION IN URANIUM AFTER 1 HR IN 5-DAY-OLD SALT BATHS AT 1350 F

Sample	Composition of Salt Bath, w/o	Partial Pressure of H ₂ O in Liner Atmosphere, mm mercury	OH ⁻ Concentration in Salt, w/o	Hydrogen Content of Metal, ppm
80	44Li ₂ CO ₃ , 56K ₂ CO ₃	70	2.24	13.0
81	Ditto	70	1.87	13.8
82	25Li ₂ CO ₃ , 75K ₂ CO ₃	70	0.79	13.3
83	Ditto	70	--	13.6
84	44Li ₂ CO ₃ , 56K ₂ CO ₃	0.5	0.18	6.5
85	Ditto	0.5	0.15	4.6
86	25Li ₂ CO ₃ , 75K ₂ CO ₃	0.5	0.07	5.1
87	Ditto	0.5	0.10	5.0
Untreated uranium				<0.1

As noted in BMI-1080, a very wet atmosphere (70 mm of mercury) is being utilized in order to achieve results which would differ significantly from those obtained with a dry atmosphere. These results show a definite correlation between atmospheric moisture and hydrogen content of the treated uranium. Although the OH⁻ concentrations of the dry samples are lower than those of the wet, the correlation between this value and the hydrogen content is not as definite.

In addition to these tests, the effect of room atmosphere on salt samples over an extended period is being investigated. Open Vycor tubes containing several salt mixes are being maintained at 1350 F, exposed to the room atmosphere. At 7-day intervals, uranium samples will be dropped in, left for 1 hr, removed, quenched, and analyzed for hydrogen. No quantitative data are available yet.

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D-3 and D-4

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When evaluation of the mixes presently under consideration is completed, other mixes and other conditions will be studied in an attempt to find an optimum system.

Properties of Ammonium Diuranate

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

Difficulties are being encountered in preparing ammonium diuranate, $(\text{NH}_4)_2\text{U}_2\text{O}_7$, in a form suitable for determination of its heat capacity and heat of formation. All dry precipitates so far prepared have had an ammonia/uranium ratio only about one-half of that for $(\text{NH}_4)_2\text{U}_2\text{O}_7$. Precipitation from a very dilute solution avoided the intermediate UO_3 hydrate-precipitate stage and produced a product, which, when analyzed wet, had an ammonia/uranium ratio very close to the theoretical 1/1. However, upon air drying, the ratio dropped to 0.4/1. Work is continuing to determine if $(\text{NH}_4)_2\text{U}_2\text{O}_7$ can be isolated in a dry form.

Equipment for differential thermal analyses of $\text{UF}_4\text{-UO}_2\text{-UO}_2\text{F}_2$ mixtures has been assembled and tested; work is now beginning on the five plant samples just received from NLO.

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E-1

E. GENERAL FUEL-ELEMENT DEVELOPMENT

H. A. Saller

Programs in the broad fields of ceramics, metallurgy, and corrosion concerned with general fuel-element development are sponsored by the Reactor Development Division of the Atomic Energy Commission and Oak Ridge National Laboratory.

The investigation of graphite, BeO, and MoSi₂ as fuel-element matrix materials has continued. The determination of favorable sintering conditions for BeO was completed. Several samples of UO₂-MoSi₂ components were prepared for radiation-damage evaluation. The study of uranium losses from graphite was continued. In the study of thermal fracture, efforts are now concentrated on UO₂. Impurity content continues to be an important factor in determining the sinterability of oxide powders.

In the study of alloys for use above 650 C, the determination of elevated-temperature properties is still under way. Low-melting casting alloys are receiving similar evaluation prior to selection of samples for radiation testing. Examination of rolled composites of U₂Ti in a Zircaloy 2 matrix showed considerable stringing of the compound. Similar composites of UC in Type 302 stainless steel revealed no reaction between the two components. There was some fracturing of the UC particles, however. Hot hardness, melting point, and fluidity of several so-called fissium alloys have been determined.

The basic study of uranium corrosion is presently concerned with the effect of pH on corrosion rate. No new results are available on the study of the H₂-O₂-H₂O system. A topical report is being prepared.

CERAMICSRefractory Fuel Elements

L. D. Loch, C. Hyde, and A. G. Allison

Refractory fuel elements based on BeO, MoSi₂, and graphite are under development. The determination of favorable sintering conditions for BeO ceramics was completed. Preparation of UO₂-MoSi₂ compacts for radiation tests and measurements of uranium losses from graphite elements were continued.

E-2

BeO

Previous work (BMI-1020) disclosed that exceptionally strong BeO ceramics could be prepared from a readily sinterable powder by sintering at temperatures to give essentially nonporous bodies, but below those at which detrimental crystal growth begins.

A series of experiments was outlined to see just how strong a BeO ceramic could be made. It was demonstrated that the most readily sinterable powder was prepared from Brush Be(OH)₂ by calcining for 2 hr at 1740 F. Specimens compacted from this powder were sintered under various conditions of time and temperature to determine the relationship between modulus of rupture and crystal size. This study was completed during the month by repeating sintering trials at 2100 F for 1 and 4 hr.

The data, which are summarized in Table E-1, indicate that, with the particular BeO powder used, the strongest specimens were obtained by densifying under conditions which produced an average crystal size of about 3 to 5 μ . A modulus of rupture of 40,000 psi was obtained. Microscopic examination showed that sintering conditions that produced maximum strength resulted in the development of only a few coarse crystals. As the number and size of these increased with more severe sintering conditions, the strength of the specimens decreased.

TABLE E-1. BEND STRENGTH AND CRYSTAL SIZE OF BeO COMPACTS SINTERED IN HYDROGEN AT VARIOUS TEMPERATURES

Sintering Conditions		Bulk Density		Average Modulus of Rupture ^(b) , psi	Average Crystal Size, μ
Temperature, F	Time, hr	G Per Cm ³	Per Cent of Theoretical ^(a)		
2100	1	2.07	68.5	9,450	--
	4	2.32	76.7	21,500	--
2200	1	2.99	98.7	36,100	3.1
	2	2.95	97.5	40,350	3.0
2300	1	2.98	98.5	36,580	5.6
	2	2.99	98.7	23,240	26.8
2400	1	3.00	99.0	23,660	21.5
2500	1	2.99	98.7	22,300	31.0
2600	1	2.98	98.5	21,480	40.0

(a) The theoretical density of BeO is 3.025 g per cm³.

(b) Determined at room temperatures by midpoint loading on a 2-in. span.

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This work is being recessed, and studies of diffusion of UO_2 in the selected dense BeO ceramics will be started.

MoSi₂

Work was continued on fabrication of 30 w/o UO_2 -MoSi₂ specimens for radiation-damage experiments. Cored specimens, 3/16 by 3/16 by 2 in. in size, were made by hot pressing. The UO_2 was added to the core as minus 44- μ powder or as 300 to 350- μ nodules. A cladding of unfueled MoSi₂ was used.

If the fuel dispersion and cladding thickness in these specimens are found to be sufficiently uniform, this technique will be used to prepare specimens containing enriched UO_2 for in-pile tests.

Graphite

Experiments were continued to measure rates of uranium loss from graphite at high temperatures when UC_2 or UO_2 is incorporated in graphite-matrix elements.

The equipment for direct measurements of uranium loss was repaired, and a 120-hr test was made on a Cr_3C_2 -coated graphite tube loaded with UO_2 . Results are not available as yet.

To determine the extent of reaction between massive UO_2 and graphite, specimens of the two materials were heated in contact for 70 hr at 2500 F in vacuum. Examination of the samples after heating showed no evidence of uranium carbide at the interface. Uranium diffused into the graphite to the extent that the concentration was 1 mg of uranium per cm^3 at a distance of 0.05 cm from the interface. A similar experiment will be made using UC_2 to obtain comparative results.

Thermal Fracture of Ceramic Structures

A. K. Smalley and W. H. Duckworth

This work is directed toward determining the extent to which separable shape and material factors are useful in defining the resistance of ceramic structures to fracture from thermal stresses, and toward measuring shape and material factors of ceramic materials of AEC interest and reactor component shapes, respectively.

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Various production and experimental UO_2 bodies are being studied. During April, initial work was done on determining the material factor of UO_2 bodies prepared from a readily sinterable form of UO_2 . Hollow, circular cylinders, 1.1 in. in OD, 0.75 in. in ID, and 0.5 in. long, were prepared by sintering hydrostatically compacted specimens for 1 hr at 3200 F in hydrogen. These were tested in the thermal-fracture apparatus. Tests on three cylinders gave an average Q_{max} , the power per unit length at fracture, of 34.4 w per cm. The specimen temperature at failure was too low to be measured with an optical pyrometer, i. e., less than 1400 F. Determinations of specimen densities by xylene absorption and displacement indicated an average density of 10.07 g per cm^3 , or 91.8 per cent of the true density of UO_2 . Visual examination of the sintered specimens revealed small discontinuous pores. These were attributed to the presence of agglomerates in the raw batch.

By adjustment for differences in shape factor between these specimens and that of specimens of a UO_2 body similar to the WAPD-PWR fuel-element core reported last month, the following comparison of material factors can be made:

Readily sinterable UO_2	34.4
----------------------------------	------

WAPD-PWR UO_2	41.0
------------------------	------

Owing to the poor structure of the readily sinterable UO_2 body, the above comparison probably will be changed by future planned work on this material.

Work on a topical report for this project has been undertaken. This report will cover work done on the project from its inception to date.

Characterization of Sinterable Oxide Powders

J. F. Quirk and G. B. Engle

Research to investigate the relations between sinterability and other, more basic properties of refractory oxide powders was started with a study of BeO prepared from $\text{Be}(\text{OH})_2$. In previous work (BMI-1020), compacts of BeO powder prepared by calcining commercial $\text{Be}(\text{OH})_2$ were sintered to essentially theoretical density at 2400 F. Similar compacts of BeO powder prepared from laboratory-made pure $\text{Be}(\text{OH})_2$ did not approach theoretical density even when sintered at 3200 F. The preparation of the starting material, in this case $\text{Be}(\text{OH})_2$, is being studied as an approach to the more general problem of oxide sinterability and characterization.

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Since previous experiments indicated that impurities in the hydroxide affected the sinterability of the BeO, effort last month was directed toward the preparation of Be(OH)₂ of controlled impurity content.

This month, preparation of three Be(OH)₂ samples was completed. The samples were analyzed spectrographically and portions of each were calcined, compacted, and sintered. Also, the surface areas of the hydroxide powders were determined by nitrogen sorption. Table E-2 gives results of the spectrographic analyses, together with an analysis of the commercial Be(OH)₂.

TABLE E-2. IMPURITIES IN Be(OH)₂

Sample	Impurities, ppm of BeO											
	Na	Mg	Ca	Al	Si	B	Fe	Ni	Mn	Cr	Pb	Cu
LP23(a)	400	500	50	200	400	15	100	20	100	400	10	30
LP24(a)	300	150	50	<30	400	15	150	<5	10	50	8	30
LP25(a)	200	400	50	<30	300	10	200	<5	10	50	5	5
C5659(b)	2000	4000	2000	500	300	<1	75	100	400	200	5	1

(a) Prepared in the laboratory.

(b) Supplied by Brush Beryllium Company, Cleveland, Ohio.

The results show that the three laboratory-prepared hydroxides, including two (Samples LP23 and LP25) prepared from impure BeSO₄ solutions, were much purer than the commercial Be(OH)₂. All the samples were precipitated by the commercial process of adding NaOH to acid BeSO₄ solution.

Surface areas of the Be(OH)₂ samples, together with bulk densities of sintered BeO compacts made from them, are given in Table E-3.

