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**PHASE RELATIONS IN THE URANIUM-ZIRCONIUM-OXYGEN
SYSTEMS INVOLVING ZIRCONIUM AND URANIUM DIOXIDE**

by

Henry A. Saller
Frank A. Rough
Joseph M. Fackelmann
Arthur A. Bauer
J. Robert Doig

July 28, 1955

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PHASE RELATIONS IN THE URANIUM-ZIRCONIUM-OXYGEN SYSTEMS INVOLVING ZIRCONIUM AND URANIUM DIOXIDE

Henry A. Saller, Frank A. Rough, Joseph M. Fackelmann,
Arthur A. Bauer, and J. Robert Doig

A portion of the uranium-zirconium-oxygen system, including uranium dioxide and zirconium and related phase regions, has been studied at 1000, 1300, and 2000 F. Tentative isothermal sections have been established for each of these temperatures.

A two-phase region occurs between uranium dioxide and alpha zirconium solid solution at 1000, 1300, and 2000 F. Alpha zirconium contains about 28 a/o oxygen and probably about 1 a/o uranium when saturated with the two elements. Little zirconium is directly soluble in uranium dioxide, but large amounts of zirconium dioxide are soluble.

INTRODUCTION

Since zirconium might be used in contact with uranium dioxide, it is of interest to determine the phase relationships in this metal-oxide system at various temperatures. As is generally true in working on alloys across a ternary system, it was necessary to develop an understanding of various related phase regions at other compositions in order to evaluate the part of the system between uranium dioxide and zirconium. Fortunately, since the reported study was a brief one, there was already a great deal of information available. The binary systems zirconium-uranium⁽¹⁾, uranium-oxygen^(1, 2), and zirconium-oxygen^(3, 4) have been studied extensively. In addition, the quasi binary between uranium dioxide and zirconium dioxide has been determined⁽⁵⁾. With this information as a background, work was begun.

EXPERIMENTAL PROCEDURES

Preparation of Alloys

A series of alloys containing up to 95 w/o uranium dioxide was first prepared by arc melting Grade 1 crystal bar zirconium and fused uranium dioxide. The alloys containing up to 85 w/o uranium dioxide (Alloys 1 to 10 in Table 1) were sufficiently homogeneous for this program, but the others were not.

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A second series of alloys, transverse to the first series, was prepared. A master alloy (Alloy 14 in Table 1) was first prepared by arc melting Grade 1 crystal bar zirconium, fused uranium dioxide, and fused zirconium dioxide. Alloys 11, 12, and 13 of Table 1 were then prepared by arc melting appropriate amounts of uranium and the master alloy.

All of these arc-melted alloys were melted under a gettered helium atmosphere in a water-cooled copper crucible. The buttons were turned and remelted several times to make them homogeneous. The size of the ingots was kept small to make the melting easier.

Alloys up to 28.8 w/o uranium dioxide were analyzed for uranium, and for oxygen and hydrogen. The results are given in Table 1. The analyses are in good agreement with the nominal compositions, although the oxygen analyses tended to vary. No further analysis was made on alloys, since only small ingots were prepared, and nominal analyses appeared to be adequate for the immediate program. The relatively high values for hydrogen are probably due to the uranium dioxide which was fused in a hydrogen atmosphere.

Additional alloys (Alloys 15 to 19 in Table 1), containing 85 to 97 w/o uranium dioxide, were prepared by powder-metallurgy techniques. These alloys were made by mixing zirconium hydride and crushed, fused uranium dioxide. The mixed powders were compacted hydrostatically at a pressure of 100,000 psi. The green compacts were vacuum outgassed at 1300 F and sintered 1 hr at 3600 F at a pressure of 10^{-4} mm of mercury or lower. A part of one alloy, Alloy 15, was resintered 1-1/2 hr at 3900 F, but the microstructure was essentially unchanged, indicating that sintering at 3600 F was adequate.

Heat Treating

All heat treating was done in dynamic vacuum of 10^{-4} mm of mercury or better, except for one heat treatment. Samples of two alloys were heat treated for 1000 hr at 1300 F. This long-time treatment was done by sealing in Vycor with a helium atmosphere. The Vycor tube was broken to quench the samples.

