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THE ZIRCONIUM-URANIUM DIOXIDE REACTION

by

Manley W. Mallett
John W. Droege
Arnold F. Gerds
Alexis W. Lemmon, Jr.

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BATTELLE MEMORIAL INSTITUTE
505 King Avenue
Columbus 1, Ohio

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The solid-solid reaction between zirconium and UO_2 was studied in the temperature range of 750 to 2000 F by means of welded sandwich-type elements. The extent of reaction was evaluated on the basis of metallographic examinations of sample cross sections. The phases formed were identified by X-ray diffraction techniques. In the temperature range of 750 to 1200 F, months of heating were required to produce measurable reaction zones. Easily measured reaction zones were produced in about 1 month at 1300 F and in a few hours at 1600 and 2000 F. A limited number of experiments indicated that Zircaloy 2 reacted less rapidly than zirconium with UO_2 .

The reaction of zirconium with UO_2 resulted in the dissolution of UO_2 in zirconium as uranium and oxygen. These diffused into the zirconium at unequal speeds. Zirconium diffused in the opposite direction to further the reaction. Inert tungsten markers were used to mark the position of the initial interfaces. Reaction and diffusion rates were determined from analyses of thin layers machined from the zirconium.

INTRODUCTION

Fuel elements composed of UO_2 clad with zirconium or zirconium-rich alloys are under consideration for some reactor applications. The useful life of such elements might be limited by the reaction occurring between the UO_2 and the zirconium as well as by the reaction occurring between the zirconium and the coolant. This investigation was initiated to obtain information that will aid in estimating the useful life of the fuel elements on the basis of reaction of the UO_2 with the zirconium cladding.

The literature reported only one study on the zirconium-uranium-oxygen ternary phase relationships. Saller, et al.⁽¹⁾, showed sections of the ternary phase diagram at 1000, 1300, and 2000 F. This work was later supplemented by a more detailed study⁽²⁾ of the effect of oxygen on the stability of the epsilon intermetallic phase in the system. In the latter study, they showed additional ternary sections at 1022 and 1220 F (550 and 660 C) as well as a binary uranium-zirconium constitutional diagram. Additional constitutional-diagram studies were reported by Summers-Smith⁽³⁾. The zirconium-oxygen phase relationships were reported by Domagala and McPherson⁽⁴⁾. The effect of small amounts of oxygen in solid solution in zirconium on mechanical properties was studied by Treco⁽⁵⁾. Many data on the complicated uranium-oxygen phase relationships were given by Katz and Rabinowitch⁽⁶⁾.

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(1) References at end.

A rather complete summary of available pertinent thermodynamic data was presented in BMI-1028⁽⁷⁾. The reaction,

may be considered from the standpoint of available thermodynamic information. Coughlin's review⁽⁸⁾ lists the standard free energies of formation, shown in Table 1, with the corresponding free energies for the reaction.

TABLE 1. STANDARD FREE ENERGIES

Temperature, K	1000	1100
Temperature, F	1340	1520
ΔF_f° of UO_2 , kcal per mole	-218.1 ± 0.7	-214.1 ± 0.7
ΔF_f° of ZrO_2 , kcal per mole	-216.05 ± 0.25	-211.6 ± 0.25
ΔF° for Reaction (1), kcal per mole	+2.05	+2.50

If the reactants and products are considered to be in their standard states, or nearly so, then the positive free energy indicates that no reaction takes place. Consideration of the data at other temperatures indicates that, in the range of 100 to 900 F, the sign becomes negative, so the reaction would be possible at these temperatures although the kinetics would certainly be unfavorable.

There is a high solubility of oxygen in zirconium (6.75 w/o)⁽³⁾. If alpha zirconium containing oxygen is considered to be a solution of ZrO_2 in zirconium, then the activity of ZrO_2 in such a solution is less than one. Under these conditions, Reaction (1) becomes thermodynamically possible. Then, the reaction takes the form

The work reported in this present paper was undertaken to judge the validity of this hypothesis. Fundamental information on the kinetics of the reaction of zirconium with UO_2 at elevated temperatures also was sought.

SUMMARY

An experimental study of the solid-solid UO_2 -zirconium reaction was performed at temperatures between 750 and 2000 F. Although thermodynamic predictions indicated that the reaction would not take place for products and reactants in their standard states, solution of the products in the zirconium lowered the thermodynamic activities

sufficiently for reaction to proceed. The extent of reaction was evaluated on the basis of metallographic examinations of sample cross sections from welded sandwich-type specimens held at the various reaction temperatures for different lengths of time. The phases formed were identified by X-ray diffraction techniques. In some cases, reaction rates were determined from analyses of thin layers machined from the zirconium.

In the temperature range of 750 to 1200 F, months of heating were required to produce measurable reaction zones. Easily measured reaction zones were produced in about 1 month at 1300 F and in a few hours at 1600 and 2000 F. A limited number of experiments indicated that Zircaloy 2 reacted less rapidly than zirconium with UO_2 . The results are consistent with known thermodynamic, kinetic, and diffusion theory.

MATERIALS

The zirconium used for this study was low-hafnium arc-melted iodide metal. For the small elements, the arc-melted ingots were forged and rolled to about 1/2-in.-diameter rod. The large sandwich-type elements were machined directly from 2-1/2-in.-diameter arc-melted ingots. Table 2 lists a typical analysis of impurities found in arc-melted and rolled zirconium rod. Zircaloy 2, used in a few experiments, contained the following alloying elements: 1.5 w/o tin, 0.12 w/o iron, 0.10 w/o chromium, 0.05 w/o nickel, and 0.05 to 0.10 w/o oxygen. Other elements were present in about the amounts shown in Table 2.

The UO_2 cores were prepared from Mallinckrodt oxide. The oxide powder was pressed into pellets in steel dies and sintered in hydrogen at about 3200 F. The sintering in hydrogen did not reduce the UO_2 but merely removed oxygen in excess of UO_2 . These high-fired compacts had densities of about 75 per cent of the theoretical density for UO_2 and an oxygen content of $\text{UO}_{2.004}$.

The diameters of the pellets were machine ground carefully to size and the ends faced by hand on silicon carbide papers to produce flat and parallel ends. A steel V-block was used to aid in producing ends that were perpendicular to the sides. The oxide pellets were vacuum degassed at about 1300 F prior to loading the zirconium jackets.

PROCEDURE

Test Elements

The reaction between zirconium and UO_2 was studied using sandwich-type elements. Plane surfaces of the high-fired UO_2 cores were in intimate contact with plane surfaces of the zirconium jackets. The elements were of two sizes. The UO_2 cores in the large elements were approximately 1-1/2 in. in diameter and 1/4 in. thick and had flat and parallel ends. Zirconium jackets were closely fitted around these cores. The 1-1/2-in.-diameter flat zirconium end plates were 1/4 in. thick.

TABLE 2. TYPICAL COMPOSITION OF ARC-MELTED
AND ROLLED ZIRCONIUM ROD

Element	Analysis(a), ppm
Iron	100-1000
Oxygen	320(b)
Nickel	5-50
Carbon	--(c)
Nitrogen	30(d)
Hydrogen	50
Chromium	60-600
Silicon	<20
Aluminum	<50
Molybdenum	ND(e)
Copper	10-100
Lead	ND
Manganese	<10
Hafnium	ND
Boron	ND
Magnesium	<10
Tin	ND
Calcium	<10

(a) By spectrographic method unless otherwise indicated.

(b) Vacuum-fusion method.

(c) Combustion method.

(d) Kjeldahl method.

(e) ND = not detected.

The small elements contained UO_2 cores about 0.3 in. in diameter and about 1/4 to 3/8 in. thick. These cores also were encapsulated in close-fitting zirconium jackets. Some of the small elements contained a thin strip of 0.001-in. -thick tungsten foil in one end to mark the original zirconium- UO_2 interface. After pressing the caps of the capsules tightly against the cores, the caps were welded in place. The excess weld metal was removed from the ends by machining.

Reactions Above 1450 F

Elements heated in the temperature range of 1450 to 2000 F were hot pressed in graphite dies in an argon atmosphere. One loading of a composite die generally consisted of three small elements and one large element. The die was contained in a vertical Mullite furnace tube of about 3-1/2 in. in ID. Globar resistance elements were used to heat the assembly. Temperature was regulated by means of a recording controller. Pressure was applied to the ends of the capsules with a lever-arm device. The dead load applied produced a pressure of about 3000 psi on the ends of the small elements and about 750 psi on the ends of the large element.

After heating at the designated temperature for the desired period of time, the pressure on the elements was removed and the die containing the elements was lifted out of the furnace tube and quenched in cold water. The microstructures shown in this report represent elements cooled in this manner.

Reactions Below 1450 F

Elements heated at 750, 950, 1100, 1200, and 1300 F were heated in autoclaves under 5000-psi helium pressures. The autoclaves were heated by resistance-wound furnaces. Temperature was regulated by means of a controller. After having been heated for the predetermined period of time, the autoclaves were cooled by removing from the furnaces and cooling in air blown from a fan. For example, they could be cooled from 1300 F to about 300 F, inside temperature, in about 1 hr by this technique. The photomicrographs shown in this report were made from elements cooled in this manner.

Evaluation of Results From Test Elements

The small elements were sectioned longitudinally and their reaction zones examined metallographically. In some cases, hardness traverses were made in the zirconium, beginning at the metal-oxide interface. No evidence for diffusion of zirconium into UO_2 was observed.

Large reacted elements were sectioned radially and most of the brittle UO_2 chipped out. A longitudinal section was cut off which exposed the one end of the reaction zone. This section was polished, etched, and examined metallographically. If it appeared that adequate contact had been achieved and a sufficiently thick reaction zone had been formed, the elements were machined into layers, each 0.5 or 1.0 mil

thick, beginning at the zirconium- UO_2 interface. Each layer then was divided into two portions. One part was analyzed for oxygen by the vacuum-fusion method. Uranium analyses by the fluorescence method⁽⁹⁾ were obtained on the other portion of each layer. Details on the methods of analysis are given in Appendix A.

