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THE KINETICS OF THE ZIRCONIUM-URANIUM DIOXIDE REACTION

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by

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TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	7
INTRODUCTION	8
MATERIALS	9
Zirconium	9
Uranium Oxide	9
PROCEDURE	10
RESULTS	10
Reaction of Solid Zirconium Cylinders With UO_2 Powder	10
Compacted-Powder Mixtures	11
Sandwich-Type Elements	18
DISCUSSION OF RESULTS	32
Packed Zirconium Cylinders Versus Powder Compacts	34
Sandwich-Type Elements	34
CONCLUSIONS	40
ACKNOWLEDGMENT	43
REFERENCES	44
APPENDIX A	
THEORETICAL CONSIDERATIONS	47
Thermodynamics	47
Kinetics	53
APPENDIX B	
MATERIALS	59
Production of Zirconium Powder	59
Uranium Oxide	59
Attempts to Produce Substoichiometric UO_2	64
APPENDIX C	
PROCEDURE	65
Reaction of Solid Zirconium Cylinders With UO_2 Powder	65
Compacted-Powder Mixtures	65
Sandwich-Type Elements	68

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THE KINETICS OF THE ZIRCONIUM-URANIUM DIOXIDE REACTION

Manley W. Mallett, Arnold F. Gerds, Alexis W. Lemmon,
and Dan L. Chase

The kinetics of the zirconium- UO_2 reaction was studied using crystal-bar zirconium and fused UO_2 or UO_2 high-fired in hydrogen. The reaction was studied with (1) solid zirconium cylinders and UO_2 powder, (2) compacted mixtures of zirconium and UO_2 powders, and (3) sandwich-type elements. Experiments performed with sandwich-type elements yielded the most useful data both from a practical and a fundamental point of view. Exploratory experiments designed to give a wider range of experimental materials were unsuccessful in producing substoichiometric UO_2 .

Results obtained from sandwich-type experiments showed that slow reactions at 950 and 1100°F formed reaction zones less than 0.0002 in. thick in 65 days. A measurable reaction took place at 1300°F, while at 2000°F, the reaction was very rapid. The UO_2 seems to be reduced to its elements, uranium and oxygen, which diffuse simultaneously, but not with equal speed, into the zirconium.

Reactants heated at 1300°F and slowly cooled to room temperature, were found to have formed alpha zirconium and alpha uranium adjacent to the UO_2 . Deeper in the original zirconium region the epsilon uranium-zirconium intermetallic phase was found dispersed in a zirconium-oxygen solid solution.

Elements slowly cooled from 2000°F contained alpha zirconium and alpha uranium at the UO_2 -metal interface. A continuous stained band having the alpha uranium lattice structure and containing some zirconium was observed beneath the two-phase region. Oxygen had diffused beyond the uranium-containing region, forming the hard zirconium-oxygen solid solution.

On the basis of limited data obtained, it has been estimated that penetration of oxygen through the 0.030-in.-thick zirconium jacket walls probably would cause their destructive embrittlement in about 300 days at 1300°F or 2-1/2 days at 2000°F.

The reaction between Zircaloy 2 and UO_2 at 1300°F appears to be somewhat less rapid than that between unalloyed zirconium and UO_2 . The phases formed by this reaction have not been identified.

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INTRODUCTION

Fuel elements composed of uranium oxide jacketed with a zirconium alloy are being considered for use in the PWR (pressurized water reactor). The jackets will be in contact with the heat-transfer fluid, water, at 630 F and 2000-psi pressure. It is anticipated that local areas of the interface between the core and the jacket of the fuel rods may become as hot as 1300 F during the most extreme operating conditions of the reactor. The kinetics of the reaction between zirconium and UO_2 were studied as assistance to WAPD in obtaining fundamental information to estimate the useful life of the fuel elements.

The reaction between zirconium and UO_2 has been studied previously at a number of other installations. In an attempt to predict if a reaction between zirconium and uranium dioxide would occur, the free-energy change for the reaction $\text{UO}_2 + \text{Zr} \rightleftharpoons \text{ZrO}_2 + \text{U}$ was studied by Stavrolakis and Barr(1)* from values given in the literature. Free-energy values of 0.892 kcal per mole for the reaction at 588 K (600 F) and 2.985 kcal per mole for the reaction at 2078 K (3280 F) were calculated. They concluded that zirconium should not reduce UO_2 , but qualified this conclusion by stating that the free-energy values were not sufficiently accurate to make definite predictions about the reaction.

McCreight(2) of KAPL studied the extent to which the reaction $\text{Zr} + \text{UO}_2 \rightarrow \text{ZrO}_x + \text{UO}_y$ should proceed. On the basis of thermodynamic considerations and some experimental work, he predicted that very little reaction would occur at temperatures as high as 2912 F. His experiments were performed on pressed compacts of zirconium and UO_2 particles. Results were observed by metallographic, X-ray, and wet chemical analytical techniques. He separated the UO_2 from the zirconium by dissolving it with hot concentrated nitric acid, followed by water and ether rinses. The residue from this treatment was identified by X-ray diffraction as zirconium without any sign of contamination. The conclusion may be somewhat in error since in this present work it was found that hot concentrated nitric acid would remove the reaction products as well as the UO_2 . This is shown in a later section of this report.

Later work at KAPL reported by Hirsch, Peloke, and Ross(3,4) also was concerned with reaction between zirconium and UO_2 compacted-powder mixtures. They observed that the UO_2 phase disappeared when the compacts were sintered in vacuum. For example, a compacted mixture of zirconium hydride and UO_2 heated at 2120 F for 3 hr in vacuum resulted in the disappearance of the UO_2 phase as judged by X-ray evidence. Compacts heated at 1830 F still contained X-ray evidence for UO_2 . Later reports gave no

*References at end.

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additional information on this system and it is assumed that the work at KAPL was discontinued.

The literature showed no information on the zirconium-uranium-oxygen ternary equilibrium diagram. However, information was available on the binary systems of interest. A tentative phase diagram for the uranium-zirconium system was reported by Saller and Rough^(5, 6). The zirconium-oxygen phase relationships were reported by Domagala and McPherson⁽⁷⁾, while much information on the uranium-oxygen phase relationships was presented by Katz and Rabinowitch⁽⁸⁾. A detailed discussion of these data, together with calculations on the thermodynamics of the zirconium- UO_2 reaction, is presented in Appendix A. Theoretical treatment of the kinetics of this reaction also is presented.

MATERIALS

Zirconium

The zirconium used for the study was low-hafnium crystal-bar zirconium. For the studies in which massive metal cylinders were used, the crystal-bar metal was arc melted into an ingot and rolled to the desired rod diameter. This material also was machined into small sandwich-type jacket elements. Large sandwich-type elements were machined directly from an induction-melted crystal-bar ingot. These elements were vacuum degassed prior to reacting with UO_2 .

Crystal-bar zirconium was converted to powder by hydriding, crushing, and sizing the brittle hydride in an inert-atmosphere dry box. Details on this procedure, together with analyses of the products, are described in Appendix B.

Uranium Oxide

Five principal types of uranium oxides were used during the course of these experiments. These included black, calcined UO_2 , brown UO_2 as received from Mallinckrodt, hydrogen-reduced (900 C) Mallinckrodt UO_2 , Mallinckrodt UO_2 pressed and fired at 3750 F in hydrogen, and fused UO_2 . These several materials are described in more detail in Appendix B. Typical analyses also are given.

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10

An unsuccessful attempt was made to produce uranium oxide of a composition lower in oxygen than UO_2 . Details of these experimental techniques are described in Appendix B.

PROCEDURE

Initially, the reaction was studied with cylindrical zirconium specimens packed in UO_2 powder and heated in either a vacuum or an atmosphere of argon. The extent of the reaction was estimated by microscopic examination and hardness traverses of the cross section. An oxygen analysis of a slice of the cross section of the zirconium was used to determine the oxygen transfer from the UO_2 during reaction.

Later, compacted mixtures of zirconium and UO_2 powders were heated in vacuum. After separation of the UO_2 from the zirconium by mechanical-chemical means, the zirconium-powder residues were analyzed both for uranium and oxygen. These data were used to determine the reaction rates.

Reaction data also were obtained with sandwich-type elements. These consisted of high-fired UO_2 cores jacketed with zirconium or Zircaloy 2. The elements were heated in autoclaves at a 5000-psi helium pressure, to insure contact between jacket and core, at several temperatures for various periods of time. Metallographic examination and hardness traverses indicated the extent of reaction. One large element, having flat areas of contact between the zirconium and the UO_2 , was machined after reaction into thin layers in the zirconium, beginning at the UO_2 interface. The chips from each layer were analyzed for uranium and oxygen and these data were used to determine the transfer of these elements to the metallic phase.

Details of these experimental procedures, including the methods of analyses, are given in Appendix C.

RESULTS

Reaction of Solid Zirconium Cylinders With UO_2 Powder

Several preliminary experiments utilized black calcined UO_2 or as-received Mallinckrodt UO_2 . Both of these oxides were found to contain oxygen in excess of the stoichiometric ratio for UO_2 . A film of ZrO_2 was found on the surface of the zirconium cylinders that had been reacted with these

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oxides. Figure 1 shows the structure at the surface of a zirconium specimen heated in contact with black calcined UO_2 for 17-1/2 hr at 1517 F. The gray film is ZrO_2 . The cracked metallic phase beneath this film is evidence of the hard, brittle solid solution of oxygen in zirconium. Very likely the film was formed by reaction of the zirconium with the oxygen in UO_2 in excess of the stoichiometric amount.

Two experiments were performed in which zirconium cylinders were packed in hydrogen-reduced UO_2 and heated at 1517 F in vacuum for 18 and 70 hr. Microscopic examination of cross sections of these specimens revealed an almost complete absence of a surface film (see Figure 2). Hardness traverses showed evidence of only a very shallow penetration of oxygen into the zirconium. An X-ray spectrometer pattern of the surface of the specimen reacted for 18 hr showed predominantly zirconium, with a very faint trace of the epsilon (also referred to as delta)^(5,6) uranium-zirconium intermetallic phase. Oxygen analyses were obtained on a slice cut from each specimen. The dimensions of these slices were accurately measured and the surface that had been exposed to UO_2 was left unabraded for analytical purposes. Results of these analyses are tabulated below.

Exposure Time to UO_2 at 1517 F, hr	Sample Weight, g	Vacuum-Fusion Analysis, w/o oxygen	Oxygen Transferred to Zirconium, μg per sq cm of surface area
18	1.089	0.0195	226
70	0.693	0.0230	546

Compacted-Powder Mixtures

Data were obtained by the compacted-powder technique on the reaction kinetics of zirconium and UO_2 at 1300 and 1517 F in addition to a single experiment at 950 F. The observed microstructures are typical of the microconstituents found after cooling to room temperature and are no indication of the phases that were in equilibrium at the temperatures of the reaction.

