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THE REACTION OF STEAM WITH URANIUM AND
WITH VARIOUS URANIUM-NIOBIUM-ZIRCONIUM
ALLOYS AT HIGH TEMPERATURES

by

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THE REACTION OF STEAM WITH URANIUM AND WITH VARIOUS URANIUM-NIOBIUM-ZIRCONIUM ALLOYS AT HIGH TEMPERATURES

Alexis W. Lemmon, Jr.

To provide data for evaluating the possible extent of the chemical reaction of steam with uranium and various uranium-niobium-zirconium alloys when contacted at high temperatures in nuclear reactors, two experimental studies were performed. These were concerned with (1) measurement of metal-water reaction rates, and (2) emissivity determinations. In addition, it was necessary to perform an experimental program to determine methods for preparing and to prepare the test specimens for the measurement programs. The materials studied were (1) unalloyed uranium, (2) uranium-10 w/o niobium, (3) 75 w/o (uranium-10 w/o niobium)-25 w/o Zircaloy 2, (4) 50 w/o (uranium-10 w/o niobium)-50 w/o Zircaloy 2, and (5) 25 w/o (uranium-10 w/o niobium)-75 w/o Zircaloy 2.

In general, it was found that solid uranium was the most reactive (with steam at 50 psia) of all materials studied with the exception of the solid 75 w/o (uranium-10 w/o niobium)-25 w/o Zircaloy 2 alloy which behaved in an anomalous fashion. The solid uranium-10 w/o niobium alloy had the lowest reactivity and the solid 50 w/o and 25 w/o (uranium-10 w/o niobium) alloys had reaction rates with steam intermediate between uranium and the uranium-10 w/o niobium alloy and comparable with those of solid Zircaloy 2 previously studied.

The variation of reaction rate with steam pressure was not investigated; some variation with steam-flow rate was noted, but was not shown conclusively to be a factor. The reaction rate of steam with all materials in the molten state did not appear to be affected by variations in the molten-metal temperature or by differences in composition.

Spectral and total emissivities were measured for all materials in the as-rolled condition and with oxygen added. Total emissivities for the as-rolled materials ranged from 0.33 at 850 C for the 75 w/o (uranium-10 w/o niobium) alloy to 0.41 at 1075 C for the uranium-10 w/o niobium alloy. Total emissivities with oxygen added to the specimens ranged from 0.35 at 850 C for the 75 w/o (uranium-10 w/o niobium) alloy to 0.67 at 1075 C for the uranium-10 w/o niobium alloy. Spectral emissivities for the as-rolled materials ranged from 0.32 at 850 C for unalloyed uranium to 0.72 at 1075 C for the 75 w/o (uranium-10 w/o niobium) alloy. Spectral emissivities with oxygen added ranged from 0.19 at 1075 C for unalloyed uranium to 0.72 at 1075 C for the uranium-10 w/o niobium alloy.

In the preparation of specimens, all alloy ingots were prepared by the duplex-melting process in which the ingot is produced by a vacuum-induction melting step followed by a remelting as the consumable electrode of an arc-melting furnace. The 5/8-in.-diameter bar stock was produced by forging and rolling, while several annealing, quenching, and rolling steps were required to produce the 5-mil sheet for the emissivity measurements.

INTRODUCTION

In many conceivable situations, the probability of contact at high temperatures between reactive metals and water is appreciable. Consequently, it is important that the effects of such contact be known so that possible corrosion difficulties can be evaluated and, in the case where reaction rates are rapid, possible hazards can be estimated.

Of current interest for nuclear-reactor applications are zirconium (and its alloys), uranium, and uranium-niobium alloys. It is known that these materials are reactive with water to some extent. Of course, reactivity could be expected to increase with increasing temperature. Much work has been performed at temperatures below 500 C in measuring the corrosion rates of these materials with water and steam. Practically no information is available above this temperature for any material of current interest except Zircaloy 2.

Also, of importance in estimating the effects of physical configuration on the amount of over-all reaction which might occur is a knowledge of the radiation emissivities of the materials involved. Consequently, a series of experimental programs was undertaken in support of WAPD to provide data on the reaction of water (steam) with uranium-niobium-zirconium alloys at high temperatures.

Experimental programs were designed to provide (1) the reaction rates of water (steam) with the alloys, (2) the radiation emissivity of the alloy specimens, and (3) methods of preparing alloy test specimens.

MEASUREMENT OF METAL-WATER REACTION RATES

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A previous study⁽¹⁾ performed at Battelle investigated the reaction rates of steam with Zircaloy 2. Studies have also been made by Aerojet⁽²⁾ and WAPD⁽³⁾. In the Battelle studies, it was found that the solid-phase Zircaloy 2 reaction with steam between 1000 and 1830 C could be correlated best by the parabolic law. No correlation proved possible for the molten-Zircaloy 2 experiments performed at initial temperatures of 1900 and 2050 C. Lack of correlation was due either to extreme inaccuracy in measurement, a lack of control and knowledge of all physical parameters, or a misinterpretation of the rate-controlling factors. In the study of solid-Zircaloy 2 reaction with steam, rates of reaction could be expressed by

$$v^2 = 0.1132 \times 10^6 e^{-\frac{34,000 \pm 1,440}{RT}} t,$$

with v in units of ml hydrogen per cm^2 and t in units of sec. The molten-Zircaloy 2 reaction with steam was more rapid than would be predicted by extrapolating the above correlation to the molten temperatures.

In the case of uranium and its alloys with niobium, similarities exist at lower temperatures between the reaction with steam (and water) and oxygen or air. Of course, in some situations, the release of hydrogen by the reaction with steam adds a complication. Rate laws ranging from parabolic to linear have been noted⁽⁴⁾. Also, in some experiments, rates which increase with time have been noted. Additional details on previous work are given in the sections covering the information on the specific materials.

⁽¹⁾References appear in the Bibliography at end of report.

The reaction between metal and steam at 50 psia was measured for unalloyed uranium and four uranium-niobium-Zircaloy 2 alloys. Runs were made in both the solid and liquid region over a temperature range of 700 to 1600 C. The five materials studied were:

- (1) Unalloyed uranium
- (2) Uranium-10 w/o niobium
- (3) 75 w/o (uranium-10 w/o niobium)-25 w/o Zircaloy 2
- (4) 50 w/o (uranium-10 w/o niobium)-50 w/o Zircaloy 2
- (5) 25 w/o (uranium-10 w/o niobium)-75 w/o Zircaloy 2.

In general, the reaction of these materials with steam was found not to obey the parabolic or logarithmic rate laws as might be expected. However, in isolated cases, normal behavior was observed, particularly in the case of some of the data on unalloyed uranium which could be correlated by the logarithmic rate law. In the case of the 25 w/o Zircaloy 2 alloy, the rate appeared to be essentially constant. Behavior between these extremes was noted for other alloys.

The variation of reaction rate with steam pressure was not investigated; some variation with steam-flow rate was noted, but was not conclusively shown to be a factor.

The reaction rate of steam with all materials in the molten state did not appear to be affected by variations in the molten-metal temperature or by differences in the alloy composition. This type of behavior is consistent with that reported in BMI-1154⁽¹⁾ for the reaction of steam with molten Zircaloy 2.

Data for all alloys are summarized in Tables 1 and 2.

Nomenclature

A	constant in the Arrhenius equation
f	steam flow rate, g per min
k	reaction-rate constant
k'	corrosion rate, mg/(cm ²)(hr)
k _c	diffusion-rate coefficient
n	reaction-rate order
Q	Arrhenius energy of activation, cal per g-mole
R	gas constant, 1.987 cal/(g-mole)(K)
r	reaction rate, g/(cm ²)(sec)
t	reaction time, sec
v	extent of reaction by hydrogen gas evolution, ml per cm ² .

TABLE 1. SUMMARY OF EXPERIMENTAL DATA FOR THE REACTION OF SOLID URANIUM-NIOBIUM-ZIRCONIUM ALLOYS WITH STEAM

Reaction Temperature, C	Material Composition(a), w/o	Steam-Flow Rate(b), g per min	Volume of Hydrogen, STP ml H ₂ per cm ² , Collected at Indicated Time									
			0.5 Min	1 Min	2 Min	5 Min	10 Min	20 Min	40 Min	60 Min	80 Min	100 Min
800	100U	6.9	--	2.3	4.7	9.1	13.5	19.5	27.5	--	--	--
900	100U	5.0	4.8	6.7	10	16	23	33	--	--	--	--
1000	100U	1.2	--	8.1	11.1	17	23.5	32	--	--	--	--
	U-10Nb	30.1	--	--	--	1.85	3.7	7.1	13	17.5	22	25
	75(U-10Nb)-25Zr2	34.3	--	2.85	4.8	10	19.5	44	135	--	--	--
	100Zr2	--	--	--	1.04	3.8	6.9	10.9	16	20.5	24	27
1100	100U(c)	10.6	--	--	24	57	93	--	--	--	--	--
	U-10Nb	28.0	--	--	1.23	4.3	9.2	17.5	30	40	49	--
	75(U-10Nb)-25Zr2	32.4	--	1.5	2.85	6.5	14.4	43	--	--	--	--
	50(U-10Nb)-50Zr2	36.7	--	3.2	5.2	9.8	15.5	23.5	35	43	55	--
	100Zr2	--	--	4.7	6.2	9.9	14	19	26.5	34.5	42	48
1200	U-10Nb	35.2	--	--	2.35	9.0	18.5	34	55	--	--	--
	75(U-10Nb)-25Zr2	36.3	--	13.5	22	49	>150	--	--	--	--	--
	50(U-10Nb)-50Zr2	38.6	--	2.5	5.3	10.9	16.5	27	44	59	71	--
	100Zr2	--	--	5.7	9.3	17	28	40	58	72	--	--
1300	50(U-10Nb)-50Zr2	28.1	--	3.3	6.2	13.8	23.5	39	64	--	--	--
	100Zr2	--	--	8.7	14	25	40	62	93	113	--	--
1400	50(U-10Nb)-50Zr2	18.5	--	3.5	7.2	20	37	62	104	--	--	--
	25(U-10Nb)-75Zr2	33.2	8.2	11.3	17.5	34	51	73	--	--	--	--
	100Zr2	--	--	--	11	21	34.5	56	--	--	--	--
1500	50(U-10Nb)-50Zr2	22.8	27	40	60	106	--	--	--	--	--	--
	100Zr2	--	--	14.5	21.5	37	56	78	110	--	--	--
1600	25(U-10Nb)-75Zr2	35.0	24	31	49	100	147	--	--	--	--	--
	100Zr2	--	--	--	--	39	67	96	--	--	--	--
1690	100Zr2	--	--	21.5	37	67	--	--	--	--	--	--

(a) Zr2 = Zircaloy 2.