RESULTS

Reaction at 2000 F

The microstructures of the cross sections of elements heated at 2000 F were characterized by a continuous band of reaction product in the zirconium that stained readily when etched. The typical appearance of the reaction zone of an element heated for 140 hr at 2000 F is shown at 50X in Figure 1. The gray material at the bottom of the photomicrograph is UO_2 . The two-phase region lying between the UO_2 and the stained band consists of alpha zirconium (with oxygen in solution) and alpha uranium. The stained band was found by X-ray diffraction studies to have the alpha-uranium structure. A small portion of this material was isolated and found to contain 80 w/o uranium and 20 w/o zirconium. However, the zirconium content is probably lower than indicated because of mechanical difficulties in separating the uranium-rich phase from the zirconium phase. The light-etching material, deeper in the zirconium than the stained band and containing the cracks, is alpha zirconium. The cracks undoubtedly resulted from mechanical stresses acting on the oxygen-embrittled zirconium.

Elements heated for shorter times showed the same relative distribution of phases except that each region was proportionately thinner. A plot of the thicknesses of the several distinct phase regions as a function of time ($t^{1/2}$) is shown for the reaction at 2000 F in Figure 2. The thicknesses of the several regions were determined by measurements on photomicrographs of known magnification. The several phase regions appear to thicken directly as the square root of time.

Knoop hardness traverses indicated that the two-phase region adjacent to the UO_2 is hard (550 to 650 Knoop hardness number, 200-g load). The stained band is relatively soft (350 to 400 Knoop hardness number) and the adjacent alpha zirconium region, containing oxygen in solid solution again is hard (500 to 650 Knoop hardness number). The unaffected zirconium beyond the region of oxygen penetration is soft (100 to 200 Knoop hardness number).

It was not possible to obtain quantitative data on the transfer of uranium and oxygen to the zirconium for the reaction at 2000 F. The cracks that formed in the zirconium containing oxygen in solution caused severe flaking when attempts were made to machine thin layers near the interface of this element.

Reaction at 1600 F

The reaction at 1600 F also produced an almost continuous band of the uranium-rich phase in the reaction zone. The microstructures in the reaction zone of elements heated at 1600 F for 68 and 507 hr are shown at 100X in Figures 3 and 4, respectively.

Etchant: 0.5 Volume Per Cent HF
on Polishing Wheel

FIGURE 1. REACTION ZONE OF A ZIRCONIUM- UO_2 ELEMENT HEATED
AT 2000 F FOR 140 HR IN ARGON

FIGURE 2. ESTIMATION OF THICKNESSES (ON BASIS OF MICRO-STRUCTURE) OF VARIOUS ZONES IN ZIRCONIUM, MEASURED FROM THE ZIRCONIUM-UO₂ INTERFACE FOR THE REACTION AT 2000 F

100X

N27407

Etchant: 0.5 Volume Per Cent HF
on Polishing Wheel

FIGURE 3. REACTION ZONE OF A ZIRCONIUM- UO_2 ELEMENT HEATED AT 1600 F FOR 68 HR IN ARGON

100X

N34188

Etchant: 0.5 Volume Per Cent HF
on Polishing Wheel

FIGURE 4. REACTION ZONE OF A ZIRCONIUM- UO_2 ELEMENT HEATED AT 1600 F FOR 507 HR IN ARGON

The two-phase region adjacent to the UO_2 contains alpha uranium (dark-etching) and alpha zirconium (light-etching matrix). The stained uranium-rich band, which is somewhat more irregular than that in the 2000 F element, was found by X-ray diffraction studies to contain a strong pattern of the epsilon intermetallic phase of the uranium-zirconium system as well as some evidence of alpha uranium. The light-etching region, adjacent to but deeper in the zirconium than the stained band, consists of oxygen dissolved in alpha zirconium. The material in the grain boundaries at the top of the photomicrograph (Figure 3) is evidence of transformed beta, indicating that the element was heated in a two-phase alpha-beta region. The element reacted for 507 hr at 1600 F can be seen to contain voids in the UO_2 at the interface. These voids, the formation of which will be discussed in a later section in detail, appear to result from the fact that products of the reaction have higher densities than the reactants.

A plot of the thickness of the several distinct phase regions in the reaction zone as a function of time ($t^{1/2}$) is shown in Figure 5. The two-phase region adjacent to the zirconium and also the stained uranium-rich zone appear to thicken as a function of the square root of time. However, both the two-phase region, consisting of alpha zirconium and alpha uranium, and the stained uranium-rich band are much thinner for the 507-hr experiment than might be expected. The dotted line, drawn to indicate the depth of maximum oxygen penetration into the zirconium, increases uniformly through about 187 hr (not shown in Figure 5) and then drops off erratically. It is likely that these anomalous points (for 236 and 507 hr) reflect the combined influence of the voids at the interface, shown in Figure 4, and perhaps to some extent the presence of the uranium-rich band in the reaction zone.

Results of analyses for uranium and oxygen obtained on thin layers machined in the zirconium adjacent to the interface from an element heated at 1600 F for 95 hr are listed in Table 3 and shown graphically in Figure 6. The relation of each layer to the microstructure is indicated by the arrowed lines in Table 3. These data show that the uranium reaches a maximum value in the uranium-rich phase region. At this point, the oxygen content is relatively low. As the uranium concentration decreases sharply (Layers 5, 6, and 7) the oxygen increases and reaches a peak at about a 5 to 7-mil distance from the interface. The uranium content decreases very rapidly through this region and appears to level off at about 0.009 w/o in about Layer 15 (14 to 15 mils from the interface). The oxygen decreases much more slowly, approaching a value of about 0.08 w/o in Layer 25 (24 to 25 mils from the interface).

Reaction at 1525 F

On the basis of a single specimen heated for 227 hr, the distribution of phases in the microstructure is much the same as that for the 1600 F elements. Table 4 lists uranium and oxygen concentrations at known distances from the interface of the large element heated at 1525 F. The relationship between the analyses and the microstructure is indicated by the arrowed lines. The analytical values are shown graphically in Figure 7. These are much like those obtained for the 1600 F specimens. The oxygen content is high and the uranium relatively low adjacent to the UO_2 . Within the region of the uranium-rich band, the uranium reaches its maximum value and the oxygen reaches a temporary minimum. Beyond this stained band, the uranium decreases sharply and the oxygen reaches a relatively high maximum value at about 7 to 8 mils from the interface and then begins its gradual descent. The oxygen concentration

FIGURE 5. ESTIMATION OF THICKNESSES (ON BASIS OF MICRO-STRUCTURE) OF VARIOUS ZONES IN ZIRCONIUM, MEASURED FROM THE ZIRCONIUM-UO₂ INTERFACE, FOR THE REACTION AT 1600 F

TABLE 3. URANIUM AND OXYGEN CONTENTS AT VARIOUS DISTANCES FROM THE ZIRCONIUM- UO_2 INTERFACE FOR AN 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 out	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(a)	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

100X

N29272

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

FIGURE 6. COMPOSITION OF ZIRCONIUM SAMPLE AFTER HEATING IN CONTACT WITH UO_2 AT 1600 F FOR 95 HR

TABLE 4. URANIUM AND OXYGEN CONTENTS AT VARIOUS DISTANCES FROM THE ZIRCONIUM- UO_2 INTERFACE FOR AN ELEMENT HEATED AT 1525 F FOR 227 HR IN ARGON AND QUENCHED

Layer	Distance of Layer From Zirconium- UO_2 Interface, mils	Oxygen, w/o	Uranium, w/o
1	0-0.5	3.99	19.7
2	0.5-1.0	4.29	16.3
3	1.0-1.5	4.06	19.7
4	1.5-2.0	3.68	17.0
5	2.0-2.5	2.64	19.0
6	2.5-3.0	1.91	26.2
7	3.0-3.5	1.69	33.1
8	3.5-4.0	1.36	41.2
9	4.0-4.5	1.22	38.4
10	4.5-5.0	2.02	41.6
11	5.0-6.0	1.38	33.9
12	6.0-7.0	2.13	19.5
13	7.0-8.0	2.58	6.35
14	8.0-9.0	2.36	2.12
15	9.0-10.0	2.17	0.63
16	10.0-11.0	1.63	0.14
17	11.0-12.0	1.32	0.063
18	12.0-13.0	1.23	0.020
19	13.0-14.0	1.01	0.010
20	14.0-15.0	0.75	0.007
21	15.0-16.0	0.557	0.004
22	16.0-17.0	0.319	0.002
23	17.0-18.0	0.486	0.002
24	18.0-19.0	0.287	---
25	19.0-20.0	0.327	---
26	20.0-21.0	0.186	---
27	21.0-22.0	0.214	---
28	22.0-23.0	0.127	---
29	23.0-24.0	0.149	---
30	24.0-25.0	0.102	---
31	25.0-26.0	0.135	0.001
32	26.0-27.0	0.128	---

FIGURE 7. COMPOSITION OF ZIRCONIUM SAMPLE AFTER HEATING IN CONTACT WITH UO_2 AT 1525 F FOR 227 HR

appears to level off at about 0.13 w/o at 22 to 23 mils from the interface. The uranium content leveled off at 0.001 to 0.002 w/o 16 to 17 mils from the interface.