TABLE E-3. SURFACE AREAS OF Be(OH)₂ POWDERS AND DENSITY OF SINTERED BeO MADE FROM THEM

Sample	Surface Area, m ² per g	Bulk Density of Sintered BeO Compacts ^(a)	
		G per Cm ³	Per Cent of Theoretical
LP23	14	2.95	97.5
LP24	18	2.63	87.1
LP25	16	2.96	97.8
C5659	4.8	3.01	99.4

(a) Made by calcining Be(OH)₂ at 1830 F, compacting at 100,000 psi, and sintering in hydrogen at 2600 F.

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The results show that the three laboratory-prepared hydroxides were much finer grained than the commercial $\text{Be}(\text{OH})_2$. Also, in this experiment the densities of the sintered BeO compacts were in the same order as the alkaline-earth impurity contents of the hydroxide starting materials. The significantly lower sintered density of BeO made from the purest hydroxide, Sample LP24, appears by comparison with Sample LP25 to be associated with lower magnesia content.

Attempts will be made to prepare an otherwise pure $\text{Be}(\text{OH})_2$ sample containing about 0.4 w/o magnesia for use in the sinterability studies. Examinations by X-ray and microscope, and surface-area determinations, will be continued on oxide powders which show significant differences in sinterability.

METALLURGY

Uranium Alloys for High-Temperature Application

R. F. Dickerson and W. E. Murr

Some binary uranium alloys are being investigated as possible high-temperature reactor fuels. Previously, the program has been concerned with physical properties of uranium-3, -5, -7, -10, -15, and -20 w/o zirconium and uranium-3.5, -5, -7, -9, and -12 w/o molybdenum. A topical report concerning this phase of work is being prepared.

At present, the program is concerned with the determination of mechanical properties of both groups of alloys at 550, 1000, and 1275 F. The necessary specimens are ready for testing, and the results of these tests will be reported when they become available.

Preparation and Properties of Low-Melting Alloys

R. F. Dickerson and W. E. Murr

Six low-melting uranium alloys are being investigated for possible application as reactor fuels. The alloys (listed in BMI-1062) include a binary eutectic (uranium-5 w/o chromium) and five chromium-containing uranium ternaries. The binary eutectic is included in the study as a basis for evaluating the properties of the five other alloys.

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Results of some mechanical-property determinations of uranium-5 w/o chromium and uranium-5 w/o chromium-1 w/o molybdenum at 550 and 1000 F are listed in Table E-4. The alloys were cast into the form of 5/8-in. -diameter rods, machined to 3/8-in. -diameter tensile specimens, and heat treated as follows: 5 min at 780 C, 2 hr at 475 C, and water quenched.

TABLE E-4. MECHANICAL PROPERTIES OF URANIUM-5 w/o CHROMIUM AND URANIUM-5 w/o CHROMIUM-1 w/o MOLYBDENUM

Nominal Alloy Content (Balance Uranium), w/o	Temperature, F	Tensile Strength, 1000 psi	Elongation, per cent	Reduction in Area, per cent
5Cr	550	103.1	6.5	21.1
	1000	32.9	33.8	88.2
5Cr-1Mo	550	127.5	4.1	8.8
	1000	51.2	8.8	21.5

From the table, it appears that the addition of 1 w/o molybdenum has improved the strength of the basic uranium-chromium alloy at the two temperatures studied. In addition, the ductility of the base alloy is greatly reduced by the molybdenum addition.

Tensile properties are being determined on other low-melting alloys. After the information becomes available, an evaluation of physical and mechanical properties will be made, and two of the most promising alloys will be selected for a radiation-damage study.

Compartmentalized Fuel Elements

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

Research in the program for the development of cermet-type fuel elements has in the past month been directed toward fabrication procedures for the following combinations: U_2Ti in a Zircaloy 2 matrix, U_6Ni in a Zircaloy 2 matrix, and UC in a stainless steel matrix.

Two packs containing 30 volume per cent U_2Ti in Zircaloy 2 were fabricated at 1500 F. In both packs, the particles of U_2Ti were elongated and were at least partially continuous. The U_2Ti powder used in one pack was produced by ball milling, while the U_2Ti in the second pack was comminuted by hand in a steel mortar. In an effort to eliminate the problem of elongated dispersion particles, U_2Ti is now being prepared by the hydriding and dehydriding procedure. In this manner, it may be possible to obtain and maintain equiaxed fuel particles.

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Four packs containing cores of 30 volume per cent UC in Type 302 stainless steel powder have been rolled. Two packs which were rolled at 2000 F could not be reduced to the desired thickness because of cracking of the cover plates above the core. Metallographic specimens are being prepared to examine the extent of reaction or determine what caused the pack failures. One pack was rolled at 1900 F; however, examination has not been completed. The fourth pack was rolled at 1800 F. Metallographic examination indicated that there was sound core-to-cladding bond and that there was no reaction between the UC and stainless steel. However, there was indication of some fracturing of UC particles.

One pack containing a core of 30 volume per cent U_6Ni in Zircaloy 2 was rolled at 1500 F. No examination of this pack has been made at this time.

Properties of Fissium Alloys

R. F. Dickerson and N. E. Daniel

Due to the interest in fissium alloys as a possible fuel for power reactors, a program for the determination of the physical properties of such an alloy is in progress. Those properties which have been determined include the melting point, the hot hardness, and the fluidity of the alloy. Specimens have also been submitted for the determination of tensile properties, thermal stability, thermal expansion, and thermal conductivity.

The hot-hardness determinations were obtained for the temperature range from 300 to 800 C at 50 C intervals on the as-fabricated alloy, and the data are listed below.

<u>DPH,</u> <u>kg per mm²</u>	<u>Temperature,</u> <u>C</u>
264	300
394	400
324	450
179	500
89	550
22.5	600
10.6	650
7.1	700
4.8	750
3.7	800

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Melting-point determinations were made on a series of six samples from various parts of an ingot. The temperature at which melting began was found to be 1836 F, and the end of melting occurred at 1977 F. The fluidity tests were conducted in vacuum utilizing a foundry-type spiral graphite mold, and the results of these tests are listed below.

<u>Pouring Temperature, F</u>	<u>Superheat, F</u>	<u>Amount of Flow, in.</u>
2102	125	3/16
2277	300	1/2
2402	425	1

Because of an obvious need for more than a cursory examination of the heat treatability of the alloy, this phase of the program is being expanded, and the results of the study will be reported as they become available.

CORROSIONMechanism of Uranium Corrosion

J. B. Schroeder and C. M. Schwartz

The study of the mechanism of uranium corrosion is continuing. It has been shown that: (1) the products of aqueous uranium corrosion are nonstoichiometric oxides with the UO_2 structure, a hydrated UO_3 , and an unidentified soluble phase; (2) UO_2 which is readily air oxidized is also apparently oxidized by 60 C water; (3) UH_3 reacts slowly with water after it has been coated with a very thin oxide film; and (4) the corrosion rate of uranium is not constant with time.

At the present time tests are under way to find what effect pH has upon the corrosion rate of uranium and how far the oxidation of UO_2 proceeds in 60 C water. No results are available at the present time.

Correlation of Microstructure With Corrosion
Behavior of Uranium Alloys

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

A study is being made of the relationship between microstructure and corrosion behavior of uranium alloys as a part of the general fuel-element-development program.

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During the past month, an effort was made to follow the progress of corrosion in boiling water of uranium alloys containing 0.5, 1, and 2 w/o aluminum, 0.5 and 1.0 w/o silicon, or 1, 2, and 4 w/o zirconium. Samples of each alloy exposed more than 1000 hr were subjected to a metallographic examination to determine the cause of the observed pitting attack. Although hydride needles were observed near the surface of several of the alloys, no changes in structure were noted which would account for the pitting attack. Additional microsections of each alloy are being prepared.

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

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

There are no additional experimental data this month. The results of the entire study are being correlated and a topical report is being prepared.

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F. STUDIES OF ZIRCONIUM-URANIUM ALLOYS

H. A. Saller

Wide-spread interest in zirconium-uranium alloys has led to an investigation of this system for alloys containing up to 70 w/o uranium. This program is sponsored by the Reactor Development Division of the Atomic Energy Commission.

The current program is concerned with studies of the constitutional diagram, transformation kinetics, heat treatment, corrosion resistance, and radiation stability of these alloys. Progress on the various phases of the programs is reported in the following sections.

Constitution of Zirconium-Uranium Alloys

F. A. Rough and A. A. Bauer

In order to determine the solubility limits of the alpha-plus-beta zirconium region of the zirconium-uranium system, a quantitative study of the effect of oxygen and nitrogen, respectively, on the region is being made with the aim of analyzing the results obtained with ternary alloys to determine the binary limits by extrapolation.

Quantitative lineal data have been obtained on a series of 22 and 40 w/o uranium alloys with varying oxygen contents. An attempt was made to estimate the oxygen content of the alpha zirconium present in these samples by determining lattice-parameter expansions and correlating these expansions with those reported by DeBoer and Fast* for a series of zirconium-oxygen alloys. The estimated oxygen contents were found to be higher than appeared reasonable. Therefore, a check on the values reported by DeBoer and Fast was made on a specimen containing 0.97 w/o oxygen, as determined by vacuum-fusion analysis. The lattice-parameter expansion observed in this specimen was equivalent to the expansion reported by DeBoer and Fast for zirconium containing about 2 w/o oxygen. As a result, additional zirconium-oxygen alloys are being prepared for a redetermination of the effect of oxygen on the zirconium lattice parameters.

Meanwhile, additional zirconium-uranium alloys containing various amounts of oxygen and nitrogen, respectively, have been arc melted and are being prepared for fabrication to rod.

*DeBoer, J. H., and Fast, J. D., "Electrolysis of Solid Solutions of Oxygen in Metallic Sodium", Rec. trav. chim., 59, 161 (1940).

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Transformation Kinetics and Hardening Reaction 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-rich uranium alloys are being determined so that a better insight of the possible heat treatments and resultant structures may be obtained.

In the study of transformation, isothermal heat treatments of beta-quenched alloys have been performed on 7, 10, 15, and 20 w/o uranium alloys at 500, 550, 650, and 750 C for times varying from 1 min to 15,000 min. Metallographic examination of the samples is currently being performed along with X-ray diffraction phase analysis. The familiar "C" curves for start of transformation are being determined. Current plans call for the use of lineal analysis to determine the finish of α precipitation in the $\alpha + \beta$ region.

There is no further progress to be reported on the hardening reaction studies.

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

F. A. Rough and A. A. Bauer

A study of the transformation kinetics of zirconium alloys containing 20 to 70 w/o uranium is being made with the aim of achieving a description of the beta zirconium-to-epsilon transformation. Work at present is concentrated on the 50 w/o uranium alloy, and metallographic, X-ray, hardness, resistivity, internal-friction, and dynamic-modulus data are being obtained.

Internal-friction and dynamic-modulus measurements have indicated that beta decomposition begins between 100 and 200 C on heating. A series of 50 w/o uranium specimens prepared to investigate this effect were transformed at 200, 300, and 400 C, both isothermally after 1 hr at 800 C and by annealing after water quenching from 800 C. Hardness measurements show that transformation begins practically instantaneously under all these conditions. In fact, less than 10 sec at 200 C, after water quenching from 800 C, is required for an increase in hardness to be noted.

Internal-friction data obtained on beta-quenched 50 w/o uranium specimens during transformation on heating to 525 C and during transformation

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at 184 and 384 C indicate that the initial structural modification which occurs during transformation may be an ordering of the beta phase. This is followed by a transformation of ordered beta to epsilon. These steps in beta decomposition would apparently coincide with the hardening and overaging phenomena observed. No evidence for dependence upon strain amplitude was observed during the internal-friction measurements, which indicates that the beta and epsilon phases may be noncoherent.