Reaction at 1517 F

Photomicrographs of a compact reacted at 1517 F in vacuum for 63 hr are shown in Figures 3 and 4. The structure is typical for compacts reacted at 1517 F. The dark gray UO_2 particles surround the light metallic zirconium particles. The grain-boundary phase in the zirconium particles is evidence of the epsilon intermetallic phase. Microhardness traverses indicated that the zirconium powder particles were saturated with oxygen in times as short as 63 hr.

FIGURE 1. ZIRCONIUM CYLINDER PACKED IN BLACK CALCINED UO_2 AND HEATED AT 1517 F FOR 17-1/2 HR IN ARGON

Note gray ZrO_2 surface film.

FIGURE 3. $Zr-UO_2$ MIXED POWDERS REACTED AT 1517 F FOR 63 HR IN VACUUM

Gray UO_2 particles; light metallic zirconium with epsilon $Zr-U$ phase in grain boundaries.

FIGURE 2. ZIRCONIUM CYLINDER PACKED IN HYDROGEN-REDUCED UO_2 AND HEATED AT 1517 F FOR 18 HR IN VACUUM

Note extremely thin reaction zone at surface of zirconium specimen.

FIGURE 4. SAME SPECIMEN AS FIGURE 3 SHOWING DISTRIBUTION OF ZIRCONIUM IN DARK GRAY UO_2 MATRIX

Gray UO_2 particles; light metallic zirconium with epsilon $Zr-U$ phase in grain boundaries.

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The results of the uranium and oxygen analyses of zirconium residues (separated from the UO_2 by the mechanical-chemical method) from compacted specimens are shown in Figure 5 and Table 1. The spread between the oxygen analyses of the residue samples from duplicate compacts is about 50 times the expected error of the oxygen analytical method. It is possible that this is indicative of cumulative errors that occur at several stages in the experimental technique. In general, the results obtained are rather inconsistent. If it is a valid assumption that oxygen and uranium enter the zirconium in the ratio of UO_2 , it appears that much of the error of the method lies in incomplete recovery of uranium. This is shown by comparing the calculated uranium values with analytical results as has been done in Table 1.

Reaction at 1300 F

Figures 6 and 7 show the microstructure of a compacted-powder mixture reacted for 120 hr at 1300 F in vacuum. The epsilon phase is again present but does not appear in the cores of the particles in this time of heating. However, microhardness measurements of individual particles showed no gradients, indicating that oxygen had penetrated to the particle cores.

Data obtained by analysis of reacted compacts for several time intervals at 1300 F are shown in Figure 8 and Table 1. These data again show a rather large spread between analyses on duplicate specimens. The agreement between the uranium equivalent to the oxygen in the residue (assuming uranium and oxygen enter the zirconium in the ratio of UO_2) and the direct uranium determinations is not good. The uranium equivalents calculated on the basis of the oxygen contents of the residues are roughly double the direct uranium determinations.

Comparison of analytical data for the compacted mixtures heated for 1 day at either 1300 or 1517 F and data for longer times seems to indicate the approach of saturation with respect to both oxygen and uranium in the zirconium metal particles in heating times as short as 63 hr. The levels of apparent saturation are different for the two reaction temperatures, as would be expected.

Reaction at 950 F

The results obtained on the compacted-powder mixture heated at 950 F for 261 hr also are shown in Table 1. These data show a much lower oxygen and uranium level than was obtained at either 1300 or 1517 F. The zirconium particles showed only a very narrow reaction zone and no apparent evidence of epsilon phase formation. It appears likely that the zirconium in these compacts is not saturated with respect to either uranium or oxygen, even though the equilibrium concentrations probably are lower at this temperature.

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FIGURE 5. RESULTS OF URANIUM AND OXYGEN ANALYSES OF ZIRCONIUM RESIDUES FROM COMPACTED-POWDER MIXTURES HEATED AT 1517 F FOR VARIOUS PERIODS OF TIME

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TABLE 1. ANALYSES^(a) FOR URANIUM AND OXYGEN
IN DUPLICATE COMPACTS

Temperature, F	Time at Temperature, hr	Oxygen in Residue ^(b, c) , w/o	Uranium in Residue ^(d) , w/o	Uranium Equivalent to Oxygen in Residue, w/o
1517	20	2.5	13.1	18.6
1517	20	3.0	13.0	22.4
1517	63	3.9	25.5	29.1
1517	63	3.2	18.6	23.8
1517	118	3.8	22.9	28.3
1517	118	3.1	22.2	23.1
1517	246	3.7	20.6	27.9
1517	246	4.2	19.2	31.7
1300	26	1.1	3.3	8.2
1300	26	0.76	4.0	5.7
1300	65	2.0	7.7	14.9
1300	65	1.8	6.2	13.4
1300	120	1.8	8.3	13.4
1300	120	1.9	7.6	14.2
1300	216	2.1	7.7	15.7
1300	216	2.3	7.8	17.1
950	261	0.42	3.2	3.2
950	261	(e)	1.1	--

(a) Analysis of zirconium residue separated by mechanical-chemical method.

(b) Corrected for oxygen content of control sample.

(c) Vacuum-fusion analysis.

(d) Fluorescence method.

(e) Sample lost during vacuum-fusion analysis.

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16

250X Etchant: 0.5% HF on Polishing Wheel N21531

FIGURE 6. ZIRCONIUM- UO_2 MIXED POWDER COMPACT
REACTED AT 1300 F FOR 120 HR IN VACUUM
Shows appearance of epsilon phase in grain
boundaries of zirconium particles.

100X Etchant: 0.5% HF on Polishing Wheel N21530

FIGURE 7. DISTRIBUTION OF ZIRCONIUM PARTICLES IN THE ZIRCONIUM
 UO_2 POWDER COMPACT SHOWN IN FIGURE 6

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17

FIGURE 8. RESULTS OF URANIUM AND OXYGEN ANALYSES OF ZIRCONIUM RESIDUES FROM COMPACTED-POWDER MIXTURES HEATED AT 1300 F FOR VARIOUS PERIODS OF TIME

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Sandwich-Type Elements

Reaction at 2000 F

The microstructures of sandwich-type elements reacted at 2000 F at a 2000-psi pressure in argon and slowly cooled were always characterized by a continuous band of material which was easily stained. Figures 9 and 10 show the microstructure in the zirconium jacket adjacent to the UO_2 in an element reacted for 14 hr at 2000 F and slowly cooled*. These microconstituents do not represent the phases in equilibrium at 2000 F but are merely transformation products formed during the slow cooling to room temperature.

The different phase regions shown in Figures 9 and 10 were identified by X-ray diffraction studies. The dark-gray phase at the bottom of the photomicrographs is UO_2 . The two-phase region, adjacent to the UO_2 , is composed of alpha uranium (dark phase in grain boundaries) and alpha zirconium (light matrix phase). The darkened continuous band, located deeper in the zirconium jacket and adjacent to the two-phase region, was found to have the alpha uranium structure. This band also contains zirconium in some form, as indicated by spectrographic analysis. The light-appearing phase adjacent to the stained band is alpha zirconium. The cracks noted probably were produced by strain during cooling or sectioning of the hard, brittle, high-oxygen zirconium. All phases in the film are probably nearly saturated with oxygen. The soft, unaffected zirconium metal with little dissolved oxygen is the region deeper into the zirconium and next to the hard zirconium-oxygen solid-solution region (Figure 10).

Sandwich-type elements reacted for longer or shorter times at 2000 F and slowly cooled merely showed differences in thickness of the various zones. A plot of the thickness of these regions as a function of reaction time ($t^{1/2}$) at 2000 F is shown in Figure 11. Justification for this type of plot is discussed in Appendix A. Thickness measurements are based on microscopic examination. Knoop hardness measurements indicate that the two-phase region adjacent to the UO_2 is hard (550-650 Knoop hardness number, 200-g load), the stained band is relatively soft (350 to 400 Knoop hardness number), and the adjacent alpha zirconium region with oxygen in solid solution, again, is hard (550-650 Knoop hardness number). The unaffected zirconium, beyond the region of oxygen penetration is soft (100-200 Knoop hardness number).

The cross section of a sample of a sandwich-type element reacted at 2000 F was exposed to corrosion in 650 F water for 1 hr. The two-phase alpha uranium plus alpha zirconium zone as well as the stained zone were

*Sandwiches cooled to room temperature from 2000 F in about 10 hr.

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19

250X Etchant: 0.5% HF on Polishing Wheel N22319
FIGURE 9. ZIRCONIUM- UO_2 SANDWICH-TYPE ELEMENT
HEATED AT 2000 F FOR 14 HR AT 2000-PSI
LOAD IN ARGON AND SLOWLY COOLED

100X Etchant: 0.5% HF on Polishing Wheel N22318
FIGURE 10. SAME SPECIMEN AS FIGURE 9 SHOWING
SHARP LINES OF DEMARCATION BE-
TWEEN THE SEVERAL ZONES

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20

FIGURE II. ESTIMATION OF DEPTH (ON BASIS OF MICROSTRUCTURE) OF VARIOUS ZONES IN ZIRCONIUM AT INDICATED DISTANCES FROM ZIRCONIUM-UO₂ INTERFACE FOR REACTION AT 2000 F

A-15652

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completely removed. However, the UO_2 in the sandwich and an additional UO_2 control specimen were not affected by this test. No experiments in which UO_2 was jacketed with Zircaloy 2 were performed at this temperature.

In an attempt to quench high-temperature equilibrium phases, a sandwich-type element was capsulated in a partial pressure of argon. The capsule then was heated at 2000 F for about 11 hr and cooled by breaking under cold water. The microstructure in the reaction zone of this element is shown in Figures 12 and 13. Here the distribution of phases is somewhat different than was found in the slow-cooled element. A thin, unidentified light-etching zone was found immediately adjacent to the UO_2 . Next to this, a rather broad and slightly darker etching region, which was relatively soft, was found. This layer was found spectrographically to contain zirconium and uranium. Inclusions of a second lighter-etching unidentified phase are visible in the area of this region nearest the UO_2 , see Figure 12. Because of the relative softness of this region, one would expect it to be a uranium-rich solid solution with little dissolved oxygen.

The lighter etching broader zone which contains some cracks and lies deeper into the zirconium between the slightly darkened zone and the transformed-beta structure is the very hard zirconium-oxygen solution. The sharp line of demarcation between this region and the transformed-beta structure, clearly shown in Figure 13, apparently occurs at the limit of diffusion of oxygen in the zirconium. A similar line of demarcation can be seen in Figure 10 at a slightly greater distance from the zirconium- UO_2 interface. The region showing the transformed-beta structure appears to contain only a relatively small amount of dissolved oxygen.

Reaction at 1300 F

Small Zirconium- UO_2 Elements. Sandwich-type elements were reacted at 1300 F in an autoclave under pressure. Although it would have been desirable to quench the specimen from the reaction temperature, this could not be accomplished with the equipment on hand. Consequently, the autoclaves were cooled to room temperature in about 16 hr. The microstructures of these slow-cooled specimens, therefore, are not necessarily representative of the phases in equilibrium at the reaction temperature but probably are largely transformation products formed on cooling.