Reaction at 1450 F

The stained, uranium-rich band also was found in elements heated at 1450 F. However, it was not very continuous when produced at this temperature. Figure 8 shows, at 100X, the microstructure in the reaction zone of an element heated for 335 hr (14 days) in argon and water quenched. The two-phase region adjacent to the UO_2 again consists of alpha uranium in an alpha zirconium matrix. The two-phase structure nearest the UO_2 contains many voids in addition to the alpha uranium and alpha zirconium and appears to be separated by a rather sharp line of demarcation from the balance of the two-phase region. Presumably voids formed in the reaction zone are healed by diffusion of zirconium toward the UO_2 , in a manner somewhat analogous to the process of sintering powders into a dense mass. The line of demarcation may indicate the extent to which this process has taken place.

The bulky, dark-etched uranium-rich material consists principally of the epsilon intermetallic phase. Spikes of this material penetrated quite deeply into the core structure along grain boundaries. The oxygen-rich zirconium lies next to this phase and deeper into the zirconium. The core structure appears to consist of a fine Widmanstätten precipitate of zirconium hydride in a zirconium matrix.

A large element that had been heated at 1450 F for 495 hr was machined into thin layers beginning at the zirconium- UO_2 interface. Results of oxygen and uranium analyses, obtained on these layers, are listed in Table 5 and shown graphically in Figure 9. Because no photomicrograph of the large element was available, one from a small element heated in the same experiment was substituted in Table 5. This small element had been heated under an external pressure of 3000 psi while the large element from which the analytical data were obtained was under a pressure of only 700 psi. Because of the probable effect of this difference in pressure on interfacial contact of the reacting materials, the degrees of reaction in the two elements are not exactly comparable. However, the arrowed lines are drawn to indicate the probable positions of the analyses with respect to the microstructure.

The uranium content rises from a low value near the interface and reaches a peak value at 3 to 4 mils from the interface. At this point the oxygen content, which has dropped sharply from a high value adjacent to the interface, appears to be at a minimum value. This region of the element must correspond to the uranium-rich stained area of the photomicrograph. Unfortunately, the oxygen content (nearer to the interface) adjacent to this low value is not known. However, on the basis of the microstructure and also data obtained at 1525 and 1600 F, it appears likely that the oxygen content increases from this relatively low value to a higher level in the two-phase region nearer to the UO_2 .

The oxygen content rises steadily from a temporary minimum value to reach a maximum at 10 to 11 mils from the interface. While the oxygen content is increasing, the uranium content decreases rather sharply from its maximum value. The decrease, however, is not as sharp as it was at the higher temperatures (1600 and 1525 F) because of the relatively broad area covered by the discontinuous stained band of uranium-rich material. The uranium analyses appear to begin leveling off at about 0.06 w/o

Etchant: 0.5 Volume Per Cent HF
on Polishing Wheel

FIGURE 8. REACTION ZONE OF AN ELEMENT HEATED AT 1450 F
FOR 335 HR (14 DAYS) IN ARGON AND WATER QUENCHED

TABLE 5. URANIUM AND OXYGEN CONTENTS AT VARIOUS DISTANCES FROM THE ZIRCONIUM- UO_2 INTERFACE FOR AN ELEMENT HEATED AT 1450 F FOR 495 HR IN ARGON AND QUENCHED

Layer	Distance of Layer From Zirconium- UO_2 Interface, mils	Oxygen, w/o	Uranium, w/o
1	0-2.0	3.36	16.3
2	2.0-3.0	--	25.9
3	3.0-4.0	0.39	32.4
4	4.0-5.0	0.54	31.3
5	5.0-6.0	0.66	25.9
6	6.0-7.0	--	21.5
7	7.0-8.0	1.33	12.5
8	8.0-9.0	1.49	6.73
9	9.0-10.0	0.06(a)	3.73
10	10.0-11.0	1.47	2.27
11	11.0-12.0	1.60	1.62
12	12.0-13.0	0.35	1.09
13	13.0-14.0	1.10	0.55
14	14.0-15.0	--	0.25
15	15.0-16.0	0.81	0.25
16	16.0-17.0	0.75	0.14
17	17.0-18.0	0.51	0.057
18	18.0-19.0	0.46	0.056
19	19.0-20.0	0.34	0.042
20	20.0-21.0	0.37	0.078(a)
21	21.0-22.0	0.13	0.031
22	22.0-23.0	0.16	0.096
23	23.0-24.0	0.19	0.096
24	24.0-25.0	0.18	0.032
25	25.0-26.0	0.17	0.032
26	26.0-27.0	0.11	0.016
27	27.0-28.0	0.14	0.015
28	28.0-29.0	0.12	0.012

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

FIGURE 9. COMPOSITION OF ZIRCONIUM SAMPLE AFTER HEATING IN CONTACT WITH UO_2 AT 1450 F FOR 495 HR

about 18 mils from the interface and decrease very slowly from this level. The oxygen decreases more slowly from its maximum value and approaches an average level of 0.15 w/o beyond a point 21 mils from the interface.

Figure 10 shows the thicknesses of the several distinct phase regions as a function of time ($t^{1/2}$) for the reaction at 1450 F. Only a few data points were available because of the small number of specimens reacted at this temperature. This plot is similar to previous ones shown for other temperatures, except that here the uranium-rich region is much less continuous than that formed at higher temperatures. For this reason, the region in which the uranium-rich phase existed is designated as a two-phase region in Figure 10. Deeper in the zirconium, and adjacent to this region, is a thin alpha-zirconium region between the relatively unaffected zirconium and the region in which the uranium-rich phase existed.

Reaction at 1300 F

Zirconium- UO_2

Figure 11 shows at 100X and 250X the microstructure in an element heated at 1300 F for 18 days (432 hr) and slowly cooled. The two-phase region adjacent to the gray UO_2 consists of alpha uranium precipitated in an alpha-zirconium matrix. Deeper in the zirconium, the discontinuous bulky spikes of the epsilon intermetallic, uranium-rich phase can be seen. This phase appears to lie in grain boundaries in the alpha-zirconium matrix. This matrix material contains oxygen in solid solution. X-ray diffraction identification of the several phase regions in this microstructure were obtained. The gray irregularly shaped precipitate particles between the two Knoop hardness impressions in the top photomicrograph in Figure 11 are evidence of the hydride of zirconium.

Elements heated at 1300 F for longer or shorter times merely showed thicker or thinner phase regions than those shown in Figure 11. Figure 12 is a plot of the thicknesses of the several phase regions as a function of time ($t^{1/2}$). Thickness measurements were made from photomicrographs. Straight lines resulted, indicating that the thicknesses of the regions vary directly with the square root of time.

Results of oxygen and uranium analyses of chip samples machined from the zirconium at 1-mil increments from the zirconium- UO_2 interface for an element heated at 1300 F for 37 days (888 hr), are listed in Table 6 and shown graphically in Figure 13. The arrowed lines in Table 6 indicate the positions of the analytical samples with respect to the microconstituents. The uranium content rises from a moderately high value to a maximum value at a distance of 4 mils from the interface. The microstructure shows a preponderance of the stained epsilon intermetallic phase in this position. It then drops sharply and appears to level off at a low but measurable constant value of 0.015 w/o at 14 to 15 mils from the interface. The oxygen decreases from a relatively high value near the interface to a minimum value in the region of the uranium-rich intermetallic phase at 4 mils from the interface. The oxygen concentration then rises to a maximum value at about 6 mils from the interface, and then decreases rather sharply from this value. The maximum oxygen concentration occurs in a region of the element containing oxygen in solid solution in the zirconium. At 16 mils from the interface, the greatest depth for which oxygen analyses were obtained, the base oxygen

FIGURE 10. ESTIMATION OF THICKNESS (ON BASIS OF MICRO-STRUCTURE) OF VARIOUS ZONES IN ZIRCONIUM, MEASURED FROM THE ZIRCONIUM-UO₂ INTER-FACE, FOR THE REACTION AT 1450 F

Etchant: 0.5 Volume Per Cent HF
on Polishing Wheel

Etchant: 0.5 Volume Per Cent HF
on Polishing Wheel

FIGURE 11. ZIRCONIUM- UO_2 ELEMENT HEATED AT 1300 F
FOR 18 DAYS (432 HR) AND SLOWLY COOLED

FIGURE 12. ESTIMATION OF DEPTH (ON BASIS OF MICROSTRUCTURE) OF VARIOUS ZONES IN ZIRCONIUM AT SEVERAL DISTANCES FROM THE ZIRCONIUM-UO₂ INTERFACE FOR THE REACTION AT 1300 F

TABLE 6. URANIUM AND OXYGEN CONTENTS AT VARIOUS DISTANCES FROM THE ZIRCONIUM- UO_2 INTERFACE FOR AN ELEMENT HEATED AT 1300 F FOR 37 DAYS (888 HR) AND SLOWLY COOLED

Layer	Distance of Layer From Zirconium- UO_2 Interface, mils	Oxygen, w/o	Uranium, w/o
1	0-1.5	--	38(a)
2	1.5-2.5	2.60	12.2
3	2.5-3.5	2.17	--
4	3.5-4.5	1.49	26.8
5	4.5-5.5	1.75	21.7
6	5.5-6.5	2.04	15.3
7	6.5-7.5	1.57	7.58
8	7.5-8.5	1.75	3.85
9	8.5-9.5	1.29	1.24
10	9.5-10.5	0.80	0.48
11	10.5-11.5	1.17	0.29
12	11.5-12.5	0.47	0.055
13	12.5-13.5	0.33	0.031
14	13.5-14.5	0.27	0.016
15	14.5-15.5	0.090	0.014
16	15.5-16.5	0.20	0.014

(a) UO_2 separated from zirconium by mechanical-chemical method. Analysis reported is on residue from separation.

FIGURE 13. URANIUM AND OXYGEN CONTENTS OF ZIRCONIUM AFTER HEATING IN CONTACT WITH UO_2 AT 1300 F FOR 37 DAYS (888 HR)

content of the zirconium is being approached but apparently has not been attained. These analytical data were the first obtained on thin layers machined from large elements. The scatter apparent in some of the oxygen analyses is believed to have been caused by experimental difficulties in machining and analyses. Minor changes in techniques minimized this scatter in later experiments.