Additional internal-friction and low-temperature-resistivity measurements are to be obtained to study these changes more thoroughly. An X-ray description of the changes accompanying transformation is also being obtained.

Heat Treatment of Zirconium-Uranium Alloys

F. A. Rough and W. Chubb

Zirconium-uranium alloys are being studied in an attempt to understand the severe hardness and embrittling reaction that occurs when beta zirconium containing 20 to 80 w/o uranium transforms to the low-temperature phases.

Isothermal-transformation studies on iodide-zirconium-base alloys containing 40 to 60 w/o uranium show that the transformation-hardness reaction proceeds in almost the same fashion for all these alloys. On the basis of these studies, samples of alloys containing 40 to 70 w/o uranium have been heat treated for mechanical testing. The treatments selected are representative of the alloys as (1) treated to retain beta zirconium, (2) treated to maximum hardness, (3) partly overaged, and (4) overaged. These results when available will be reported in the section on mechanical properties.

No further work is planned on this program.

Corrosion of Zirconium-Uranium Alloys

W. E. Berry and R. S. Peoples

The corrosion behavior of zirconium-uranium alloys is being studied as a part of the over-all AEC program to investigate the properties of these alloys. Tests are in progress in 680 F degassed water to determine the effects on corrosion behavior of several zirconium melting stocks and several selected heat treatments. Alloys contain 0 through 70 w/o uranium

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with crystal bar, sponge, or high-oxygen-sponge zirconium melting stock. Heat treatments studied were: (1) 650 C, 12 hr, water quench and (2) 650 C, 12 hr, quench to 550 C, hold 4 hr, furnace cool.

After 70 to 105 days of exposure, the following trends have been observed:

- (1) The crystal bar zirconium-7 and 10 w/o uranium alloys in both heat-treated conditions and the crystal bar zirconium-15 w/o uranium alloy in the water-quenched furnace-cooled condition continue to possess adherent corrosion films. The water-quenched crystal bar-15 w/o uranium alloy and specimens from both heat treatments of the sponge zirconium-22 w/o uranium alloy developed an adherent film and gained weight at a linear rate until after approximately 70 days of exposure, when the oxide film on these samples began to flake. Samples of the oxide have been submitted for X-ray analysis in an attempt to determine the progress of corrosion. A sponge zirconium-15 w/o uranium alloy and a high-oxygen-sponge zirconium-22 w/o uranium alloy, water quenched from 650 C, are alternately gaining weight at a linear rate over a 28 to 35-day period, then losing weight over a 7 to 14-day period.
- (2) With the exception of the above alloys, all other alloy compositions of the three zirconium base stocks lost weight at a linear rate after an initial 7 to 14-day period during which an oxide film formed and then flaked off.
- (3) Epsilon phase uranium-crystal bar zirconium base alloys water quenched from 650 C have a tendency to crack during corrosion testing.

A beta-quenched crystal bar zirconium-55 w/o uranium alloy which was cold reduced 50 per cent exhibited laminar cracking when corrosion tested in 680 F water. Striations were found in a duplicate piece which had not been corrosion tested. The original hot-rolled sheet before cold reduction also contained striations. Further studies will be made to determine the origin of the striations and their role in the peculiar corrosion behavior noted.

The above studies are being continued. Future work will be directed toward establishing the relationship between water temperature and corrosion rates of these alloys.

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Radiation Stability of Zirconium-Uranium Alloys

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

The investigation of the radiation effects on zirconium-uranium alloys is being continued. The initial work is being done on five of eight zirconium-uranium alloy specimens which had been irradiated at KAPL and were made available to Battelle. Two specimens are zirconium-22 w/o uranium alloy clad with Zircaloy 2 and three specimens are bare zirconium-40 w/o uranium alloy.

Dimensional measurements, density measurements, and photomicrographs were made on each specimen. The specimens were then sealed in small Vycor vials under a pressure of 4×10^{-5} mm of mercury. Three specimens were given an isothermal heat treatment at a temperature of 725 C for 50 hr, and the remaining two specimens were thermal cycled between 400 C and 700 C for 226 cycles and 100 cycles. A Zircaloy 2-clad specimen was given each type of heat treatment. Post-heat-treatment density measurements, dimensional measurements, photomicrographs, and a visual examination for each specimen will be made on these specimens.

The work is continuing on the radiation-effects program for zirconium-22 w/o uranium alloy specimens which have been prepared by Battelle. Pre-irradiation tests and measurements on 18 specimens representing three different conditions of heat treatment have been completed. Electrical-resistivity measurements have been made on four specimens of each different heat treatment at temperatures of -200 (liquid nitrogen), 25 and 150 C. It is planned to irradiate four specimens from each heat treatment and to use the remaining six specimens for destructive tests and control studies. The specimens will be irradiated in both a temperature-controlled capsule at 725 C and in noncontrolled capsules at about 400 C. A burnup of 2 total a/o is planned for each alloy.

A temperature-controlled capsule is currently being designed and fabricated. The special heating element for this capsule has been delivered and is now being tested to determine if it will supply the required output.

A device for opening irradiation capsules in an inert atmosphere or under vacuum is now being designed. This device will facilitate the direction of the fission gas which is released during irradiation to a fission-gas-analysis apparatus.

A fission-gas-analysis apparatus is in the initial stages of design. Several possible systems of counting and measuring fission gas are being investigated. A system will be designed which will give accurate

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measurement determinations of small quantities of fission gas released from a fuel-alloy specimen during irradiation and also during postirradiation heat treatments.

The investigation of the zirconium-uranium alloy system is being continued. The purpose of this work is to determine additional alloy compositions which will give the most useful information from irradiation tests. At present, it is planned to irradiate both zirconium-50 and 70 w/o uranium alloys with several different heat treatments.

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G. CORROSION STUDIES OF ZIRCONIUM

R. S. Peoples

Described in the following sections is the program for the AEC Reactor Development Division on the corrosion behavior of zirconium-base cladding materials. The ORNL-supported research on electrocladding of zirconium with platinum also is outlined.

The corrosion studies guided by the Zirconium Corrosion Committee's program to develop new corrosion-resistant zirconium sponge-base alloys have been continued. Ternary and quaternary alloys containing combinations of iron, nickel, and tin are being evaluated in 750 F steam and 680 F and 600 F water. Results continue to indicate that the most promising compositions are those containing 0.25 to 0.5 w/o tin plus 0.1 to 0.25 w/o iron and/or nickel. Reaction rates of hydrogen with zirconium and zirconium alloys at 400 C have been determined for three heat-treatment conditions. Corrosion rates for similar heat-treated samples were determined in 750 F steam.

In other investigations, a study is being made of the reaction of zirconium with water vapor at subatmospheric pressures. Rate constants for reactions at 670 and 770 C follow a parabolic law.

The studies for ORNL have included electrocladding of the new flat-type specimens with nickel plus platinum and just platinum.

Corrosion of Zirconium and Zirconium Alloys

W. K. Boyd and R. S. Peoples

Corrosion investigations to determine compositional variations which affect the corrosion behavior of zirconium and zirconium alloys are being conducted in 750 F steam (1500 psi) and 680 and 600 F degassed water.

No indication of breakaway in 600 F water has been noted for specimens representing seven different melts of Zircaloy 2. Corrosion rates are of the order of 5 mg/(dm²)(month) after up to 34 months of exposure.

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Evaluation of a series of Zircaloy 2 melts intentionally contaminated with various amounts of hydrogen, nitrogen, or oxygen has been continued. Corrosion data based on 322 days in 680 F degassed water continue to indicate no effect of hydrogen in the range 500 to 1500 ppm. Oxygen contents of more than 6000 ppm accelerate corrosion, as do nitrogen additions of more than 200 ppm. Corrosion resistance is completely destroyed with nitrogen additions above 390 ppm.

Zirconium Corrosion Committee Program

Corrosion studies have been continued for ternary and quaternary sponge-base melts prepared at Battelle and at the BuMines containing 0.25 to 0.50 w/o tin plus 0.04 to 0.45 w/o iron and/or nickel. After an additional month of exposure (up to a total of 308 days in both 750 F steam and 680 F water), corrosion data are similar to those summarized in Tables G-1, G-2, and G-3 of BMI-1080. The tin-nickel ternary alloys continue to evince somewhat better resistance to 750 F steam than do the tin alloys containing like additions of iron. However, the reverse is true for 680 F degassed water. In general, heat treatments based on a slow cool from 775 C or a quench from 900 C do not significantly alter the corrosion properties of the alloy systems studied. Nitrogen contents of 150 ppm and above accelerate corrosion at tin levels of 0.5 w/o or less. Additions of 200 ppm aluminum also reduce corrosion resistance.

Effect of Heat Treatment

Corrosion data based on more than 8 months of exposure in 750 F steam continue to indicate that binary zirconium-iron and zirconium-nickel alloys are more resistant if the structures are composed of a fine dispersion of compound particles in an alpha matrix. Structures containing large colonies of compound particles separated by alpha platelets are the least resistant.

All the above studies are being continued.

Mechanism of Zirconium Corrosion

C. M. Schwartz and D. A. Vaughan

An investigation is being made of the effect of hydrogen, picked up by zirconium during exposure to high-temperature water or steam, upon the corrosion of zirconium. Previous studies had shown that a layer of hydride is formed between the oxide film and the metal at breakaway, and that the

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reaction of hydrogen with zirconium or Zircaloy 2 reduces the corrosion resistance of the metal. A comparison of the hydrogen-reaction rates and corrosion rates of several zirconium alloys is being made.

In order to test the same surface both as to hydrogen reaction and corrosion, both tests were made on the as-heat-treated surface. A summary of the results obtained to date are given in Table G-1. For the alloys studied, the hydrogen-reaction rates follow either a linear or a parabolic rate law. The corrosion data are much more complex and do not appear to agree with previous results on corresponding alloys. This difference in corrosion behavior is probably due to substitution of the heat-treated surface for the conventional pickled surface; hence, the corrosion tests are being discontinued. The hydrogen reaction-rate studies on the sponge zirconium and the zirconium-iron alloy will be completed during the next period.

Zirconium-Gas Reactions

M. W. Mallett and W. M. Albrecht

Zirconium-Water Vapor

A study is being made of the kinetics of the reaction of zirconium with water vapor at subatmospheric pressures.

Additional work was carried out to check the operation of the micro-balance used to obtain kinetic data. The reaction of a zirconium specimen with oxygen at 800 C at 1/2 atm pressure followed the cubic rate law with a rate constant of $6.9 \times 10^5 (\mu\text{g}/\text{cm}^2)^3/\text{sec}$. This is in agreement with results of a previous study* of the zirconium-oxygen reaction carried out at atmospheric pressure in a Sieverts apparatus (volumetric technique) where a cubic rate constant of $2.7 \times 10^6 (\mu\text{g}/\text{cm}^2)^3/\text{sec}$ [$9.3 \times 10^{-4} (\text{ml}/\text{cm}^2)^3/\text{sec}$] at 800 C was obtained.

Kinetic data of the zirconium-water vapor reaction are being obtained at water-vapor pressures of 33 mm of mercury (vapor pressure of water at room temperature). Rate constants for reactions at 670 and 770 C reported last month were in error. A check of the calculations gave parabolic constants of 72 and 300 $(\mu\text{g}/\text{cm}^2)^2/\text{sec}$ at 670 and 770 C, respectively.

A rate experiment was carried out at 770 C and a water-vapor pressure of 1 mm of mercury to determine the pressure dependency of the reaction. A parabolic rate constant of 350 $(\mu\text{g}/\text{cm}^2)^2/\text{sec}$ was obtained which is

* Belle, J., and Mallett, M. W., J. Electrochem. Soc., 101, 339 (1954).