(b) Flow-rate values for Zircaloy 2, uranium, and uranium-10 w/o niobium were for a 3.45-cm-ID Vycor tube. For 75 w/o (uranium-10 w/o niobium)-25 w/o Zircaloy 2, 50 w/o (uranium-10 w/o niobium)-50 w/o Zircaloy 2, and 25 w/o (uranium-10 w/o niobium)-75 w/o Zircaloy 2, a 2.7-cm-ID Vycor tube was used. Mass-flow, velocities past the specimens at equal flow rates are 1.8 times as large for the smaller tube.

(c) Sample studied at 1125 C.

TABLE 2. SUMMARY OF EXPERIMENTAL DATA FOR THE REACTION OF MOLTEN AND SEMIMOLTEN URANIUM-NIOBIUM-ZIRCONIUM ALLOYS WITH STEAM

Reaction Temperature, C	Material Composition ^(a) , w/o	Steam-Flow Rate, g per min	Volume of Hydrogen, STP ml H ₂ per cm ² , Collected at Indicated Time						
			0.5 Min	1 Min	2 Min	5 Min	10 Min	20 Min	40 Min
1200	100U ^(b)	7.0	--	12.5	25	55	90	132	--
1300	100U ^(c)	7.0	--	14	27	46	80	115	--
1400	U-10Nb	14.6	--	9.2	23.5	55	92	140	205
	75(U-10Nb)-25Zr2	32.7	--	19	35	75	140	--	--
1500	75(U-10Nb)-25Zr2	33.3	--	14	27	68	107	188	--
1600	U-10Nb	13.5	--	19.5	33	64	105	170	--
	75(U-10Nb)-25Zr2	33.8	--	20.5	31.5	65	114	200	--

(a) Zr2 = Zircaloy 2.

(b) Sample studied at 1230 C.

(c) Sample studied at 1280 C.

Experimental Methods

The techniques and apparatus used for this program were essentially the same as those used in the previous study reported in BMI-1154(1). As before, the solid and molten specimens were heated by electrical induction and reacted with flowing steam at a pressure of 50 psia. Extent of reaction was determined by measuring the hydrogen formed, by metallographic examination of the reacted specimens, or by vacuum-fusion analysis. However, a number of changes in the apparatus were made to facilitate operation and control of the equipment and improve the precision of the data. The more important changes were:

- (1) Use of much higher steam-flow rates
- (2) Relocation of the rotameter
- (3) Use of special joints and fittings to insure a gastight apparatus
- (4) Addition of pressure gages as an aid in checking the system for leaks and estimating better the pressure existing in the reaction chamber
- (5) Addition of a vacuum-pumping system
- (6) Use of crucibles made of morganite*, stabilized zirconia, and urania in place of graphite for containing the molten metal in performing the molten metal-steam reactions
- (7) Use of direct immersion of the thermocouple well in the molten metal
- (8) Use of a baffle arrangement for deflecting the steam down into the crucible during the molten runs.

Concurrent with these changes, the general technique of gas measurement was modified. The system, from the steam valve to the bottom of the condenser, was evacuated just prior to the start of a run, which was initiated by opening the steam valve. After an elapsed time of 0 to 50 sec, at which time the pressure near the bottom of the condenser had reached 1 atm absolute, the valve at the bottom of the condenser was opened and the measurement of gas evolution begun.

Materials

The uranium and the four alloys of uranium-niobium-zirconium were prepared by the Fuel-Element Development Division of Battelle as described in a later section. Forged rods of about 0.6 in. in diameter were machined to the form and size indicated in Figure 1. The surface was polished dry with 60-grit emery paper and finished with 180-grit emery paper. Pieces were then washed with benzene and carbon tetrachloride just prior to the run and protected thereafter by a blanket of argon. Samples for the liquid runs were machined from the same stock. In most cases, cylinders 0.5 in. in diameter by 0.5 in. long were used. Final preparation was the same as for the solid runs.

* Triangle RR, recrystallized alumina.

FIGURE 1. METAL ROD SPECIMEN

Steam at 60 psig was obtained from the building service lines. Periodic checks showed that noncondensable gases amounted to less than 0.1 per cent by volume and that other impurities were negligible. A standard grade of argon as supplied by Linde Air Products was used. It is rated at 2 grains of water per 1000 ft³ of gas at atmospheric pressure and contains 7 ppm oxygen. No attempt was made to remove these impurities prior to use. Urania crucibles were furnished by Westinghouse Atomic Power Division. Degussit thermocouple wells of high-temperature-fired alumina were obtained by Battelle-Frankfurt. Commercial zirconia and morganite crucibles and commercial porcelain thermocouple wells were used.

Equipment

For Runs 1 through 13, the equipment was arranged as described in BMI-1154, pages C-3 to C-6. The arrangement of equipment used for the remaining runs is illustrated in Figure 2. The transfer of the rotameter unit to the upstream side of the reaction chamber made it possible to neglect small leaks in the rotameter. Beginning with Run 24, no rotameter was used. Proper flow and pressure were then maintained by precalibration of the steam flow and presetting of Valves V₄ and V₅. Periodic manual adjustment of V₁ kept the reading of Pressure Gage G₁ constant at a pressure sufficient to maintain the average of G₂ and G₃ between 35 and 36 psig. With the rotameter in the system, V₄ and V₅ were periodically adjusted to maintain the float at a precalibrated position and also maintain the average of G₂ and G₃ between 35 and 36 psig. Larger fluctuations were taken out by V₁.

For the uranium and a portion of the uranium-10 w/o niobium runs, a 3.45-cm-ID Vycor tube was used. For the remainder of the uranium-10 w/o niobium runs and the (uranium-10 w/o niobium)-25, 50, and 75 w/o Zircaloy 2 runs, a 2.7-cm-ID Vycor tube was used. All valve joints and other metal-metal fittings were silver soldered. All neoprene and natural rubber connections were joined with Glyptal. Silicon rubber gaskets were used instead of lead gaskets for the Vycor-metal seal. The 3-1/2-in. bronze pressure gages, G₂, G₃, and G₄, were of the vacuum-pressure type, 30 in. vacuum, 60 psig pressure.

The vacuum system was designed for rapid pumping. It contained two 10-liter bottles in parallel with a high-speed mechanical pump. By suitable manipulation of stopcocks, the combination could evacuate the system to about 2 mm in 15 to 20 sec when V₅ was sufficiently open. Morganite, stabilized zirconia, and urania crucibles were used in the setup shown in Figure 3. Stabilized zirconia crucibles fabricated from hollow cylinders were used in the setup of Figure 4.

Procedure for Measuring Reaction Rates Between Solid Metals and Steam

After the system had been heated by heating tapes to about 320 F, the steam-flow rate was calibrated at the desired value by passing steam through the system and measuring the rate of condensate formation. When all water had been flushed out of the system with argon, the polished sample was placed in the system. A final leak check was then made. Using an argon flow comparable with the steam flow expected in the run, the spacing on the induction coil was adjusted to give a minimum temperature variation on the surface of the specimen. After the desired temperature was finally reached, the argon valve, V₃, was closed and, after a short time, V₆ was closed. Stopcock S₁ was

FIGURE 2. APPARATUS FOR MEASUREMENT OF GAS EVOLUTION IN METAL-STEAM REACTIONS

FIGURE 3. MODIFIED ASSEMBLY FOR LIQUID RUNS

FIGURE 4. LATEST ASSEMBLY FOR LIQUID RUNS

then opened. When the gages read close to 30 in. vacuum, S_1 was closed. During this period, a slight readjustment of power level had to be made. As soon as this was accomplished, the run was begun.

To initiate the run, the steam valve, V_2 , was opened. Immediate adjustments of Valves V_1 , V_4 , and V_5 were made to maintain the float at the desired position and to keep the reaction chamber at the desired pressure of 35 to 36 psig. The input voltage to the Lepel spark gap was immediately increased manually by means of an autotransformer. The increase in voltage required to maintain the specimen at the constant temperature was estimated from knowledge of the behavior of similar previous runs. As soon as the reading of the G_4 pressure gage approached zero, indicating that the condenser pressure was 1 atm absolute, V_6 was opened. The time interval between opening of Valves V_2 and V_6 was recorded. The run was stopped when 2 to 3 liters of gas was collected.

Procedure for Measuring Reaction Rates Between Molten Metals and Steam

The techniques used for making molten runs differed only in the setup used in the reaction chamber. The following description is illustrated by Figures 3 and 4. The first setup used for making molten runs used an assembly similar to that shown in Figure 4 except that no baffle had been added and the thermocouple did not protrude into the molten-metal region. Temperature control was by means of optical-pyrometer readings of the surface of the molten metal or floating oxide layer. Calibration for these readings was accomplished in a manner described in a later section of this report. Figure 3 shows a different setup for making molten runs. Since thermocouple temperatures were not used, the manner of supporting the crucible was changed as shown. A baffle was added in this second setup to encourage movement of steam into the crucible. In both the first and second setup, the liquid level was relatively low in the crucible so that black body conditions would be more closely approximated. Figure 4 shows the third setup used. Temperature control was by means of thermocouple measurements and the pyrometer was used as an auxiliary measuring device.

Results and Discussion

Reaction Between Unalloyed Uranium and Steam

The reaction between uranium and steam has been studied up to 400 C, as reported by Brugman and Hoxeng⁽⁴⁾. In the description of one experiment they state: "Saturated steam at 140 psi (183 C) reacts with U during the first few hours at the same rate as liquid distilled water at the same temperature. Then, at more or less localized areas, metal is corroded at a very much higher rate (40x). In some cases, the metal is deeply pitted while in others swelled areas or craterlike formations occur... It is conceivable that steam could enter along the grain boundaries and give the appearance of an unusually high specific rate of attack because of the larger surface area". At these low temperatures, some of these effects may be due to hydrogen or hydride formation.