Zircaloy 2- UO_2

Zircaloy 2 appears to react with UO_2 less rapidly than zirconium on the basis of metallographic examinations of only a few samples. The microstructure in an element reacted at 1300 F for 51 days (1224 hr) is shown at 250X in Figure 14. The phases shown somewhat resemble those produced in the unalloyed zirconium. A two-phase region exists adjacent to the UO_2 . This region is somewhat similar to the alpha uranium-alpha zirconium region found in the unalloyed zirconium elements. Next to this region is a band of what also appears to be a two-phase material. An occasional tongue of one of these phases penetrates more deeply into the Zircaloy 2, apparently by way of grain boundaries. A bulky phase, similar in appearance to the phase identified as epsilon in the unalloyed elements, lies still deeper in the Zircaloy 2. Beyond the bulky phase, a rather narrow region, containing oxygen in solid solution, may be noted. The width of this solid-solution region is much narrower than the similar region found in the unalloyed zirconium. The quantity of the bulky epsilon phase appears to be much less than that found in a similar element containing unalloyed zirconium.

Reaction at 1200 F

The reaction zones in zirconium- UO_2 elements heated at 1200 F are somewhat different from those produced at higher temperatures. Figure 15 shows, at 100X and 250X, the structure in the reaction zone of an element heated at 1200 F for 216 days (5184 hr) under a 5000-psi helium pressure in an autoclave. The two-phase structure, adjacent to the gray UO_2 , again consists of alpha uranium in an alpha-zirconium matrix. Here a greater proportion of alpha uranium appears to be present than in those elements heated at higher temperatures. The identity of the few patches of the bulky discrete outlined particles inside of the two-phase structure is not known, although its appearance is similar to that of the uranium-rich phase. No identification of this phase by X-ray diffraction techniques was obtained because of the small proportion present in the structure. The bright metallic regions, on both sides of the large crack, probably consist of a solid solution of oxygen in zirconium. This solid solution is quite hard and brittle. The more bulky precipitated needles, lying deeper into the zirconium than the hard, solid-solution region, are evidence that hydrides formed during cooling.

The initial fit between the zirconium jacket and the UO_2 core in the large element was not good enough to obtain the needed intimate contact even under the 5000-psi pressure in the autoclave. Therefore, no quantitative data on the transfer of oxygen and uranium to zirconium at this temperature were obtained. However, some estimate of the depth of penetration of the various phases into the zirconium has been possible by visual observation of the microstructures of various specimens. These estimates are shown in Figure 16.

Etchant: 0.5 Volume Per Cent HF
on Polishing Wheel

FIGURE 14. ZIRCALOY 2-UO₂ ELEMENT HEATED AT 1300 F FOR 51 DAYS (1224 HR) AND SLOWLY COOLED

100X

N34575

Etchant: 0.5 Volume Per Cent HF
on Polishing Wheel

250X

N34576

Etchant: 0.5 Volume Per Cent HF
on Polishing Wheel

FIGURE 15. ZIRCONIUM- UO_2 ELEMENT HEATED AT 1200 F
FOR 216 DAYS (5184 HR)

Note high proportion of dark-etching alpha
uranium adjacent to the UO_2 and the almost
complete absence of bulky uranium-rich phase.

FIGURE 16. ESTIMATION OF DEPTH (ON BASIS OF MICROSTRUCTURE) OF VARIOUS ZONES IN ZIRCONIUM AT SEVERAL DISTANCES FROM THE ZIRCONIUM-UO₂ INTERFACE FOR THE REACTION AT 1200 F

Reaction at 1100 F

The microstructure of an element heated at 1100 F for 329 days (7896 hr) is shown at 500X in Figure 17. The two-phase region adjacent to the gray UO_2 consists of dark-etching alpha uranium in an alpha-zirconium matrix. The bulky uranium-rich phase is completely absent in this microstructure. The bright metallic phase, adjacent to the two-phase region and deeper in the zirconium, consists of oxygen in solid solution in the metal. The dark needlelike markings probably are evidence of hydride precipitated during cooling of the specimen. Figure 18 shows the depth of penetration of the various zones as a function of time.

A large element that was heated at 1100 F for 394 days (9456 hr) was machined into thin layers in the zirconium, beginning at the zirconium- UO_2 interface. The chips from each layer were analyzed for oxygen and uranium. Results of these analyses are listed in Table 7 and shown graphically in Figure 19. The lines to the photomicrograph in Table 7 indicate the positions of the layers with respect to the microconstituents. Both the uranium and oxygen contents decrease rapidly from their highest values at the interface. The phases present adjacent to the interface are alpha uranium and alpha zirconium. The oxygen is in solid solution in the zirconium. The uranium appears to reach a constant low, but measurable, content of about 0.015 w/o at about 4 mils from the interface. The oxygen decreases less rapidly, and appears to level off at about 10 mils from the interface. The oxygen content at this point is about 0.16 w/o.

Reaction at 950 F

Zirconium- UO_2

The reaction between zirconium and UO_2 was extremely slow at 950 F. The microstructure at 100X and 500X is shown in Figure 20 for an element heated for 503 days (12,072 hr). The gray material between the zirconium and the UO_2 is evidence of resin intrusion when the core became separated from its jacket during mounting for polishing. Very little evidence of reaction can be detected in the zirconium adjacent to the UO_2 . The few small markings at the interface in the zirconium adjacent to the UO_2 may be evidence of hydrides precipitated on cooling. The larger, irregularly shaped light-gray inclusions in the zirconium are precipitated hydrides.

Zircaloy 2- UO_2

On the basis of relatively short time studies, Zircaloy 2 appears to be at least as inert as zirconium with regard to UO_2 at 950 F. The microstructure in the reaction zone of a Zircaloy 2- UO_2 element heated at 950 F for 70 days (1680 hr) is shown at 250X in Figure 21. Again, no evidence of reaction is visible. The apparent dark-gray film lying between the Zircaloy 2 and the UO_2 is merely an intrusion of resin which occurred when the UO_2 core and its jacket were separated in mounting the specimen for metallographic polishing. Oxygen penetration into the Zircaloy 2 was less than 1 mil on the basis of hardness measurements.

500X

N35648

Etchant: 0.5 Volume Per Cent HF
on Polishing Wheel

FIGURE 17. REACTION ZONE OF AN ELEMENT HEATED AT 1100 F
FOR 7896 HR (329 DAYS) UNDER 5000-PSI HELIUM
PRESSURE

FIGURE 18. ESTIMATION OF DEPTH (ON BASIS OF MICROSTRUCTURE) OF VARIOUS ZONES IN ZIRCONIUM AT SEVERAL DISTANCES FROM THE ZIRCONIUM-UO₂ INTERFACE FOR THE REACTION AT 1100 F

TABLE 7. URANIUM AND OXYGEN CONTENTS AT VARIOUS DISTANCES FROM THE ZIRCONIUM- UO_2 INTERFACE FOR THE ELEMENT HEATED AT 1100 F FOR 394 DAYS IN AUTOCLAVE

Layer	Distance of Layer From Zirconium- UO_2 Interface, mils	Oxygen, w/o	Uranium, w/o
1	0-0.5	--	35.0
2	0.5-0.75	3.26	46.9
3	0.75-1.25	2.80	34.9
4	1.25-1.75	2.88	26.7
5	1.75-2.25	3.12	23.8
6	2.25-2.5	2.04	8.68
7	2.5-2.75	1.52	2.80
8	2.75-3.0	0.93	0.372
9	3.0-3.5	0.57	0.040
10	3.5-4.0	0.67	0.020
11	4.0-4.5	0.60	0.016
12	4.5-5.5	0.36	0.067(a)
13	5.5-6.0	0.36	0.020
14	6.0-7.0	0.35	0.012
15	7.0-8.0	0.38	0.018
16	8.0-9.0	0.26	--
17	9.0-10.0	0.16	--
18	10.0-11.0	0.073(a)	--
19	11.0-12.0	0.210	0.013
20	12.0-12.5	0.214	--
21	12.5-13.5	0.178	--

250X

N36455

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

FIGURE 19. COMPOSITION OF ZIRCONIUM SAMPLE AFTER HEATING IN CONTACT WITH UO_2 AT 1100 F FOR 394 DAYS (9456 HR)

100X

N35660

Etchant: 0.5 Volume Per Cent HF
on Polishing Wheel

500X

N35663

Etchant: 0.5 Volume Per Cent HF
on Polishing Wheel

FIGURE 20. REACTION ZONE OF AN ELEMENT HEATED AT 950 F FOR 503 DAYS (12, 072 HR) UNDER A 5000-PSI HELIUM PRESSURE

Etchant: 0.5 Volume Per Cent HF
on Polishing Wheel

FIGURE 21. REACTION ZONE OF ZIRCALOY 2- UO_2 ELEMENT
HEATED AT 950 F FOR 70 DAYS (1680 HR) UNDER
A 5000-PSI HELIUM PRESSURE

Reaction at 750 F

Only very limited data were obtained on the reaction of zirconium with UO_2 at 750 F. Figure 22 shows at 50X and 250X the microstructure in the reaction zone of an element heated at 750 F for 578 days (13, 872 hours) under a 5000-psi helium pressure. Again, no evidence of reaction between the zirconium and the UO_2 was noted. The large discrete light-gray particles in the zirconium are evidence of zirconium hydride which was precipitated on cooling from the reaction temperature. It appears possible that the source of some of the hydrogen in these reaction elements is the UO_2 , which was heated at about 3200 F in hydrogen during sintering. Subsequent brief vacuum degassing of the UO_2 at 1300 F apparently was not adequate to remove all of the hydrogen.