Metallography

Alloys containing up to 80 w/o uranium dioxide were polished mechanically with stannic oxide on a wheel covered with Forstmann's

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TABLE 1. ALLOY COMPOSITIONS AND ANALYSES

Alloy	Nominal Composition, w/o	Analysis, w/o			Remarks
		Uranium	Oxygen	Hydrogen	
1	5.6UO ₂	5.7	0.54-0.84(a)	0.010	Arc melted
2	9.9UO ₂	8.7	1.2	0.0072	Arc melted
3	19.3UO ₂	17.4	2.4	0.005-0.013(a)	Arc melted
4	28.8UO ₂	25.1	3.2-4.1(a)	0.003-0.004(a)	Arc melted
5	43.0UO ₂				Arc melted
6	58.7UO ₂				Arc melted
7	68.9UO ₂				Arc melted
8	74.0UO ₂				Arc melted
9	79.2 and 80.0UO ₂				Arc melted
10	84.4UO ₂				Arc melted
11	28.1Zr, 67.2U, 4.7 O				Arc melted
12	34.9Zr, 59.3U, 5.8 O				Arc melted
13	47.7Zr, 44.4U, 7.9 O				Arc melted
14	61.0Zr, 28.8U, 10.2 O				Arc melted
15	85.0UO ₂				Prepared by powder metallurgy
16	90.0UO ₂				Prepared by powder metallurgy
17	92.5UO ₂				Prepared by powder metallurgy
18	95.0UO ₂				Prepared by powder metallurgy
19	97.0UO ₂				Prepared by powder metallurgy

(a) Duplicate samples.

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cloth. These alloys were etched with a mixture of acids which varied from 50 cm³ lactic, 50 cm³ nitric, and 5 drops hydrofluoric to 30 cm³ lactic, 50 cm³ nitric, and 5 drops hydrofluoric.

Alloys containing more than 80 w/o uranium dioxide were polished mechanically with diamond paste as the abrasive, again on a Forstmann's cloth. These alloys were etched electrolytically in a solution composed of 1 part chromic and 18 parts acetic acids. The samples were etched 1/2 to 2 min at 20 v.

X-Ray Diffraction

Samples were examined by X-ray diffraction in a variety of ways. Metallographic specimens were examined with the General Electric XRD-3 spectrometer unit with filtered copper radiation. Some unmounted specimens were examined in powder form in Debye cameras after crushing in glass or diamond mortars. These samples were especially suitable for examination of the oxide phase. Samples of high uranium dioxide content were also examined after etching for a long time in concentrated nitric acid. This treatment dissolved the uranium dioxide and made it possible to obtain alpha zirconium and alpha uranium patterns free of mechanical strains. It is likely that the nitric acid dissolved some of the alpha uranium, since that pattern was sometimes no stronger in the etched sample than in the crushed sample.

Some samples of low uranium dioxide content were prepared by etching into slivers. This preparation was especially useful in the identification of the uranium-zirconium epsilon phase, which is hard to identify when cold worked. The etching solution for the preparation of slivers was 50 parts nitric, about 20 parts hydrofluoric, and sufficient water to prevent deposition of green salts on the sliver.

RESULTS

Isothermal sections of a part of the uranium-zirconium-oxygen system for temperatures of 1000, 1300, and 2000 F are shown in Figures 1, 2, and 3. These diagrams are based on a study of alloys having compositions plotted on the diagrams and on existing data for the systems zirconium-uranium⁽¹⁾, uranium-oxygen^(1, 2), zirconium-oxygen^(3, 4), and UO₂-ZrO₂⁽⁵⁾.

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FIGURE 1. TENTATIVE ZIRCONIUM-URANIUM-OXYGEN TERNARY SECTION AT 1000 F

A-15484

FIGURE 2. TENTATIVE ZIRCONIUM-URANIUM-OXYGEN TERNARY SECTION AT 1300 F

FIG. 2 1708 A-15485

A-15485

FIG 3 1708 A-15486

FIGURE 3. TENTATIVE ZIRCONIUM-URANIUM-OXYGEN TERNARY SECTION AT 2000 F A-15486

In order to best present the data relating to the isothermal sections, the presentation is broken down according to the composition ranges studied: zirconium-rich alloys, intermediate alloys, and UO_2 -rich alloys.

The compositions of the alloys studied, and the analyses, where available, are given in Table 1. The alloy number of Table 1 corresponds with the numbers given on the isothermal sections shown in Figures 1, 2, and 3.