Brugman and Hoxeng⁽⁴⁾ also report the results of experiments on the reaction of uranium metal with air and oxygen up to temperatures of 1000 C, although results above 650 C were reportedly inconclusive. They state that the oxide formed for temperatures

above 300 C tends to flake off rapidly and that laminar-scale formation may depend on the previous heat treatment of the metal. From 100 to about 650 C, the results from various laboratories may be correlated by

$$\log k' = \frac{-2300}{T} + 4.80.$$

In an effort to extend the range of temperatures over which the reaction rates of uranium metal with steam are known, this present series of experiments was undertaken. For the unalloyed uranium, runs were made with the solid material at 700, 800, 900, 1000, and 1125 C. (The run at 1125 C was made using the techniques and apparatus for liquid runs.) In addition, a series of runs was made at 800 C to determine the effect of steam-flow rate on the reaction rate. Liquid runs were made at 1230 C and 1280 C. Steam at 50 psia was used on all the runs.

Three crystalline forms of uranium are known. These are denoted as the α , β , and γ forms in order of increasing transition temperatures. According to Saller and Rough⁽⁵⁾, phase transformations from α to β and β to γ occur at 662 C and 769 C, respectively. The γ phase melts at 1130 C. Consequently, all solid runs except the one at 700 C, were made in the γ -phase region.

The composition of the uranium used in these experiments was:

<u>Impurity</u>	<u>Concentration, ppm</u>
Carbon	50
Nitrogen	50
Oxygen	10
Hydrogen	2 to 10
Silicon	300 (varies)
Molybdenum	40
Nickel	30
Iron	100
Chromium	20
Aluminum	40
Uranium	Remainder

Based on these analyses, the uranium has a minimum purity of 99.93 w/o.

Experimental Methods. The reaction between uranium and steam is expected to follow the equation,

Thus, the reaction was followed volumetrically as previously described. Two techniques were used in making the solid runs. In Runs 1 to 13, argon (at 1 atm) was present in the system just before steam was admitted. In these runs experimental volumes were corrected for an "argon blank", which measured the volume-time relation of argon purged from the system by steam under "no-reaction" conditions. In Runs 14 to 22, the equipment was evacuated just prior to admission of steam. These runs were accordingly corrected only for the time lag between the opening of the steam valve and the opening of the valve at the bottom of the condenser. Temperatures were measured by means of a

platinum-platinum 10 w/o rhodium thermocouple. Temperature control at the beginning of the runs fluctuated from run to run. Some runs showed an initial drop in temperature, whereas others exhibited an initial rise.

All runs with uranium were made using a 3.45-cm-ID Vycor tube. The two liquid runs and the solid run at 1125 C (Runs 10, 11, and 17) were made using the arrangement described by BMI-1154(1), Figure C-3. However, the thermal gradient across the slurry was too great to permit thermocouple readings to be of any value. Temperature control was therefore manual by means of pyrometer readings and temperature fluctuations were much greater than in the case of solid runs. Pyrometer readings were made on the hottest portion of the top surface of the reacted specimen. It was noted in earlier runs with solid specimens that the pyrometer readings were often higher than the thermocouple readings. Since emissivity and absorption errors would lower the apparent optical temperature, the readings were probably affected by reflection of light from the Vycor tube. As a consequence of this, an empirical correlation of pyrometer and thermocouple readings was used.

Results. As in the previous work on the steam oxidation of Zircaloy 2 described in BMI-1154(1), the experimental gas volume was plotted against time for each run. The results are shown in Figures 5 and 6. Figure 6 shows only the runs made at 800 C, whereas Figure 5 shows one 800 C run plus all the other uranium runs. Unfortunately, in this type of plot there exists an inherent inconsistency due to the hydrogen being produced at the metal at one time and this same gas being measured in the burette at a later time. To circumvent this problem, reciprocal rate was plotted against volume for all the uranium runs. In this way, the time difference is inconsequential because rate of change of volume at a given volume is the same at both the metal and at the burette. The rate obtained, as in the previous work on Zircaloy 2(1) was the interval rate, i. e., $\Delta v / \Delta t$. The results correlated in this fashion are shown in Figures 7 and 8.

In Figures 7 and 8, those runs for which the data can be fitted by straight lines drawn through the origin follow the parabolic law:

$$v^2 = kt \quad .$$

The runs for which the data curve upward on this type of plot, e. g., Run 13, could be replotted as volume versus the logarithm of the reciprocal rate to obtain a straight line. This plot is not shown. These runs obey the logarithmic law of the form

$$v = k \log_{10} (C_1 t + C_2) \quad .$$

The remaining runs are seen to be parabolic but displaced so that the straight lines representing the data do not pass through the origin. In the case of Run 19, this anomaly could be explained qualitatively by assuming preoxidation of the uranium specimen. Preoxidation would shift the parabolic line to the right if the volume corresponding to a given rate were actually larger due to neglect of the volume corresponding to the initial oxidation. Above- or below-normal temperatures at the start of a run should not have any effect on a plot of reciprocal rate versus volume except for those points which are not at the nominal temperature.

In order to correlate the data with temperature and steam-flow rate, a reaction-rate constant was computed for each of the runs. To evaluate a parabolic constant for the logarithmic runs, the best line was drawn through the points and the origin. In those

FIGURE 5. EXPERIMENTAL DATA FOR THE REACTION BETWEEN UNALLOYED URANIUM AND STEAM

FIGURE 6. EFFECT OF STEAM FLOW ON THE REACTION BETWEEN UNALLOYED URANIUM AND STEAM AT 800 C

FIGURE 7. EFFECT OF FLOW RATE ON THE REACTION BETWEEN URANIUM AND STEAM AT 800 C

FIGURE 8. EFFECT OF TEMPERATURE ON REACTION OF URANIUM AND STEAM

cases in which a best line could not be drawn, the line drawn represented the limiting case of maximum reaction. These statements also are illustrated by Figures 7 and 8. The parabolic reaction-rate constants are given in Table 3 with the corresponding values of temperature and steam-flow rate. A value of the modified reaction-rate constant, k/f , is included. This represents a semiempirical attempt at correlation in which the reaction rate is divided by the steam-flow rate.

TABLE 3. PARABOLIC REACTION-RATE CONSTANTS

Run	Temperature, C	Steam-Flow Rate, g per min	Reaction-Rate Constant, k , cm^2 per min	Specific Reaction- Rate Constant, k/f , cm^2 per g
1	800	1.2	10.0	8.33
2	700	1.2	1.93	1.61
3	900	1.2	13.5	11.25
4	1000	1.2	42.2	35.1
9	1050	0.8	41.8	52.2
10	1280	7.0	634	90.5
11	1230	7.0	870	124
12	900	5.0	56.8	11.35
13	800	5.0	47.5	9.50
14	800	3.0	9.6	3.20
15	800	27.1	97.5	3.60
16	800	4.4	6.37	1.45
17	1125	10.6	1070	101
19	800	12.5	17.1	1.37
20	800	15.8	11.4	0.721
21	800	20.8	65.2	3.13
22	800	6.9	20.0	2.90

These values of k/f are plotted against reciprocal absolute temperature in Figure 9. In drawing a line through these points, a logarithmic average of the 800 C values was used as an aid in determining the best fit. An activation energy of 31,800 cal per mole was obtained. Therefore, the reaction rate between 800 C and the melting point can be represented by

$$v^2 = 9.7 \times 10^6 \text{ ft e}^{-\frac{31,800}{RT}},$$

where

v = volume of hydrogen gas collected, STP ml H_2 per cm^2

f = flow rate, g per min

t = reaction time, min.

An additional attempt at correlation was made using logarithmic reaction-rate constants. For each of the uranium runs, the logarithm of reciprocal rate was plotted against the volume of gas collected. As previously mentioned, some of the runs yielded straight-line plots. The parabolic runs generally were concave down. A limiting slope was used to obtain the logarithmic constant in these cases. The reaction-rate constants

FIGURE 9. EFFECT OF TEMPERATURE ON THE PARABOLIC SPECIFIC REACTION-RATE CONSTANT

were divided by the steam-flow rate and plotted against reciprocal absolute temperature as shown in Figure 10. As before, a logarithmic average of the 800 C runs was used in determining the best fit of the line. From this line an activation energy of 30,000 cal per mole was obtained.

As in the parabolic-rate plot, Figure 9, the 700 C run does not correlate with the other runs. This may be because this is the only run made with the β -phase uranium. The liquid runs also did not correlate on this type of plot.

Discussion. It is fairly obvious from the attempts at correlation which were described in the previous section that one or more controlling variables were not recorded. In view of the previous work in this field, as briefly discussed, one of these variables might have been the previous heat-treatment history of the material used. It is conceivable that variations in handling occurred during fabrication but, in view of the high temperatures at which the experiments were performed, it is difficult to see how this effect could remain.

Another feature of these uranium runs was the lack of correlation of the 800 C runs with the steam-flow rate. The scatter of these runs can be readily seen by inspection of Table 3 and Figures 9 and 10. Although the logarithmic average of the specific reaction constants of the 800 C runs agree with the other solid runs in Figures 9 and 10, correlation has not proved possible. The two 900 C runs essentially merge even though made at different flow rates.

In order to evaluate the possibility that the flow rate may affect the over-all reaction rate, a theoretical estimate was made of the relative resistance to reaction offered by diffusion of steam through the gas phase as compared with the over-all rate. At all flow rates used in the uranium work, the Reynolds number was well in the laminar region. Since no correlational data could be found for mass or heat transfer for flow past a cylinder in the longitudinal direction for low Reynolds numbers, use was made of the data of Treybal⁽⁶⁾ on flow past single spheres. The cylindrical specimen was treated as a sphere and an equivalent Reynolds number was calculated. Using a reaction-rate value obtained at the beginning of Run 9, the difference in concentration of the steam between the bulk phase and the surface of the metal was estimated to be about 5.4 per cent of the bulk-phase concentration. According to Smith⁽⁷⁾, since this value is already more than a few per cent, diffusional resistance through the gas is becoming important. However, since the most extreme case was chosen, i. e., the one with the lowest flow rate, it would appear that gas diffusional resistances are not important for the runs in general. The data obtained for the 800 C runs do not appear to confirm this.

According to Figure 10, the specific reaction rate "levels out" abruptly at the melting point of uranium and, thus, appears to be independent of temperature. The non-increasing character of the points for the molten runs shown in Figure 11, may be caused by scatter due to uncertainty in surface area. However, it is felt that it is more likely that some physical process within the metal-oxide system (other than normal solid diffusion of cations and/or anions in the oxide layer) is a major factor in determining the over-all rate. Some confirmation of the accuracy of the surface-area estimates for these "crucible" runs can be obtained from the results of Run 17. Run 17 was made at 1125 C, in the solid region, under liquid-run conditions. A reaction constant which falls in line with the other solid runs lends support to the essential correctness of the area-estimating technique.