Figure 14 shows the microstructure in the cross section of an element reacted at 1300 F for 18 days and slowly cooled in the autoclave overnight. Phases present were identified by metallographic and X-ray diffraction studies. The dark-gray material at the bottom of the photomicrograph is the UO_2 . The two-phase region adjacent to the UO_2 was found to consist of alpha

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22

250X Etchant: 0.5% HF on Polishing Wheel N23119
FIGURE 12. ZIRCONIUM- UO_2 SANDWICH-TYPE ELEMENT
ENCAPSULATED IN VYCOR UNDER PARTIAL
PRESSURE OF ARGON, HEATED AT 2000 F FOR
11 HR AND WATER QUENCHED

100X Etchant: 0.5% HF on Polishing Wheel N23118
FIGURE 13. SAME ZIRCONIUM- UO_2 SANDWICH-TYPE SPECIMEN
AS FIGURE 12

Note sharp boundary between the hard zirconium-
oxygen solid solution and the transformed beta phase.

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uranium and alpha zirconium. The faintly visible third phase may be a phase that was in equilibrium at 1300 F. The metallographically discernible subregion is evidence of the outward movement of the UO_2 -metal interface as UO_2 was consumed by the reaction. The epsilon phase appears as the bulky phase apparently at the grain boundaries. The slender acicular phase in the zirconium away from the reaction zone is evidence of zirconium hydride in the unreacted metal. All phases in the reaction zone were at least partially saturated with oxygen, as evidenced by the expanded lattice found for the alpha zirconium.

A cross section of this specimen was corroded in 650 F water for 1 hr. Figure 15 shows the same field, after corrosion, as was shown in Figure 14. The regions containing alpha uranium have been removed by the hot-water corrosion. Neither the zirconium nor the epsilon phase appears noticeably affected. The UO_2 also was not attacked, although it was loosened by removal of the alpha uranium from the adjacent region. The darkened blotches in the unaffected zirconium metal suggest pits formed in corrosion or local deposits of corrosion products. Since the phases subjected to corrosion probably were not those in equilibrium at 1300 F but were mostly transformation products formed on cooling from 1300 F, these corrosion results may have no practical value as far as predicting the corrosion behavior of ruptured fuel elements in service.

Figure 16 is a plot of the increase in thickness of the several zones near the metal-oxide interface as a function of time ($t^{1/2}$) at 1300 F. Estimations of the thicknesses of the respective zones were based on microscopic measurement techniques. Hardness measurements indicated that the region in which the epsilon phase existed was softer than either of the adjacent regions.

Large Zirconium- UO_2 Elements. The results of analyses of chip samples, machined in 0.001-in. increments from the zirconium reaction zone adjacent to the UO_2 for an element reacted under pressure at 1300 F for 37 days, are listed in Table 2 and plotted in Figure 17. The microstructure of this region is shown in Figure 18. The identifying layer numbers, used in Table 2, appear at the side of the photomicrograph in Figure 18. This structure again represents transformation products formed on slow cooling from 1300 F. The reaction zone shown has the same phases present as those previously described for the smaller test specimens.

Comparison of the analytical results with those obtained by metallographic examination discloses substantial agreement between the two methods. Interpretation also depends upon relative solubility of oxygen in the various microconstituents. The solubility of oxygen in alpha zirconium is quite high (about 28 a/o at 1300 F) while the solubility of oxygen in alpha uranium is only a few parts per million. The solubility of oxygen in the various

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24

250X Etchant: 0.5% HF on Polishing Wheel N21528

FIGURE 14. ZIRCONIUM- UO_2 SANDWICH-TYPE ELEMENT HEATED AT 1300 F AND A 5000-PSI HELIUM PRESSURE FOR 18 DAYS AND SLOWLY COOLED

250X Etchant: 0.5% HF on Polishing Wheel N21748

FIGURE 15. ZIRCONIUM- UO_2 SANDWICH-TYPE ELEMENT (SAME FIELD AS SHOWN IN FIGURE 14) AFTER 1 HR OF CORROSION IN 650 F WATER

Note erosion of area where alpha uranium was present.

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FIGURE 16. ESTIMATION OF DEPTH (ON BASIS OF MICROSTRUCTURE) OF VARIOUS ZONES IN ZIRCONIUM AT INDICATED DISTANCES FROM ZIRCONIUM-UO₂ INTERFACE FOR REACTION AT 1300 F

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TABLE 2. ANALYSIS OF CHIP SAMPLES FROM KNOWN POSITIONS IN
REACTION ZONE OF SANDWICH-TYPE ELEMENT HEATED
UNDER PRESSURE AT 1300 F FOR 37 DAYS

Layer	Distance of Cut From UO ₂ -Metal Interface, mils	Oxygen(a)		Uranium(b)		Phases Represented by Cut(c)
		w/o	a/o	w/o	a/o	
1	0-1.5	--	--	--	--	Cleaning cut
2	1.5-2.5	2.6	14.2	12.2	4.46	Majority alpha Zr, some alpha U
3	2.5-3.5	2.2	12.6	Lost	--	Mainly epsilon phase, some alpha Zr, little or no alpha U
4	3.5-4.5	1.5	9.4	26.8	11.35	Epsilon plus alpha Zr
5	4.5-5.5	1.8	10.8	21.7	8.77	Mainly alpha Zr, some epsilon
6	5.5-6.5	2.0	11.4	15.3	5.86	Mainly alpha Zr, little epsilon
7	6.5-7.5	1.6	9.9	7.58	2.82	Mainly alpha Zr, very little epsilon
8	7.5-8.5	1.8	10.7	3.85	1.40	Mainly alpha Zr, very little epsilon
9	8.5-9.5	1.3	7.5	1.24	0.45	Alpha Zr plus trace epsilon
10	9.5-10.5	0.8	4.4	0.48	0.18	Nearly all alpha Zr
11	10.5-11.5	1.2	6.5	0.29	0.10	Alpha Zr
12	11.5-12.5	0.5	2.8	0.055	0.02	Alpha Zr
13	12.5-13.5	0.3	1.7	0.031	0.01	Alpha Zr
14	13.5-14.5	0.3	1.7	0.016	0.01	Alpha Zr
15	14.5-15.5	0.1	0.6	0.014	0.01	Alpha Zr
16	15.5-16.5	0.2	1.1	0.014	0.01	Alpha Zr

(a) Vacuum-fusion analysis.

(b) Fluorescence analysis.

(c) See Figure 15.

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FIGURE 17. URANIUM AND OXYGEN VERSUS DISTANCE FROM ZIRCONIUM- UO_2 INTERFACE FOR SANDWICH-TYPE ELEMENT HEATED UNDER PRESSURE AT 1300 F FOR 37 DAYS

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28

250X Etchant: 0.5% HF on Polishing Wheel N23295

FIGURE 18. REACTION ZONE OF LARGE SANDWICH-TYPE
ELEMENT HEATED AT 1300 F UNDER PRESSURE
FOR 37 DAYS

Numbers at side of photomicrograph indicate
layer numbers.

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other uranium phases is also believed to be quite low and this is assumed in the following presentation of data.

As described in the procedure section, successive cuts were made, by machining in a lathe, from this large reacted specimen. The first layer, approximately 0.0015 in. in thickness, contained portions of the adherent UO_2 phase and, since this sample would not have represented the true situation in the surface metallic layer, no analysis was made.

The second layer was obtained from a two-phase region containing, as metallographically observed (Figure 18), mostly alpha zirconium with a small amount of uranium. This layer analyzed relatively high in oxygen and low in uranium content.

Layer 3, taken from a two-phase region identified as consisting mainly of epsilon phase and alpha zirconium, contained less oxygen and probably more uranium than Layer 2. Unfortunately, this sample was lost during analysis for uranium. Logically, one would expect much more uranium in this sample because it contained a part of the region identified as having an abundant amount of epsilon compound in an alpha zirconium matrix.

Layer 4 represents the heart of the two-phase region identified as the epsilon phase in the alpha zirconium matrix. This layer analyzed as having the highest uranium content. For this sample, the amount of oxygen as determined by vacuum fusion continues the decrease set by the pattern established in Layers 2 and 3.

Beginning with Layer 5, the concentration of uranium begins to decrease as the amount of epsilon diminishes and the amount of alpha zirconium increases. This decrease continues in Layer 6, which contains the last of the epsilon phase, as well as through the remaining ones, Layers 7 through 16. Oxygen, on the other hand, increases significantly in Layer 5 and again in Layer 6 before beginning to decrease again. This decrease continues, somewhat erratically, throughout the remainder of the sample, Layers 7 through 16. Undoubtedly there is some scatter in the oxygen analyses because of the difficulties which are inherent in performing a vacuum-fusion analysis on chip samples, but the sustained rise in oxygen content indicated by Layers 4 through 6 is believed to be real. A proposed explanation of this is given in a later section of this report.

Zircaloy 2*- UO_2 Elements. Specimens have been examined metallographically after 14 and 51 days of exposure at 1300 F in the autoclave under

*Zirconium containing, nominally, 1.5 w/o tin, 0.12 w/o iron, 0.1 w/o chromium, and 0.05 w/o nickel.

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pressure followed by slowly cooling to room temperature. Figures 19 and 20 show the microstructure in the reaction zone for an element reacted for 51 days. These microconstituents again are the transformation products formed on slowly cooling to room temperature.

The dark-gray phase at the bottoms of the figures is UO_2 . Adjacent to the UO_2 is a two-phase region clearly shown in Figure 20. These phases appear similar to those identified as alpha uranium and alpha zirconium for the zirconium- UO_2 elements. However, X-ray identification of the phase regions in this specimen has not been obtained. Adjacent to this two-phase region, and deeper into the zirconium, a band appears to exist. An occasional tongue of this material penetrates deeper into the zirconium. The composition of this phase has not been determined. The large bulky phase apparently at the grain boundary next to this band is similar in appearance to the material previously identified as epsilon phase. Beyond this region is a very narrow region containing oxygen in solid solution in the metal phase.

On the basis of the metallographic examination of these two specimens, it appears that the reaction between UO_2 and the metal phase is less rapid with a Zircaloy 2 jacket than with a zirconium jacket. The zone in which the apparent epsilon phase is formed certainly is much narrower than was observed for the zirconium- UO_2 elements. The depth of oxygen penetration into the Zircaloy 2 appears to be only about one-third of that found for a similar zirconium jacket.

Reaction at 1100 F

Only limited data were obtained on the zirconium- UO_2 reaction at 1100 F. Small sandwich-type elements composed of UO_2 jacketed with zirconium and, also, UO_2 jacketed with Zircaloy 2 were examined after heating in an autoclave at a 5000-psi helium pressure. The zirconium-jacketed sandwich was heated for 23 days at 750 F and 75 days additionally at 1100 F. It showed only a very slight evidence of reaction. The microstructure in the reaction zone (of this specimen) is shown in Figure 21. Only limited evidence of reaction can be seen (reaction zone is less than 0.0002 in. thick) and oxygen penetration appears to be of the order of 0.015 in., as determined from hardness measurements.