Zirconium-Rich Alloys

The as-cast structures of zirconium-rich Alloys 1, 2, 3, and 4, containing 5.6 to 28.8 w/o uranium dioxide, are shown in Figures 4 to 7. The alloys up to 19.3 w/o UO_2 were largely beta which transformed to alpha zirconium during cooling. In the 28.8 w/o UO_2 alloy (Figure 7), the alpha phase was stabilized by the oxygen and was present as the principal phase at all temperatures. Inverse-rate thermal analyses indicated that a small amount of second phase present in these alloys was transforming during heating and cooling. In Alloys 1, 2, and 3, Figure 1, the transformation occurred at about 580 to 600 C on heating and was suppressed to around 550 C on cooling. This transformation corresponds well with the beta-to-epsilon transition of zirconium-uranium binary alloys⁽¹⁾ (epsilon is sometimes designated as delta). In Alloy 4 (28.8 w/o UO_2), and higher, thermal analyses indicated that transformation of the second phase occurred at higher temperatures which correspond with a uranium-rich transformation.

X-ray diffraction data from samples of Alloys 1, 2, and 3, after furnace cooling from 1000 F, indicated that these samples contained alpha zirconium solid solution, and epsilon phase. These and other X-ray data on Alloys 1, 2, 3, and 4 are summarized in Table 2. It is apparent that Alloy 3 (19.3 w/o UO_2) treated at 1300 F was in the $\alpha_{\text{Zr}} + (\beta_{\text{Zr}} - \gamma_{\text{U}})$ field, as shown in Figure 2. Alloy 4 (28.8 w/o UO_2) was in the $\alpha_{\text{Zr}} + \gamma_{\text{U}}$, or $\alpha_{\text{Zr}} + \gamma_{\text{U}} + \text{UO}_2$ field according to these X-ray data, but metallographic inspection did not reveal any UO_2 . Alloy 4 is shown in the $\alpha_{\text{Zr}} + \gamma_{\text{U}}$ field in Figure 2.

At 2000 F, Alloys 1, 2, 3, and 4 were all in the $\alpha_{\text{Zr}} + (\beta_{\text{Zr}} - \gamma_{\text{U}})$ region. As indicated in Table 2, beta ($\beta_{\text{Zr}} - \gamma_{\text{U}}$) was not retained by quenching Alloys 1 and 2 from 2000 F, but transformed largely to epsilon.

The beta ($\beta_{\text{Zr}} - \gamma_{\text{U}}$) tended to be retained in Alloys 3 and 4, but some transformation probably occurred. Since the composition of beta is shifting with the UO_2 content in this region, varying stability of the beta ($\beta_{\text{Zr}} - \gamma_{\text{U}}$) phase is to be expected during quenching. The microstructures of

250X

N18532

FIGURE 4. ZIRCONIUM-5.6 w/o UO_2 ALLOY

As Arc Melted

250X

N18533

FIGURE 5. ZIRCONIUM-9.9 w/o UO_2 ALLOY

As Arc Melted

250X

N18534

FIGURE 6. ZIRCONIUM-19.3 w/o UO_2 ALLOY

As Arc Melted

250X

N18535

FIGURE 7. ZIRCONIUM-28.8 w/o UO_2 ALLOY

As Arc Melted

TABLE 2. PHASE IDENTIFICATION IN ZIRCONIUM ALLOYS CONTAINING UP TO 28.8 w/o UO_2

Alloy	Nominal UO_2 , w/o	Heat Treatment	Sample Preparation	Method of Examination	Pattern Intensities ^(a)					Unknowns		
					UO_2	α_{Zr}	α_{U}	β_{Zr}	ϵ_{UZr}	X	Y	Others
1	5.6	1000 F, F.C.	Sliver	Debye camera	-	S	-	-	S	-	-	F
2	9.9	1000 F, F.C.	Sliver	Debye camera	-	S	-	-	MF	-	-	-
3	19.3	1000 F, F.C.	Sliver	Debye camera	-	S	-	-	S	-	-	-
3	19.3	240 hr, 1300 F, W.Q.	Sliver	Debye camera	-	S	-	F	-	-	-	-
4	28.8	240 hr, 1300 F, W.Q.	Crushed	Debye camera	F	S	MF	-	-	-	-	-
1	5.6	24 hr, 2000 F, W.Q.	Metallographic	Spectrometer	?	MS	-	?	MF	-	-	VVF
2	9.9	24 hr, 2000 F, W.Q.	Metallographic	Spectrometer	?	MS	-	?	M	-	-	VVF
3	19.3	24 hr, 2000 F, W.Q.	Metallographic	Spectrometer	-	S	-	M or	M	-	-	VVF
4	28.8	24 hr, 2000 F, W.Q.	Metallographic	Spectrometer	-	MS	VF	F+ or	F+	-	-	-

- (a) S = strong
M = medium
F = faint
V = very
? = identification questionable.

