

## X-Ray Studies on Solid Solutions of Oxygen in $\alpha$ -Zirconium

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The solubility of oxygen in  $\alpha$ -zirconium in the temperature region, 400°–800°C, has been investigated by X-ray methods. The solubility, which is independent of temperature, is 28.6 at % ( $\text{ZrO}_{0.40}$ ). With increasing oxygen content, the length of the  $c$  axis increases over the entire solubility range while that of the  $a$  axis passes through a maximum at the composition  $\text{ZrO}_{0.25}$ . In the solubility range there exist two phases, *viz.*  $\text{ZrO}_{0+x}$ , with randomly distributed oxygen atoms, and  $\text{Zr}_3\text{O}_{1+y}$ , with partly ordered oxygen atoms. At the limiting composition ( $\text{ZrO}_{0.33}$ ), the oxygen atoms are completely ordered ( $\text{Zr}_3\text{O}$ ).

Previous studies on the solubility of oxygen in the hexagonal, close-packed  $\alpha$ -modification of zirconium have shown that oxygen can enter into solid solution up to the composition  $\text{ZrO}_{0.395}$  (28.3 at % O)<sup>1</sup>. The solubility mechanism deduced has been thought to imply that the oxygen atoms occupy the major interstices of the metal structure, *i.e.* the octahedral holes, in a perfectly random way<sup>2</sup>. The incorporation of the oxygen atoms in the  $\alpha$ -structure has been reported to be accompanied by a considerable expansion of the  $c$  axis and by only a slight change in the  $a$  axis<sup>3</sup>.

### EXPERIMENTAL

The starting materials for the syntheses were zirconium metal and zirconium dioxide. Two series of alloys were prepared, one with metal from A. D. Mackay Inc. (lump, low in hafnium) and the other with metal from the Foote Mineral Comp. (crystal bar, 99.9 % Zr with 260 ppm O, the principal impurity, and 70 ppm Hf). For the first set of alloy preparations, a Mackay "hafnium free" dioxide was used and, for the second, a dioxide obtained by heating the Foote metal in a stream of oxygen.

The preparation of the alloys was carried out by arc melting the appropriate mixtures of the starting materials in an argon atmosphere as described earlier<sup>4</sup>. After pulverisation, the samples were homogenized by heat-treatment in sealed, evacuated silica capsules. The heat-treatment was always abruptly stopped by quenching in water. The Mackay alloys were heat-treated at 400°C for 1 month and thereafter at 600°C or at 800°C for 1 week and the Foote alloys at 600°C for 1 month. At these temperatures, no reaction was found to occur between the silica and the specimens.

Table 1. Comparison between analytically found ( $x_a$ ) and starting composition ( $x_s$ ), their differences and the corrected composition ( $x_c$ ) for samples  $ZrO_x$  heat-treated at 600°C and 400°C for 1 month.

$x_a$	$x_s$	$x_a - x_s$	$x_c$
Foote alloys			
0.148	0.100	0.048	0.118
0.225	0.200	0.025	0.195
0.263	0.240	0.023	0.233
0.351	0.320	0.031	0.321
0.366	0.340	0.026	0.336
0.378	0.350	0.028	0.348
0.400	0.370	0.030	0.370
0.427	0.400	0.027	0.397
0.443	0.420	0.023	0.413
0.475	0.450	0.025	0.445
0.547	0.500	0.047	0.517
Mackay alloys			
0.275	0.240	0.035	0.245
0.314	0.280	0.034	0.284
0.361	0.320	0.041	0.331
0.382	0.340	0.042	0.352
0.409	0.350	0.059	0.379
0.447	0.400	0.047	0.417
0.463	0.420	0.043	0.433
0.492	0.450	0.042	0.462
0.551	0.500	0.051	0.521

The oxygen contents of the heat-treated samples were determined by chemical analysis. Weighed samples of about 0.2 g were heated in silica boats in an oxygen stream at 950°C for some hours, admixed with a known amount of  $TiO_2$  (rutile form) to avoid spitting and reduce sintering. The compositions of the preparations were thus determined from the increase in weight upon oxidation to dioxide.

The analytically found compositions differ slightly from the starting compositions (*cf.* Table 1). The difference amounts for Foote samples to about 0.03 units and for the Mackay samples to about 0.04 units in the ratio O to Zr. These differences depend most likely on a systematic error in the analysing method rather than on composition changes caused by the syntheses and heat-treatments. So with pure Foote metal a result was obtained corresponding to an oxygen content of about 1 % which is much higher than the correct one of 260 ppm. The somewhat higher difference for the Mackay samples can be explained by the fact that the starting metal contained oxygen. The hafnium content of the Mackay starting materials has been found spectrographically to be 220–250 ppm.