The Zircaloy 2-jacketed sandwich was examined after heating for 65 days at 1100 F in the autoclave. Again only very slight evidence of reaction is evident, as can be seen in Figure 22.

250X Etchant: 0.5% HF on Polishing Wheel N23301

FIGURE 19. REACTION ZONE OF UO_2 CORE JACKETED WITH ZIRCALOY 2 AND HEATED AT 1300 F FOR 51 DAYS UNDER PRESSURE AND SLOWLY COOLED

500X Etchant: 0.5% HF on Polishing Wheel N23302

FIGURE 20. SAME AS FIGURE 19 SHOWING TWO-PHASE REGION ADJACENT TO THE DARK-GRAY UO_2 . Bulky phase in zirconium resembles epsilon phase.

250X Etchant: 0.5% HF on Polishing Wheel N23491

FIGURE 21. REACTION ZONE OF UO_2 CORE JACKETED WITH ZIRCONIUM AND HEATED UNDER PRESSURE AT 750 F FOR 23 DAYS AND 1100 F FOR 75 DAYS ADDITIONALLY AND SLOWLY COOLED

250X Etchant: 0.5% HF on Polishing Wheel N23494

FIGURE 22. REACTION ZONE OF UO_2 CORE JACKETED WITH ZIRCALOY 2 AND HEATED UNDER PRESSURE FOR 65 DAYS AT 1100 F AND SLOWLY COOLED

Reaction at 950 F

A sandwich-type element composed of UO_2 jacketed with zirconium and a similar element jacketed with Zircaloy 2 were examined after heating at 950 F in the autoclave for 70 days. Both elements showed very little if any evidence of a reaction zone. Figure 23 shows the reaction zone in the zirconium-clad element. Oxygen penetrated into the zirconium to a depth of less than 0.001 in., as judged from a hardness traverse. The large gray inclusions in the zirconium are evidence of precipitated hydrides.

The microstructure of the Zircaloy 2-clad element is shown in Figure 24. The apparent gray film lying between the UO_2 and the metal is merely an intrusion of resin which occurred when the UO_2 and its jacket were separated in mounting the specimen for metallographic polishing. The oxygen penetration into the Zircaloy 2 was as little as that observed for unalloyed zirconium.

DISCUSSION OF RESULTS

Data on the kinetics of reaction of zirconium with uranium dioxide have been obtained principally by three methods. It appears that each method has several advantages as well as a number of drawbacks. Using massive cylindrical zirconium specimens packed in powdered UO_2 , it is possible to analyze the extent of reaction by observing penetration of oxygen and/or uranium in the zirconium. The reaction zone can be machined into concentric layers and the oxygen and uranium content of each layer determined. Hardness data and metallographic information also can be obtained from the solid specimen. Since the UO_2 powder was not pressed around the zirconium cylinders by high pressure, but merely tamped in place, the extent of the contact between the zirconium and the UO_2 was not known. However, as Figure 2 shows, contact was imperfect. The same thing is probably true of powder compacts, as shown by Figure 3. In addition, in only two of the experiments in which this technique was used, was the UO_2 sufficiently free of excess oxygen and other impurities to yield useful data.

The method of compacted-powder mixtures provides reasonably good contact between the individual powder particles. However, in this method it was found that it was difficult to obtain a clean separation of the UO_2 from the zirconium particles. Any adherent UO_2 on the zirconium renders the results of both uranium and oxygen analyses meaningless. Some of the products of the reaction were dissolved during leaching and this is discussed in Appendix C. Also, the relatively fine particles of zirconium used, 70 to 100 mesh (0.149 to 0.210-mm sieve-size openings), were rapidly saturated with oxygen and uranium.

250X Etchant: 0.5% HF on Polishing Wheel N23874

FIGURE 23. REACTION ZONE OF UO_2 CORE JACKETED WITH ZIRCONIUM AND HEATED AT 950 F FOR 70 DAYS UNDER PRESSURE AND SLOWLY COOLED

250X Etchant: 0.5% HF on Polishing Wheel N23877

FIGURE 24. REACTION ZONE OF UO_2 CORE JACKETED WITH ZIRCALOY 2 AND HEATED AT 950 F FOR 70 DAYS UNDER PRESSURE AND SLOWLY COOLED

Of the three methods, the use of the sandwich-type elements appears to offer the best approach to the problem. The heating of these elements in autoclaves in an inert gas at a pressure of about 5000 psi insured good contact between the zirconium jacket and the UO_2 core. If the surfaces of contact are large enough, as was the case with the large sandwich-type elements, analyses for oxygen and uranium can be obtained at known distances from the metal-oxide interface. This method enables one to determine accurately the transfer of both oxygen and uranium to the zirconium.

Packed Zirconium Cylinders Versus Powder Compacts

Data were obtained on the kinetics of the zirconium- UO_2 reaction at 1517 F (825 C) by two methods: (1) packing of massive zirconium cylinders in UO_2 powder, and (2) using mixed-powder compacts. Assuming that the zirconium powder particles are cubes, the amount of oxygen transferred to the zirconium powder from the UO_2 was expressed in terms of μg of oxygen (transferred) per cm^2 of surface area. By this means it is possible to compare directly the data obtained by both methods. Table 3 lists the oxygen transfer on this basis. These values are plotted in Figure 25 along with the two values obtained from the cylindrical-specimen experiments. The single points plotted for the mixed-powder compact experiments are the average of two analyses. The data obtained from the zirconium cylindrical specimens, in Figure 25, appear somewhat lower than those obtained on the mixed-powder compacts. However, the difference is well within the experimental error of the methods. Agreement between the two methods would be expected only in the initial stages of reaction, since the powder particles are quite rapidly saturated with oxygen at this temperature.

Sandwich-Type Elements

Results for the sandwich-type elements have been presented in Figures 11 and 16, which indicate the depth of penetration of each of the reaction zones as a function of time for the several temperatures being considered. The reaction rates are slow for temperatures of 950 F and 1100 F but become significant at 1300 F. Rates of reaction at 2000 F are extremely rapid. The break from the slow reaction observed at 1100 F to the more rapid reaction at 1300 F may occur at the temperature of the epsilon-to-gamma transformation.

Inasmuch as 1300 F is approximately the estimated maximum temperature at the UO_2 -Zircaloy 2 interface, it is interesting to predict for this condition the expected maximum life of a fuel element operating at this temperature. It has been noted that the depth of penetration increases directly as

CONFIDENTIAL

35

TABLE 3. KINETIC DATA ON THE REACTION AT 1517 F
ON THE BASIS OF SURFACE AREA

Time Exposed to UO ₂ , hr	Average Zirconium Particle Size, mm	Oxygen ^(a) , w/o	Oxygen Transfer, μg per cm ²
20	0.163	2.75	485.
63	0.194	3.55	745.
118	0.194	3.45	725.
246	0.194	3.95	847.
18	Cylinder	0.0195	226. ^(b)
70	Cylinder	0.0230	546. ^(b)

(a) Oxygen values are the average of vacuum-fusion analyses of zirconium residues from duplicate compacts shown in Table 4.

(b) Data obtained by packing zirconium cylindrical specimens in hydrogen-reduced UO₂.

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FIGURE 25. COMPARISON OF OXYGEN TRANSFER TO ZIRCONIUM AT 1517 F FOR DATA OBTAINED BY TWO METHODS

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the square root of time of reaction. That is, the depth of penetration can be expressed as:

$$d = k t^{1/2},$$

where

d = depth of penetration, in.;

k = a constant at given temperatures; and

t = time of reaction, days.

From the data presented for the runs made at 1300 F, it is possible to derive a series of equations of the above form representing the depth of penetration, relative to the original interface, of the various phases observed. For the movement of the interface,

$$d \text{ (in in.)} = 0.00017 t^{1/2} .$$

For the maximum penetration of the alpha zirconium plus alpha uranium phase,

$$d \text{ (in in.)} = 0.00037 t^{1/2} .$$

For the maximum penetration of the alpha zirconium plus epsilon phase

$$d \text{ (in in.)} = 0.00130 t^{1/2} ,$$

and for the maximum penetration of dissolved oxygen in the alpha zirconium phase

$$d \text{ (in in.)} = 0.00172 t^{1/2} .$$

If one assumes an idealized isothermal system rather than one in which the temperature is decreasing through the zirconium jacket, the time required for oxygen to penetrate a given thickness of zirconium can be estimated. For a jacket thickness of 0.030 in. and a temperature of 1300 F, about 300 days would be required for the oxygen to penetrate to the exterior of the zirconium jacket. This time may well represent the usable life of a reactor fuel element of this type if the criterion is truly the time required for penetration to the exterior surface. However, the above assumption ignores any reaction that may occur between the jacket and the cooling water.

The jacket lifetime at 950 and 1100 F could not be estimated from the results of the present study because of the slowness of the reaction. At

2000 F, it appears that the limit of usefulness of the 0.030-in. jacket would be about 60 hr.

The corrosion resistance of the original materials as well as the reaction products produced are also of interest. Photomicrographs of prototype fuel-element sections before and after exposure for 1 hr to water at 650 F show that the original materials, UO_2 and zirconium, are unaffected, but that alpha uranium-bearing phases, resulting from the reaction, are completely removed. This indicates that if small leaks existed or developed in the zirconium jackets the major portion of the reaction products would find their way into the water, probably causing serious contamination. It is, however, extremely uncertain what might happen if a very small leak developed in the jacket. It is likely that both oxygen and hydrogen might react quite rapidly in addition to speedily diffusing into the high-temperature phases that exist.

Reaction

All evidence obtained during the course of this study seems to indicate that the reaction between UO_2 and zirconium (or Zircaloy 2) reaches measurable speed at temperatures of the order of 1100 F. The reaction proceeds, despite an unfavorable free-energy driving force for the reactants and products in their standard states, because of the decreased activities of the uranium and oxygen when dissolved in the zirconium (see Appendix A). Reduction of the UO_2 evidently occurs at the surface of the metallic phase simultaneously with solution of its component elements. The over-all rate of reaction is evidently controlled then by the solid-state rate of diffusion of the oxygen and uranium into the zirconium matrix. All types of the experiments believed to be valid substantiate this premise.

Unfortunately, the test of only one of the large practical sandwich-type samples was completed. However, a number of conclusions are possible because of the complete and interrelated nature of the information obtained.