Alloys 1, 2, 3, and 4 quenched from 2000 F are shown in Figures 8 to 11. These specimens were etched to show the phase distribution that existed before quenching rather than the transformation effects. In the alloys up to 19.3 w/o UO_2 , Figures 8, 9, and 10, the phase which is distributed along former grain boundaries is alpha zirconium solid solution. This distribution is related to the transformed structures of the as-cast alloys shown in Figures 4, 5, and 6. In the 28.8 w/o UO_2 alloy quenched from 2000 F, Figure 11, the beta phase is distributed along the grain boundaries of the alpha which was stabilized by the oxygen.

No direct evidence of the $\alpha_{\text{U}} + \alpha_{\text{Zr}} + \epsilon$ region in the 1000 F section, or of the $\gamma_{2\text{U}} + (\gamma_{1\text{U}} - \beta_{\text{Zr}}) + \alpha_{\text{Zr}}$ region in the 1300 F section, has been obtained. These regions must be present, however, if the data for the system uranium-zirconium⁽¹⁾ and the data presented here are correct.

Additional information as to the nature of the zirconium-rich corner can be deduced from knowledge of the systems zirconium-oxygen and zirconium-uranium and from lattice constants determined during this investigation. Domagala⁽³⁾ has shown that 6.75 w/o oxygen (about 29 a/o) is soluble in alpha zirconium while only 0.8 w/o uranium (about 0.3 a/o) is soluble in alpha zirconium.

The lattice constants of the alpha zirconium in Alloys 9, 13, and 14 are given in Table 3 along with those of pure alpha zirconium⁽⁶⁾ and of oxygen-saturated zirconium⁽⁴⁾. If uranium is assumed to have no effect on the lattice constants and the lattice constant c_0 varies linearly with oxygen content, an approximate oxygen level can be calculated giving the results shown in Table 3. These data indicate that the oxygen content of alpha zirconium varies only slightly in going from the $\text{ZrO}_2 + \text{UO}_2 + \alpha_{\text{Zr}}$ region to the $\text{UO}_2 + (\gamma_{2\text{U}} - \beta_{\text{Zr}}) + \alpha_{\text{Zr}}$ region. The solubilities in alpha zirconium are essentially the same at 1000 F and 2000 F (Figures 1 and 3).

Additional data would be needed to give precise information on the solubilities of uranium and oxygen in the alpha zirconium ternary solid solution.

Intermediate Alloys

Discussion of the intermediate alloys includes data on Alloys 5 to 10 and 11 to 14, as plotted in Figure 2.

Samples of Alloys 5 to 10 were found to contain three phases at 1000 F, at 1300 F, and at 2000 F: a uranium-rich phase which varies according to the temperature, alpha zirconium, and uranium dioxide.

250X

N23776

FIGURE 8. ZIRCONIUM-5.6 w/o UO_2 ALLOY
Heat Treated 24 Hr at 2000 F and
Water Quenched

250X

N23777

FIGURE 9. ZIRCONIUM-9.9 w/o UO_2 ALLOY
Heat Treated 24 Hr at 2000 F and
Water Quenched

250X

N23778

FIGURE 10. ZIRCONIUM-19.9 w/o UO_2 ALLOY
Heat Treated 24 Hr at 2000 F and
Water Quenched

500X

N23779

FIGURE 11. ZIRCONIUM-28.8 w/o UO_2 ALLOY
Heat Treated 24 Hr at 2000 F and
Water Quenched

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TABLE 3. LATTICE CONSTANTS OF THE ALPHA ZIRCONIUM SOLID SOLUTION

Alloy	Nominal Composition, w/o			Heat Treatment	Lattice Constants, A		Estimated Oxygen in Solution,	Remarks
	Zirconium	Uranium	Oxygen		a_0	c_0	a/o	
--	100	--	--	--	3.23	5.145 ^(a)	--	Pure zirconium
--	93.0	--	7.0	--	3.24	5.20 ^(a)	--	Oxygen saturated
9	20.0	70.5	9.5	240 hr, 1300 F, W.Q.	3.243 ± 0.001	5.198 ± 0.001	~ 28	
13	47.7	44.4	7.9	16 hr, 1300 F, W.Q.	3.243 ± 0.001	5.196 ± 0.001	~ 27	
14	61.0	28.8	10.2	16 hr, 1300 F, W.Q.	3.242 ± 0.001	5.199 ± 0.001	~ 28.5	

(a) Reference (4).