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TABLE G-1. COMPARISON OF 400 C HYDROGEN REACTION RATES WITH 400 C CORROSION DATA FOR SEVERAL ZIRCONIUM ALLOYS

Sample	Zirconium Alloy, w/o	Heat Treatment	Hydrogen-Reaction ^(a) Rate at 1 Atm Pressure	Weight Gain, mg per dm ² , During Exposure to 400 C Steam ^(a)					
				18 Hr	36 Hr	54 Hr	108 Hr	252 Hr	396 Hr
V1	Fabricated crystal bar	800 C anneal	0.72 (ml/cm ²) ² /sec ^(b)	8	25	32	32	37	Flaked badly
V2	Ditto	1050 C anneal	0.57 (ml/cm ²) ² /sec ^(b)	4	21	30	30	35	43
V3	Ditto	1050 C quenched	0.72 (ml/cm ²) ² /sec ^(b)	2	22	40	52	46	36
V4	Fabricated sponge	800 C anneal	--	9	105	119	21	28	39
V5	Ditto	1050 C anneal	--	89	114	127	123	135	172
V6	Ditto	1050 C quenched	--	10	36	88	44	46	61
V7	Zircaloy 2	800 C anneal	2.3 ml/(cm ²)(sec) ^(c)	12	19	22	28	32	67
V8	Ditto	1050 C anneal	1.9 ml/(cm ²)(sec) ^(c)	6	17	25	27	34	99
V9	Ditto	1050 C quenched	2.2 ml/(cm ²)(sec) ^(c)	5	13	25	24	31	40
V10	Crystal bar + 0.1 Fe	800 C anneal	--	11	22	29	30	36	47
V11	Ditto	1050 C anneal	--	7	86	37	Lost weight		
V12	Ditto	1050 C quenched	--	4	27	40	49	53	110
V13	Crystal bar + 2.5 Sn	800 C anneal	3.8 ml/(cm ²)(sec) ^(c)	15	53	83	168	393	4305
V14	Ditto	1050 C anneal	6.1 ml/(cm ²)(sec) ^(c)	16	27	37	64	249	297
V15	Ditto	1050 C quenched	3.8 ml/(cm ²)(sec) ^(c)	9	12	23	19	125	91
V16	Crystal bar + 0.05 Ti	800 C anneal	0.55 (ml/cm ²) ² /sec ^(b)	15	65	71	67	73	91
V17	Ditto	1050 C anneal	0.52 (ml/cm ²) ² /sec ^(b)	8	110	121	119	126	132
V18	Ditto	1050 C quenched	0.59 (ml/cm ²) ² /sec ^(b)	6	130	132	134	145	153

(a) The reactions were studied on the as-heat-treated surface, heating done in vacuum.

(b) A parabolic rate constant, the reaction products were adherent to the specimens.

(c) A linear rate constant, the reaction products flaked off during reaction.

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in good agreement with the constant, $300 (\mu\text{g}/\text{cm}^2)^2/\text{sec}$, obtained at a water-vapor pressure of 33 mm of mercury. From this, it appears that the reaction is not pressure dependent.

The above reaction experiments were made with small cylindrical zirconium specimens, 1/8 in. in diameter with surface areas of about 1 cm^2 . However, to make rate runs at lower temperatures, specimens with larger surface areas are desirable. Therefore, a supply of sheet zirconium, 0.012 in. thick has been obtained. For a run made at 500 C at a water-vapor pressure of 33 mm of mercury, using the sheet material, the reaction followed a cubic rate law. The calculated rate constant was $2.3 \times 10^3 (\mu\text{g}/\text{cm}^2)^3/\text{sec}$. To confirm that the cubic rate at 500 C with sheet material was not an effect of specimen geometry, a reaction run was made at the same temperature using a cylindrical specimen. This reaction also followed the cubic rate law, with a rate constant of $1.2 \times 10^3 (\mu\text{g}/\text{cm}^2)^3/\text{sec}$. Apparently, the reaction of zirconium with water vapor may follow the cubic rate law at even lower temperatures. Rate data will be obtained at 300 and 400 C to check this.

Electrocladding of Zirconium With Platinum Metals

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

Work has proceeded on the preparation of the new flat, rectangular corrosion coupons.

Three types of electrocladding were used on the zirconium test strips. The first consisted of a nickel undercoat covered with platinum and with no diffusion bonding of nickel to zirconium. Platinum alone comprised the second type of coating and it was not diffusion bonded. The third type was the duplex nickel and platinum cladding with the nickel diffusion bonded to the zirconium.

Following the electrocladding operation, the coupons were cut from the strips and ground to size. The first two types of coatings were not sufficiently well bonded to withstand the machining operations and they separated from the basis metal. The third group has not been machined as yet.

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H. REACTOR MATERIALS DEVELOPMENT

H. A. Saller

The programs covered in this section of the report are concerned with the development of materials for general reactor application. These programs are sponsored by the Reactor Development Division of the Atomic Energy Commission and Argonne National Laboratory.

Studies of the heat treating of zirconium alloys are being brought to a close with a determination of elevated-temperature properties of two alloys in several states of heat treatment.

In the enameling studies, results on fine-grained and coarse-grained uranium showed little difference. Both were cracked.

The determination of the kinetics of the zirconium- UO_2 reaction is continuing. Results obtained on a sample heated at 1600 F for 95 hr are reported.

Adherent uniform coatings of molybdenum were deposited on the outside of small-bore stainless steel tubing by means of thermal decomposition of molybdenum carbonyl. The program is now directed toward producing thicker nonporous coatings.

Studies of Zirconium Heat Treatment

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

The primary objective of this research is a study of the heat treatability of certain zirconium alloys. These alloys contain enough beta-stabilizing elements to respond to solution treating and aging heat treatments. Strengths of up to 200,000 psi have been obtained for alloys containing molybdenum or niobium and tin. However, the tensile elongation was rather low. In the current research, attempts are being made to determine the cause of the low ductility. This research includes an investigation of the kinetics of the beta to omega to alpha transformation reaction and of what effects, if any, small amounts of hydrogen have on the tensile properties. Fifteen-pound double-melted ingots of a 5 w/o molybdenum-2 w/o tin and a 5 w/o niobium-2 w/o tin alloy are being used for the present investigation.

The age-hardening study for both alloys has been completed. X-ray diffraction data for the niobium alloy were included in BMI-1080. During

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the past month, tensile properties of the niobium-tin alloy were obtained in several conditions of heat treatment. In general, the elongation values were rather low for the strengths obtained, as shown by the following selected results:

<u>Tensile Strength,</u> <u>psi</u>	<u>0.2 Per Cent Offset</u> <u>Yield Strength, psi</u>	<u>Elongation in 1 In.,</u> <u>per cent</u>
190,500	178,000	2
177,500	159,500	4

Because these values are lower than expected from experience with an earlier 5-lb heat of the 5 w/o niobium-2 w/o tin alloy, a complete analysis of both heats is being obtained.

Also during the past month, X-ray diffraction patterns have been obtained for many of the aged conditions for the 5 w/o molybdenum-2 w/o tin alloy. This alloy behaves as expected, showing the transformation of beta to omega to alpha-plus-compound with increasing aging times; the time required for the changes to take place decreases as the aging temperature increases. Tensile properties will be obtained for this alloy in several heat-treated conditions.

The investigation of the effect of hydrogen is concerned with the partitioning of hydrogen due to heat treatment. The partitioning is being determined by autoradiography, using tritium as the radioactive tracer for hydrogen.

In addition to autoradiography, limited stress-rupture tests will be made on the 5 w/o molybdenum-2 w/o tin and 5 w/o niobium-2 w/o tin alloys heat treated to a high-strength condition.

Enameling of Special Metals

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

A study is being made of the possibilities of enameling certain metals of interest to the AEC and of some of the properties of such coatings. The enameling of uranium is currently under investigation.

In the work to date, difficulties in enameling uranium have been due to cracking of the coating during cooling. As an aid in determining the cause of cracking, a plate of uranium-0.5 w/o chromium alloy has been obtained for enameling studies. This alloy, after beta quenching, has been found to have small, randomly oriented grains. A grain structure of this type should alleviate cracking caused by differential thermal expansion of the metal.

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Enameling studies of the alloy, this month, revealed little difference in the tendency of the enamels to crack, irrespective of whether they were applied to the beta-quenched alloy or to pure beta-quenched uranium.

Two enamel compositions reported in KAPL-1479 were smelted at Battelle and applied to uranium plate. An enamel based on the $\text{Na}_2\text{O-PbO-SiO}_2$ eutectic, with CuO introduced to promote adherence, had excellent adherence to the metal. Although no cracks were apparent at the glass surface, reflections of light from the interface indicated that cracking had occurred. The other composition cracked fairly severely.

Future work will include a fairly broad study of phosphate-enamel compositions which might be applicable to uranium.

Kinetics of the Zirconium-Uranium Dioxide Reaction

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

Fuel elements composed of uranium dioxide are being considered for some reactor applications. In order to prevent contamination of the reactor coolant, the UO_2 must be protected by a suitable jacket. Alloys of zirconium are possible jacket materials and this study is being made to obtain information on the compatibility of zirconium in contact with UO_2 at elevated temperatures.

The heating of sandwich-type elements at 950, 1100, and 1200 F in autoclaves is continuing. The heating of an additional element at 1600 F for 500 hr has been completed and analyses will be obtained. It is planned to begin the heating of similar elements at 1450 F in the very near future.

Analyses for oxygen and uranium of chip samples machined from the zirconium in layers near the interface of a large element heated at 1600 F for 95 hr have been completed. These analyses, together with the microstructure in the reaction zone of this element, are shown in Table H-1. Layer 1 was a cleaning cut and no analyses were obtained. The uranium content is moderately high and the oxygen content also is relatively high in the two-phase alpha uranium-alpha zirconium region adjacent to the UO_2 (Layer 2). In Layer 3, the uranium content increases and the oxygen decreases. This layer was immediately adjacent to the stained band. Layer 4 shows the highest uranium content of any of the layers analyzed and also has a relatively low oxygen content. This layer was taken from a section of the sample which included a good part of the stained band. Although X-ray diffraction identification of this stained material has not been obtained, it appears likely that it will have either the structure of alpha uranium or of

TABLE H-1. URANIUM AND OXYGEN CONTENTS AT INDICATED DISTANCE FROM ZIRCONIUM- UO_2 INTERFACE FOR ELEMENT HEATED AT 1600 F FOR 95 HR IN ARGON AND QUENCHED

Layer	Distance of Layer From Zirconium- UO_2 Interface, mils	Oxygen, w/o	Uranium, w/o
1	0 - 1.5	Cleaning cut	No analysis
2	1.5 - 2.5	3.66	15.5
3	2.5 - 3.0	2.45	37.5
4	3.0 - 4.0	1.06	58.6
5	4.0 - 5.0	1.47	40.6
6	5.0 - 6.0	2.56	6.9
7	6.0 - 7.0	2.52	0.15
8	7.0 - 8.0	1.94	0.051
9	8.0 - 9.0	1.94	0.058
10	9.0 - 10.0	1.51	0.028
11	10.0 - 11.0	1.28	0.016
12	11.0 - 12.0	0.864	0.075(a)
13	12.0 - 13.0	0.909	0.018
14	13.0 - 14.0	0.214(a)	0.018
15	14.0 - 15.0	0.450	0.008
16	15.0 - 16.0	0.515	0.009
17	16.0 - 17.0	0.383	0.015
18	17.0 - 18.0	0.280	0.009
19	18.0 - 19.0	0.338	--
20	19.0 - 20.0	0.225	--
21	20.0 - 21.0	0.165	--
22	21.0 - 22.0	0.189	--
23	22.0 - 23.0	0.153	--
24	23.0 - 24.0	0.135	--
25	24.0 - 25.0	0.084	0.009

(a) Small deviations from the general trend of the analyses are indications of the normal spread of analytical results. However, the indicated analyses appear to be the results of random analytical errors.