FIGURE 10. EFFECT OF TEMPERATURE ON THE LOGARITHMIC SPECIFIC REACTION-RATE CONSTANT

A fortuitous comparison is possible between the present studies and the correlation of Brugman and Hoxeng⁽⁴⁾ for the reaction of uranium metal with air and oxygen between 100 and 650 C as previously discussed. Table 4 shows this comparison. The initial experimental rates are shown for the first 2-min period. Numbers shown in parentheses are computed from the first available volume measurement; this is at 1 min for 800 and 1000 C and at 1/2 min for 900 C. In view of the fact that these early (in each run) volumes are subject to considerable uncertainty, the agreement is probably sufficiently good to attach significance to it. It is possible that the same reaction mechanism is controlling for both air and oxygen oxidation of uranium at low temperatures and steam oxidation at high temperatures.

TABLE 4. COMPARISON OF EXTRAPOLATED REACTION RATES OF BRUGMAN AND HOXENG⁽⁴⁾ WITH PRESENT EXPERIMENTS

Temperature, C	Extrapolated Rate ^(a) , mg/(cm ²)(hr)	Initial Experimental Rate, mg/(cm ²)(hr)
800	83.1	100.8(98.6)
900	174	214(411)
1000	316	238(347)
1125	575	515

(a) Extrapolated from the relation

$$\log k' = \frac{-2300}{T} + 4.80.$$

Conclusions and Recommendations. From the preceding discussion, it appears that even a crude mechanism for the reaction between uranium and steam cannot be proposed even though some correlation has been possible. However, since some empirical understanding of the reaction rates has been obtained, future workers should have some basis for predicting the extent of reaction of uranium with steam. Obviously, as a casual inspection of Table 1 and 2 will show, uranium is considerably more reactive, at the same temperature, than any of the other materials studied.

In addition to effort required on studying the basic reaction, more work of a fundamental nature is needed to understand the problem of reaction-rate dependence on gas-flow velocity. One phase of this work should include the study of a larger range of Reynolds numbers. It is recommended that additional runs be made in the molten region to verify the possibility that the over-all reaction rate is independent of temperature for a given flow rate.

Reaction Between Uranium-10 w/o Niobium and Steam

Some information is available on the behavior of uranium-niobium alloys in oxidizing atmospheres at low temperatures. Brugman and Hoxeng⁽⁴⁾ indicate that niobium is a γ -phase stabilizer and, as such, decreases the rate of corrosion by water at low temperatures. The present study was undertaken to determine the reaction rate of this alloy with steam at high temperatures.

According to a phase diagram prepared by Baldwin Sawyer, and reported by Saller and Rough⁽⁵⁾, this present uranium-10 w/o niobium alloy begins to melt from a single-phase region at about 1220 C and completes melting at about 1570 C. Accordingly, the solid material was reacted with 50-psia steam at 1000, 1050, 1100, 1150, and 1200 C. Runs were made on the partially molten material at 1400 C and on the completely molten material at 1585 and 1600 C.

Experimental Methods. For making the solid runs the setup shown by Figure C-3 of BMI-1154(1) was used. A 3.45-cm-ID Vycor tube was used as the test section for the 1000, 1100, and 1200 C solid runs. All other runs were made with a 2.7-cm-ID tube. A platinum-platinum 10 w/o rhodium thermocouple was used for measuring temperature. In addition, an optical pyrometer was used as an auxiliary temperature-measuring device. Its primary function was to show that proper spacing on the turns of the induction coil had been achieved so as to have a reasonably small temperature variation from the top to the bottom of the sample.

The temperature control for the five solid runs was quite good. In all cases, the temperature returned to within 5 C of its nominal value within 3 min. The sharpest and largest drop came in the 1150 C run when the temperature dropped 83 C but held steady at 1150 C after 2 min. The other runs held between the following limits in the first 3 min: 1000 C, 998-1013 C; 1050 C, 1049-1073 C; 1100 C, 1094-1104 C; and 1200 C, 1163-1207 C. If the reaction is allowed to proceed longer than 30 min these initial disturbances should not affect significantly the ultimate course of the reaction. Most of these runs were longer than 30 min.

Two methods were used for carrying out the reactions when making the molten runs. For the 1585 C run, the setup shown in Figure 3 was used. Here total reliance was placed on optical readings, and manual temperature control was used. For the 1400 and 1600 C runs, the setup shown by Figure 4 was used. Temperature control was almost instantaneous. A 3 C rise was noted in the 1600 C run; the 1400 C run gave no indication of a change in the nominal temperature.

The method of controlling temperature illustrated in Figure 4 has been the most successful used in this study.

Results. To illustrate the results of the reaction, 100X photomicrographs are shown in Figure 11 and Figure 12. These correspond to runs made at 1050 and 1200 C, respectively.

Figure 13 illustrates the results of the solid and liquid runs for this alloy. The volume of hydrogen evolved per square centimeter of sample surface* was plotted against the time in minutes. The steam-flow rates are indicated in grams per minute in the key above the plots. Figure 14 is a plot of the reaction-rate constant k versus the reciprocal of the absolute temperature.

Not evident from inspection of Figure 13 is a characteristic common to all the plots, viz., a region of constant slope near the center of each plot that has nearly the same value on each plot. It is this feature that was arbitrarily selected to correlate the runs on the basis of temperature.

* The total surface area was chosen for the liquid runs.

100X

1 Per Cent HF on Polishing Wheel

N36464

FIGURE 11. URANIUM 10 w/o NIOBIUM AFTER REACTION AT 1050 C WITH
50 PSIA STEAM FOR 50 MIN

100X

1 Per Cent HF on Polishing Wheel

N36463

FIGURE 12. URANIUM 10 w/o NIOBIUM AFTER REACTION AT 1200 C WITH
50 PSIA STEAM FOR 40 MIN

FIGURE 13. EFFECT OF TEMPERATURE ON THE REACTION BETWEEN URANIUM-10 w/o NIOBIUM AND STEAM

FIGURE 14. EFFECT OF TEMPERATURE ON THE REACTION-RATE CONSTANT FOR STEAM WITH URANIUM-10 w/o NIOBIUM

By assuming that the reaction follows the law

$$v^n = kt,$$

the runs could be assigned a value of n according to the principles outlined in the previous paragraph. The value of n varied from 1.31 to 1.50 with an average value of 1.41. For each run, k was calculated from the above formula. The Arrhenius plot of k is shown in Figure 14. From it, the activation energy for the over-all reaction appears to be 42,500 cal per mole. The correlating equation is then:

$$v^{1.41} = 1.78 \times 10^7 e^{-\frac{42,500}{RT}} t.$$

Discussion. The use of the correlational method just described may be open to question, but the reaction rate observed in these samples failed to follow any known rate laws. Heindlhofer and Larson⁽⁸⁾ and Smirnov⁽⁹⁾ have shown that a binary alloy would never be expected to behave in a parabolic fashion toward oxidation. However, this present behavior may best be described as a combination of parabolic and logarithmic functions. Therefore, any method used for correlation is likely to be arbitrary.

The value used for the surface area of the liquid runs was also somewhat arbitrary. By inspection of a cross section of reacted sample, it was found that the oxide coating generally appeared to be as thick on the sides and bottom of the sample as on the exposed top. However, the attack was far from uniform since some sites were much more readily attacked than others. It is believed, nevertheless, that steam rather than the crucible material is responsible for the "side-wall" reaction.

The use of the total surface area has additional support from the values of k computed for the liquid runs. On the Arrhenius plot, these values compare favorably with the values of k for the solid runs. However, too much weight should not be attached to this confirmation due to the manner in which the values of k were computed. Furthermore, if it is assumed that the 1400 and 1600 C runs are reliable and the 1585 C run is not reliable because of inherent inaccuracies occurring in that run, it would appear that the value of k is essentially constant for these three runs. Therefore, change in temperature may no longer be of primary importance in determining the over-all reaction rate in this region.

Inspection of Table 1 shows that the reaction rate of solid uranium-10 w/o niobium with steam is of the order of 10 per cent of the reaction rate of unalloyed uranium at corresponding temperatures. In the case of the molten runs, the reaction rate of the uranium-10 w/o niobium alloy at 1400 C approximately corresponds to the reaction rate of molten uranium at 1230 and 1280 C. This behavior lends further weight to the thesis that the reaction rates of molten materials are unaffected by temperature or, within some undefined limits, composition.

Conclusions and Recommendations. Although the mechanism of reaction of the uranium-10 w/o niobium alloy with steam cannot be determined, it has been possible to correlate the data for the solid runs in an empirical manner. Rates of reaction for this alloy with steam are approximately 10 per cent of the rates with unalloyed uranium at corresponding temperatures. Rates for the molten alloy approximately correspond to the rates for molten uranium even though the reaction temperature is somewhat higher.

In order to resolve the question as to whether or not the effective reaction-rate constant for the molten alloy is independent of temperature, it is recommended that a number of additional runs be made in the molten and near-molten regions. To minimize the possibility of surface-area errors, low, flat vessels might be used instead of crucibles.

The problem of the real behavior of the solid specimens, i. e., whether they behave parabolically, logarithmically, or in a truly unpredictable fashion is a more difficult one. Additional work of a more fundamental nature is probably needed to find an answer.

Reaction Between the 75 w/o (Uranium-10 w/o Niobium)-25 w/o Zircaloy 2 Alloy and Steam

For this alloy, no specific information could be found in the literature for either the reaction rates with oxidizing materials or phase behavior. However, the phase diagram given by Saller and Rough⁽⁵⁾ for the system zirconium-uranium indicates that the 25 w/o zirconium alloy begins to melt at approximately 1320 C; at 1600 C it should be completely molten. Assuming similar behavior for this system, runs were made on the solid material at 1000, 1100, 1200, 1275, and 1300 C. Molten runs were made at 1400, 1500, and 1600 C.

Experimental Methods. Solid runs with this material were made according to the methods described in BMI-1154⁽¹⁾, Figure C-3. For the molten runs, the method illustrated by Figure 4 of this report was used. For these runs a 2.7-cm-ID Vycor tube, rather than a 3.45-cm-ID tube, was used for the test section. Thus, for a given steam rate, the mass velocity past the test specimen is 1.8 times as high as for the uranium runs.