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Microstructures of as-cast samples of these alloys are shown in Figures 12 to 17. The light-etching phase is alpha zirconium, and the gray material is uranium dioxide. Inverse-rate thermal analysis of Alloys 5, 6, 7, and 8 indicated that a small amount of material was transforming at about 695 to 750 C on heating, and between 650 and 670 C during cooling. This corresponds approximately to the gamma uranium ($\gamma_{\text{U}}-\beta_{\text{Zr}}$) solid solution transformation in uranium-rich alloys⁽¹⁾. Microstructures of the alloys quenched from 2000 F after 24 hr revealed that a third phase was present. The three phases can best be distinguished in Alloy 5, which contains 43.0 w/o UO_2 (Figure 18), but were present in the entire series. The gray phase in Figure 2 is the oxide, the minor light-etching phase is uranium rich, and the balance is alpha zirconium solid solution. The uranium-rich phase, not readily visible in Figures 19, 20, 21, 22, and 23, could be distinguished by over-etching with concentrated hydrofluoric acid, but microphotographs were not obtained in this condition. Similar metallographic observations were made for samples treated at 1300 and 1000 F.

The X-ray data obtained on these intermediate alloys are summarized in Table 4. Alloys 5 and 6, containing 43.0 and 58.7 w/o uranium dioxide and quenched from 2000 F, were undoubtedly three phase, as plotted in Figure 3.

It is apparent from the X-ray data that transformation of the uranium-rich phase in these alloys occurred during the quench, giving α_{U} and ($\beta_{\text{Zr}}-\gamma_{\text{U}}$) or ϵ_{UZr} . Epsilon was probably present, rather than beta, but it is difficult to distinguish between the two phases, especially when working with small amounts. The diagram for 1300 F, Figure 2, has been drawn to conform to data on the binary uranium-zirconium system which show the gamma transformation occurring at 685 C. Additional data would, of course, be needed to interpret the uranium-rich portion of the system more accurately.

Data for other samples treated at 1000 F and in the as-cast condition are included in Table 4. These samples were also three phase, corresponding to the positions in Figure 1.

In order to be certain that an equilibrium had been achieved in these studies, Alloys 9 and 10, containing 80.0 and 84.4 w/o uranium dioxide, were heat treated 1000 hr at 1300 F. These samples gave the same results as those which were as cast and those heat treated 240 hr at 1300 F (Table 4).

Also in the intermediate range was a series of alloys which runs transverse to the zirconium- UO_2 two-phase region (Alloys 11, 12, 13, and 14 in Figure 2). Samples of these alloys were examined metallographically and by X-ray diffraction. Both methods showed that the amount of uranium-rich