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the epsilon intermetallic phase in the uranium-zirconium system. Both of these phases have low oxygen solubilities.

In Layer 5, the oxygen content begins to increase and the uranium content, although still high, decreases from the maximum value obtained in Layer 4. The region of this cut also appears to be partly in the stained band. Beginning with Layer 6, the uranium content decreases very sharply. The oxygen content of Layer 6 rises above the value of Layer 5 and appears to be at a peak value. This layer probably comprises a region which contains the last of the spires from the stained band in an oxygen-saturated zirconium matrix. Layer 7 shows a relatively low uranium content and a continuing high oxygen content. This cut appears to have been taken from a region of alpha solid solution of oxygen (and perhaps a small amount of uranium) in zirconium. In Layers 8 through 25, the oxygen content decreases steadily to approach its base value. It appears that the base value of uranium is obtained at about Layer 15. The microstructure for this region appears to consist of a single phase of alpha zirconium with oxygen (and a slight amount of uranium) in solid solution. At about Layer 24 or 25, the two-phase core structure of the zirconium begins to appear in the microstructure. All of these data are being studied further.

Vapor Deposition of Molybdenum Coatings on
Stainless Steel Tubing

C. F. Powell and I. E. Campbell

As part of a program of assistance to the Argonne National Laboratory, Battelle is developing processes for the vapor deposition of molybdenum on the inside and outside of small-bore Type 304 stainless steel tubing. Previous work on the deposition of molybdenum on the outside of 0.183-in. OD stainless steel tubing by thermal decomposition of molybdenum carbonyl had resulted in an adherent coating being deposited only over the first inch or two of tubing at the inlet end of the plating chamber. The work for this month was directed toward improving coating uniformity and coverage by minor modifications in coating-chamber design.

The existing coating apparatus was altered so that the mixture of hydrogen and molybdenum carbonyl vapor, at a total pressure of 0.1 to 0.4 mm mercury, was injected into the coating chamber through a water-cooled helical slit which ran the length of the chamber along its central axis. The specimens, 20-in. lengths of tubing, were spaced about 0.5 in. from this slit with their axes parallel to the axis of the slit. The products of the coating reaction were exhausted from one end of the coating chamber by a vacuum pump.

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This arrangement provided uniform, adherent coatings over 10 to 14-in. lengths of tubing. The coatings obtained during a 4-hr coating period at 800 C were too thin to be completely nonporous, as indicated by exposure to hydrochloric acid.

The present vaporizer design will be improved to provide more uniform injection of the coating atmosphere into the deposition chamber, and longer coating periods will be tried in an effort to form the desired 1-mil-thick coatings.

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I. PHYSICAL METALLURGY

H. A. Saller

The Research Division of the Atomic Energy Commission sponsors a number of fundamental research projects in the fields of ceramics, metallurgy, and gas-metal studies.

Results of isothermal transformation and quench and aging studies of uranium-titanium alloys containing 8 and 26 a/o titanium have been completed and are reported.

In the study of the tensile transition of uranium, metallographic examination reveals that it is not a simple change in mechanism that occurs at the transition temperature.

In the program on oxidation-resistant niobium alloys, corrosion tests of a number of the alloys are now completed.

Other programs show normal progress.

Properties of Uranium Compounds

L. D. Loch, G. B. Engle, and M. J. Snyder

Fundamental research on the properties of uranium compounds that may be useful nuclear fuels was continued. A number of thermally stable compounds that have relatively high uranium contents are being investigated.

In the past, efforts have been made to prepare pure intermetallic compounds in the uranium-rich region of the uranium-silicon system and two compounds with nonmetals, US and UN. U_3Si , αUSi_2 , and UN have been prepared and progress has been made on US. This month U_3Si_2 was prepared and work on USi was continued.

Two as-cast samples of compositions corresponding to U_3Si_2 (7.25 w/o silicon) and USi (10.5 w/o silicon) were annealed in vacuo for 8 hr at 1400 C. The annealed sample of 7.25 w/o silicon was a one-phase material which was identified as U_3Si_2 by X-ray diffraction. The annealed sample of 10.5 w/o silicon was essentially USi, but some U_3Si_2 phase was present. This sample will be annealed again.

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Ball-milled samples of U_3Si_2 and alpha USi_2 were hydrostatically pressed at 100,000 psi and sintered in argon at 1450 C. The resulting samples were relatively free from cracks and imperfections and will be used for the measurement of physical properties.

Arc melts of UC, UC_2 , and UAl_2 were made and are being fabricated into usable forms.

In future work, the hardnesses and thermal properties of the uranium silicides will be measured. UB_2 and UB_4 will be prepared.

Development of Uranium-Titanium Alloys

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

The response of uranium-rich uranium-titanium alloys to heat treatment is being studied and the effect of heat treating upon mechanical properties is being evaluated.

Isothermal Transformation

Alloys containing 8 and 26 a/o titanium were solution treated for 1 hr at 750 and 850 C and isothermally transformed at 300, 400, and 500 C for times of 1/2 to 16 hr. Isothermal transformation of the 8 a/o alloy, solution treated at 850 C, showed a slight hardening reaction at 1 hr at 500 C. Transformation at 400 C resulted in a slight softening at 6 hr followed by a small increase in hardness. Transformation at 300 C resulted in a large hardness increase (340 $\rightarrow$ 450 DPH) at 8 hr.

Treatment of the 8 a/o alloy, solution treated at 750 C, at 300 C showed no hardness change. However, at 400 C a marked hardness increase occurred after 16 hr.

Transformation of the 26 a/o alloy produced little hardening compared with the 8 a/o alloy. Samples solution treated at 750 C and isothermally transformed at 300 and 400 C showed no trends or changes. Solution treating at 850 C resulted in a moderate hardening upon transformation at 500 C (from 460 to 500 DPH). No appreciable changes occurred at 400 C. A sudden hardness increase resulted upon transforming at 300 C for 6 to 8 hr.

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Quench and Aging Studies

X-ray diffraction results for several representative samples are listed below:

<u>Sample</u>	<u>Titanium Content, a/o</u>	<u>Solution Treating Temperature, C</u>	<u>Aging Cycle</u>		<u>Hardness, DPH</u>	<u>Phases Present</u>
			<u>Temperature, C</u>	<u>Time, hr</u>		
1	0	750	--	--	225	<i>a</i>
2	8	750	--	--	450	<i>a</i>
9	0	850	--	--	258	<i>a</i>
10	8	850	--	--	496	<i>a</i>
11	8	850	300	1	492	<i>a</i>
12	8	850	400	1	670	<i>a</i>
13	8	850	500	1	618	<i>a</i>
14	8	850	500	2	611	<i>a</i>
16	8	850	500	8	546	<i>a</i>
17	26	750	--	--	496	<i>a</i> + U ₂ Ti
24	26	850	--	--	606	<i>a</i> + U ₂ Ti
27	26	850	500	1	456	<i>a</i> + U ₂ Ti
30	26	850	500	8	424	<i>a</i> + U ₂ Ti
36	8	850	200	1	430	<i>a</i>
37	8	850	600	1	429	<i>a</i>
38	8	850	500	1/2	599	<i>a</i>
39	8	850	500	20	413	<i>a</i>
49	26	850	500	20	496	<i>a</i> + U ₂ Ti

Contrary to X-ray results, photomicrographs of all 8 a/o alloys solution treated at 750 C showed small amounts of U₂Ti. This compound is an equilibrium phase at the solution-treating temperature of 750 C.

The high hardness associated with the aging of 8 a/o titanium alloys solution treated at 850 C might be attributed to a fine precipitate of U₂Ti observed in the photomicrographs but undetected by X-ray diffraction.

Mechanical Properties

An attempt to heat treat tensile bars of the 8 a/o titanium alloy at 750 C resulted in severe warping and a growth of about 1/2 in. in 6 in. The 26 a/o alloys appeared much more stable.

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Investigation of the Tensile Transition in Alpha Uranium

L. L. Marsh and G. K. Manning

The tensile transition in alpha uranium is being studied in an effort to learn more about the nature of the process resulting in the loss of tensile ductility. The variation of microstructure with the temperature of deformation has provided evidence that the transition phenomenon is not simply related to a change in the primary mode of deformation.

Replicas obtained from the surface of deformed specimens indicate that the deformation process at 200 F, nominally above the transition, is exceedingly complicated. The microstructure exhibits many twinning systems and a complete array of slip structure that is most difficult to analyze. At room temperature (75 F), the microstructure of specimens which are strained the same amount as at 200 F is comparatively much simpler. Both twinning and slip processes are active at 75 F. However, the slip structure at 75 F generally consists of single lines, whereas at 200 F there is a tendency for the slip structure to band together in a manner common to most metals. Another item observed is that the deformation markings with respect to twinning versus slip are very inhomogeneous from grain to grain, suggesting a possible orientation dependence for the various deformation modes.

At -75 F the microstructure (light microscopy) revealed twinning and final fracture by cleavage. A secondary cleavage crack that did not result in specimen fracture followed the twin edges, jumping from one to another as each twin stopped. The point of departure was generally associated with a region of intersecting twins. This behavior at -75 F along with the behavior at 75 F and 200 F is remarkably similar to the behavior of iron on passing through its tensile transition.

Constitutional Diagrams of Uranium Alloys

F. A. Rough and A. A. Bauer

A study of the phase relationships between the delta phases of the uranium-molybdenum and uranium-titanium systems is being conducted by examination of a series of alloys ranging in composition from uranium-31.5 a/o molybdenum to uranium-34 a/o titanium.

The general phase relationships in this system have been mapped out, and additional alloys are now being prepared for the purpose of obtaining

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further information on the solubility limits of the delta phases. Alloys of the two delta-phase compositions with small added amounts of titanium and molybdenum, respectively, have been arc melted and are now being fabricated to sheet for heat treatment and subsequent metallographic and X-ray examination.

Study of Bonding Fundamentals

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

The formation of a macroscopic bond is assumed to result from the bonding of numerous individual asperities at the interface. Work has continued on investigations of single-asperity bonding in which gold needles with a spherical tip radius of about 0.01 cm are bonded to flat gold surfaces.

A simplified torsion-balance enclosure has been constructed to allow more efficient operation in controlled atmospheres.

Experimental work will be continued in May. Included in plans for the immediate future are more extensive electron-microscope observations, both on single-asperity bonded regions and on areas of macroscopic bonding. These are to be made with the viewpoint of studying progressive changes in bond-interface structure as they are related to changes in experimental conditions, such as temperature, load, and time. Bonding studies of dissimilar metals also will be carried out.

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.

The effects of hydride and of grain size on the tensile-impact properties of zirconium have been noted. Examination of the surface structure of deformed samples in the light and electron microscopes is in progress.

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Solid-State Studies of Thorium-Uranium Alloys

A. E. Austin and C. M. Schwartz

The thorium end of the thorium-uranium phase diagram is being studied to determine uranium solubility in thorium and its effect upon the thorium transformation. Alloys of 1, 2, 5, and 10 w/o uranium have been used. Above 1300 C, the solubility of uranium in alpha thorium increases markedly upon approach to the beta transformation. Alloys of 3 w/o and 7 w/o uranium are currently being examined to further define the solubility limit.

The transformation of thorium remains at about 1500 C up to 7 w/o uranium. A two-phase region of alpha and beta thorium was observed, apparently over a very narrow temperature range. Present experimental work is being directed toward outlining the extent of the alpha-plus-beta region.