Results. Results of these experiments are best shown by a series of photomicrographs and photographs. For comparison with other photographs shown in this section, Figure 15 shows a part of the interior of an unreacted specimen of this alloy. The characteristic feature of the solid runs made on this material was the excessive flaking off of the oxides formed by reaction. This is best illustrated by Figure 16. The two samples shown there were exposed to steam at 1275 or 1100 C. The tendency was for part of the reacting alloy to "drip off", leaving an appreciably shorter piece than the original specimen.

Results of solid runs made at 1000 C and 1200 C are illustrated by Figures 17, 18, 19, and 20. Complete sections of the two reacted specimens are shown in Figures 17 and 19, whereas Figures 18 and 20 show a small part of the interface region between the oxide layer and unreacted alloy. In the case of the 1200 C run, reaction appeared to take place preferentially at the top of the specimen. Figure 21 illustrates a highly reacted region of the 1300 C run. Numerous oxide inclusions appear in the metallic phase.

100X

1 Per Cent HF on Polishing Wheel

N36521

FIGURE 15. 75 w/o (URANIUM-10 w/o NIOBIUM)-
25 w/o ZIRCALOY 2 UNREACTED ALLOY

N39295

FIGURE 16. PHOTOGRAPH OF 75 w/o (URANIUM-10 w/o NIOBIUM)-25 w/o ZIRCALOY 2 AFTER
REACTION WITH 50-PSIA STEAM AT 1275 AND 1100 C AND 7 AND 40 MIN,
RESPECTIVELY

2X

50 Ml Lactic Acid, 30 Ml HNO_3 , 1-1/2 Ml HF

N36481

FIGURE 17. 75 w/o (URANIUM-10 w/o NIOBIUM)-25 w/o ZIRCALOY 2
AFTER REACTION AT 1000 C WITH 50-PSIA STEAM FOR
31 MIN

100X

1 Per Cent HF on Polishing Wheel

N36472

FIGURE 18. 75 w/o (URANIUM-10 w/o NIOBIUM)-25 w/o ZIRCALOY 2
AFTER REACTION AT 1000 C WITH 50-PSIA STEAM FOR
31 MIN

2X

50 Ml Lactic Acid, 30 Ml HNO_3 , 1-1/2 Ml HF

N36480

FIGURE 19. 75 w/o (URANIUM-10 w/o NIOBIUM)-25 w/o ZIRCALLOY 2
AFTER REACTION AT 1200 C WITH 50-PSIA STEAM FOR
8 MIN

100X

1 Per Cent HF on Polishing Wheel

N36471

FIGURE 20. 75 w/o (URANIUM-10 w/o NIOBIUM)-25 w/o ZIRCALLOY 2
AFTER REACTION AT 1200 C WITH 50-PSIA STEAM FOR
8 MIN

60X

1 Per Cent HF on Polishing Wheel

N39585

FIGURE 21. 75 w/o (URANIUM-10 w/o NIOBIUM)-25 w/o ZIRCALOY 2 AFTER REACTION AT 1300 C WITH 50-PSIA STEAM FOR 5 MIN

4X

1 Per Cent HF on Polishing Wheel

N39587

FIGURE 22. 75 w/o (URANIUM-10 w/o NIOBIUM)-25 w/o ZIRCALOY 2 AFTER REACTION AT 1400 C WITH 50-PSIA STEAM FOR 23 MIN (ALLOYS CONTAINED IN STABILIZED ZrO_2 CRUCIBLE)

The specimens oxidized at 1400, 1500, and 1600 C are shown in full section in Figures 22, 25, and 27, respectively. In Figure 22, the position of the thermocouple well indicates that uniform melting had not taken place. There appears to be a line of demarcation across the center of the section. To explore further the significance of the separation into two apparently different regions, a higher magnification (100X) photomicrograph was taken of the border region and is shown in Figure 23. From this 100X photomicrograph there appear to be oxide inclusions on the demarcation line. A possible explanation is that steam had penetrated along the side of the melt (see Figure 22) and had blown across through the center along the demarcation line. Since both regions are much different in appearance than the metallic phase of the specimen reacted at 1200 C (see Figure 20), it appears that some melting has taken place throughout the alloy. Since 1400 C is not far above the solidus, one would expect a rather high viscosity due to the high percentage of solids. Such a high viscosity might explain why the semimolten material did not flow down into the crucible.

To further illustrate the character of the oxidation products of the runs made with this alloy, photomicrographs of the oxide layer at the top of the reacted specimen are presented in Figures 24, 26, and 28.

Figure 29 shows a plot of volume of hydrogen evolved as a function of time for the solid and liquid runs. An estimate of 10 cm² of surface area, based on dimensions of the specimen and crucible, was used to compute the values for the three liquid runs. Observation of the full sections of the reacted specimens shown in Figures 22, 25, and 27 shows that the estimate based on the dimensions of the specimen and crucible is adequate. Data on the 1300 C run are not included because of difficulties encountered with temperature control. Comparison of the data shown in Figure 29 with the data for uranium should be made at similar mass-flow velocities. To permit this, the flow rates in Figure 29 should be multiplied by 1.8.

Discussion. Inspection of Figure 29 and Table 1 shows that, at temperatures of 1100 C and below, the reaction of the 75 w/o (uranium-10 w/o niobium)-25 w/o Zircaloy 2 alloy with steam seems to behave in a predictable fashion. The reaction rate appears to be about 15 per cent of the rate for unalloyed uranium and somewhat higher than the rate of the uranium-10 w/o niobium alloy at corresponding temperatures. However, some increase in reaction rate with time was noted.

However, the "solid"-phase reaction at 1200 and 1275 C behaved in an anomalous manner. In these cases, rates of reaction increased more rapidly with time. The behavior of the specimen was unusual as well. As illustrated by Figure 16, portions of the reacting specimen "dripped off" as the reaction proceeded. The most probable explanation for this is that the phase behavior of this alloy in this temperature range is somewhat abnormal. A two-phase solid or a liquid-solid structure is a possible explanation. Certainly, considerably more effort is needed in a study of both the phase behavior and the reaction rates in this region.

Inspection of Table 2 shows that the reaction rates of this molten alloy with steam are comparable to those of uranium and the uranium-10 w/o niobium alloy. At 1400 C, the rates are about 50 per cent higher than those of the uranium-10 w/o niobium alloy. However, this is believed to be simply a random variation and not of true significance.

100X

1 Per Cent HF on Polishing Wheel

N39579

FIGURE 23. 75 w/o (URANIUM-10 w/o NIOBIUM)-25 w/o ZIRCALOY 2 AFTER REACTION AT 1400 C WITH 50-PSIA STEAM FOR 23 MIN (ALLOYS CONTAINED IN STABILIZED ZrO_2 CRUCIBLE)

40X

1 Per Cent HF on Polishing Wheel

N39576

FIGURE 24. 75 w/o (URANIUM-10 w/o NIOBIUM)-25 w/o ZIRCALOY 2 AFTER REACTION AT 1400 C WITH 50-PSIA STEAM FOR 23 MIN (ALLOYS CONTAINED IN STABILIZED ZrO_2 CRUCIBLE)

4X

1 Per Cent HF on Polishing Wheel

N39588

FIGURE 25. 75 w/o (URANIUM-10 w/o NIOBIUM)-25 w/o ZIRCALOY 2 AFTER REACTION AT 1500 C WITH 50-PSIA STEAM FOR 25 MIN (ALLOYS CONTAINED IN STABILIZED ZrO_2 CRUCIBLE)

40X

1 Per Cent HF on Polishing Wheel

N39582

FIGURE 26. 75 w/o (URANIUM-10 w/o NIOBIUM)-25 w/o ZIRCALOY 2 AFTER REACTION AT 1500 C WITH 50-PSIA STEAM FOR 25 MIN (ALLOYS CONTAINED IN STABILIZED ZrO_2 CRUCIBLE)

4X

1 Per Cent HF on Polishing Wheel

N39589

FIGURE 27. 75 w/o (URANIUM-10 w/o NIOBIUM)-25 w/o ZIRCALOY 2 AFTER REACTION AT 1600 C WITH 50-PSIA STEAM FOR 23 MIN (ALLOYS CONTAINED IN STABILIZED ZrO_2 CRUCIBLE)

40X

1 Per Cent HF on Polishing Wheel

N39574

FIGURE 28. 75 w/o (URANIUM-10 w/o NIOBIUM)-25 w/o ZIRCALOY 2 AFTER REACTION AT 1600 C WITH 50-PSIA STEAM FOR 23 MIN (ALLOYS CONTAINED IN STABILIZED ZrO_2 CRUCIBLE)

FIGURE 29. REACTION BETWEEN 75 w/o (URANIUM-10 w/o NIOBIUM)-25 w/o ZIRCALLOY 2 AND STEAM AT 50 PSIA

Conclusions and Recommendations. It can be concluded that the reaction of the 75 w/o (uranium-10 w/o niobium)-25 w/o Zircaloy 2 alloy with steam is somewhat similar to the previous materials reported except for the "solid" material above 1200 C. Reaction rates at 1100 C and below are about 15 per cent of those of unalloyed uranium at the same temperature. Rates for the molten material are seemingly unaffected by temperature, and are equivalent to those for the other materials reported. Behavior between 1200 C and the melting point is not understood. Therefore, it is recommended that additional effort be spent in studying the phase behavior and the reaction with steam in this region.

Reaction Between 50 w/o (Uranium-10 w/o Niobium)-50 w/o Zircaloy 2 Alloy and Steam

As far as is known, the corrosion behavior of this particular alloy has not been studied previously. However, the phase behavior and the oxidation rates at low temperatures of the 50 w/o uranium-zirconium alloy are known.

Barnartt, Charles, and Gulbransen⁽¹⁰⁾ recently reported the rates of reaction of the 50 w/o uranium-zirconium alloy with oxygen at a 1-atm pressure over the range 200 to 500 C: "Two forms of the alloy, the stable ϵ -phase and the quenched γ -phase, were reacted to an oxide-scale thickness of 0.1 mm at the higher temperatures. In general, the weight gain increased linearly with time, although in many cases the oxidation curve showed a bend and could be represented by two straight lines. At 400 C and above, the stable ϵ -phase reacted considerably faster than the γ -phase. The thick oxide scales were porous and showed uranium enrichment. During the formation of thin oxide films at 200 C and 250 C the reaction followed the parabolic rate law approximately. The alloy oxidizes somewhat more rapidly than pure Zr, but very much more slowly than U."

Saller and Rough⁽⁵⁾ reported that the solidus temperature for the 50 w/o uranium-zirconium alloy is approximately 1580 C. Assuming similar behavior for this 50 w/o (uranium-10 w/o niobium)-50 w/o Zircaloy 2 alloy, reaction rates with steam were measured for the solid alloy at 1100, 1200, 1300, 1400, 1450, and 1500 C.