250X

N18536

FIGURE 12. ZIRCONIUM-43.0 w/o UO_2 ALLOY

As Arc Melted

250X

N18537

FIGURE 13. ZIRCONIUM-58.7 w/o UO_2 ALLOY

As Arc Melted

250X

N18538

FIGURE 14. ZIRCONIUM-68.9 w/o UO_2 ALLOY

As Arc Melted

250X

N18539

FIGURE 15. ZIRCONIUM-74.0 w/o UO_2 ALLOY

As Arc Melted

250X

N18540

FIGURE 16. ZIRCONIUM-79.2 w/o UO_2 ALLOY

As Arc Melted

250X

N18541

FIGURE 17. ZIRCONIUM-84.4 w/o UO_2 ALLOY

As Arc Melted

500X

N18542

FIGURE 18. ZIRCONIUM-43.0 w/o UO_2 ALLOY

Heat Treated 24 Hr at 2000 F and
Water Quenched

500X

N18543

FIGURE 19. ZIRCONIUM-58.7 w/o UO_2 ALLOY

Heat Treated 24 Hr at 2000 F and
Water Quenched

500X

N23772

FIGURE 20. ZIRCONIUM-68.9 w/o UO_2 ALLOY

Heat Treated 24 Hr at 2000 F and
Water Quenched

500X

N23773

FIGURE 21. ZIRCONIUM-74.0 w/o UO_2 ALLOY

Heat Treated 24 Hr at 2000 F and
Water Quenched

500 X

N23774

FIGURE 22. ZIRCONIUM-79.2 w/o UO_2 ALLOY

Heat Treated 24 Hr at 2000 F and
Water Quenched

500X

N23775

FIGURE 23. ZIRCONIUM-84.4 w/o UO_2 ALLOY

Heat Treated 24 Hr at 2000 F and
Water Quenched

TABLE 4. PHASE IDENTIFICATION IN ZIRCONIUM ALLOYS CONTAINING 43.0 to 84.4 w/o UO₂

Alloy	Nominal Composition, w/o	Heat Treatment	Sample Preparation	Method of Examination	Pattern Intensities ^(a)					Unknowns		
					UO ₂	α Zr	α U	$(\beta \text{Zr}-\gamma \text{U})$	ϵUZr	X	Y	Others
5	43.0UO ₂	24 hr, 2000 F, W.Q.	Metallographic	Spectrometer	M	S	S	F? or F?	-	-	-	-
6	58.7UO ₂	24 hr, 2000 F, W.Q.	Metallographic	Spectrometer	MF	MF	VF	VF?	VF?	-	-	-
8	74.0UO ₂	240 hr, 1300 F, W.Q.	Crushed ^(b)	Debye	S	M	VF	-	-	-	-	VVF?
8	74.0UO ₂	240 hr, 1300 F, W.Q.	Etched ^(c)	Debye	VVF-F	S	F+	-	-	VVF	F	-
9	80.0UO ₂	240 hr, 1300 F, W.Q.	Crushed	Debye	VSD	M	F+	-	-	-	-	M
9	80.0UO ₂	240 hr, 1300 F, W.Q.	Etched	Debye	-	VS	MF+	-	-	MF+	F	-
10	84.4UO ₂	240 hr, 1300 F, W.Q.	Crushed	Debye	VSD	F	VF	-	-	-	-	VVF
10	84.4UO ₂	240 hr, 1300 F, W.Q.	Etched	Debye	-	VS	MF	-	-	MF	VVF	-
9	80.0UO ₂	1000 hr, 1300 F, W.Q.	Crushed	Debye	Sd	MF	VF+	-	-	VVF	-	-
10	84.4UO ₂	1000 hr, 1300 F, W.Q.	Crushed	Debye	Sd	M	F	-	-	VVF	-	-
9	80.0UO ₂	1000 F, F.C.	Crushed	Debye	VSD	MF	F	-	-	-	-	VF
9	80.0UO ₂	1000 F, F.C.	Etched	Debye	-	VS	MF	-	-	VF	VF	-
10	84.4UO ₂	1000 F, F.C.	Crushed	Debye	VSD	F	F	-	-	-	-	VVF
10	84.4UO ₂	1000 F, F.C.	Etched	Debye	-	VS	M	-	-	F	MF	-
9	79.2UO ₂	As arc melted	Crushed	Debye	VSD	M	MF	-	-	-	-	VF
9	79.2UO ₂	As arc melted	Etched	Debye	-	VS	MF+	-	-	-	F	-
10	84.4UO ₂	As arc melted	Crushed	Debye	VSD	F	F	-	-	-	-	VVF
10	84.4UO ₂	As arc melted	Etched	Debye	-	VS	F	-	-	VF	VVF+	-
11	28.1Zr, 67.2U, 4.7 O	16 hr, 1300 F, W.Q.	Metallographic	Spectrometer	MF	MS	MF	-	-	-	-	-
12	34.9Zr, 59.3U, 5.8 O	16 hr, 1300 F, W.Q.	Metallographic	Spectrometer	MS	M	MF	-	-	-	-	-
13	47.7Zr, 44.4U, 7.9 O	16 hr, 1300 F, W.Q.	Metallographic	Spectrometer	MS	M	VF	-	-	-	-	VVF
13	47.7Zr, 44.4U, 7.9 O	16 hr, 1300 F, W.Q.	Crushed CCl ₄	Debye	M	M	VF	-	-	-	-	-
14	61.0Zr, 28.8U, 10.2 O	16 hr, 1300 F, W.Q.	Metallographic	Spectrometer	VF ^(d)	M	VVF	-	-	-	-	XY other
14	61.0Zr, 28.8U, 10.2 O	16 hr, 1300 F, W.Q.	Crushed CCl ₄	Debye	MF ^(e)	MS	VVF	-	-	-	-	VVF
					VF ^(d)							
					MS ^(f)							
11	28.1Zr, 67.2U, 4.7 O	As arc melted	Crushed	Debye	S	MS	F+	?	-	-	-	VVF
11	28.1Zr, 67.2U, 4.7 O	As arc melted	Etched	Debye	-	S	F	-	-	VVF	-	-
12	34.9Zr, 59.3U, 5.8 O	As arc melted	Crushed	Debye	S	S	MF+	?	-	-	-	-
12	34.9Zr, 59.3U, 5.8 O	As arc melted	Etched	Debye	-	VS	F	-	-	-	WF-	-
13	47.7Zr, 44.4U, 7.9 O	As arc melted	Crushed	Debye	VS	VS	MF	-	-	-	-	VF
13	47.7Zr, 44.4U, 7.9 O	As arc melted	Etched	Debye	-	S	F	-	-	-	-	-
14	61.0Zr, 28.8, 10.2 O	As arc melted	Crushed	Debye	-	S	-	-	-	-	-	-

(a) Intensities: S = strong, M = medium, F = faint, V = very, d = diffuse.