Oxidation-Resistant Niobium Alloys

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

Niobium would be attractive as a structural material for nuclear reactors if its low oxidation resistance could be improved. Since the oxide is not volatile, the possibilities of increasing the oxidation resistance of niobium by alloying are promising and are being investigated in this work.

Results obtained from an oxidation test on pure niobium in dry oxygen at 1150 C indicate that oxidation is linear after about 20 min. The slope of the straight-line portion of the oxidation curve is equivalent to 3.44 ml oxygen consumed per cm^2 per min. This rate is very close to the 1200 C rate reported earlier, 3.33 ml oxygen per cm^2 per min. The 1100 C data, also reported earlier, show an inflection after about 80 min, increasing from 0.84 to 3.38 ml oxygen per cm^2 per min. The behavior of these samples indicates that a change in the rate-determining factor probably exists in the range 1100 to 1200 C.

Weight-gain data for the pure-niobium marker-experiment samples discussed previously are given in Table I-1. The weight gains for these specimens, oxidized in one 2-hr test instead of in an interrupted test, increased with increasing temperature. This is in contrast to several earlier series of pure niobium samples which showed higher weight gains at 800 C than at 1000 C. This point will be checked by additional tests.

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Oxidation tests were also completed on nine niobium-base alloys; the results of these tests are also given in Table I-1. The addition of 1 a/o aluminum to niobium-5 a/o molybdenum appeared to be slightly beneficial, while a similar addition of silicon greatly increased the oxidation rate. Ternary alloys of niobium-20 a/o titanium-5 a/o vanadium, and niobium-5 a/o molybdenum-5 a/o vanadium had excellent oxidation resistance. These ternary combinations are more effective than either addition added singly.

The niobium-7.5 a/o molybdenum binary alloy had a much higher weight gain than the niobium-5 a/o molybdenum alloy, reported earlier. Thus, the optimum concentration of molybdenum in a niobium binary alloy is between zero and 7.5 a/o. Data on the niobium-titanium-molybdenum ternary alloys indicate that, with 5 a/o molybdenum, the oxidation rate decreases with increasing titanium. Increasing the molybdenum to 10 a/o increases the rate of oxidation. With the exception of niobium-5 a/o titanium-5 a/o molybdenum, combinations of the two addition elements are more effective in decreasing the oxidation rate than either one alone.

Oxidation tests were completed on duplicate samples of alloys which separated into several pieces during routine oxidation exposures. Each of the samples was cut in half, one-half of which was homogenized 2 hr at 1500 C. Oxidation rates varied between the two halves, and showed that the homogenizing treatment was ineffective. Radiographic inspection of several ingots also indicated inhomogeneity. To eliminate inhomogeneity, all alloys are now given four arc melts instead of three and are radiographed before machining.

Knoop hardness traverses have been completed on the niobium-base binary alloys containing iron, tantalum, and tungsten. Depths of contamination after oxidation are given in Table I-2. Comparison of these data with the contamination data for pure cast niobium, reported in BMI-1070, indicates that none of these three elements has any significant effect on the depth of contamination.

Two additional elements, beryllium and boron, will be evaluated as binary additions to niobium. Twenty-gram ingots containing 0.2, 1, and 5 a/o of these elements are being prepared and will be oxidation tested in the usual manner.

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

Alloy Composition (Balance Niobium), a/o	VHN	Weight Gain, mg/(cm ²)(hr)		
		600 C	800 C	1000 C
100Nb ^(a)	124	5.89	19.16	38.36
5Mo ^(b)	166	0.25	2.1	4.6
5Mo-1Al	172	0.19	1.85	3.63
5Mo-1Si	235	0.93	9.75	15.4
20Ti-5V	194	0.10	0.94	2.8
5Mo-5V	197	0.12	2.8	3.15
7.5Mo	231	0.13	5.75	10.35
5Ti-5Mo	166	0.11	9.7	7.1
10Ti-5Mo	314	0.10	7.35	3.85
15Ti-5Mo	212	0.11	3.53	3.05
10Ti-10Mo	225	0.16	7.05	3.33
100Nb (control)	--	9.3	--	--

(a) These samples were air oxidized for 2 hr, with one face painted with Cr₂O₃. The fourth sample, exposed at 1200 C, gained 57.62 mg/(cm²)(hr).

(b) Data from previous tests included for comparison.

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TABLE I-2. DEPTH OF CONTAMINATION OF OXIDIZED NIOBIUM-BASE ALLOYS

Alloy Composition (Balance Niobium), a/o	Base Hardness, KHN ^(a)	Oxidation Conditions		Depth ^(b) of Contamination, cm
		Time, hr	Temperature, C	
1Ta	127	10	600	0.008
		5	800	0.046
		1	1000	0.077
5Ta	119	10	600	0.013
		5	800	0.064
		5	1000	>0.1
10Ta	104	10	600	0.019 ^(c)
		5	800	0.043
		5	1000	>0.1
25Ta	140	10	600	0.017
		5	800	0.073
		1	1000	0.069
1W	145	10	600	0.030
		5	800	0.1
		1	1000	0.079
5W	188	10	600	0.029
		5	800	0.086
		1	1000	0.052 ^(c)
10W	176	10	600	0.019 ^(c)
		5	800	>0.1
		5	1000	>0.1
25W	383	10	600	0.0
		1	800	0.040
		1	1000	0.069
1Fe	164	10	600	0.027
		5	800	>0.1
		5	1000	>0.1
5Fe	212	10	600	0.016
		5	800	0.066
		5	1000	>0.1

(a) Hardness of the uncontaminated alloy.

(b) The depth of contamination was determined as the point on the hardness-versus-depth curve which was 25 KHN above the base hardness of the sample.

(c) Depth of contamination was estimated, since the curve leveled out above the base hardness.

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Uranium-Hydrogen Reactions

M. W. Mallett and W. M. Albrecht

A fundamental investigation is being made of the kinetics of the reaction of hydrogen with uranium and uranium alloys under the conditions that $p-p_0$ is a constant, where p is the system pressure and p_0 is the dissociation pressure of the uranium hydride. Additional rate runs were made with a uranium-5 w/o zirconium alloy. The results are listed below.

Temperature, C	Linear Reaction Rate, ml STP hydrogen consumed per cm ² of surface per sec	
	$p-p_0 = 70$ Mm	$p-p_0 = 150$ Mm
100	5.0×10^{-3}	--
200	--	1.1×10^{-2}
250	4.5×10^{-3}	--

From the results obtained thus far, it appears that the reaction rates go through a maximum at about 225 C at all levels of $p-p_0$. A few additional rates will be obtained to establish definitely the maximum for a uranium-5 w/o chromium alloy.

The solubility of hydrogen in the chromium alloy was obtained at 700 C. A value of 10 ppm by weight was obtained. This is in agreement with the solubility of hydrogen in beta uranium at this temperature.

Solubilities of hydrogen in a uranium-5 w/o zirconium alloy were obtained at 650 and 750 C. Values of 840 and 775 ppm hydrogen by weight, respectively, were obtained. The marked increase in hydrogen "solubility" of the uranium-5 w/o zirconium alloy over that of pure uranium may be due in part to formation of a zirconium-containing hydride phase. Additional solubility data are being obtained.

Study of Hydrides

M. W. Mallett and M. J. Trzeciak

Hydrides are being studied to determine how various factors influence their thermal stabilities. The effects of different alloying elements on zirconium hydride are currently being evaluated.

No finished data were obtained during the month, although planned experiments are continuing.

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J. DEVELOPMENTAL STUDIES FOR THE PWR

A. W. Lemmon, Jr.

In one program being performed as assistance to WAPD on the PWR, a study is being made of the factors which affect the amount of chemical reaction between water and Zircaloy 2 at high temperatures. Experimental studies include those on radiation emissivities, chemical-reaction rates, diffusion rates in the solid materials, and the phenomenon of meltdown, while computational analyses are being made of the cooling mechanism of molten droplets in water and the probable total extent of reaction.

Emissivities of Zircaloy 2 have been obtained by both the hole-in-tube and wire-loop methods. The values check closely. For both methods, the spectral emissivity ranges from 0.43 at 1200 C to 0.46 at 1750 C, while the values for the total emissivity range from 0.21 (or 0.22) at 1200 C to 0.26 at 1750 C. Measurements on solid Zircaloy B, Zircaloy B and Zircaloy 2 with dissolved oxygen and oxide coatings, and stabilized oxide are under way. Work is also being performed on the measurement of emissivities of the molten materials.

Diffusion coefficients for oxygen in Zircaloy 2 have been determined experimentally. Values for diffusion in alpha Zircaloy 2 are 1.8×10^{-8} cm² per sec at 1000 C and 7.9×10^{-7} cm² per sec at 1400 C. Work is essentially complete on the measurement of diffusion rates in alpha and beta Zircaloy 2 at 100-degree intervals between 1000 and 1500 C. The experimental determination of diffusion rates at 1600 C and above has proved impossible. However, extrapolation of values for lower temperatures to the higher temperatures can be made. Measurement of diffusion rates in Zircaloy 3 will be completed soon.

Some information has been obtained on the reaction rates of steam with Zircaloy 2. Experiments at 50 psia give reaction rates between 1000 and 1500 C that check closely those Bostrom (WAPD-104) obtained under considerably different conditions. Insensitivity of the reaction to pressure is thus indicated. Measurements of the reaction rates for solid Zircaloy 2 at higher temperatures and for the molten material will be made soon.

An initial test has been performed in the experimental meltdown study. Heating rates of the Zircaloy 2 plate assembly were low because of excessive heat losses to the furnace. At no time during the tests (at temperatures up to 1600 C) did the addition of steam increase the heating rate. Modifications of the apparatus and the experimental techniques will be made.

Methods of computing the cooling rate and extent of reaction of a molten Zircaloy 2 droplet falling through steam and water are being

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programmed for machine calculation. Computations should be performed during May. Calculations for determining the probable maximum extent of the reaction of Zircaloy 2 with steam during meltdown are also progressing. A few simple experiments are being made on the reaction of molten drops of Zircaloy falling through water.

In another program, assembly of the apparatus has been completed for the study of flow in a model of the PWR pressure vessel, and testing has begun. Additional studies of flow-measuring and restricting orifices, and on flow in the shield region, have been started.

In the study of modified fuel-element cores, modified uranium dioxide materials containing BeO, CeO₂, or ZrO₂ have essentially the same corrosion characteristics as does UO₂ without additives. Samples of UO₂ containing BeO were somewhat more resistant to thermal fracture than the base material. Studies of other additives are continuing.

Emissivity Measurements on Zircaloy

C. F. Lucks, G. B. Gaines, H. W. Deem, W. D. Wood,
and W. E. Nexsen, Jr.

Measurements have been completed on the emissivity of Zircaloy 2 in the as-received condition by using both the hole-in-tube and wire-loop methods. The values for the spectral and total emissivities have been recalculated and corrected, and the final values are given in the following tabulation.

<u>Temperature,</u> <u>C</u>	<u>Spectral</u> <u>Emissivity</u>	<u>Total Emissivity</u>	
		<u>Hole-In-Tube Method</u>	<u>Wire-Loop Method</u>
1200	0.43	0.21	0.22
1300	0.44	0.22	0.22
1400	0.44	0.23	0.23
1500	0.44	0.24	0.24
1600	0.45	0.25	0.25
1700	0.45	0.26	0.25
1750	0.46	0.26	0.26

Differences (about 10 per cent) were found between the four wire-loop runs for the total-emissivity evaluation. The diameters of the short and long loops were found to vary considerably on two of these runs and to be the equal on the other two. The data from the latter runs were used for the final results.