Experimental Methods. Solid runs with this material were made according to the methods described in BMI-1154⁽¹⁾, Figure C-3. However, a 2.7-cm-ID Vycor tube was used in place of the 3.45-cm-ID tube. Thus, for a given steam rate, the mass velocity past the test specimen was 1.8 times as high as for the uranium runs. The steam pressure was 50 psia and Reynolds' numbers for the steam varied from 660 to 1420.

Results. To illustrate the internal changes as a result of the reaction, three photos are presented in Figures 30, 31, and 32 for the 1200 C run. Inspection of Figure 30 shows that uniform reaction has taken place over the entire surface of the specimen. Figure 31 is a photomicrograph of a portion of the lower part of the specimen where the thermocouple well is inserted. Figure 32 is a 100X photomicrograph of the specimen.

The results of these runs are presented in Figure 33, where the volume of hydrogen collected is plotted against the time elapsed. It is believed that the run made

2X

50 Ml Lactic Acid, 30 Ml HNO_3 , 1-1/2 Ml HF

N36478

FIGURE 30. 50 w/o (URANIUM-10 w/o NIOBIUM)-50 w/o ZIRCALOY 2 AFTER REACTION AT 1200 C WITH 50-PSIA STEAM FOR 82 MIN

32X

1 Per Cent HF on Polishing Wheel

N36466

FIGURE 31. 50 w/o (URANIUM-10 w/o NIOBIUM)-50 w/o ZIRCALOY 2 AFTER REACTION AT 1200 C WITH 50-PSIA STEAM FOR 82 MIN

100X

1 Per Cent HF on Polishing Wheel

N36467

FIGURE 32. 50 w/o (URANIUM-10 w/o NIOBIUM)-50 w/o ZIRCALOY 2 AFTER
REACTION AT 1200 C WITH 50-PSIA STEAM FOR 82 MIN

FIGURE 33. EFFECT OF TEMPERATURE ON THE REACTION BETWEEN 50 w/o (URANIUM-10 w/o NIOBIUM)-50 w/o ZIRCALOY 2 AND STEAM

at 1400 C involved pre-exposure of the specimen due to a leaky steam valve. This would explain the relatively low values for volume collected at the beginning of the run.

Several methods of correlation, including parabolic and logarithmic laws, were attempted but did not prove applicable. However, it is believed that some method of correlation might be possible if the data were treated more exhaustively than was feasible in this study. Obviously, without an applicable correlation, reaction-rate constants and an activation energy could not be evaluated.

Discussion. Inspection of Table 1 shows that the 50 w/o (uranium-10 w/o niobium)-50 w/o Zircaloy 2 alloy has about the same reactivity as Zircaloy 2 at about 1100 and 1400 C, has less reactivity at 1200 and 1300 C, and has a higher reactivity at 1500 C. There is no apparent explanation for this behavior, and correlation of the results has not proved possible. Also, comparison of these results with those of Barnartt, Charles, and Gulbransen⁽¹⁰⁾ for the oxidation of the 50 w/o uranium-zirconium alloy has not been possible. However, a similar conclusion seems possible. This alloy reacts with steam somewhat more rapidly than pure zirconium but very much more slowly than pure uranium.

Conclusions and Recommendations. Since correlation of these results has not proved possible, it is obvious that additional experimental work should be performed. However, it has been established in a qualitative fashion that this alloy is much less reactive than uranium and has about the same reactivity as Zircaloy 2.

Reaction Between 25 w/o (Uranium-10 w/o Niobium)-75 w/o Zircaloy 2 Alloy and Steam

Again, similarity between this alloy and the 25 w/o uranium-zirconium alloy for purposes of setting run conditions was assumed. According to Saller and Rough⁽⁵⁾, the solidus temperature for this alloy is approximately 1710 C. Solid runs were made at 1400 and 1600 C. No liquid runs were made.

Experimental Methods. Solid runs with this material were made according to the methods described in BMI-1154⁽¹⁾, Figure C-3. However, a 2.7-cm-ID Vycor tube was used in place of the 3.45-cm-ID tube for the test section. Thus, for a given steam rate, the mass velocity past the test specimen was 1.8 times as high as for the uranium runs. The steam pressure was 50 psia.

Results. The photomicrograph shown in Figure 34 illustrates the appearance of the oxide layer and adjacent regions for the run made at 1600 C. Results of the two runs made with this material are given in Figure 35 where volume of hydrogen evolved is shown as a function of time. Limiting slopes were found to correspond to a parabolic reaction. The two runs may, accordingly, be described by the equations

$$v^2 = 2100 t \text{ at } 1600 \text{ C}$$

and

$$v^2 = 270 t \text{ at } 1400 \text{ C.}$$

100X

1 Per Cent HF on Polishing Wheel

N36475

FIGURE 34. 25 w/o (URANIUM-10 w/o NIOBIUM)-75 w/o ZIRCALOY 2
AFTER REACTION AT 1600 C WITH 50-PSIA STEAM FOR
10 MIN

FIGURE 35. REACTION OF 25 w/o (URANIUM-10 w/o ZIRCALOY 2)-75 w/o ZIRCALOY 2 WITH STEAM AT 50 PSIA

On the basis of these two runs, an activation constant of 63,500 cal per mole was calculated.

Discussion. From an inspection of the limited information available, the reaction of the 25 w/o (uranium-10 w/o niobium)-75 w/o Zircaloy 2 alloy with steam appears to follow the parabolic law and correlation has been made on that basis. Rates of reaction for this alloy are greater than for Zircaloy 2, as shown by Table 1.

Conclusions and Recommendations. Although firm conclusions cannot be reached on the basis of only two experimental runs, the reaction of this alloy with steam appears to behave in a predictable manner and to be somewhat faster than the reaction of Zircaloy 2 with steam. Obviously, additional data are needed for this material and should be obtained when possible.

EMISSIVITY DETERMINATIONS

H. W. Deem, E. A. Eldridge, and C. F. Lucks

Spectral- and total-emissivity measurements have been made on:

- (1) Unalloyed uranium
- (2) Uranium-10 w/o niobium
- (3) 75 w/o (Uranium-10 w/o Niobium)-25 w/o Zircaloy 2
- (4) 50 w/o (Uranium-10 w/o Niobium)-50 w/o Zircaloy 2
- (5) 25 w/o (Uranium-10 w/o Niobium)-75 w/o Zircaloy 2.

Measurements of emissivity versus temperature were first made with the materials in an as-rolled condition. These measurements were followed by others made at temperature with various amounts of oxygen added, and, finally, emissivities of the oxidized materials were measured over a temperature range. Smoothed emissivity values, after a first thermal cycle in a vacuum, at temperatures of 850 and 1075 C are given in Table 5.

Specimens

The specimen metals were hot rolled at 815 C in helium to a thickness of 30 mils. They were then annealed and quenched after which they were cold rolled to 5 mils. The strips were wavy, and those containing Zircaloy 2 showed varying amounts of edge cracking.

Specimens for the hole-in-tube method of measuring emissivities were tubes nominally 1/2 in. in diameter and 11 in. long made from the 5-mil-thick sheet metals.

TABLE 5. SUMMARY OF EMISSIVITY VALUES FOR URANIUM-NIOBIUM-ZIRCONIUM ALLOYS

Material	Total Emissivity		Spectral Emissivity	
	At 850 C	At 1075 C	At 850 C	At 1075 C
Uranium				
As rolled	0.36	0.34	0.32	0.38
With oxygen added ^(a)	0.44 ^(b)	0.43	0.21 ^(b)	0.19
Uranium-10 w/o niobium				
As rolled	0.39	0.41	0.59	0.62
With oxygen added ^(a)	0.60	0.67	0.61	0.72
75 w/o (uranium-10 w/o niobium)-25 w/o Zircaloy 2				
As rolled	0.33	0.34	0.72	0.72
With oxygen added ^(a)	0.35	0.38	0.68	0.65
50 w/o (uranium-10 w/o niobium)-50 w/o Zircaloy 2				
As rolled	0.35	0.36	0.53	0.57
With oxygen added ^(a)	0.41 ^(b)	0.46	0.61 ^(b)	0.64
25 w/o (uranium-10 w/o niobium)-75 w/o Zircaloy 2				
As rolled	0.37	0.38	0.61	0.66
With oxygen added ^(a)	0.47	0.50	--	--

(a) See Table 10 for amounts of oxygen added.

(b) At 900 C.

These tubes were formed by rolling a strip of the metal on a mandrel and heating it in a vacuum for 4 hr at 600 C while constrained.

One metal, the 25 w/o (uranium-10 w/o niobium)-75 w/o Zircaloy 2 alloy, was too brittle in the cold-rolled condition to be formed on the mandrel. The strip of this alloy was annealed in a vacuum for 1 hr at 735 C and water quenched before being placed on the forming mandrel.

Methods and Apparatus

Spectral- and total-emissivity measurements were made using the hole-in-tube method as previously described in BMI-1154⁽¹⁾. Measurements made with both the hole-in-tube and wire-loop methods showed that the hole-in-tube method, with potential leads affixed above and below the hole, could be used for both spectral- and total-emissivity measurements.

The apparatus for the measurement of emissivities by the hole-in-tube method consisted of a cylindrical water-cooled vessel which could be evacuated. A Vycor window in one side permitted measuring specimen temperature with an optical pyrometer. Corrections for the Vycor window were applied to the optical-pyrometer readings.

A 3/64-in. hole was drilled through one wall near the center of the tubular specimen and two 6-mil-diameter zirconium wire potential leads were resistance welded to the tube about 1-1/2 in. above and below the hole. Water-cooled current leads were affixed to each end of the tube and the assembly placed in the water-cooled vacuum chamber.

Measurements were taken of the current flowing through the tube and the voltage drop across the potential wires. Optical-pyrometer readings were taken through the Vycor window of the black-body temperature through the hole in the specimen and the surface temperature beside the hole. The spectral emissivity was determined by the following relationship:

$$\ln \epsilon_{\lambda} = \frac{-C_2}{\lambda} \frac{T-S}{(ST)},$$

where

ϵ_{λ} = spectral emissivity

λ = observed wavelength = 0.65 μ

C_2 = radiation constant = 1.438 cm-K

S = surface temperature, K

T = true (black body) temperature, K .