Although the experiment was performed at 1300 F, the metallographic structure as shown in Figure 18 represents that which would exist at a lower temperature because of the slow cooling rather than a quench, that the specimen received at the end of the experimental run. Figure 26 is a tentative uranium-zirconium-oxygen ternary section at 1000 F. This was prepared as a result of another part of this program⁽⁹⁾. Here are plotted the data representing the compositions (in atomic per cent) of the various layers as presented in Table 2 and Figure 17. The phases as observed in the photomicrograph (Figure 18) correspond closely to those which would be predicted from this phase diagram. Two conclusions are possible. First, the work of the two parts of this study are in substantial agreement and, second, the slow

FIGURE 26. TENTATIVE ZIRCONIUM-URANIUM-OXYGEN TERNARY SECTION AT 1000 F

A-15484

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40

cooling from 1300 F results in a structure which is representative of the structure at about 1000 F. This 1000 F section also may represent structures below 1000 F, since no further phase changes are likely to occur.

In the same manner the data also are plotted on a similar diagram in Figure 27, representing the ternary section at 1300 F. It is observed that Layers 2 through 6 lie close to or within the two-phase region in which the phases are the alpha zirconium phase and the gamma-prime uranium-beta zirconium solid-solution phase. It will be observed that the concentration of uranium increases greatly in crossing the phase boundary, Layer 2 to Layer 4. The explanation for this is believed to be that the activity coefficient for the uranium in this phase is so much lower than in the adjacent phase that the uranium concentration must take a stepwise increase to maintain a proper activity gradient for diffusion into the zirconium matrix. Substantiation of this hypothesis should be attempted by further theoretical and experimental study.

As previously hypothesized, if oxygen is substantially insoluble in the uranium-bearing phases, the experimental oxygen diffusion gradient can be rationalized. Assuming that the gamma-prime uranium beta-zirconium solid-solution phase is 56 a/o zirconium and 44 a/o uranium (32.8 w/o zirconium, 67.2 w/o uranium), the per cent oxygen can be calculated as if it were contained in the alpha zirconium phase alone. The resultant data are shown in Table 4. Within the limit of experimental error, ± 10 per cent, the calculated oxygen values show the smoothly decreasing oxygen gradient normally expected in a simple diffusion system.

Results at other temperatures do not disagree with the interpretations presented here, but also are not sufficiently complete to permit an unqualified conclusion that the system behaves the same at all temperatures. Additional work should be undertaken to substantiate more fully the tentative conclusions reached.

CONCLUSIONS

This study of the kinetics of the reaction between zirconium and UO_2 was made using three experimental methods. The most useful method, from the viewpoint of obtaining practical as well as fundamental information on the reaction, appears to be the one using large sandwich-type elements. The zirconium end disks from these elements can be suitably machined and analyzed to determine the transfer of oxygen and uranium to the zirconium.

The reaction of UO_2 with zirconium appears to take place without formation of zirconium dioxide, ZrO_2 . The UO_2 seems to be reduced by

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FIG. 27/
FIGURE 27. TENTATIVE ZIRCONIUM-URANIUM-OXYGEN TERNARY SECTION AT
1300 F A-15485

42

TABLE 4. DISTRIBUTION OF OXYGEN AND URANIUM
IN 1300 F REACTION PRODUCTS

Layer (a)	Uranium Analysis, w/o	Uranium in Solid Solution (b), w/o	Uranium in Alpha Zirconium, w/o	Oxygen Analysis, w/o	Oxygen Calculated in Alpha Zirconium Phase, w/o
2	12.2	18.1	81.9	2.6	3.2
3	--	--	--	2.2	--
4	26.8	39.9	60.1	1.5	2.5
5	21.7	32.3	67.7	1.8	2.7
6	15.3	22.8	77.2	2.0	2.6
7	7.6	11.3	88.7	1.6	1.8
8	3.9	5.8	94.2	1.8	1.9
9	1.2	1.8	98.2	1.3	1.3
10	0.5	0.7	99.3	0.8	0.8

(a) See Table 2.

(b) Solid solution, consisting of alpha-prime uranium and beta zirconium, assumed to be composed of 32.8 w/o zirconium and 67.2 w/o uranium.

reaction with the zirconium. The reduced elements, oxygen and uranium, simultaneously diffuse into the zirconium.

Reactions below 1100 F are quite slow. At 1300 F, the reaction proceeds at a measurable rate. At 1517 F, the reaction is rapid and at 2000 F, very rapid.

Calculations based on results obtained under the isothermal conditions of the autoclave experiments here reported indicate that a zirconium-jacketed (0.030-in. wall) UO_2 fuel element might have a useful life of about 300 days at 1300 F and only about 60 hr at 2000 F.

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- (2) Petrographic studies of the UO_2 were made by Mr. A. Durbin.
- (3) The X-ray diffraction work was carried out by Mr. D. A. Vaughan.
- (4) Vacuum-fusion oxygen analyses were done under the supervision of Mr. C. B. Griffith.
- (5) Tentative uranium-zirconium-oxygen ternary sections were made available for use by Mr. F. A. Rough.
- (6) Many of the thermodynamic calculations were performed by Dr. J. J. Ward.

We also thank Dr. R. W. Dayton for his advice and encouragement during the course of this work.

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45 45 and 46

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APPENDIX A

THEORETICAL CONSIDERATIONS

Thermodynamics

In a solid-solid reaction of the type being considered here, the initial state of the reactants has an important bearing upon the thermodynamics of the process. At the outset very little was known about the behavior of this system, and a phase diagram was not available. Consequently, many exploratory thermodynamic calculations performed would not have been necessary if the information on the ternary phase diagram, now completed, had been available at the outset of this work.

Interest in the thermodynamics of the possible reactions between uranium dioxide and zirconium necessitates a consideration of the free energies of formation of all compounds entering as possible reactants, intermediates, or products into this problem. Consequently, uranium, zirconium, and their probable and possible oxide forms, and oxygen solubilities were studied in preparation for a complete thermodynamic analysis.

Uranium-Oxygen System

The experimental and theoretical information (of an unclassified nature) available on this system up to the year 1951 is concisely summarized by Katz and Rabinowitch(8)*. The evidence reported by them shows that oxygen is soluble in uranium only to the extent of 0.003 w/o at 1133 C (2071 F) with lower solubilities at lower temperatures and somewhat higher solubilities at higher temperatures. In samples containing oxygen in the composition range U to UO, only uranium and uranium monoxide X-ray diffraction patterns were observed. This UO has been observed only as a thin surface layer on uranium metal.

Uranium dioxide was reported to exist as a single phase between the limits $\text{UO}_{1.75}$ to $\text{UO}_{2.30}$, although there is some claim that a distinct phase with a composition $\text{UO}_{1.75}$ may exist (experiments in the present study showed no evidence of substoichiometric UO_2 compositions such as $\text{UO}_{1.75}$). Phases having compositions between UO and $\text{UO}_{1.75}$ are evidently not

*These numbers refer to the list of references following the main body of the report.

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possible and two phases, nominally uranium and UO_2 , are necessary to satisfy the conditions for this composition range.

In the range from $\text{UO}_{2.30}$ to $\text{UO}_{2.67}$, nominally U_3O_8 , a continuous range of compositions is evidently possible, although there is some evidence for the existence of an orthorhombic crystal structure purported to be U_2O_5 . Material of this composition can be converted to U_3O_8 , having a somewhat different orthorhombic structure, by gradual uptake of oxygen without the formation of a new phase.

Uranium trioxide, UO_3 , has a reported composition range of $\text{UO}_{2.67}$ to UO_3 . X-ray observations confirm the gradual transition from U_3O_8 to UO_3 . It has been pointed out that the hexagonal uranium lattice in one crystalline form of UO_3 can be obtained from the orthorhombic uranium lattice of U_3O_8 by a gradual change in the parameters of the lattice of the uranium atoms.

Additional understanding of uranium-oxygen compositions can be obtained from the decomposition information summarized by Katz and Rabinowitch⁽⁸⁾. Beginning with the composition UO_3 , uranium oxide can be decomposed down to the composition U_3O_8 quite easily. Conditions of 10 mm of mercury oxygen pressure and about 580 C (1076 F) were sufficient to obtain U_3O_8 which then remained stable up to a temperature above 650 C (1202 F) at this same pressure. Between 750 and 1360 C (1382 and 2480 F), U_3O_8 loses oxygen gradually down to the composition $\text{UO}_{2.62}$. At 1360 C (2480 F) oxygen is lost at this same pressure of 10 mm of mercury down to the composition $\text{UO}_{2.30}$. This constant-temperature decomposition is indicative of the diphasic region which exists. Further decomposition required lower pressures and $\text{UO}_{2.20}$ was obtained at 1160 C (2120 F) and 0.022 mm of mercury. The conversion of $\text{UO}_{2.20}$ to $\text{UO}_{2.00}$ requires much higher temperatures.

From a study of the thermodynamics of the uranium-oxygen system, recommended values for the free energy of formation of the various uranium oxides can be presented. These values from Coughlin⁽¹⁰⁾, Glassner⁽¹¹⁾, and Brewer⁽¹²⁾ represent the ones believed to be the best available. These recommended values are given in Table A-1 and shown graphically in Figure A-1.

Of interest in the graphical presentation are the values given for the free energy of formation for $\text{UO}_{2.25}$ and $\text{UO}_{2.62}$ at 298.16 K (77.1 F) and the values given for UO at all temperatures. The significance of the value for $\text{UO}_{2.62}$ being higher than that for U_3O_8 at 298.16 K (77.1 F) is not understood and cannot be explained from the information available.

The existence or nonexistence of UO in any given temperature range could be predicted from this plot if the values were sufficiently accurate. A

147

TABLE A-1. FREE ENERGY OF FORMATION OF URANIUM OXIDES

Compound	Temperature:	K	Free Energy, kcal per g mole					Uncertainty, kcal	Reference for Data ^(a)
			298.16	500	1000	1500	2000		
	F		77.1	440.4	1340.4	2240.4	3140.4		
UO			-123.0	-120.0	-110.0	-99.0	-87.0	±5.0	10
UO ₂			-246.6	-238.2	-218.1	-197.7	-177.0	±0.70	11
UO _{2.25}			-256.0	--	--	--	--	±2.0	11, 12
UO _{2.62}			-270.0	--	--	--	--	±3.0	11, 12
U ₃ O ₈			-804.0	-770.9	-691.5	-611.0	-530.6	±3.5	10
UO ₃			-272.5	-260.0	-230.5	-200.4	-169.2	±5.0	10

(a) These numbers refer to the list of references following the main body of the report.

CONFIDENTIAL

50

FIGURE A-I. FREE ENERGY OF FORMATION OF URANIUM OXIDES

A-15649

CONFIDENTIAL

curve between U and UO_2 which was convex upward for any temperature would indicate UO as a stable form at that temperature, a straight line would indicate incipient stability, a concave line would indicate the nonexistence of this compound. However, as far as is known, the values given for UO were obtained by taking one-half of the measured values for UO_2 . Thus no significance can be attached to the shape of the curve in this region.