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Measurements of the effect of oxygen content on Zircaloy 2 have been made by using hole-in-tube specimens with approximately 7-1/2 and 15 a/o oxygen added. Calculations should be completed and results tabulated within the next three or four days. Attempts to prepare specimens with 20 a/o oxygen were not successful.

Zircaloy B specimens are being prepared for hole-in-tube measurements. Runs will be made on the material as received and with 15 a/o oxygen added. These runs should be completed and results tabulated early in May.

Work continued this month on outgassing the graphite crucible block, and on the final assembly and testing of the experimental apparatus for total-emissivity measurements on molten materials. Because the high voltages present in the 500-kc induction heater cause arcing and glow discharge when the pressure rises above 0.1μ , the outgassing has been very slow. An attempt will be made to outgas the graphite in another furnace and transfer it to the present setup. Once the outgassing is completed, the apparatus should be ready for the taking of data.

Cooling Mechanism of Molten Zircaloy 2 Droplets in Water

W. S. Hogan, R. F. Redmond, J. W. Chastain, and S. L. Fawcett

The object of this phase is to determine analytically the extent of oxidation of a molten Zircaloy 2 droplet as it falls through steam and then water.

The problem has been formulated on the basis of a model which considers the variation of heat-transfer and oxidation rates over the droplet surface. The heat of reaction is postulated to be released at the droplet surface. Equations which govern the heat transfer and reaction rates have been derived on the basis of available experimental data.

An approximate form of the solution of the time-dependent heat-transfer equation with a surface heat flux varying arbitrarily with time and azimuthal angle is being coded for IBM computation. Some preliminary calculations are being performed. The results of the calculations should be obtained in May.

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Diffusion of Oxygen in Zircaloy 2 and Zircaloy 3

M. W. Mallett and W. M. Albrecht

An investigation is being made of the diffusion of oxygen in alpha and beta Zircaloy 2 and Zircaloy 3 in the range 1000 to 1800 C. Diffusion coefficients for oxygen in alpha Zircaloy 2 at 1000 and 1400 C are 1.8×10^{-8} and 7.9×10^{-7} cm² per sec, respectively. Calculations are being made to evaluate coefficients at 1100 and 1300 C. Experimental work is being completed to determine the rate of diffusion of oxygen in alpha Zircaloy 2 at 1500 C.

Diffusion specimens containing oxygen gradients have been prepared at 1100, 1300, and 1500 C in beta Zircaloy 2. The gradients are being analyzed. No gradient could be prepared at 1600 C because of the rapidity of the reaction. The time needed to quench the specimens adequately was too long compared with the 5-min reaction time to prepare a diffusion gradient.

From the results obtained thus far, the diffusion coefficients for oxygen in beta Zircaloy 2 are of the order of 10^{-6} cm² per sec. This is about 10 times as great as the diffusion coefficient (order of 10^{-7} cm² per sec) for nitrogen in beta iodide zirconium* at corresponding temperatures, not lower as was reported last month. The differences in the coefficients probably result from the difference in the size of the solute atoms, oxygen and nitrogen, and not from the alloying metals in Zircaloy 2.

It is planned to spot check the rates of diffusion of oxygen in alpha and beta Zircaloy 3. A supply of Zircaloy 3 is being fabricated for this work.

Measurement of Steam-Zircaloy 2 Reaction Rates

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

Experimental data on the reaction rates of steam with Zircaloy 2 as a function of temperature are needed to permit the calculation of the amount of reaction that will occur in various proposed systems. Previous summaries have described the experimental apparatus and procedures. During April, experiments on the reaction rates between steam and Zircaloy 2 were begun and a total of 11 runs were made. Reaction rates have been determined for the reaction at 50-psia steam pressure in the temperature range from 1000 to 1500 C when reaction times were from 1 to 50 or more minutes.

*M. W. Mallett, J. Belle, and B. B. Cleland, J. Electrochem. Soc., 101, 1 (1954).

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The reaction in the 1000 to 1500 C range does not follow the parabolic law, but shows exponential values for n between 1.5 and 2.4 when v , the total amount of gas evolved, is plotted against t , the reaction time, as:

$$v^n = k t .$$

The quantities of gas collected per cm^2 of specimen surface are shown in Table J-1 for reaction times of 1 and 10 min, as taken from the experimental curves. In some cases, a slight extrapolation was necessary to obtain gas-volume values for the 1-min reaction times. Tentative values for the reaction-rate constant, k , and the exponent, n , are given to characterize the curves which represent the experimental data.

TABLE J-1. STEAM - ZIRCALOY 2 REACTION DATA

Steam Pressure, 50 psia

Steam-Flow Rate, 1.1 to 10 g per min

Reaction Temperature, C	Specific Gas Volume		Reaction- Rate Constant (k)	Exponent Value (n)
	At 1 Min (v_1)	At 10 Min (v_{10})		
1000	2.0	7.3	3.2	1.74
1100	(5.5) ^(a)	(14.)	(62.)	(2.42)
1200	6.0	27.	15.	1.51
1300	9.3	40.	34.	1.58
1400	(6.8)	(34.)	(16.)	(1.43)
1500	(19.)	(54.)	(680.)	(2.21)
1500	14.	56.	92.	1.70

Note: v_t = specific gas volume collected to time t , ml (STP) per cm^2 surface, where t = reaction time, min. The symbols n and k are the constants for the equation $v^n = k t$.

(a) Parentheses indicate relatively uncertain values.

Material balances between the weight gain of the Zircaloy 2 specimens and the volumes of gas collected indicate that approximately 15 per cent of the hydrogen liberated in the reaction is absorbed by the specimen. Therefore, the actual rates of reaction would be about 15 per cent greater than the gas-evolution measurements indicate. These data are in close agreement with those of Bostrom* even though the pressure is considerably different.

*W. A. Bostrom, WAPD-104 (March 19, 1954).

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Measurements of the steam-Zircaloy 2 reaction rates at temperatures of 1600 C, 1700 C, and 1750 C will be made as soon as the high-temperature platinum thermocouples (Degussa) are received. Delivery of these thermocouples has been promised for the first week of May. In addition, experiments are planned with reaction times of less than 1 min in order to determine more closely the initial rates of reaction. Reaction rates between molten Zircaloy 2 and steam will be measured; graphite cups will be used as containers for the molten metal. For the determination of extent of reaction in the short-time and the molten Zircaloy 2 experiments, the oxygen and hydrogen contents of the samples will be measured by vacuum-fusion analysis and metallographic examination will also be made.

A few experiments have been performed in which molten droplets of Zircaloy 2 were allowed to fall through a column of water at atmospheric pressure. The primary objective was to provide information to be used in checking the calculations on the cooling of molten droplets. Additional information on reaction rates has also been obtained.

Rough quantitative results were obtained which showed that weight gain and both time and distance of fall were functions of water temperature and increased with increasing temperature. The data are given in the following tabulation.

<u>Average Water Temperature, F</u>	<u>Average Time to End of Luminescence, sec</u>	<u>Average Distance of Fall to End of Luminescence, ft</u>	<u>Average Weight Gain, per cent</u>
129	3.5	8.9	6.9
148	6.2	14.8	10.6
196	9.3	21.6	13.0

Additional results are being obtained by analyzing reacted pellets by vacuum-fusion and metallographic techniques. These will be reported later.

Experimental work will be terminated at the end of May.

Experimental Study of Meltdown

A. E. Klickman, J. W. Chastain, and S. L. Fawcett

An experimental program is being performed in an attempt to determine the phenomena which occur during meltdown of Zircaloy 2 plates

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in a steam atmosphere. The models used in the tests are similar to PWR elements but they contain only four plates 12 in. long.

The first test has been completed. The resistance heating was approximately 2 w per g and the steam-flow rate simulated a PWR generation rate of 100 lb per min. The model temperature was raised to 500 C by resistive heating before the steam was introduced. The experiment continued until a short in the model blew a fuse in the heating circuit. This occurred when the estimated maximum plate temperature was 1600 C.

Although there was some reaction during this period, the reaction never became autocatalytic. After the fuse blew, steam was still supplied to the model, but the plate temperatures dropped rapidly. An examination of the model after it cooled revealed that a flaky oxide crust approximately 10 mils thick had been deposited on the surfaces of the plates and their thickness had been reduced by about 5 mils. Metallographic and chemical analyses are being made to obtain more information on the extent of the oxidation.

Tests are planned with higher steam flow and higher heating rates in an attempt to get the reaction to become autocatalytic. This work should be completed early in May. Complete results of all of the tests will be presented in the report for May.

Analysis of the Extent of Reaction and Efficacy
of Cooling

J. F. Foster, C. J. Geankoplis, A. W. Lemmon, Jr.,
and R. B. Filbert, Jr.

Previous work on this calculational program to determine the maximum amount of reaction between Zircaloy 2 and steam during meltdown has included: the review of previous WAPD reports, organization and calculation of thermodynamic and physical property data, and the completion of exploratory calculations made to establish limits of the more important variables. In this program, the experimental and analytical information being obtained in other phases is being used.

Additional progress has been made during the month in the development of the calculational techniques and methods to be used in performing the final calculations. A number of simplifications in the calculational procedure have been found possible as a result. The final selection of primary conditions will be established, with the help of WAPD, during the first part of May. Preliminary discussions with Battelle's Computing Laboratory

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personnel have paved the way for rapid programming of the computational procedure, which is expected to be performed during the latter part of May.

Reactor Flow Studies

J. M. Allen and H. R. Hazard

An experimental investigation of the coolant flow throughout a model of the PWR pressure vessel is being made in assistance to WAPD. Previously reported work has included the installation of the air-supply facility with associated ducting and instrumentation, the design of orifice systems for the model core and thermal-shield regions, the calibration of the core orifice system, and the construction of a large manometer board.

Following the installation of the model in the laboratory, the construction and assembly of test equipment was completed. The inlet and outlet ducts were built and attached to the model. Vernier rods were installed to extend into each duct to equalize the flow both through inlet ducts and through the associated outlet ducts. The manometer board was assembled to include the 340 tubes from appropriate pressure taps on the model. The yaw tubes were installed in the shield region of the model, and their reference indicators were aligned. Three sensitive inclined manometers were calibrated for use with the yaw tubes, fixed pressure taps in the thermal-shield region, and the control-rod guides.

Construction was completed and tests begun during the week of April 16. Three tests were conducted by using three-loop, four-loop, and two-loop operations, respectively, and a fourth test was run to determine the flow distribution in the core with a different three-loop configuration. Preliminary analysis of the flow distribution through the several regions of the core indicates that the deviation from the average is within 7 per cent, except for five tubes which have, in one or more tests, shown larger deviation. The cause of these few consistently large deviations will be investigated in May before the program of model modifications is continued, as they do not appear to be related to conditions in the lower plenum.

The flow distribution through the shield region is regular and uniform, showing no evidence of eddies or dead regions except for that in the lower portion of the outer shield channel. A severe warping of the steam lines opposite the inoperative inlet during three-loop operation is indicated. This effect will be studied in more detail during May. Yaw tubes have not proven satisfactory for flow measurements in this region of disturbed flow because of fluctuation in flow direction and static pressure. Use of a combined impact-reverse impact tube to measure velocities in this region will be investigated in May.

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Studies of the design and calibration of flow-measuring and flow-restricting orifices for use in the model core and for study of flow in a large model of the shield region have begun. Work on core orifices has already been completed, and work on the flat-plate shield-region model was started. After preliminary design, a model 1-1/2 times the size of the prototype was found to yield the maximum Reynolds numbers with the air facility available. The mechanical design of this model has been started.

In May, work on the PWR model will continue. Data for Tests 1 to 4 will be analyzed further in an attempt to determine the reasons for the excessive flow variations in a few tubes, following which remedial action will be taken and additional tests will be run.