(b) Crushed or powder sample.

(c) Crushed and etched to remove UO₂.(d) a₀ = 5.40.(e) a₀ = 5.30.(f) a₀ = 5.29.

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phase present tended to decrease in the 1300 F treated samples of Alloys 11, 12, and 13 (Figure 4). Alloy 14, on the other hand, showed evidence, especially after heat treating at 1300 F, that it was in the $\text{UO}_2\text{-ZrO}_2 + \alpha\text{Zr}$ region. This is indicated by the two lattice constants of $a_0 = 5.40 \pm 0.01$ and $a_0 = 5.29 \pm 0.01$ Å (Table 4), corresponding with uranium dioxide and zirconium dioxide solid solutions. On the basis of a plot of lattice constants for the $\text{UO}_2\text{-ZrO}_2$ system⁽⁵⁾, the values of $a_0 = 5.40$ and 5.29 Å correspond with about 23 and 53 mole per cent zirconium dioxide. Limits of 40 and 80 mole per cent zirconium dioxide were reported for these solid solutions in the work of Lambertson and Mueller⁽⁵⁾.

X-ray data for the transverse series of alloys in the as-cast conditions are also given in Table 4.

Uranium Dioxide-Rich Alloys

Studies of the system uranium-oxygen indicate that uranium dioxide exists from about $\text{UO}_{1.9}$ ⁽²⁾ to $\text{UO}_{2.2}$ ^(1, 2), although these values are controversial. The system $\text{UO}_2\text{-ZrO}_2$ has been studied by Lambertson and Mueller⁽⁵⁾. They have demonstrated that the two oxides have extensive intersolubility which increases at high temperatures. Existing data on the lattice constants for uranium dioxides are summarized in lines 1 and 2 of Table 6. It has been assumed that the highest lattice constant for uranium dioxide corresponds with $\text{UO}_{1.9}$ and the lowest with $\text{UO}_{2.2}$.

For this study UO_2 -rich alloys were prepared by powder metallurgy to contain 85 to 97 w/o UO_2 . Alloys of up to 95 w/o UO_2 were also prepared by arc melting, but were not homogeneous above about 85 w/o UO_2 .

Only limited solubility was observed in the uranium dioxide, except for Alloy 14 (Figure 2), which was discussed with the intermediate alloys.

Microstructures of as-sintered powder-metallurgy samples containing 90 and 95 w/o UO_2 are shown in Figures 24 and 25. The presence of second, or, perhaps, second and third phases can be detected on both structures, along with considerable porosity. Identification of phases in the powder-metallurgy series of samples is summarized in Table 5. Alpha zirconium and alpha uranium or alpha zirconium, were detected in all but the 97 w/o UO_2 sample. The solubility is probably considerably less than 3 w/o zirconium, since small amounts of extra phases would not be detected.

Considerable information can also be deduced from the lattice constants of the uranium dioxide phase of various samples in the intermediate composition range. Lattice constants were calculated for Alloys 9 to 14 and are given in Table 6. Comparison with other photograms indicate that

250X

N23780

FIGURE 24. ZIRCONIUM-90.0 w/o UO_2 ALLOY

Pressed and Sintered

250X

N23781

FIGURE 25. ZIRCONIUM-95.0 w/o UO_2 ALLOY

Pressed and Sintered

TABLE 5. PHASE IDENTIFICATION IN UO_2 -RICH ALLOYS^(a)

Alloy	Nominal UO_2 , w/o	Pattern Intensities ^(b)					Unknowns		
		UO_2	α_{Zr}	α_{U}	β_{Zr}	ϵ_{UZr}	X	Y	Others
15	85.0	S	MF	VF	-	-	-	-	VF ^(c)
16	90.0	S	F	VF	-	-	-	-	VF ^(c)
17	92.5	S	F	VF	-	-	-	-	VF ^(c)
18	95.0	S	VF	?	-	-	-	-	VF ^(c)
19	97.0	S	?	?	-	-	-	-	VF ^(c)

(a) Examined in the as-sintered condition by X-ray spectrometer and with metallographic samples.