50X

N35883

Etchant: 0.5 Volume Per Cent HF
on Polishing Wheel

250X

N35885

Etchant: 0.5 Volume Per Cent HF
on Polishing Wheel

FIGURE 22. REACTION ZONE OF A ZIRCONIUM- UO_2 ELEMENT HEATED AT 750 F FOR 578 DAYS (13, 872 HR) UNDER A 5000-PSI HELIUM PRESSURE

Corrosion Tests

Cross sections of a few elements that had been polished metallographically were exposed to water at 650 F for 1-hr periods. As might be expected, the uranium in the two-phase region in the zirconium was completely removed by the water corrosion. Figure 23 shows at 250X, after water corrosion, the reaction zone of an element heated at 1300 F for 18 days and slowly cooled. This field is identical to that shown in Figure 11 before corrosion. A comparison of Figure 23 with the lower photomicrograph in Figure 11 clearly shows that all areas that contained uranium were completely removed. The balance of the constituents, alpha zirconium and the intermetallic epsilon phase, were apparently little affected by the exposure to 650 F water. The UO_2 core was loosened by the reaction of the water with the uranium and dropped out of the zirconium jacket. However, it did not appear to have reacted with the water.

Similar results were obtained in corrosion tests of the cross sections of elements reacted at other temperatures.

250X

N21748

FIGURE 23. REACTION ZONE OF ZIRCONIUM- UO_2 ELEMENT HEATED AT 1300 F FOR 18 DAYS AND SLOWLY COOLED

This field is the same as that shown in the lower photomicrograph in Figure 11 after corrosion in 650 F water for 1 hr.

Marker Experiments

In order to understand better the reactions that occurred, some experiments were performed in which attempts were made to mark the positions of the original interfaces between the zirconium and the UO_2 . Tungsten was found to be nonreactive with both zirconium and UO_2 up to at least 2000 F. Strips of tungsten foil, 1 mil thick and 1/32 to 1/16 in. wide, were placed between the plane zirconium and UO_2 surfaces in one end of some of the small reaction elements. After heating the welded elements for suitable periods of time at the several temperatures, the elements were sectioned longitudinally through the end plugs and the tungsten markers located under the microscope in a polished and etched specimen. The position of the markers relative to the phases produced indicated the direction of movement of the boundary as a result of the reactions.

Figures 24, 25, 26, and 27 show the positions of the markers after reaction at 2000, 1600, 1450, and 1200 F, respectively. For the experiments at 2000, 1600, and 1450 F, the markers, after reaction, appear to lie at about the interface between the two-phase (alpha uranium plus alpha zirconium) region and the stained bulky uranium-rich phase. The bending of the marker, shown in Figure 24 for the reaction at 2000 F, must have resulted from the displacement of the UO_2 by the reaction products during reaction. For the 1200 F experiment, the final position of the marker is about at the deepest penetration of uranium into zirconium. The final position of the marker with respect to the two-phase alpha uranium-plus-alpha zirconium region is approximately at the deepest penetration of uranium into zirconium for the four reaction temperatures studied. It is obvious that the two-phase region, containing alpha uranium and alpha zirconium, was produced by the consumption of UO_2 as a result of the reaction.

Uranium as a Diffusion Barrier

The presence of the uranium-rich phase in the reaction zone caused speculation on its effect on the diffusion that must occur to sustain the reaction. In order to study the effect of uranium as a diffusion barrier, experiments were set up in which uranium foils, 1 to 2 mils thick, were placed at the original interface prior to welding and heating of the elements. One element containing the foil was heated at 1450 F and another element was heated at 1600 F. Photomicrographs of longitudinal sections through one end of each element are shown in Figures 28 and 29. These figures also show comparative photomicrographs from the other ends of the elements, which did not contain the uranium foils.

In general, the reaction layers occur in the same sequence and represent the same phases regardless of the initial presence of the uranium foil. The two-phase region adjacent to the UO_2 , consisting of alpha uranium and alpha zirconium, appears slightly thinner in the ends of the elements in which the foils were placed. Conversely, the stained uranium-rich regions are thicker and more continuous in the ends of the elements which initially contained the foils. This stained uranium-rich material appears to penetrate quite deeply into the zirconium by way of grain boundaries in the element heated at 1450 F (see Figure 28). In the 1600 F element, the stained phase appears to be agglomerated and concentrated in a relatively thin but nearly continuous band without the grain-boundary penetration noted in the 1450 F element (see Figure 28).

40X

N35323

Etchant: 0.5 Volume Per Cent HF
on Polishing Wheel

FIGURE 24. REACTION ZONE OF ZIRCONIUM- UO_2 ELEMENT HEATED AT 2000 F FOR 140 HR UNDER A 3000-PSI PRESSURE IN ARGON AND WATER QUENCHED

Note inert tungsten marker at original interface.

100X

N28183

Etchant: 0.5 Volume Per Cent HF
on Polishing Wheel

FIGURE 25. REACTION ZONE OF ZIRCONIUM- UO_2 ELEMENT AFTER HEATING AT 1600 F FOR 119 HR UNDER A 3000-PSI PRESSURE IN ARGON AND WATER QUENCHED

Note inert tungsten marker at original interface.

Etchant: 0.5 Volume Per Cent HF
on Polishing Wheel

FIGURE 26. REACTION ZONE OF ZIRCONIUM- UO_2 ELEMENT AFTER HEATING AT 1450 F FOR 335 HR UNDER A 2450-PSI PRESSURE IN ARGON AND WATER QUENCHED

Note inert tungsten marker at original interface.

Etchant: 0.5 Volume Per Cent HF
on Polishing Wheel

FIGURE 27. REACTION ZONE OF ZIRCONIUM- UO_2 ELEMENT AFTER HEATING AT 1200 F FOR 70 DAYS (1680 HR) UNDER A 5000-PSI HELIUM PRESSURE AND COOLING RAPIDLY

Note position of inert tungsten marker.

100X

N36457

a. Contained No Uranium Foil at
Original Interface

100X

N36456

b. Contained 1-Mil-Thick Uranium Foil
at Initial Zirconium- UO_2 Interface

Etchant: 0.5 Volume Per Cent HF on Polishing Wheel

FIGURE 28. REACTION ZONE OF ZIRCONIUM- UO_2 ELEMENT HEATED AT 1450 F FOR 524 HR
UNDER A 3000-PSI PRESSURE IN ARGON AND WATER QUENCHED

100X

N34562

a. Contained no Uranium Foil at
Original Interface

100X

N34560

b. Contained 1-Mil-Thick Uranium Foil
at Original Interface

Etchant: 0.5 Volume Per Cent HF on Polishing Wheel

FIGURE 29. REACTION ZONE OF ZIRCONIUM- UO_2 ELEMENT HEATED AT 1600 F FOR 236 HR
UNDER A 3000-PSI PRESSURE IN ARGON AND WATER QUENCHED

The presence of dissolved oxygen in zirconium is evidenced by the bright metallic solid-solution region adjacent to but deeper in the zirconium than the stained material. In the element heated at 1600 F, the oxygen appears to have penetrated more deeply in the absence of the foil than in the presence of the foil. On the other hand, in the element heated at 1450 F, a lesser penetration of oxygen appeared to occur in the absence of the foil than in its presence. This may have been caused by the presence of the voids at the final zirconium- UO_2 interface in the end of the element that was initially free of foil. The end of this element which initially contained the uranium foil has relatively fewer and smaller voids.

SUMMARY OF EXPERIMENTAL RESULTS

The microstructures of all elements heated in the temperature range of 1300 to 2000 F were characterized by the formation of a uranium-rich phase which formed mainly in the zirconium. Reaction at 2000 F produced a continuous band that had the alpha-uranium structure. This band was found by analysis to contain 80 w/o uranium and 20 w/o zirconium on a sample isolated from an element heated for 140 hr at 2000 F.

At lower temperatures in this range, the uranium-rich band became less continuous. Reaction at 1300 F produced the material as a very bulky grain-boundary deposit. This material was identified as having the structure of the epsilon inter-metallic phase in the uranium-zirconium system. The uranium-rich phase in elements heated between 1300 and 2000 F was found to contain mixtures of alpha uranium and the epsilon compound, more alpha uranium being found at increasing reaction temperatures. Experiments with uranium foil at the initial zirconium- UO_2 interface indicate that the uranium is not an effective diffusion barrier in this system.

The two-phase region, existing between the UO_2 and the uranium-rich region for elements heated in this temperature range, consisted of alpha uranium in an alpha-zirconium matrix. Marker experiments indicated that this region was produced by consumption of the UO_2 as a result of the reaction. Voids adjacent to the UO_2 were noted in the microstructure of elements heated for long times at 1600 F and lower.

Beyond the bulky uranium-rich phase and deeper in the zirconium, the microstructure showed solid solution of oxygen in zirconium. This region contained cracks in the hard oxygen-embrittled zirconium metal in some cases. At 1300 and 1450 F, grain-boundary penetration of the uranium-rich phase into this region was evident. Some precipitated hydrides were noted in the zirconium.

Elements heated at 1200 F and lower showed an almost complete absence of the uranium-rich phase in the zirconium which had characterized the reactions at higher temperatures. Adjacent to the UO_2 , the two-phase alpha zirconium-alpha uranium region existed. In some elements, voids existed near the UO_2 . Oxygen penetration into the zirconium beyond this two-phase region was evident. Precipitation of hydrides in the zirconium also was noted. At 750 and 950 F the reactions were very slow.

ANALYSIS OF RESULTS

Although plots of the analytical data from the large elements are interesting in themselves, it seemed desirable also to attempt to interpret the results in terms of diffusion constants, total amounts of UO_2 reacting, and volume changes in the reaction. Such an interpretation would make possible a comparison with diffusion measurements for oxygen in zirconium and might aid in better understanding of the process. This would also permit a more reliable extrapolation of the results to other times and temperatures.