Table 2. Observed densities of samples  $ZrO_x$  heat-treated at 600°C for 1 month and calculated densities for interstitial solutions.

$x$	$d_{obs}$	$d_{calc}$
0	6.49 <sup>5</sup>	6.50 <sup>6</sup>
0.118	6.52	6.55
0.195	6.60	6.60
0.233	6.64	6.63
0.321	6.76	6.73
0.336	6.76	6.75
0.348	6.75	6.77
0.370	6.79	6.80
0.397	6.82	6.83

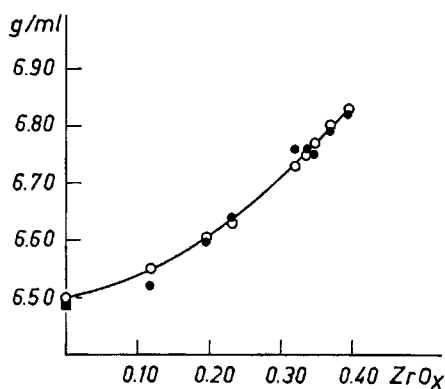


Fig. 1. Observed density of samples  $ZrO_x$  heat-treated at 600°C for 1 month (filled circles) and calculated density for interstitial solutions (open circles).

The results of the analyses have therefore been corrected, using a constant equal to 0.030 units, to give the ratios of oxygen to zirconium in the alloys.

Density determinations have been carried out by measuring the weight of the samples in air and benzene. Table 2 and Fig. 1 show the observed densities for samples heat-treated at 600°C for 1 month and the calculated densities for interstitial solutions.

X-Ray powder photographs were taken of all the samples using a Guinier set-up with monochromatized  $CuK\alpha_1$  radiation. Potassium chloride ( $a = 6.2919 \text{ \AA}$  at 20°C<sup>7</sup>) was always added to the specimens as an internal standard. Details about the techniques employed in the X-ray powder work have been given elsewhere<sup>8</sup>.

Table 3. Lattice parameters of specimens  $ZrO_x$  heat-treated at various temperatures.

$x$	$a \text{ \AA}$		$c \text{ \AA}$			
	0	3.2323 <sup>7</sup>	5.1477 <sup>7</sup>			
Footé alloys	600°C	~ 1 800°C	600°C	~ 1 800°C		
0.118	3.2470	3.2455	5.1689	5.1703		
0.195	3.2528	3.2518	5.1790	5.1776		
0.233	3.2540	3.2542	5.1825	5.1813		
0.321	3.2527	3.2532	5.1875	5.1864		
0.336	3.2510	3.2515	5.1937	5.1889		
0.348	3.2485	3.2495	5.1954	5.1940		
0.370	3.2470	3.2487	5.1987	5.1974		
0.397	3.2448	3.2448	5.2014	5.1985		
0.413	3.2437	3.2439	5.2043	5.2017	(two-phase region)	
0.445	3.2436	3.2445	5.2046	5.2014	→→	
0.517	3.2434	3.2441	5.2043	5.2006	→→	
Mackay alloys	400°C	600°C	800°C	400°C	600°C	800°C
0.245	3.2562	3.2541	3.2548	5.1854	5.1837	5.1858
0.284	3.2557	3.2536	3.2548	5.1903	5.1861	5.1889
0.331	3.2518	3.2497	3.2509	5.1941	5.1920	5.1941
0.352	3.2503	3.2480	3.2494	5.1975	5.1983	5.1985
0.379	3.2504	3.2456	3.2474	5.2023	5.2010	5.2005
0.417	3.2458	3.2441	3.2437	5.2031	5.2019	5.2021
0.433	3.2463	3.2447	3.2444	5.2065	5.2045	5.2038
0.462	3.2454	3.2438	3.2447	5.2044	5.2073	5.2020
0.521	3.2469	3.2442	3.2442	5.2045	5.2040	5.2041