The total-emissivity values were determined using the following equation:

$$\epsilon_{T'} = \frac{IV}{2\pi r \ell \sigma T^4},$$

where

$\epsilon_{T'}$ = total hemispherical emissivity

I = current through specimen, amp

V = potential drop across measured section, v

r = radius of the specimen, cm

ℓ = length of measured section, cm

σ = Boltzmann's constant = 5.673×10^{-12} w/(cm²)(K⁴)

T = true (black body) temperature, K.

Oxygen was added to specimens by adding individual charges of oxygen (2.5 cm³ at atmospheric pressure per charge) to the vacuum chamber while the specimen was maintained at approximately 900 C. The system was at a pressure of about 2×10^{-5} mm of mercury when each charge of oxygen was added and was evacuated between charges. Subsequent oxygen analyses of the specimens indicated that one such charge of oxygen resulted in an oxygen content in the specimen of about 0.04 w/o.

Results

Spectral and total emissivities for the metals in an as-rolled condition and with oxygen added are shown by experimental points and curves, and as smoothed tabular values.

Five uranium specimens were measured, with varying results. The uranium specimens had a dark, oxidized surface before their emissivities were measured but they were bright and clean after being heated in a vacuum in the apparatus.

Figures 36, 37, 38, and 39 show observed values of spectral and total emissivities for three as-rolled uranium specimens. Figure 40 shows total emissivity versus charges of oxygen added to the specimens shown in Figures 37, 38, and 39. Analyses after the emissivity measurements showed the specimen in Figures 37 and 38 to contain 0.27 w/o oxygen and the specimen in Figure 39 to contain 0.20 w/o oxygen. Figure 41 shows spectral and total emissivities for another as-rolled uranium specimen which burned out when oxygen was added. Figure 42 shows spectral and total emissivities of still another as-rolled uranium specimen and also for the same specimen with two charges of oxygen added.

The spectral and total emissivities of uranium decrease with the first heating in a vacuum. After the first heating the emissivities are more constant with thermal cycling. This decrease of emissivity with the first heating evidently occurs as the surface brightens.

FIGURE 36. SPECTRAL AND TOTAL EMISSIVITY VERSUS TEMPERATURE FOR URANIUM SPECIMEN 1

FIGURE 37. TOTAL EMISSIVITY VERSUS TEMPERATURE FOR URANIUM SPECIMEN 2

FIGURE 38. SPECTRAL EMISSIVITY VERSUS TEMPERATURE FOR URANIUM SPECIMEN 2

FIGURE 39. SPECTRAL AND TOTAL EMISSIVITY VERSUS TEMPERATURE FOR URANIUM SPECIMEN 3

FIGURE 40. TOTAL EMISSIVITY OF URANIUM VERSUS "CHARGES" OF OXYGEN FOR URANIUM SPECIMENS 2 AND 3

Each charge represents approximately 2.5 cm^3 of oxygen admitted at atmospheric pressure to the vacuum chamber of the apparatus.

FIGURE 41. SPECTRAL AND TOTAL EMISSIVITY VERSUS TEMPERATURE FOR URANIUM SPECIMEN 4

FIGURE 42. SPECTRAL AND TOTAL EMISSIVITY VERSUS TEMPERATURE FOR URANIUM SPECIMEN 5 AS ROLLED AND WITH ADDED OXYGEN

FIGURE 43. TOTAL AND SPECTRAL EMISSIVITY VERSUS TEMPERATURE FOR URANIUM-10 w/o NIOBIUM, SPECIMEN 12

Each charge represents approximately 2.5 cm^3 of oxygen admitted at atmospheric pressure to the vacuum chamber of the apparatus.

FIGURE 44. SPECTRAL AND TOTAL EMISSIVITY OF 75 w/o (URANIUM-10 w/o NIOBIUM)-25 w/o ZIRCALOY 2, SPECIMEN 9

FIGURE 45. SPECTRAL AND TOTAL EMISSIVITY OF 50 w/o (URANIUM-10 w/o NIOBIUM)-50 w/o ZIRCALOY 2, SPECIMEN 8

FIGURE 46. SPECTRAL AND TOTAL EMISSIVITY OF 25 w/o (URANIUM-10 w/o NIOBIUM)-75 w/o ZIRCALOY 2, SPECIMEN 10

FIGURE 47. TOTAL EMISSIVITY OF URANIUM-10 w/o NIOBIUM VERSUS "CHARGES" OF OXYGEN FOR SPECIMEN NO. 12

Each charge represents approximately 2.5 cm^3 of oxygen admitted at atmospheric pressure to the vacuum chamber of the apparatus.

Total Emissivity of 75 w/o (Uranium-10 w/o Niobium)- 25 w/o Zircaloy 2, Specimen 9

Total Emissivity of 50 w/o (Uranium-10 w/o Niobium) - 50 w/o Zircaloy 2, Specimen 8

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FIGURE 48. TOTAL EMISSIVITY VERSUS "CHARGES" OF OXYGEN FOR SPECIMENS 8 AND 9

Each charge represents approximately 2.5 cm^3 of oxygen admitted at atmospheric pressure to the vacuum chamber of the apparatus.

FIGURE 49. TOTAL EMISSIVITY OF 25 w/o (URANIUM-10 w/o NIOBIUM)-75 w/o ZIRCALOY 2 VERSUS "CHARGES" OF OXYGEN FOR SPECIMEN NO. 10

Each charge represents approximately 2.5 cm^3 of oxygen admitted at atmospheric pressure to the vacuum chamber of the apparatus.

TABLE 6. EMISSIVITY OF URANIUM

Specimen(a)	Temperature, C	Total Emissivity of Uranium						Spectral Emissivity of Uranium, $\lambda = 0.65 \mu$					
		First Heating	First Cooling	Second Heating	Second Cooling	Third Heating	Third Cooling	First Heating	First Cooling	Second Heating	Second Cooling	Third Heating	Third Cooling
1	850	0.44	0.29	0.32				0.45	0.25	0.22			
	925	0.37	0.29	0.29				0.32	0.25	0.27			
	1000	0.33	0.29	0.29				0.26	0.25	0.32			
	1075	0.29	0.29	0.29(b)				0.24	0.24	0.38(b)			
2	850	0.48	0.41	0.40	0.38	0.35	0.34	0.53	0.34	0.27	0.35	0.23	0.23
	925	0.39	0.38	0.40	0.37	0.33	0.32	0.38	0.34	0.29	0.34	0.24	0.24
	1000	0.37	0.37	0.38	0.37	0.32	0.31	0.34	0.34	0.31	0.33	0.25	0.25
	1075	0.34	0.34	0.34	0.34	0.31	0.31	0.34	0.34	0.32	0.32	0.26	0.26
3	850	0.54	0.41	0.38	0.35			0.77	0.45	0.47	0.54		
	925	0.45	0.40	0.38	0.34			0.59	0.45	0.56	0.58		
	1000	0.40	0.39	0.36	0.33			0.51	0.46	0.60	0.60		
	1075	0.39	0.39	0.35	0.35			0.47	0.47	0.61	0.61		
4	850	0.46						0.59					
	925	0.42						0.51					
	1000	0.39						0.49					
	1075	0.37(c)						0.49(c)					
5	850	0.43						0.39					
	925	0.39	0.35					0.27	0.27				
	1000	0.36	0.35					0.27	0.27				
	1075	0.34	0.34					0.27	0.27				

(a) All specimens were in the as-rolled condition.

(b) Specimen tube burned out.

(c) Specimen tube collapsed

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TABLE 7. EMISSIVITY OF ALLOYS

Specimen(a)	Composition, w/o	Temperature, C	Total Emissivity				Special Emissivity, $\lambda = 0.65 \mu$			
			First Heating	First Cooling	Second Heating	Second Cooling	First Heating	First Cooling	Second Heating	Second Cooling
12	Uranium-10 niobium	850	0.45	0.40	0.39	0.39	0.66	0.59	0.66	0.59
		925	0.44	0.40	0.39	0.39	0.63	0.60	0.63	0.60
		1000	0.43	0.41	0.40	0.40	0.62	0.61	0.62	0.61
		1075	0.43	0.43	0.41	0.41	0.62	0.62	0.62	0.62
9	75 (uranium-10 niobium)- 25 Zircaloy 2	850	0.36	0.33	0.33	0.33	0.53	0.74	0.72	0.72
		925	0.35	0.33	0.33	0.33	0.55	0.67	0.71	0.71
		1000	0.34	0.33	0.33	0.33	0.60	0.62	0.71	0.71
		1075	0.34	0.34	0.34	0.34	0.60	0.60	0.71	0.71
8	50 (uranium-10 niobium)- 50 Zircaloy 2	850	0.37	0.35	0.35	0.35	0.60	0.53	0.53	0.53
		925	0.37	0.36	0.36	0.36	0.59	0.57	0.57	0.57
		1000	0.37	0.36	0.36	0.36	0.58	0.59	0.59	0.59
		1075	0.36	0.36	0.36	0.36	0.57	0.57	0.57	0.57
10	25 (uranium-10 niobium)- 75 Zircaloy 2	850	0.39	0.37	0.37	0.37	0.63	0.63	0.61	0.61
		925	0.38	0.37	0.37	0.37	0.63	0.63	0.64	0.64
		1000	0.38	0.38	0.38	0.38	0.63	0.63	0.65	0.65
		1075	0.38	0.38	0.38	0.38	0.63	0.63	0.66	0.66

(a) All specimens in as-rolled condition.

TABLE 8. EFFECT OF OXYGEN ADDITION ON THE TOTAL EMISSIVITY OF URANIUM AND URANIUM ALLOYS

Specimen	Composition, w/o	Cumulative(a) Number of Charges Added	Temperature, C	Total Emissivity
2	100 uranium	0	895	0.33
		1	895	0.46
		3	895	0.48
		5	895	0.50
		10	895	0.53
		15	895	0.54
		20	895	0.55(b)
3	100 uranium	0	895	0.33
		1	895	0.54
		3	895	0.57
		5	895	0.58
		10	895	0.59(b)
12	Uranium-10 niobium	0	900	0.40
		1	900	0.48
		3	900	0.51
		5	900	0.53
		10	900	0.60
		15	900	0.64
9	75 (uranium-10 niobium)- 25 Zircaloy 2	0	900	0.33
		1	900	0.35
		3	900	0.37
		5	900	0.39
		6	900	0.40
8	50 (uranium-10 niobium)- 50 Zircaloy 2	0	900	0.35
		1	900	0.35
		3	900	0.35
		5	900	0.35
		6	900	0.36
		10	900	0.36
		14	900	0.40
10	25 (uranium-10 niobium)- 75 Zircaloy 2	0	900	0.37
		1	900	0.37
		3	900	0.37
		5	900	0.38
		10	900	0.39
		15	900	0.40
		20	900	0.42
		25	900	0.45
		29	900	0.49

(a) Each charge represents approximately 2.5 cm³ of oxygen admitted at atmospheric pressure to the vacuum chamber of the apparatus.