Distribution of Oxygen and Uranium

It is apparent that, at temperatures of 1300 F and above, most of the uranium was found in a layer some distance, about 4 mils in most of the large elements, from the UO_2 -zirconium interface. A large amount of oxygen was found beyond this layer. However, it is interesting to take note of the distribution of oxygen and zirconium in the first layer.

If, for each layer, the concentrations of oxygen and uranium are divided by their respective molecular and atomic weights, the number of moles of oxygen and g atoms of uranium per 100 g of sample is obtained. A comparison of these figures shows the relative rates at which the decomposition products of UO_2 move into the zirconium. The results of this calculation are shown in Table 8. The table shows an excess of oxygen over uranium near the interface, indicating a rapid removal of uranium from the reaction zone through the first few mils of intervening zirconium toward the uranium-rich phase. This behavior is in marked contrast to that observed at greater distances from the interface, where oxygen is found to diffuse much further than uranium.

For runs at 1100 F and below, there has probably been some movement of uranium away from the interface. However, the data in Table 8 indicate that this movement (in the case of the 1100 F run) has not been marked enough to show an excess of oxygen in any of the layers.

Concentration of Oxygen in the Zirconium Phase

Figures 6, 7, 9, 13, and 19 show the concentrations of oxygen and uranium plotted against the distance from the interface. The maximum in the uranium curve corresponds to the minimum in the oxygen curve. Since the solubility of oxygen in uranium is known to be very low, the oxygen found by analysis is presumed to be present in the zirconium phase. By making some assumptions with regard to the concentrations in the two phases, it is possible to plot the concentration of oxygen in zirconium as a continuously decreasing function.

If, for any machined layer, $C_{\text{U}, \text{U}}$ is the concentration of uranium in the uranium-rich phase, $C_{\text{U}, \text{Zr}}$ is the concentration of uranium in the zirconium-rich phase, $C_{\text{U}, \text{T}}$ is the experimentally determined total concentration of uranium in the layer, and f_{U} and f_{Zr} are, respectively, the fractions of uranium-rich and zirconium-rich phases in the layer, then

TABLE 8. OXYGEN AND URANIUM CONCENTRATIONS NEAR THE EFFECTIVE INTERFACE

Temperature, F	Layer	Distance From Interface, mils	Concentration of Oxygen, w/o	Concentration of Uranium, w/o	Concentration of Oxygen, moles per 100 g	Concentration of Uranium, g atoms per 100 g
1100	1	0-0.5	--	35.0	--	0.147
	2	0.5-0.75	3.26	46.9	0.102	0.197
	3	0.75-1.25	2.80	34.9	0.088	0.147
1300	1	0-1.5	--	--	--	--
	2	1.5-2.5	2.6	12.2	0.081	0.051
	3	2.5-3.5	2.2	--	0.069	--
	4	3.5-4.5	1.5	26.8	0.047	0.113
1450	1	0-2	3.36	16.3	0.105	0.068
	2	2-3	--	25.9	--	0.109
	3	3-4	0.39	32.4	0.012	0.136
1525	1	0-0.5	3.99	19.7	0.125	0.083
	2	0.5-1	4.29	16.3	0.134	0.068
	3	1-1.5	4.06	19.7	0.127	0.083
	4	1.5-2.0	3.68	17.0	0.115	0.071
	5	2.0-2.5	2.64	19.0	0.082	0.080
	6	2.5-3.0	1.91	26.2	0.060	0.110
1600	1	0-1.5	3.86	24.1	0.121	0.101
	2	1.5-2.5	3.66	15.5	0.114	0.065
	3	2.5-3.5	2.45	37.5	0.076	0.158

$$C_{U, U} f_U + C_{U, Zr} f_{Zr} = C_{U, T}. \quad (3)$$

Similarly, for the corresponding oxygen concentrations,

$$C_{O, U} f_U + C_{O, Zr} f_{Zr} = C_{O, T}. \quad (4)$$

$C_{O, T}$ is the experimentally determined concentration of oxygen in the layer. Assuming that only two phases are present,

$$f_U + f_{Zr} = 1. \quad (5)$$

The concentration of uranium in the zirconium phase, $C_{U, Zr}$, can be estimated from the work of Summers-Smith⁽³⁾. This concentration term is very small and has little effect on the calculation. The concentration of oxygen in uranium was assumed to be negligibly small. This gave three relationships among four unknowns. This difficulty was resolved as follows: A value was arbitrarily assigned to $C_{U, U}$. For each layer, the equations were then solved for $C_{O, Zr}$. This procedure was followed for several choices of values for $C_{U, U}$. The resulting curves of $C_{O, Zr}$ as a function of penetration into the zirconium were examined and that one was chosen which showed a smoothly descending function. Figure 33 illustrates the procedure as applied to the data obtained from the element heated at 1525 F. Similar treatment of the data from runs at other temperatures results in the following "best choices" for $C_{U, U}$. An estimation is included of the range within which the choice might be made.

<u>Temperature, F</u>	<u>$C_{U, U}$, w/o</u>	<u>Range, w/o</u>
1100	90	70-100
1300	67 ⁽⁷⁾	40-70
1450	39	37-42
1525	50	40-70
1600	80	75-90

The corresponding curves are shown in Figures 30 through 34. It is evident that, for the layers of high uranium concentration, small analytical errors are greatly exaggerated by this treatment, so the calculated points are not expected to lie close to the curves.

Estimation of Diffusion Coefficients

If the rate of the process is controlled by the rate of diffusion of oxygen in zirconium, then the data may be treated in terms of the laws of diffusion.

The diffusion constant, D , is given by Fick's second law:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}, \quad (6)$$

FIGURE 30. COMPUTED DIFFUSION GRADIENT OF OXYGEN IN ZIRCONIUM AFTER 9456 HR AT 1100 F

FIGURE 31. COMPUTED DIFFUSION GRADIENT OF OXYGEN IN ZIRCONIUM AFTER 888 HR AT 1300 F

FIGURE 32. COMPUTED DIFFUSION GRADIENT OF OXYGEN IN ZIRCONIUM AFTER 495 HR AT 1450 F

FIGURE 33. COMPUTED DIFFUSION GRADIENT OF OXYGEN IN ZIRCONIUM AFTER 227 HR AT 1525 F

FIGURE 34. COMPUTED DIFFUSION GRADIENT OF OXYGEN IN ZIRCONIUM AFTER 95 HR AT 1600 F

where C is concentration, t is time, and x is distance. If it is assumed that the concentration of oxygen at the interface is determined by the decomposition pressure of UO_2 and is, therefore, constant, the solution for Equation (6) is as follows⁽¹⁰⁾:

$$C(x, t) = C_0 \left[1 - \frac{2}{\pi} \int_0^{\frac{x}{2\sqrt{Dt}}} e^{-y^2} dy \right], \quad (7)$$

where C_0 is the constant concentration of oxygen at the UO_2 -zirconium interface and y is an arbitrary variable. Values of the integral may be found in tables of the "error function".

A series of curves of C/C_0 versus x was plotted from tables for various values of $1/2 (Dt)^{1/2}$. For each run, the data were expressed in terms of C/C_0 for various values of C_0 . Plots of the data so expressed were then compared with the "theoretical" C/C_0 curves and the values of $1/2 (Dt)^{1/2}$ and C_0 giving the best fit were selected. In these comparisons, the greater weight was assigned to the points lying, in general, between 7 and 20 mils from the interface.

The position of the interface changed during the course of the reaction and, furthermore, the zero position of the cutting tool in machining the samples was of necessity selected in a somewhat arbitrary manner. It was necessary, therefore, in matching the curves to the data, to select a position for the "effective interface". In some cases, it also seemed to be necessary, in order to obtain a reasonable fit, to assume a "base" concentration of oxygen to be subtracted from each oxygen-concentration datum.

In adjusting four constants in this way to the data for each run, it is apparent that the confidence to be placed in each is somewhat limited. Indeed, the purpose here is not so much to determine D and C_0 as to show that, with reasonable assumptions, the data may be made to fit diffusion curves fairly well. In particular, little reliance is placed in the values of C_0 since these depend primarily on an extrapolation of points near the interface, which are, for this purpose, the least reliable. Less uncertainty is involved in determining the apparent diffusion constant. Because of the complexity of the process, however, the calculated diffusion constants are not claimed to be reliable values for the true diffusion constant of oxygen in zirconium.

The calculated values of the w/o oxygen subtracted, x_0 , C_0 , and D , are shown in Table 9. The curves of Figures 30 through 34 are based on these values of C_0 and D . The parameters of Table 9 were selected to fit the data. The physical significance of these numbers is doubtful. The "w/o oxygen subtracted" may be related to the concentration of oxygen originally present in the zirconium. The "effective interface" has been designated as x_0 . The choice of the position of x_0 is arbitrary and is affected by several factors. The C_0 is considered to be the equilibrium concentration of oxygen in the zirconium-rich phase in contact with UO_2 . However, if the contact was not good, the experimentally chosen C_0 may no longer have this significance. Thus, in the case of the run at 1450 F, there were indications that voids between the UO_2 and the zirconium interrupted the reaction. If this interpretation is correct, then the oxygen diffusing into the zirconium would not have been replaced by oxygen from the UO_2 , and the apparent C_0 would be lower than the equilibrium value. This is probably the explanation for the low value for C_0 found in this case. Also, in no case would C_0 be expected to have a value higher than the limit of solubility of oxygen in zirconium (6.75 w/o).