(b) Intensities: S = strong, M = medium, F = faint, V = very, D = diffuse.

(c) A common impurity indicated by a reflection at 1.95 Å.

TABLE 6. LATTICE CONSTANTS OF THE UO_2 PHASE

Alloy	Nominal Composition, w/o	Heat Treatment	Lattice Constants, A	Remarks
--	$\text{UO}_{1.86}^{(a)}$	--	$a_0 = 5.461 \pm 0.0007^{(b)}$	--
--	$\text{UO}_{2.2}^{(b)}$	--	$a_0 = 5.4297 \pm 0.0008^{(b)}$	--
9	79.2 UO_2	As arc melted	$a_0 = 5.42 \pm 0.01$	} Typical of arc-melted samples
9	80.0 UO_2	As arc melted	$a_0 = 5.425 \pm 0.01$	
9	80.0 UO_2	1/2 hr, 1000 F and F.C.	$a_0 = 5.42 \pm 0.01$	Typical of samples treated at 1000 F
8	74.0 UO_2	240 hr, 1300 F, W.Q.	$a_0 = 5.45 \pm 0.01$	} Typical of samples treated similarly at 1300 F
9	80.0 UO_2	240 hr, 1300 F, W.Q.	$a_0 = 5.45 \pm 0.01$	
11	28.1Zr, 67.2U, 4.7 O	16 hr, 1300 F, W.Q.	$a_0 = 5.44 \pm 0.01$	--
12	34.9Zr, 59.3U, 5.8 O	16 hr, 1300 F, W.Q.	$a_0 = 5.44 \pm 0.01$	--
13	47.7Zr, 44.4U, 7.9 O	16 hr, 1300 F, W.Q.	$a_0 = 5.42 \pm 0.01$	Probably in α_{Zr} and UO_2 field
14	61.0Zr, 28.8U, 10.2 O	16 hr, 1300 F, W.Q.	$a_0 = 5.40 \pm 0.01$ and $a_0 = 5.29 \pm 0.01^{(c)}$	Probably UO_2 and ZrO_2 solid solutions

(a) Reference (2).

(b) Reference (1).

(c) ZrO_2 is tetragonal.

similar values would be calculated for additional samples. Values of $a_o = 5.42 \pm 0.01$ and $a_o = 5.425 \pm 0.01$ were obtained for as-cast 79.2 and 80.0 w/o UO_2 alloys. Similar values were obtained for 80 w/o UO_2 samples when heat treated 1/2 hr at 1000 F and furnace cooled. On the other hand, Samples 8 and 9, heat treated 240 hr at 1300 F and quenched, and Samples 11 and 12, heat treated 16 hr at 1300 F and quenched, had lattice constants of 5.45 and 5.44 Å, respectively. This lattice shift indicates that zirconium or oxygen, or both, was removed from solid solution by the heat treatments. Sample 13, with a lattice constant of $a_o = 5.42$ Å, even after heat treating 16 hr at 1300 F, was probably in the $\alpha_{Zr} + UO_2$ field, although the nominal composition does not fall within the field as shown in Figure 2.

Sample 14, heat treated at 1300 F, indicates that the lattice constant shifts even more as the composition moves across the $\alpha_{Zr} + UO_2$ phase region (Figure 2). The two lattice constants for Sample 14, $a_o = 5.40$ and $a_o = 5.29 \pm 0.01$ Å correspond with the uranium dioxide and zirconium dioxide solid solutions, respectively.

The uranium dioxide solid solution has been drawn to correspond approximately with the data discussed (Figure 2). Comparison of X-ray photograms indicate that the UO_2 solid solution is similar at 1300 and 2000 F. It is probably also similar at 1000 F, since the as cast and 1000 F treated samples, although different, do not represent equilibrium. Additional data would be needed to define the uranium dioxide solid solution.

CONCLUSIONS

Tentative isothermal sections of a part of the uranium-zirconium-oxygen system have been determined for 1000, 1300, and 2000 F. Uranium dioxide and zirconium solid solutions coexist in equilibrium at each of these temperatures. Alpha zirconium in equilibrium with uranium dioxide contains about 28 at/o oxygen, but very little uranium. Little zirconium is soluble directly in uranium dioxide, but extensive solubility exists between uranium dioxide and zirconium dioxide.

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