Also of interest is the interpretation that U_3O_8 becomes more stable than UO_3 at a temperature between 1000 and 1500 K (1340.4 and 2240.4 F). This conclusion can be reached from consideration of the relative free energies of formation (per gram-atom of uranium) of UO_3 and U_3O_8 in this temperature range.

Zirconium-Oxygen System

The zirconium-oxygen system appears to be considerably less complex than the uranium-oxygen system. In the first place, oxygen has a significant solubility in metallic zirconium, about 6.75 w/o, according to Domagala and McPherson⁽⁷⁾. However, oxygen in an amount of about 0.25 w/o is sufficient to cause severe embrittlement, according to Treco⁽¹³⁾.

Zirconium dioxide (ZrO_2) appears to be the only compound between zirconium and oxygen, and evidently exists as a definite compound rather than as an indistinct range of compositions as in the case of uranium dioxide. Consequently, the free energy of formation of this compound is known with more certainty than is the case with the uranium-oxygen compounds. The recommended values are given in Table A-2. This information was originally reported by Coughlin⁽¹⁰⁾.

TABLE A-2. FREE ENERGY OF FORMATION
OF ZIRCONIUM DIOXIDE(a)

Temperature		Free Energy of Formation(b), kcal per g mole
K	F	
298.16	77.1	-247.8
500	440.4	-238.5
1000	1340.4	-216.1
1500	2240.4	-193.9
2000	3140.4	-172.5

(a) After Coughlin⁽¹⁰⁾.

(b) Uncertainty: ± 0.25 kcal per g mole.

Equilibrium Conditions

Using the free energy of formation information already presented, the reaction equilibrium situation for a number of assumed conditions was computed. Several situations were hypothesized. Among these are:

- (1) Reactants and products in ideal standard states with complete immiscibility assumed
- (2) Reactants and products completely miscible with ideal solid solution assumed
- (3) Reactants and products in actual conditions which would be predicted from information available from phase diagrams for binary and ternary systems.

Table A-3 gives values of the standard free-energy change as a function of the temperature for a number of reactions of interest. It can be concluded from these data (Reactions 4, 5, and 6 of Table A-3) that it is thermodynamically possible for any uranium oxide, UO_x , where $x > 2$, to corrode zirconium.

However, with uranium oxides where $x < 2$, if solid solution with ZrO_2 does not occur, the thermodynamic data along with phase-rule considerations show that no interaction will occur. If ideal solid solution of the oxides does occur, as has been reported by Lambertson and Mueller⁽¹⁴⁾, the conversion of zirconium will be greater than 20 per cent, as shown in Table A-3, under equilibrium conversions. Also, in regard to Reactions 2 and 3, the uncertainties in the data are so large that further experimental investigation of these reactions at elevated temperatures would certainly appear worthwhile. Reactions 7 and 8 show that disproportionation of UO_2 will not occur.

The reaction of metallic zirconium with UO_2 , $\text{Zr (c)} + \text{UO}_2 \text{ (c)} \rightarrow$ products, also could be written in terms of half reactions similar to half-cell reactions in electrochemistry. For the UO_2 half reaction, $\text{UO}_2 \text{ (c)} \rightarrow \text{U (c)} + \text{O}_2 \text{ (g)}$. Data from Coughlin⁽¹⁰⁾ show that for this reaction $\Delta F_{1300 \text{ F}} = 219.00 \text{ kcal per mole}$ or that $\log K = 48.971$ where $K = \frac{P_{\text{O}_2} \cdot a_{\text{U}}}{a_{\text{UO}_2}}$

The partial pressure of oxygen over this system (representing half of the reaction of interest), which can be calculated for various assumed conditions of the state of the uranium metal produced, can be thought of as the oxidizing potential of this half reaction toward other substances. Thus, any other half reaction which has a lower oxidizing potential (lower calculated oxygen partial pressure) will be forced to receive oxygen as a product of this reaction.

In a similar fashion the half reaction for ZrO_2 decomposition is $\text{ZrO}_2 (\text{c}) \rightarrow \text{Zr} (\text{c}) + \text{O}_2 (\text{g})$. In this case Coughlin⁽¹⁰⁾ reports that $\Delta F_{1300 \text{ F}} = 217.04 \text{ kcal per mole}$ or $\log K = -48.533$ where $K = \frac{a_{\text{Zr}} \cdot P_{\text{O}_2}}{a_{\text{ZrO}_2}}$.

Various conditions of interest can now be assumed, calculations performed, and results compared to determine the net oxidizing potential of each of these half reactions to the other.

From the results shown in Table A-4, it is evident that UO_2 is oxidizing to zirconium under all conditions considered in the table where the uranium reaction product is dissolved in the zirconium phase. The activity coefficients shown were estimated from the binary phase diagram by a rather crude procedure, but are believed to represent, approximately, the values in the ternary system uranium-zirconium-oxygen at the same atomic percentage composition. However, the estimating procedure is crude and does not justify further discussion at this time. Refinements and verification of the procedure will be made at some future time.

Kinetics

In considering any chemical reaction, once the existence of a positive driving force has been established by the use of thermodynamic principles, the question of kinetics then becomes of interest. The cases of reactions which take place in liquid or gas phases have been studied and treated extensively in the literature. However, the kinetics of reactions which take place between two solid phases have been inadequately studied. This is probably due not only to the inherent difficulties in solving the kinetic relationships involved but also to the lack of understanding of the phase relationships in solid systems in general.

In spite of this lack of coordinated methods for treating solid-solid reactions, the basic principles of kinetics can still be applied to achieve partial solutions. For example, consideration can be given to the three steps which must occur in sequence if a solid-solid reaction takes place. First, the reactants must diffuse to the point at which reaction occurs; second, chemical reaction must occur; and third, the products of the reaction must be removed, probably by diffusion, so that additional reaction can then take place. Any of these steps can be the rate-controlling one, if its rate is appreciably slower than that of the others. Or, if the rate for each step is approximately the same, they may all have appreciable influence on the over-all rate. Also, the relative influence of any step may increase or decrease with a change in temperature level. In any actual case, the rate-controlling step might be determined by comparing the experimental variation in rate with time and temperature.

TABLE A-3. FREE-ENERGY CHANGE OF THE REACTIONS

Reaction	Temperature K F	Standard Free-Energy Change,			
		298.16 77.1	500 440.4	1000 1340.4	1500 2240.4
1. $\text{Zr}(\alpha, \beta) + \text{UO}_2(\text{c}) \rightarrow \text{ZrO}_2(\alpha, \beta) + \text{U}(\alpha, \beta, \gamma, \ell)$		-1.15	-0.25	+2.05	+3.85
2. $\text{Zr}(\alpha, \beta) + 2\text{UO}_2(\text{c}) \rightarrow \text{ZrO}_2(\alpha, \beta) + 2\text{UO}(\text{c})$		-0.55	-2.05	+0.15	+3.55
3. $\text{Zr}(\alpha, \beta) + 2\text{UO}(\text{c}) \rightarrow \text{ZrO}_2(\alpha, \beta) + 2\text{U}(\alpha, \beta, \gamma, \ell)$		-1.80	+1.50	+3.90	+4.10
4. $\text{Zr}(\alpha, \beta) + 2\text{UO}_3(\text{hex}) \rightarrow \text{ZrO}_2(\alpha, \beta) + 2\text{UO}_2(\text{c})$		-195.95	-194.85	-191.25	-188.50
5. $\text{Zr}(\alpha, \beta) + 6\text{UO}_3(\text{hex}) \rightarrow \text{ZrO}_2(\alpha, \beta) + 2\text{U}_3\text{O}_8(\text{c})$		-220.75	-220.25	-216.10	-213.50
6. $\text{Zr}(\alpha, \beta) + \text{U}_3\text{O}_8(\text{c}) \rightarrow \text{ZrO}_2(\alpha, \beta) + 3\text{UO}_2(\text{c})$		-183.60	-182.20	-178.90	-176.00
7. $5\text{UO}_2(\text{c}) \rightarrow 2\text{UO}(\text{c}) + \text{U}_3\text{O}_8(\text{c})$		+183.00	+180.10	+179.00	+179.00
8. $2\text{UO}_2(\text{c}) \rightarrow \text{UO}(\text{c}) + \text{UO}_3(\text{hex})$		+97.70	+96.40	+95.70	+96.00

(a) Assuming complete miscibility and ideal solid-solution behavior of the oxides from the products and reactants.

OF THE URANIUM OXIDES WITH ZIRCONIUM

kcal 2000 3140.4	Uncertainty, kcal		Equilibrium Conversion(a), per cent				
	Probable	Maximum	298.16	500	1000	1500	2000 K 3140.4 F
+4.50	±0.75	±0.95	88	56	26	22	24
+7.50	±7.10	±11.65	75	84	66	53	47
+1.50	±7.10	±10.25	88	27	20	29	48
-188.10	±7.10	±11.65	>99.999	>99.999	>99.999	>99.999	>99.999
-218.50	±13.20	±37.25	>99.999	>99.999	>99.999	>99.999	>99.999
-172.90	±3.8	±5.85	>99.999	>99.999	>99.999	>99.999	>99.999
+180.40	±7.2	±17.0	<0.001	<0.001	<0.001	<0.001	<0.001
+97.80	±7.1	±11.4	<0.001	<0.001	<0.001	<0.001	<0.001

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TABLE A-4. OXIDIZING POTENTIALS AT 1300 F

Decomposition Reaction	Assumed Conditions	P_{O_2} , atmospheres
UO_2	Ideal conditions - $a_{UO_2} = 1$, $a_U = 1$	1.07×10^{-49}
UO_2	Ideal solid solution of U in Zr phase, 0.01% reacted - $a_{UO_2} = 1$, $a_U = 0.0001$	1.07×10^{-45}
UO_2	Ideal solid solution of U in Zr phase, 10% reacted - $a_{UO_2} = 1$, $a_U = 0.10$	1.07×10^{-48}
UO_2	Ideal solid solution of U in Zr phase, 30% reacted - $a_{UO_2} = 1$, $a_U = 0.30$	3.56×10^{-49}
UO_2	Estimated solid solution of U in Zr phase, 30% reacted - $a_{UO_2} = 1$, $\gamma_U = 0.57$, $a_U = 0.171$	6.25×10^{-49}
ZrO_2	Ideal conditions - $a_{ZrO_2} = 1$, $a_{Zr} = 1$	2.93×10^{-49}
ZrO_2	Estimated solid solution of U in Zr phase, 30% reacted - $a_{ZrO_2} = 1$, $\gamma_{Zr} = 1.47$, $a_{Zr} = 1.03$	2.84×10^{-49}

CONFIDENTIAL

When the speed of the over-all rate in a chemical reaction is determined by the actual interaction of the reacting species themselves, the speed is said to be reaction-rate controlled. In the case of a solid-solid reaction, the over-all rate would be independent of time for the reaction-rate-controlled case. That is to say, the diffusion rates of the products and reactants are sufficiently rapid in comparison with the over-all rate that the driving force for reaction is essentially constant and results in a constant rate at any given temperature. However, for this type of controlling mechanism the increase in rate with increasing temperature is extremely rapid. The rapidity of increase depends upon the energy required to activate the molecules for reaction. The usual form of a rate equation for a reaction-rate-controlling mechanism would be

where

r	= rate of reaction
A	= constant
E*	= activation energy for reaction
R	= gas constant
T	= absolute temperature.