TABLE 9. CONSTANTS FOR THE DIFFUSION OF OXYGEN IN ZIRCONIUM

Temperature, F	Time, hr	Oxygen Subtracted, w/o	x_o , mils	C_o , w/o	D , cm ² per sec
1100	9456	0.15	0.5	7.0	3.0×10^{-13}
1300	888	0.00	0.5	6.0	4.2×10^{-11}
1450	495	0.00	0.5	3.8	2.5×10^{-10}
1525	227	0.08	0.75	6.5	3.1×10^{-10}
1600	95	0.12	0.5	5.5	5.8×10^{-10}

The apparent diffusion constants are shown in Figure 35. The straight line, corresponding to the equation

$$D = 5.2 \exp -50,800/RT, \quad (8)$$

was taken from Pemsler's work⁽¹¹⁾. It fits his data for the diffusion of oxygen in zirconium at lower temperatures as well as those of Mallett Albrecht, and Wilson⁽¹²⁾ for the diffusion of oxygen in Zircaloy 2 at 1000 to 1500 C.

Quantity of UO₂ Reacted

From the analyses of the layers machined from the zirconium and from the densities of the layers, the total amount of uranium and oxygen per unit cross section may be determined. For each layer, the densities were obtained on the assumption of additive volumes for uranium and zirconium and from the work of deBoer and Fast⁽¹³⁾ on the zirconium-oxygen system. From the analyses and the densities, the weights of uranium and oxygen in each layer were found. The weights were converted to moles of oxygen and g atoms of uranium by dividing by 32 and 238, respectively. The total amounts of each per cm² of cross section are shown in Table 10. The total weights of UO₂, based on the uranium analyses, also are shown. The agreement between moles of oxygen and g atoms of uranium is probably no worse than is to be expected because of the difficulties involved in the machining and analytical procedures.

The manner in which the total amount of oxygen may be expected to vary with time and temperature may be determined by a return to a consideration of the diffusion equations. The amount of solute transported across the interface is given by⁽¹⁰⁾:

$$W = - \int_0^t D \left(\frac{\partial C}{\partial x} \right)_{x=0} dt. \quad (9)$$

FIGURE 35. APPARENT DIFFUSION CONSTANTS FOR OXYGEN IN ZIRCONIUM

TABLE 10. AMOUNT OF UO_2 REACTING

Temperature, F	Time, hr	Total Oxygen, moles per cm^2	Total Uranium, g atoms per cm^2	Total UO_2 , g per cm^2	$Wt^{-1/2}$, $\text{g}/(\text{cm}^2)(\text{hr}^{1/2})$
1100	9456	0.58×10^{-4}	0.54×10^{-4}	1.45×10^{-2}	0.15×10^{-3}
1300	888	1.12×10^{-4}	0.90×10^{-4}	2.44×10^{-2}	0.82×10^{-3}
1450	495	1.21×10^{-4}	1.52×10^{-4}	4.11×10^{-2}	1.85×10^{-3}
1525	227	1.89×10^{-4}	1.75×10^{-4}	4.72×10^{-2}	3.13×10^{-3}
1600	95	1.52×10^{-4}	1.51×10^{-4}	4.08×10^{-2}	4.18×10^{-3}

Substituting Equation (7) and carrying out the mathematics on the assumption that D is independent of t and x at any one temperature, it is found that

$$W = 2(\pi)^{-1/2} C_0 (Dt)^{1/2}. \quad (10)$$

D may be expressed in the form of Equation (8):

$$D = D_0 \exp -E/RT, \quad (11)$$

where D_0 and E are constants. If it is assumed that C_0 does not vary greatly with temperature, substituting Equation (11) into Equation (10) gives

$$\ln (Wt^{-1/2}) = A - B/T, \quad (12)$$

where $A = \ln (2\pi^{-1/2} C_0 D_0^{1/2})$ and, for natural logarithms, $B = E/2R$. Using for W the number of g per cm^2 of UO_2 reacting, and expressing t in hr, the results found in the last column of Table 10 are plotted in Figure 36. The straight line corresponds to the equation

$$\log_{10} W_{\text{UO}_2} t^{-1/2} = 2.118 - 5110 T^{-1}, \quad (13)$$

where W now denotes the weight in g of UO_2 reacting per cm^2 , t is in hr, T in deg K, and common logarithms are used.

Volume Change

Several experiments seem to show the formation of voids at the UO_2 -zirconium interface. In some cases there are indications that the reaction may have been interrupted on this account. An attempt was made, therefore, to calculate from densities the change in volume to be expected. The weights of uranium, oxygen, and zirconium for a cross section of 1 cm^2 were calculated for each layer, as described

FIGURE 36. TOTAL AMOUNT OF UO_2 REACTING

in the previous section. From the totals for all layers, the weights of UO_2 and zirconium entering into reaction were found. The volumes of these materials before reaction were then compared with the final volume of the machined portion of the element. For these calculations the bulk density of the UO_2 was assumed to be 75 per cent of its theoretical density. The results are shown in Table 11. Figure 37 shows the final result plotted in a manner similar to that used in Figure 36. The line fits the equation

$$\log_{10} (St^{-1/2}) = 0.984 - 5060 T^{-1}, \quad (14)$$

where S is the shrinkage in cm, t is in hr, and T in deg K.

TABLE 11. VOLUME CHANGE ON REACTION

Temperature, F	Total Weight, g per cm^2		Volume of Reactants, cm^3 per cm^2			Final Volume of Products, cm^3 per cm^2	Shrinkage	
	UO_2	Zr	UO_2	Zr	Total		Cm	Mils
1100	1.45×10^{-2}	21.13×10^{-2}	0.177×10^{-2}	3.231×10^{-2}	3.408×10^{-2}	3.304×10^{-2}	0.104×10^{-2}	0.41
1300	2.44×10^{-2}	24.77×10^{-2}	0.298×10^{-2}	3.787×10^{-2}	4.085×10^{-2}	3.937×10^{-2}	0.148×10^{-2}	0.58
1450	4.11×10^{-2}	44.94×10^{-2}	0.503×10^{-2}	6.872×10^{-2}	7.375×10^{-2}	7.112×10^{-2}	0.263×10^{-2}	1.03
1525	4.72×10^{-2}	43.13×10^{-2}	0.577×10^{-2}	6.595×10^{-2}	7.172×10^{-2}	6.858×10^{-2}	0.314×10^{-2}	1.24
1600	4.08×10^{-2}	38.36×10^{-2}	0.499×10^{-2}	5.865×10^{-2}	6.364×10^{-2}	6.096×10^{-2}	0.268×10^{-2}	1.06

If the lattice expansion of zirconium containing oxygen is correct as determined by deBoer and Fast⁽¹¹⁾, the accuracy of the density reported by them is not critical for this calculation. If it is desired to determine such a relationship for UO_2 of another density, the results of Table 11 may be recalculated from the total weight of UO_2 given in the table. Thus, using the theoretical density for UO_2 , 10.9 g per cm^2 , the equation

$$\log_{10} (St^{-1/2}) = 0.868 - 5350 T^{-1} \quad (15)$$

is obtained.

Penetration of Oxygen and Uranium Into the Zirconium Phase

From microscopic examination of the small elements, the thicknesses of the several layers formed during reaction can be estimated. These results have been reported in Figures 2, 5, 10, 12, 16, and 18. These data may be correlated in a manner similar to that used in the two preceding sections. Values of the thickness of each layer divided by the square root of time have been averaged for each temperature and, in Figure 38, the logarithms are plotted against the reciprocals of the temperatures. All the points fell within the indicated limits.

FIGURE 37. CALCULATED SHRINKAGE, BASED ON 75 PER CENT OF MAXIMUM DENSITY FOR UO_2

FIGURE 38. VARIATION OF ZONE THICKNESS WITH TEMPERATURE

The lowest curve represents the thickness of the two-phase alpha uranium-alpha zirconium layer. Since the boundary between this region and the adjacent uranium-rich phase was, in most cases, well defined, there is relatively little scatter about this line in Figure 38. The results provide good evidence for a break in the curve at about 1300 F. Above this temperature the curve fits the equation

$$\log_{10} (dt^{-1/2}) = 0.20 - 3680 T^{-1}, \quad (16)$$

where d is in cm, t in hr, and T in deg K. From 1100 to 1300 F, the equation is

$$\log_{10} (dt^{-1/2}) = 4.81 - 8200 T^{-1}. \quad (17)$$

The presence of spikes of the uranium-rich phase extending into the zirconium, especially at the intermediate temperatures, made the estimation of the thickness of this region difficult. This difficulty is reflected in the scatter of points around the second line of Figure 38. The points also reflect the more compact nature of this region at higher temperatures. Since the uranium-rich phase did not occur significantly at temperatures below 1300 F, the line extends only from 1300 F upward to 2000 F.

The uppermost series of points in Figure 38 represents the extent of penetration of oxygen into the zirconium. The points representing visual observation are too uncertain to establish the line. The line was drawn through points obtained from the oxygen analyses of the large elements. These points represent the distance from the interface to the layer at which the oxygen concentration was found to be 0.25 w/o. In this case, the line below 1300 F is not well established. From 1300 to 2000 F, the line corresponding to 0.25 w/o oxygen fits the equation

$$\log_{10} (dt^{-1/2}) = 1.22 - 4040 T^{-1}. \quad (18)$$

Similar equations could be derived for other concentration levels.

DISCUSSION OF RESULTS

As presented in the introduction to this report, the thermodynamics of the zirconium- UO_2 reaction predicted that the reaction to form ZrO_2 was not possible. However, reaction, with the products of reaction in solid solution, was presented as thermodynamically possible. This has been found experimentally to be the case.

On the basis of theoretical considerations and experimental results, a reaction mechanism can be proposed. It is evident that the oxygen from the UO_2 diffuses away rapidly into the zirconium while the resulting reduced uranium acts as a solvent for zirconium. In the presence of oxygen, it is likely that uranium is only very slightly soluble in zirconium. Since oxygen has an extremely limited solubility in uranium, the uranium-rich phase contains dissolved zirconium but very little dissolved oxygen. Thus, two solid solutions are formed, one a solution of oxygen in zirconium, and the other a solution of zirconium in uranium.