Construction of the flat-plate shield model will begin early in May and should be completed by June 1, following which the test program will begin.

Modified UO₂ Fuel-Element Cores

D. J. Bowers, W. A. Hedden, and M. J. Snyder

As part of the WAPD-PWR program, research is being conducted to determine whether the service performance of UO₂ fuel-element cores is improved by the addition of selected oxide or metallic materials. The oxide additives under study are BeO, CeO₂, SiO₂, and ZrO₂, and the metal additives are silicon and beryllium. The initial criterion in evaluating the additives is that sintered compacts contain a minimum of 80 volume per cent of UO₂, and present work is on mixes whose solid volume is at least 5 per cent of additive. Corrosion-resistance and thermal-fracture tests are being conducted on bodies meeting this requirement.

In past work, results of corrosion-resistance tests in 650 F water showed that the weight losses of experimental bodies made with BeO, CeO₂, or ZrO₂ were essentially the same as those of UO₂ bodies containing no additive. During the current month, corrosion tests of these materials in 750 F steam were completed. Results are given in Table J-2. The corrosion resistance in 750 F steam for all bodies tested compared favorably with that of unmodified UO₂ specimens. Although the weight loss for two of the bodies containing BeO appears high, it is probable that this resulted from an initial spalling of the samples. The change of weight was negligible after the initial 24-hr test period.

Thermal-fracture studies were continued. Data were obtained on specimens made from 90 volume per cent of UO₂ and 10 volume per cent of BeO sintered for two different periods. The results are given in Table J-3.

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TABLE J-2. CORROSION TESTS ON FUEL-ELEMENT CORE BODIES
IN STEAM AT 750 F

UO ₂ ^(a) , volume per cent	Additives		Sintering Temperature, F ^(b)	Cumulative Change in Weight per Unit Area, mg per cm ² , After Indicated Exposure		
	Material	Amount, volume per cent		24 Hr	96 Hr	168 Hr
100	None	--	3200	-0.39	-0.37	-0.31
100	None	--	3200	-1.54	-1.57	-1.57
95	ZrO ₂ ^(c)	5	3050	-0.23	-0.23	-0.23
95	ZrO ₂	5	3050	-0.28	-0.25	-0.25
95	CeO ₂ ^(d)	5	3050	-0.34	-0.31	-0.31
95	CeO ₂	5	3050	-0.24	+0.02	-0.02
90	BeO ^(e)	10	3200	-0.35	-0.28	-0.33
90	BeO	10	2800	-0.86	-0.86	-0.81
90	BeO	10	2800	-1.97	-1.89	-1.78
100 ^(f)	None	--	--	-0.21	-0.33	-0.33

(a) As-received UO₂ from Mallinckrodt.

(b) All compacts sintered in hydrogen for 2 hr at temperatures shown after being hydrostatically pressed at 100,000 psi.

(c) Pure ZrO₂ from U. S. Bureau of Mines; average particle size, 37 μ .(d) 99 $\pm$ w/o CeO₂ from A. D. McKay; average particle size, 8 μ .(e) Refractory-grade BeO from Brush Beryllium Company; average particle size, 13 μ .

(f) WAPD production core.

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TABLE J-3. RESULTS OF THERMAL-FRACTURE TESTS OF
90 w/o UO₂-10 w/o BeO BODY SPECIMENS

Test	Dimensions, in.			Sintering Conditions	Bulk Density, per cent of theoretical	Power per Unit Length at Fracture, per cm
	Outer Diameter	Inner Diameter	Length			
1	0.930	0.55	0.461	6 hr ^(a) at 3200 F in dry hydrogen	93.6	38.5
2	0.945	0.56	0.462	Ditto	90.6	38.5
3	0.927	0.56	0.454	Ditto	<u>90.4</u>	<u>34.0</u>
Average					91.5	37.0
4	0.951	0.56	0.455	4 hr at 3200 F in dry hydrogen	86.4	55.6
5	0.892	0.56	0.488	Ditto	90.9	44.6
6	0.950	0.55	0.467	Ditto	<u>90.2</u>	<u>43.4</u>
Average					89.1	46.5
Reference UO ₂					86.0	28.4 ^(b)

(a) Sintered 2 hr at 3200 F; resintered 4 hr at 3200 F.

(b) Average of four specimens as reported in BMI-1080.

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Specimens sintered for 4 hr required an average power input of 46.5 w per cm for fracture as compared with a value of 28 w per cm for reference UO_2 specimens of similar size and density. Specimens sintered for 6 hr, although not appreciably more dense than those sintered for 4 hr, required an average power input of only 37 w per cm for fracture. It is suspected that the increased sintering time resulted in grain growth and thereby a lower thermal-fracture resistance. In view of the encouraging improvement in thermal-fracture resistance obtained by the incorporation of BeO, further study will be made of UO_2 -BeO bodies.

Difficulty was encountered in sintering the thermal-fracture specimens containing ceria and silica to a density required for the minimum 80 volume per cent of UO_2 . Resintering of UO_2 - CeO_2 specimens at 2640 F for 1 hr, with the introduction of steam in place of hydrogen at temperatures above 2370 F, increased the density from 82 to 85 per cent of theoretical. With this increase, the minimum UO_2 content was achieved. These specimens will be tested for resistance to thermal fracture. Thermal-fracture specimens made with SiO_2 , however, have not met the minimum UO_2 -content requirement, and further resintering will be necessary before proceeding with thermal-fracture tests. Indications are that sintering at 2640 F in steam for a period longer than 2 hr may increase the bulk density sufficiently to meet the minimum UO_2 -content requirement.

In further exploration of UO_2 -BeO bodies, compacts were prepared from mixtures of UO_2 and readily sinterable BeO. Sintered compacts made from 95 volume per cent of UO_2 and 5 per cent of sinterable BeO were only slightly more dense than similar compacts made with refractory-grade BeO when sintered in dry hydrogen at 2800 F.

The hot-pressing study of UO_2 -silicon bodies was continued. Preliminary results from this study were reported in BMI-1080. The silicon content of the bodies ranged from 10 to 80 volume per cent and hot-pressing temperatures ranged from 2600 to 2900 F. The use of the high metal contents, in an attempt to insure a continuous silicon phase in the cermet, resulted in squeezing out of some of the metal during hot pressing, and data on these compacts are questionable. With 20 volume per cent of silicon in the body, hot-pressed compacts were more dense as the temperature was increased. However, none were sufficiently dense to meet the UO_2 -content requirement. X-ray diffraction studies showed the presence in these compacts of minor amounts of the same reaction product previously noted in larger amounts in sintered specimens. No additional hot-pressing studies are planned at the present time. The planned extension of the work with silicon-containing bodies involves vacuum sintering, with collection of volatiles, if any, to obtain additional information on the nature of the UO_2 -silicon reaction product. After the vacuum sinter, consideration will be given to further work with this reaction product alone, or as an additive in a modified UO_2 body.

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In other work, UO_2 compacts containing silicon powder additives were heated to 2550 F in dry nitrogen to form a Si_3N_4 bond. Compacts containing 5, 15, and 20 volume per cent of silicon powder showed increases in weight that indicated essentially complete reaction of the silicon to form Si_3N_4 . However, bulk densities of these compacts were less than 70 per cent of theoretical. It is planned to resinter nitrided compacts at temperatures up to about 3200 F in an effort to increase their bulk densities to the extent required for a minimum of 80 volume per cent of UO_2 .

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K. STUDY OF A LIQUID-METAL NEUTRON ABSORBER FOR THE
CONTROL OF A GAS-COOLED POWER REACTOR

B. B. Gordon

In January, a study of the feasibility of using a liquid-metal neutron absorber for the self-control of a gas-cooled power reactor was initiated. [REDACTED] The hot-gas coolant from the reactor would heat the liquid metal in a storage container. The resulting thermal expansion of the liquid-metal absorber would cause a greater volume of absorber to be inserted into the reactor core. During February the electronic-simulator study of this system was started.

During April thermal-time constants between the coolant gas and the liquid metal of 1/2 to 10 sec were studied. Results indicated that thermal-time constants of longer than 2 sec create instabilities. Also equivalent temperature coefficients of reactivity were studied. The results indicate that a compromise is necessary in this coefficient, since high coefficients tend to cause instability, while low coefficients give insufficient control. The best equivalent temperature coefficient, which appears to be less than 5×10^{-5} per deg F, varies with the thermal-time constant. All instabilities become more pronounced at higher power levels.

During May, this study to determine the optimum ranges of parameters will continue. Also, the physical system will be examined to determine what range of thermal-time constants is possible.

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L. EVALUATION OF A REFLECTOR-CONTROLLED HETEROGENEOUS BOILING REACTOR

J. W. Chastain

Previous analyses by Battelle have shown a reflector control system to be a stable and feasible method for controlling a boiling heterogeneous reactor. In this system, an annular water reflector is connected intimately with the core and, through a pipe line, to a surge tank. Increases in the reactor power cause increased boiling, which forces water from the reflector to the surge tank. This lowering of the reflector level causes a decrease in the reactivity and, consequently, in the power, which tends to return the reactor to its previous power level.

To verify this system experimentally, two separate experiments are planned. Data on the reactivity effects will be obtained from a critical-assembly experiment. The kinetics of the control system will be checked by a full-scale mock-up of the hydraulic system, driven by an electronic reactor simulator.

During April, the design of the critical-assembly core structure and table was started. Several bids have been received on the long-delivery items for the hydraulic system.

Critical Experiment

W. S. Hogan, R. F. Redmond, J. W. Chastain,
and S. L. Fawcett

The control range and effectiveness of the reflector and information which will permit an evaluation of the transient behavior can be obtained from a critical experiment. Such an experiment will also provide flux and power distributions and give an indication of operating-fuel requirements.

The design of the critical assembly and associated equipment is under way and should be completed in the coming month. The critical assembly will be split in two approximately equal parts and mounted on a two-part table assembly, one part of which can move horizontally. Each part of the table assembly will contain eight plate-type safety elements and a neutron source. The core will be made up of fuel elements containing aluminum, plastic, and fuel. These materials will be contained in aluminum boxes 1-1/2 x 1-1/2 x 24 in. The assembly will be surrounded by 1 ft of plastic as a reflector.

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Polyethylene has been chosen as the plastic to use to simulate water. It has a higher hydrogen density than water and can be used to simulate a wide range of conditions of water density. Void distribution and effective density may be varied by drilling holes in the material. The slowing down length for polyethylene has been computed, and calculations are nearing completion on the fast-diffusion coefficient for aluminum-polyethylene mixtures. When these calculations are completed, the proper amounts of core materials can be determined to duplicate the fast leakage and the reflector savings of the water-moderated reactor being simulated.

In the coming month, it is hoped that the construction of the table will begin, and that the Hazards Summary Report will be near completion.

Simulator Studies

B. B. Gordon, D. R. Forry, and J. J. Stone, Jr.

During the month work on the mock-up of the control system has been concerned with the design and procurement of some of the necessary components. Design work and detail drawings of four pressure vessels were prepared and sent to several fabricators for cost estimates. Two of these pressure vessels will be used to simulate the annular reflector shell and the external surge tank. The other two will serve as air supplies for the reflector and surge tanks. Bids are now being received and these indicate as a probable delivery date the end of June. An order has been placed with the Worthington Corporation for two motor-driven air compressors to be used for supplying high-pressure air to the 500-psi receiver tanks. Delivery of the compressors is expected by the middle of June. Specifications are being prepared for the simulation and control systems necessary to complete the control system.

Other items which are currently being investigated include: blow-off valves, feed-water pumps, and a liquid-level-indicating device.

It is anticipated that during the next month the orders will be placed for the pressure vessels and other items necessary to begin the assembly of the reactor control system.

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