(b) Specimen tube collapsed.

TABLE 9. EMISSIVITY OF URANIUM AND URANIUM "CHARGES"^(a) OF OXYGEN

Specimen	Composition, w/o	Oxygen Charges ^(a)	Temperature, C	Total Emissivity		Spectral Emissivity, $\lambda = 0.65\mu$	
				Heating	Cooling	Heating	Cooling
5	Uranium	2	900	0.51	0.44	0.21	0.21
			925	0.49	0.44	0.20	0.20
			1000	0.46	0.43	0.20	0.20
			1075	0.43	0.43	0.19	0.19
12	Uranium-10 niobium	15	850	0.60	0.57	0.61	0.61
			925	0.61	0.59	0.64	0.64
			1000	0.64	0.63	0.67	0.67
			1075	0.67	0.67	0.72	0.72
9	75 (uranium-10 niobium)- 25 Zircaloy 2	6	850	0.41	0.35	0.68	0.68
			925	0.41	0.35	0.66	0.66
			1000	0.40	0.36	0.66	0.66
			1075	0.38	0.38	0.65	0.65
8	50 (uranium-10 niobium)- 50 Zircaloy 2	20	900	0.47	0.41	0.63	0.61
			925	0.52	0.42	0.70	0.62
			1000	0.50	0.44	0.70	0.64
			1075	0.46	0.46	0.64	0.64
10	25 (uranium-10 niobium)- 75 Zircaloy 2	(b)	850	0.68	0.47	--	--
			925	0.61	0.48	--	--
			1000	0.53	0.49	--	--
			1075	0.50	0.50	--	--

(a) Each charge represents approximately 2.5 cm^3 of oxygen admitted at atmospheric pressure to the vacuum chamber of the apparatus.

(b) Heavy addition of oxygen - amount not measured.

TABLE 10. OXYGEN ANALYSIS FOR URANIUM AND ALLOYS

Specimen	Composition, w/o	Specimen Condition	Number of "Charges"(a)	Amount of Oxygen, w/o
-	100 Uranium	As rolled	0	0.06
2	100 Uranium	Oxygen added	21	0.27
3	100 Uranium	Oxygen added	10	0.20
4	100 Uranium	Thermally cycled in vacuum	0	0.08
-	Uranium-10 niobium	As rolled	0	0.07
12	Uranium-10 niobium	Oxygen added	19	0.37
-	75 (Uranium-10 niobium) - 25 Zircaloy 2	As rolled	0	0.11
9	75 (Uranium-10 niobium) - 25 Zircaloy 2	Oxygen added	6	0.22
-	50 (Uranium-10 niobium) - 50 Zircaloy 2	As rolled	0	0.16
8	50 (Uranium-10 niobium) - 50 Zircaloy 2	Oxygen added	20	0.57
-	25 (Uranium-10 niobium) - 75 Zircaloy 2	As rolled	0	0.11
10	25 (Uranium-10 niobium) - 75 Zircaloy 2	Oxygen added	Unknown large amount of oxygen added	1.03

(a) Each charge represents approximately 2.5 cm^3 of oxygen admitted at atmospheric pressure to the vacuum chamber of the apparatus.

Figure 43 shows observed emissivities values versus temperature for a uranium-10 w/o niobium alloy.

Figures 44, 45, and 46 show, respectively, observed spectral and total emissivities for the 75 w/o (uranium-10 w/o niobium)-25 w/o Zircaloy 2, 50 w/o (uranium-10 w/o niobium)-50 w/o Zircaloy 2, and 25 w/o (uranium-10 w/o niobium)-75 w/o Zircaloy 2 alloys in an as-rolled condition and with oxygen added. Figures 47, 48, and 49 show the total emissivities at temperature versus the oxygen charges added to the specimens shown in Figures 43, 44, 45, and 46.

Curves are not shown for spectral-emissivity measurements at temperature versus charges of oxygen added because of the wide scatter of data. For uranium the spectral-emissivity values ranged from 0.12 to 0.62 with no definite trend with temperature. The uranium-10 w/o niobium specimen had a range of spectral emissivities from 0.69 to 0.85. The ranges of spectral emissivities for the alloys containing Zircaloy 2 are as follows: 25 w/o Zircaloy 2, from 0.58 to 0.75; 50 w/o Zircaloy 2, from 0.55 to 0.72; and 75 w/o Zircaloy 2, from 0.62 to 0.83.

There was a decided mottled appearance to the outside surface of the specimens when charges of oxygen were added. This prevented an accurate measurement of the outside-surface temperature by the optical pyrometer. Total-emissivity measurements were not affected by the mottled condition of the outside surface because only black-body temperatures (through the hole in the specimen wall) are involved. Spectral emissivities could, however, be measured on specimens containing oxygen after the oxygen had been given time to diffuse into the metal and the mottled surface condition had largely disappeared. It is apparent from the emissivity data shown in the curves that there is more scatter in the spectral- than in the total-emissivity measurements, mainly because it was difficult to accurately measure the outside-surface temperatures.

Table 6 shows smoothed emissivity values at selected temperatures for all uranium specimens measured, and Table 7 shows values for all the uranium alloys measured.

Table 8 shows smoothed total-emissivity values at temperature for six specimens to which varying amounts of oxygen were added.

Table 9 shows smoothed emissivity values versus temperature for the five specimens to which oxygen was added.

Table 10 shows oxygen contents of the metals in the as-rolled condition and also after oxygen had been added.

PREPARATION OF TEST SPECIMENS

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The uranium-10 w/o niobium alloy and a series of uranium-10 niobium-base alloys with varying additions of Zircaloy 2 were prepared for use in the study of metal-water reaction rates and emissivities. The techniques used for the preparation of these alloys into the form of rod and foil are described on pages 70 and 71.

Uranium-10 w/o Niobium Alloy

Three uranium-10 w/o niobium alloy ingots were prepared by the duplex-melting process. This process produces a vacuum-induction melted ingot which is remelted as the consumable electrode of an arc melting furnace. The induction-melted ingot was prepared from reactor-grade uranium and single-sintered bar niobium. These materials were melted in a zirconia crucible and cast into a cylindrical graphite mold. The induction-melted ingot was then cleaned by vapor blasting and welded to an adapter to form an electrode for consumable melting. This electrode was melted into a 2-1/2-in.-diameter ingot.

After melting, the ingots were cropped to remove the starter charge and spatter ring and samples for chemical analyses were taken from the top and bottom of the ingots. The results of these analyses are listed in Table 11.

TABLE 11. CHEMICAL ANALYSES OF URANIUM-10
w/o NIOBIUM INGOTS

Ingot	Location of Sample	Analyses, w/o		
		Niobium	Carbon	Nitrogen
I	Top	9.33	0.008	0.008
I	Bottom	9.04	0.005	0.008
II	Top	9.78	0.008	0.008
II	Bottom	9.60	0.006	0.008
III	Top	10.00	0.008	0.008
III	Bottom	10.00	0.005	0.008

The cropped ingots were then arc conditioned to remove surface imperfections which would impair the quality of the finished product. The arc-conditioned ingots were forged from a chloride salt bath at 2200 F to 1-in.-square rod. This rod was rolled to 5/8-in.-diameter stock from a helium-atmosphere furnace at 1550 F. Although the major portion of this material was fabricated to rounds, some of the material was produced in the form of 5-mil foil.

Initial efforts to obtain this foil were unsuccessful because it was impossible to obtain cold reductions of more than 30 per cent with the heat treatments in use. Therefore, the hot-rolled material was jacketed with Ti-Namel and rolled at 1175 F to 9-mil sheet. The Ti-Namel was then removed and the sheet was annealed at 1750 F for 4 hr in vacuum and cooled rapidly in air. Foil of the desired thickness with extremely good surfaces was obtained by rolling this annealed sheet in a four-high rolling mill.

Alloys Containing Zircaloy 2

Three ingots were prepared. The composition of the ingots was varied by alloying different quantities of the uranium-10 w/o niobium with Zircaloy 2. The uranium-niobium-alloy ingots were prepared by the vacuum-induction melting procedure described in the preceding section. The 1-1/2-in.-diameter vacuum-cast ingots were cut longitudinally and Zircaloy 2 in the form of 1-1/4-in.-wide strip was placed between the halves. This formed an elongated assembly of the desired nominal composition. The composite shapes were welded together and arc melted as consumable electrodes to 2-3/4-in.-diameter ingots. The ingots were quartered by sawing longitudinally, and these quarters were welded end to end to form the second-melt electrode. After the second melt, the ingots were cropped and samples for chemical analyses were obtained from the top and bottom of each ingot. The results of these analyses and the nominal composition of these ingots are given in Table 12.

TABLE 12. CHEMICAL ANALYSES OF INGOTS
CONTAINING ZIRCALOY 2

Ingot	Location of Sample	Nominal Amount of Zircaloy 2 in Ingot, w/o	Analysis, w/o		
			Zirconium	Nitrogen	Carbon
I	Top	25	26.4	0.014	0.024
I	Bottom	25	27.6	0.014	0.017
II	Top	50	52.1	0.009	0.025
II	Bottom	50	53.4	0.009	0.028
III	Top	75	74.8	0.007	0.023
III	Bottom	75	75.3	0.007	0.019

All of the alloys were forged to rod without difficulty. However, the forging temperature was different for each composition. A temperature of 1850 F was used to forge the 25 w/o (uranium-10 w/o niobium) - 75 w/o Zircaloy 2 alloy, the 50 w/o (uranium-10 w/o niobium) - 50 w/o Zircaloy 2 alloy was forged at 1750 F, and the 75 w/o (uranium-10 w/o niobium) - 25 w/o Zircaloy 2 alloy was forged at 1500 F. The forged alloy rods were then rolled to 5/8 in. in diameter from a helium atmosphere at 1500 F.

After investigating various methods of preparing the foil, it was found that good-quality material could be produced by rolling the 5/8-in. rod to 30-mil flat stock at 1250 F. The 30-mil strip was then water quenched from the rolling temperature. After quenching, it was possible to cold roll in the four-high rolling mill to 5-mil foil without further heat treating.

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