Diffusion Controlling

Diffusion in a solid occurs in much the same manner as gaseous and liquid diffusion except that practically no steady-state cases occur in solid diffusion. This means that over-all rates that are diffusion controlled vary with time as well as with temperature and concentration. As a means of confirming this, Jost⁽¹⁵⁾ gives Fick's second law of diffusion, assuming that D , the coefficient of diffusion, is constant, as:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} .$$

This equation can also be derived and written in terms of the activities as

$$\frac{\partial a}{\partial t} = D \frac{\partial^2 a}{\partial x^2},$$

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A number of solutions of this differential equation are possible for various assumed conditions and many of the cases are treated by Jost⁽¹⁵⁾ and others. Solutions for the case of one-dimensional diffusion into an infinite solid show that x_m , the maximum penetration distance of the diffusing species, is proportional to $t^{1/2}$.

The coefficient of diffusion, D , for solids varies with the absolute temperature as $D = A \exp - \frac{Q}{RT}$ where Q = activation energy for diffusion.

It is apparent that the expected variation in reaction rate of a solid-solid reaction with temperature would be about the same for the reaction-rate- and diffusion-controlled cases. The absolute variation, of course, would depend upon the relative values of the activation energies in the two cases. However, for the diffusion-controlled case, the dependence of the rate upon time would be evident.

CONFIDENTIAL

APPENDIX B

MATERIALSProduction of Zirconium Powder

Conversion of the crystal-bar zirconium to powder for the powder-compact experiments was accomplished as follows:

- (1) The crystal bar was pickled in 50 per cent HNO_3 to which about 60 g per liter of ammonium bifluoride was added
- (2) The metal was dried and then hydrided, using hydrogen produced by the decomposition of UH_3
- (3) The hydrided metal was crushed with a diamond mortar and pestle in a dry box filled with argon
- (4) The crushed hydride was sieved in the dry box. The minus 60 plus 100-mesh material was separated for use
- (5) The hydride was decomposed by heating in a vacuum at 825 C, yielding zirconium-metal powder, slightly sintered
- (6) The sintered powder again was crushed and sieved in the dry box and stored in small batches in argon-filled desiccators until used.

Impurities in a typical batch of zirconium powder and in a sample of arc-melted and rolled rod are shown in Table B-1. With the exception of iron, which appears slightly high, all of the impurities are at a nominally low level.

Uranium Oxide

Five principal types of uranium oxides were used during the course of this work.

- (1) Initial experiments were carried out with black calcined UO_2 heated in vacuum 1 hr at 800 C to remove adsorbed gases and moisture

TABLE B-1. TYPICAL COMPOSITIONS OF ZIRCONIUM^(a)

Element	Zirconium Powder, ppm	Arc-Melted and Rolled Rod, ppm
Iron	500	100-1000
Oxygen ^(b)	300	320
Nickel	100	5-50
Carbon ^(c)	70	-
Nitrogen ^(d)	70	30
Hydrogen ^(b)	50	50
Chromium	40	60-600
Silicon	30	< 20
Aluminum	20	< 50
Molybdenum	20	ND ^(e)
Copper	< 10	10-100
Lead	< 10	ND
Manganese	2	< 10
Hafnium	ND	ND
Boron	ND	ND
Magnesium	ND	< 10
Tin	ND	ND
Calcium	ND	< 10

(a) By spectrographic method unless otherwise indicated.

(b) Vacuum-fusion method.

(c) Combustion method.

(d) Kjeldahl method.

(e) ND = not detected.

- (2) Later, chocolate-brown UO_2 was used as received from the Mallinckrodt Chemical Works (MCW)
- (3) To further improve the material, MCW UO_2 was heated in hydrogen at 900 C for 20 hr to a dewpoint of -60 C to remove excess oxygen
- (4) Other MCW UO_2 was pressed into bars and fired at 3750 F in hydrogen; this material then was crushed and sized in an argon-filled dry box
- (5) Finally, fused oxide was produced by arc melting pressed MCW UO_2 , using an inert tungsten electrode in a water-cooled copper crucible.

Gravimetric Determination of Oxygen in Uranium Dioxide

The oxygen contents of the various types of UO_2 were determined by a gravimetric method. In this method, the UO_2 was burned in oxygen to an oxidation state of U_3O_8 . The water driven off during burning was absorbed and weighed. Weights of the oxide before and after burning, compensated for the weight of water, permitted the determination of the oxide composition. The reproducibility of the results indicated the good precision of the method, e.g., $\text{UO}_{2.000} \pm 0.004$. The method is more completely described in MDDC-1435(16).

Some check analyses were made with a volumetric method of analysis. In this method a known excess of ceric sulfate was employed as a combined dissolving and oxidizing agent for the UO_2 . The excess ceric sulfate was determined by back titrating with ferrous sulfate. This method also is described in detail in MDDC-1435.

Analyses on a sample of Mallinckrodt UO_2 by both methods showed little difference in results. However, the gravimetric method had the advantage of also giving an estimate of the moisture contents of the oxides and, therefore, was adopted for all of the analyses for oxygen in the UO_2 .

Data on the oxygen contents of the several grades of UO_2 as determined by the gravimetric method are listed in Table B-2. Fused UO_2 was found to be very nearly stoichiometric in composition as also were the hydrogen-reduced UO_2 and the oxide pressed and sintered at 3750 F in hydrogen.

TABLE B-2. COMPOSITION OF SEVERAL TYPES OF URANIUM OXIDE

Type	Color	Moisture, w/o	Oxygen-Uranium Ratio	Phases Detected by X-Ray Diffraction
Calcined	Black	-	2.100	UO ₂ and U ₃ O ₈
MCW, as received	Chocolate	0.07	2.022	UO ₂
MCW, hydrogen reduced to -60 C dewpoint	Rusty red	0.04	2.004	UO ₂
MCW, pressed and sintered in hydrogen at 3750 F	Dark red	<0.01	2.004	UO ₂
MCW, fused in arc	Reddish brown	<0.01	2.001	UO ₂

Production of Fused UO₂

In an effort to produce a stoichiometric product of high density, a number of batches of UO₂ were fused by means of an inert tungsten electrode under argon at a 1-atmosphere pressure. Some of the charge of pressed wafers of minus 325-mesh MCW UO₂ was contained in the water-cooled copper crucible. Additional UO₂ was fed into the crucible as melting progressed. The electrode was struck to the copper crucible. Melting, accomplished at about 40 v and 800 amp, was accompanied by a considerable amount of volatilization of UO₂, which tended to snuff out the arc. Thus, the arc could usually be maintained for only about 30 sec before it was extinguished. Because of this, the size of each fused batch was limited to about 100 g. Techniques were later developed to produce batches as large as 3000 g by reducing the current to about 300 to 400 amp at 45 v. These techniques are described in another report⁽¹⁷⁾.

The fused UO₂ was carefully hand sorted and only about 25 to 50 per cent of the batch product was found to be usable. The remainder had to be discarded because it was only partially fused or contained obvious metallic contamination. The useful fused oxide was crushed to minus 200-mesh size by means of a diamond mortar in an argon-filled dry box. The minus 200-mesh powder also was separated into various finer sieve fractions and stored in separate containers in an argon-filled desiccator until used.

The arc-melted UO₂ was analyzed by spectrographic means. The impurities are listed in Table B-3. The high tungsten content, 6900 ppm, probably was introduced from the tungsten electrode when striking the arc on the copper crucible. This may account also for the 150 ppm of copper found.

TABLE B-3. SPECTROGRAPHIC ANALYSIS
OF FUSED UO_2

Element	Amount, ppm
Tungsten	6900
Copper	150
Magnesium	100
Calcium	About 100
Iron	80
Aluminum	20
Lead	20
Nitrogen	< 20(a)
Silicon	< 20
Molybdenum	5
Boron	1
Beryllium	0.5
Manganese	0.5

(a) Kjeldahl analysis.

Petrographic Examination of Fused UO_2

Samples of the crushed, fused UO_2 powder were examined under the petrographic microscope. The internal structure was found to be dense, coarsely crystalline, and essentially free of porosity. Since UO_2 crystallizes in the isometric (cubic) system, it has only one refractive index. Its average index of refraction, $N = 2.34_{\text{Li}} \pm 0.01_{\text{Li}}$, was found using fused solid melts containing selenium and sulfur. This determination was made with the red-wave portion of transmitted white light because monochromatic yellow sodium-vapor light was absorbed in the dark-red embedding medium.

Some of the coarse crystals showed curved banded flow lines as found in pisolitic structures. Others exhibited conchoidal fracture outlines. The appearance of the crystals, expressed simply, was that of broken glass.

Powders produced from compacts sintered at 3750 F in hydrogen, closely resembled the fused oxide and had the same refractive index. However, individual crystals were more poorly formed and showed considerable pinpoint porosity. This porosity gave the appearance of small, discrete, spherical gas bubbles entrapped in a fluid.

In contrast to the above-described refractory oxide, the Mallinckrodt (MCW) UO_2 , as received, gave a refractive index between 2.27_{Li} and 2.30_{Li} .

This oxide appeared as clusters of small particles somewhat resembling hydrated alumina or hydrated UO_3 . It clearly exhibited a much greater ratio of surface area to volume than either of the high-temperature products.

Attempts to Produce Substoichiometric UO_2

An effort was made to produce uranium oxide of a composition lower in oxygen than UO_2 . It was thought that by use of the substoichiometric oxide the rate of reaction of zirconium with uranium oxide might be decreased. Also, it was hoped to gain further knowledge of the stability of uranium-oxygen compounds as a function of oxygen content in the region of UO_2 . As an approach to the problem, attempts were made to produce uranium monoxide, UO . Intimate mixtures of uranium chips with UO_2 powder in the ratio for UO were reacted by heating compacted mixtures at temperatures between 650 and 950 C for times up to about 500 hr. No UO was detected. Other experiments were performed in which a mixture of uranium chips and UO_2 powder in the ratio for UO was pressed and then arc melted in a partial pressure of helium. The resulting ingot again showed evidence of only uranium and UO_2 . Samples from this ingot also were heat treated at a number of temperatures from 650 to 1600 C but no UO was produced. The only evidence of UO obtained in this work was that a very thin surface film of a material identified as UO by X-ray diffraction was formed on massive uranium that was heated in a vacuum of the order of 10^{-3} to 10^{-4} mm of mercury. Since no massive UO was produced, work with substoichiometric UO_2 was abandoned.