Zirconium diffuses through the uranium-rich layer in the direction of the reaction zone. This was demonstrated by the experiments at 1450 and 1600 F in which uranium foil was placed between the UO_2 and zirconium in preparing the specimen. Microscopic examination showed that zirconium appeared between the UO_2 and the uranium-rich phase to about the same extent as without the initial uranium foil. The driving force for this diffusion of zirconium is presumed to be related to the lower activity of zirconium which is caused by the higher concentration of oxygen at points closer to the source of the oxygen.

As the reaction proceeds, the uranium formed at the reaction interface is transported through the intervening zirconium phase to a uranium-rich band several mils away. This band is continuous at the higher temperatures. Analyses for oxygen and uranium, summarized by Table 8, show that the uranium formed by the reaction moves through the first few mils faster than the oxygen. This uranium transport takes place by diffusion along grain boundaries of the zirconium matrix.

It should be reiterated that, for the reaction to proceed, it is necessary that good contact be maintained between the zirconium and UO_2 . Although all tests were performed under pressure, the zirconium is deformed and forced into contact with the UO_2 more readily at high temperatures and at low oxygen concentrations. In several experiments, the reaction was interrupted after a time, presumably because the dissolved oxygen made the zirconium phase less plastic, thus allowing the formation of voids.

Mechanism at High Temperatures

For reactions at high temperature (1600 and 2000 F), the microstructures of the reaction zone (see Figure 1) show a two-phase region next to the UO_2 and next to this a second two-phase region (stained band). Deeper in the metal is a one-phase solid solution of oxygen in zirconium. The (outer) first two-phase region (Region 1) appears to consist of small grains containing oxygen dissolved in zirconium, designated as $\text{O}(\text{Zr})$, enveloped in a thin grain-boundary network of zirconium dissolved in uranium and designated as $\text{Zr}(\text{U})$. The second two-phase region (Region 2) consists of small grains of $\text{O}(\text{Zr})$ in a $\text{Zr}(\text{U})$ matrix. Actually, however, the $\text{Zr}(\text{U})$ could have been produced by swelling of the originally thin grain-boundary phase of Region 1, by uptake of zirconium as the activity of the zirconium in $\text{Zr}(\text{U})$ tends to approach that in the neighboring $\text{O}(\text{Zr})$. In the meantime in Region 1, the activity of zirconium in $\text{O}(\text{Zr})$ is minimized by the high concentration of oxygen resulting from the reaction. This condition serves also to minimize the zirconium activity (content) of the grain-boundary $\text{Zr}(\text{U})$, and as a result this phase remains thin and relatively uniform in this region.

With this picture of conditions established early in the reaction, it is easy to see how the regions proceed to grow. Since grain-boundary diffusion is faster than volume diffusion, the uranium moves rapidly through the grain boundaries of Region 1 and feeds the $\text{Zr}(\text{U})$ phase of Region 2 which has expanded beyond grain-boundary proportions to become the matrix phase. Further diffusion of uranium then must take place by the slower volume diffusion.

Mechanism at Lower Temperatures

In the temperature range of 1300 and 1450 F (see Figures 8 and 11), the phase distribution in Region 1 is essentially the same as that described for higher temperatures. However, the movement of oxygen from this region is so slow that counterdiffusion of zirconium in O(Zr) cannot occur at a rate sufficient to increase the activity of zirconium in O(Zr). Consequently, expansion of the Zr(U) phase in the grain boundaries of the small grains cannot occur. Diffusion of uranium along the grain boundaries of the original metal does take place, as illustrated by Figure 39, and spikes of Zr(U) form in the position of Region 2 of higher temperatures. These intrusions of uranium expand by uptake of zirconium and by feeding of uranium from the grain boundaries of Region 1. In time, the spikes expand into quite massive deposits of Zr(U), as illustrated by Figure 40 for the uranium-rich region, which, however, do not form an integral band such as that formed at higher temperatures.

Mechanism Where No Uranium-Rich Phase is Formed

At temperatures of 1200 F and below, no uranium-rich phase is formed as at the higher temperatures. Obviously, this is a result of two contributing factors. First, the diffusion rates are now so low (comparatively) that there is insufficient uranium transferred to form this phase; and, secondly, the thermodynamic potential which resulted in the formation of this phase at higher temperatures has decreased to a low value. This latter phenomenon is confirmed by the study of Saller, et al.⁽¹⁾, of the phase relationship in this system. The best evidence for the change in mechanism at about 1300 F is contained in Figure 38. The abrupt change in slope of the correlating line at this temperature lends additional support to this explanation.

Rates of Reaction

It is possible to express the rates of reaction for this solid-solid reaction in several different ways. Each may have utility for different applications.

Amount of UO₂ Reacting

The amount of UO₂ reacting as a function of time and temperature is expressed by Equation (13) and shown by Table 10 and Figure 36. As long as the conditions of the experiments are reproduced, namely those of constant temperature and of external pressure sufficiently high to give plastic deformation, these results can be used to estimate the amount of reaction for practical situations. Unfortunately, the effects of temperature gradients are not known.

Depth of Penetration

Figure 38 and Equations (16), (17), and (18) express the rates of penetration into the zirconium of the various phases formed by the reaction as a function of time and

500X

N37608

FIGURE 39. TWO-PHASE ALPHA URANIUM-PLUS-ALPHA ZIRCONIUM
REGION FROM 1450 F EXPERIMENT

100X

N27404

FIGURE 40. URANIUM-RICH PHASE OF THE 37-DAY 1300 F SPECIMEN

temperature. The applicability of these results, of course, is subject to the same limitations of conditions as applied to the previous correlation of the amount of UO_2 reacting. The depth of penetration is perhaps the best method of expressing the data insofar as obtaining a measure of time to failure of a zirconium-clad UO_2 nuclear fuel element is concerned. Failure might occur by brittle fracture of zirconium by oxygen penetration, but it most certainly would occur by rapid water corrosion of any exposed uranium-rich phase.

Effect of Formation of Voids

Table 11 shows that the products of the reaction occupy a smaller volume than the reactants. If the pressure forcing the zirconium against the UO_2 is insufficient to overcome this shrinkage, voids may develop between the UO_2 and zirconium. This effect would be small for UO_2 of the highest possible density. In the experiments conducted in this research, such shrinkage and resultant formation of voids may have resulted in an interruption of the reaction before the element was removed from the furnace. There are a number of indications that this occurred in one run at 1450 F. The total amount of UO_2 reacting seems low in comparison with the other runs. The estimated concentration of oxygen at the interface also seems to be too low. The results of this run were, therefore, given relatively little weight in the calculations. In any practical situation, it should be estimated whether or not the external pressure is sufficient to prevent the formation of voids and thus permit estimation on the basis of these data.

Diffusion of Oxygen in Zirconium

An attempt is described at calculating the concentration of oxygen in the zirconium phase for those layers that contained both zirconium- and uranium-rich phases. Diffusion constants were determined to fit the resulting curves. The calculations were based on the assumption that the uranium-rich layer does not act as a diffusion barrier for oxygen. The assumption seems to fit the data, but evidence to support the assumption is not conclusive. However, it does provide further support as to the validity of these results.

CONCLUSIONS

The analysis of the experiments shows, as far as can be determined, that the results are consistent and valid. It has been possible to arrive at a logical explanation of the mechanism of the solid-solid reaction which takes place and express in mathematical form the results obtained. The results are best expressed by the equations [Equations (16), (17), and (18)] which give the depth of penetration of various phases formed by the reaction as a function of time and temperature.

The results are indicative of some of the difficulties to be expected from zirconium-clad UO_2 fuel elements. The high solubility of oxygen in zirconium results in a reaction which is rapid at high temperature. The reaction leads to the formation of a separate phase of uranium-rich alloy, to an over-all decrease in volume, and to rapid diffusion of oxygen into the zirconium. Presumably zirconium-clad UO_2 fuel

elements would eventually fail because of the resulting excessive oxygen in the zirconium. The time at which failure is to be expected may be estimated for 0.25 w/o oxygen by application of Equation (18). For other oxygen concentrations, similar equations may easily be derived. The experimental techniques are believed to be sufficiently refined to be applicable to the study of similar systems.

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APPENDIX

ANALYTICAL PROCEDURES

APPENDIX

ANALYTICAL PROCEDURES

Analysis for Oxygen in Zirconium

Thin layers in the zirconium at known distances from the zirconium- UO_2 interface were machined into chips and analyzed for oxygen by the vacuum-fusion technique. The chip sample was weighed on an analytical balance into a cup made of cp tin foil. The cup containing the sample was placed in the vacuum-fusion apparatus, and the apparatus was evacuated overnight. The analysis was carried out by dropping the sample in the foil onto a bed of graphite chips contained in a graphite crucible at 1200 C. The chips and crucible previously had been degassed at 2300 C until a sufficiently low blank rate was attained. The temperature of the crucible and its contents was raised to 2100 C after the sample had been dropped and the gas evolved from the sample was collected until the blank rate was restored. The collected gases were analyzed for carbon monoxide and hydrogen by the low-pressure fractional-freezing method. The oxygen content was calculated from the amount of CO formed. All of the analyses reported in this report were on a single determination on the total portion of the sample for each layer.

Analysis for Uranium in Zirconium

Chip samples machined from the zirconium at known distances from the zirconium- UO_2 interface were analyzed for uranium by the fluorescence method. The total portion of the sample was dissolved in a reagent composed of dilute nitric acid with hydrofluoric acid added. After the sample was completely dissolved, the resulting solution was diluted to a known volume with 10 per cent nitric acid. This volume and the volume of subsequent dilutions depended on the composition of the alloy.

The determination of uranium was completed by a conventional fluorescence method. Details of this method are described by Center^{(9)*}.

MWM:JWD:AFG:AWL/ims

*Listed in "References" at end of the text of the report.