APPENDIX C

PROCEDUREReaction of Solid Zirconium Cylinders With UO_2 Powder

Initial experiments were performed in which arc-melted and rolled crystal-bar zirconium specimens, each about 3/8 in. in diameter and 1-1/2 in. long, were packed in UO_2 powder retained by an Alundum thimble and heated in a Vycor reaction tube either in vacuum or argon. A resistance-wound furnace was used to heat the specimens. The temperature of reaction was measured by means of a platinum-platinum 10 per cent rhodium thermocouple spot welded to one end of the zirconium cylinder. After the reaction had proceeded for the desired period of time, the furnace was removed and a beaker of cold water was placed around the reaction tube to cool the specimen rapidly. The extent of the reaction was estimated by microscopic examination and hardness traverses of a cross section of the specimen. An oxygen analysis also was obtained on a slice of the cross section to determine the transfer of oxygen from the UO_2 to the zirconium during reaction.

Compacted-Powder Mixtures

Intimate mixtures of zirconium and UO_2 powders were compacted at about 100,000 psi. The compacts were heated in vacuum for predetermined times at temperatures of interest. The UO_2 powder then was separated from the zirconium powder and the extent of the reaction was determined by analysis of the zirconium-powder residue for oxygen and uranium. The greatest difficulty in the method was to obtain a clean separation of the zirconium from the UO_2 powder.

Preliminary experiments indicated that a ratio of 1 part of zirconium powder to 4 parts of UO_2 powder (by weight) was required to insure that all of the zirconium particles would be surrounded by UO_2 . The zirconium powder used was minus 70 plus 80-mesh size (0.177 to 0.210-mm screen opening). The UO_2 powder was minus 230 plus 270-mesh size (0.053 to 0.062-mm screen opening). The constituent powders were weighed using about 1/2 g of zirconium and about 2 g of UO_2 for each compact. After mixing thoroughly by hand, the powders were pressed and the compact was expelled directly from the 1/2-in.-diameter die into small individual preweighed Vycor cups. A group of three mixed compacts together with unpressed samples of the zirconium and UO_2 powders constituted the charge for a run.

The cups containing the compacts and unpressed powders were loaded into a Vycor reaction tube. The tube was attached vertically to a vacuum-pumping system by means of Apiezon W wax. The system was evacuated to a pressure of 10^{-5} to 10^{-6} mm of mercury. The reaction tube then was heated by means of a resistance-wound furnace. The reaction temperature was measured by means of a platinum-platinum 10 per cent rhodium thermocouple positioned adjacent to the cups inside the reaction tube. Temperature was controlled to about ± 5 F by means of a controller which operated on a maximum-minimum basis.

After reaction, the furnace was removed and the reaction tube was cooled rapidly by a blast of cool air. The zirconium was separated from the UO_2 in two compacts and analyzed for uranium and oxygen to determine the extent of the reaction. The entire zirconium residue from one compact constituted a single sample. The third compact was examined under the microscope. The zirconium control powder also was analyzed for oxygen to determine the effect of extraneous factors on the course of the experiment.

Method of Powder Separation

Initially, the reacted compacts were boiled in 40 per cent nitric acid for 45 min to dissolve the UO_2 . The residue was filtered on a weighed filtering crucible, washed with hot 40 per cent nitric acid and hot water, and dried overnight in an oven in air at 250 F. After cooling, the crucible containing the dry residue was weighed. Separate portions of the residue then were analyzed for oxygen and uranium.

Oxygen and uranium analyses of these residues showed only about half the uranium that would be expected from the oxygen analyses, assuming that oxygen and uranium enter the zirconium in the ratio for UO_2 . Tests with sandwich-type elements indicated that free uranium was one of the phases in the reaction layer formed at the metal- UO_2 interface during reaction, and that some of this phase was lost during leaching in the 40 per cent nitric acid.

In an attempt to minimize dissolution of products of the zirconium- UO_2 reaction, a combination mechanical-chemical powder-separation method was used. The reacted compacts were broken apart by lightly treating with a mortar and pestle. The resultant powder mixture was sieved on a 100- or 120-mesh screen to roughly separate the zirconium from the UO_2 . The coarse 70 to 100-mesh zirconium-rich particles were retained on the screen while the finer 230 to 270-mesh UO_2 particles fell through the screen. The zirconium powder was leached lightly with hot 10 per cent nitric acid for several 5-min intervals to remove the adherent UO_2 . It was filtered on a weighed filtering crucible, washed with hot 10 per cent nitric acid and hot

water, and dried for about 1 hr in a vacuum* at about 250 F. The crucible was cooled in the vacuum and portions of the residue were analyzed for oxygen and uranium.

In order to evaluate this new method of separation, a compacted-powder mixture, heated for 234 hr at 1517 F, was separated by the mechanical-chemical method, and dried. This zirconium-rich residue was divided into four samples each weighing 0.100 g. Each sample was leached consecutively for a number of time increments in one of four concentrations of boiling nitric acid. Uranium analyses were obtained on the solutions from these leachings after each incremental treatment. These results are shown in Table C-1.

TABLE C-1. URANIUM DISSOLVED FROM ZIRCONIUM-RICH POWDER RESIDUES BY LEACHING IN SEVERAL CONCENTRATIONS OF BOILING NITRIC ACID

Nitric Acid Concentration, volume per cent	Mg per 100 Mg of Uranium Dissolved in Consecutive Indicated Time Increment, min				
	5	10	15	20	Total Time 50
10	2.6	1.5	2.2	2.4	8.7
20	4.7	3.2	3.6	5.0	16.5
30	7.2	4.5	5.0	4.2	20.9
40	9.9	7.6	5.0	0.1	22.6

These data clearly show that substantially all of the uranium-rich phase was dissolved in about 30 min in the 40 per cent HNO_3 solution. On the other hand, only 10 to 20 per cent of the uranium-rich phase was dissolved in the 5 to 10-min increment used in the modified method of powder separation.

Analysis for Uranium in Zirconium

The zirconium-powder residues were analyzed for uranium by the fluorescence method. The sample was dissolved in a reagent composed of dilute nitric acid with hydrofluoric acid added. After solution was complete, the resulting solution was diluted to a known volume with 10 per cent nitric

*Duplicate samples air and vacuum dried showed consistently lower oxygen contents when vacuum dried. This was assumed to indicate a pickup of oxygen in air drying.

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68

acid. This volume and the volume of subsequent dilutions, as well as sample size, depended on the composition of the alloy.

The determination of uranium was completed by a conventional fluorescence method, details of which are described by Center⁽¹⁸⁾.

Analysis for Oxygen in Zirconium

Zirconium-rich powder residues were analyzed for oxygen by a previously developed vacuum-fusion technique. The 0.10-g sample was weighed on a balance and wrapped in cp tin foil. It was placed in the vacuum-fusion apparatus and the system containing the specimen was pumped for about 16 hr. The analysis was carried out by dropping the sample onto a bed of graphite chips contained in a graphite crucible at 1200 C. Prior to the analysis, the chips and crucible were degassed at 2300 C. After dropping the sample, the temperature was raised to 2100 C and the gas evolved from the sample collected until the blank rate was restored. The collected gas was analyzed for carbon monoxide and hydrogen by the low-pressure fractional-freezing method. The oxygen content was calculated from the amount of CO formed. The same technique was used to analyze the chip samples obtained from the large sandwich-type element.

Sandwich-Type Elements

Sandwich-type elements were used to study the reaction of a high-fired UO_2 core with its zirconium jacket to simulate operating conditions of the reactor. Ground UO_2 rods, 3/8 in. in diameter, were cut into 1-in. lengths. The density of these rods was about 88 per cent of the theoretical density of UO_2 . The cut ends were faced flat by hand through 600-grit silicon carbide papers.

Arc-melted crystal-bar zirconium was rolled to 1/2-in.-diameter rod. The rod was machined to a 0.470-in. OD and bored to 3/8-in.-ID tube and the tube was cut into 1-1/2-in. sections. A 1/4-in.-thick end plug was welded into one end of each tube section. After testing the closure for leaks, the UO_2 cores were fitted into the zirconium jackets and the second 1/4-in. end plug was inserted and welded in place in a helium-filled tank. Similar elements with Zircaloy 2 jackets were prepared by similar techniques.

Sandwich-type elements were heated in autoclaves at a 5000-psi helium pressure (to insure that contact existed between core and jacket over a large fraction of the surface) at 950, 1100, and 1300 F for various periods of time. After reaction, the autoclaves were slowly cooled to room temperature in about 16 hr. Quenching of the sandwiches was desirable, but could

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69 69 and 70

not be attained in the autoclave. The extent of the reaction was estimated by metallographic examination and hardness traverses on cut sections of the elements. Knoop hardness traverses were made to estimate the extent of oxygen penetration as a function of time at reaction temperature. Phases appearing in the vicinity of the zirconium- UO_2 interface in the slow-cooled samples were identified by means of X-ray diffraction techniques.

Slightly modified elements were made to study the reaction between zirconium and UO_2 at 2000 F. These comprised UO_2 cores, 3/8 in. in diameter and 1/4 in. thick in jackets with 1/8-in. walls and 1/4-in. end plugs.

The experiments at 2000 F were performed by inserting a group of three elements in a graphite die. By means of a graphite plunger and a lever arm, the elements were dead loaded at 2000 psi. Tank argon was bled into the Globar-heated furnace chamber. Temperature was controlled within the die to ± 10 F. After the experiment had continued for the desired period of time, the specimens were allowed to cool slowly to room temperature. A quench was desirable but could not be effected in the available equipment. By inserting a new specimen for each short-time experiment and reheating two of the originally charged specimens, reaction data could be obtained for several time intervals with a minimum number of experiments.

Four large sandwich-type elements also were used to obtain data on the kinetics of the reaction. These elements contained high-fired (3250 F in hydrogen) UO_2 cores 3/8 in. thick and 1-1/2 in. in diameter. These were enclosed in jackets with 1/8-in. walls and a 1/4-in.-thick bottom machined from a 2-in.-diameter arc-melted ingot. Closure was made by inserting two 1/4-in.-thick zirconium disks into the jacket on top of the UO_2 disk and welding the top disk to the jacket walls in a helium-filled chamber. These sandwich-type elements were heated in the autoclaves at several temperatures along with the smaller zirconium and Zircaloy 2 disks.

One of these large elements was analyzed after heating for 37 days at 1300 F. The jacket was cut open radially and most of the brittle UO_2 chipped out. The bottom of the zirconium jacket was accurately aligned in a lathe and the side walls were turned off. This left the part of the jacket bottom which had been in contact with UO_2 . After removing the adherent UO_2 with a thin cleaning cut, chip samples of the metal were removed at 0.001-in. increments. Adjacent cuts were analyzed for oxygen and uranium and the data were used to determine the depth and extent of transfer of these elements into the zirconium. Metallographic examination and a hardness traverse were made from the zirconium disk in contact with the opposite face of the UO_2 . These data were correlated with the results of analyses obtained on the chip samples.

MWM:AFG:AWL:DLC/pa:mm

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