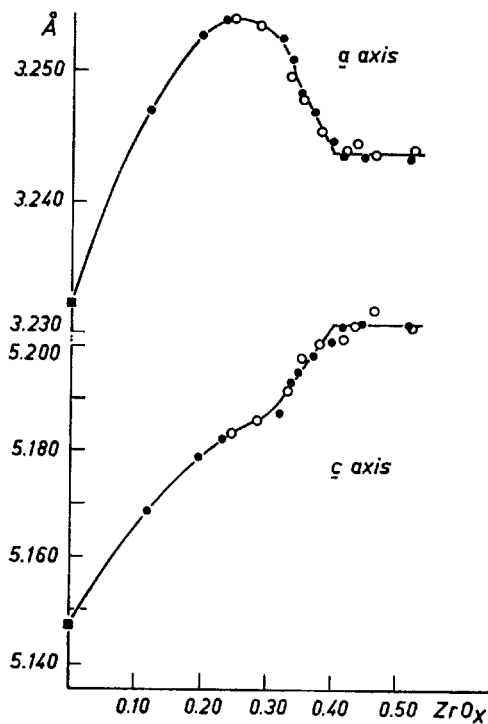


Fig. 2. Lattice parameters of samples  $ZrO_x$  heat-treated at 600°C for 1 month (filled circles) and 1 week (open circles).

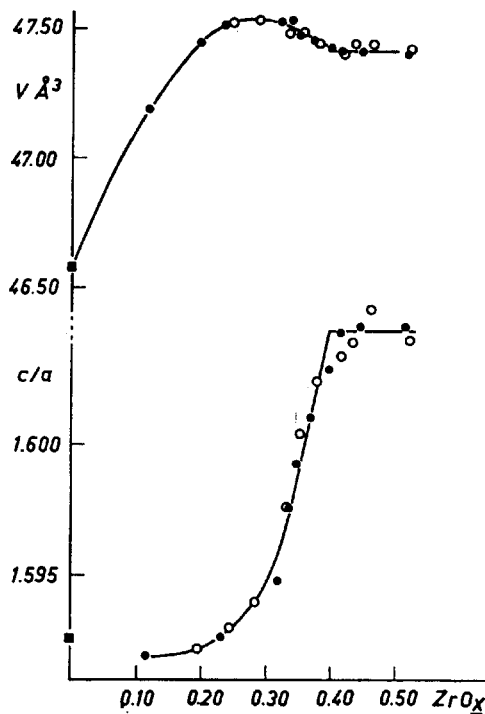


Fig. 3. Unit cell volume and axial ratio of samples  $ZrO_x$  heat-treated at 600°C for 1 month (filled circles) and 1 week (open circles).

The single-crystal photographs were taken in a Weissenberg camera using  $CuK$  radiation.

## RESULTS

The dependence of the metal lattice parameters of preparations  $ZrO_{0-0.52}$  on the oxygen content is shown in Table 3.

For each composition the lattice parameters are, within the experimental error, independent of the heat-treatment. Fig. 2 gives the  $a$  and  $c$  axes as functions of the oxygen contents for both sets of alloys heat-treated at 600°C. The agreement between the two series is good.

The incorporation of oxygen atoms in the  $\alpha$ -zirconium lattice causes a considerable increase in the  $c$  axis over the entire range of solid solubility. A marked change in the rate of increase of the  $c$  axis is observed at the composition  $ZrO_{\sim 0.32}$ . The length of the  $a$  axis is less affected by the oxygen content but passes through a pronounced maximum at the composition  $ZrO_{0.25}$ .

Table 4. Unit cell volume and  $c/a$  of samples  $ZrO_x$  heat-treated at 600°C for 1 month (Foote alloys) and 1 week (Mackay alloys).

	$x$	$V \text{ \AA}^3$	$c/a$	
	0	46.58 <sup>7</sup>	1.5926 <sup>7</sup>	
Foote alloys	0.118	47.19	1.5919	
	0.195	47.45	1.5922	
	0.233	47.52	1.5927	
	0.321	47.53	1.5948	
	0.336	47.54	1.5976	
	0.348	47.48	1.5993	
	0.370	47.46	1.6011	
	0.397	47.43	1.6030	
	0.413	47.42	1.6044	(two-phase region)
	0.445	47.42	1.6046	—»—
	0.517	47.41	1.6046	—»—
Mackay alloys	0.245	47.53	1.5930	
	0.284	47.54	1.5940	
	0.331	47.49	1.5977	
	0.352	47.49	1.6005	
	0.379	47.45	1.6025	
	0.417	47.41	1.6035	—»—
	0.433	47.45	1.6040	—»—
	0.462	47.45	1.6053	—»—
	0.521	47.43	1.6041	—»—

The changes in the values of the lattice parameters are such that the  $c/a$  ratio is almost constant up to the composition  $ZrO_{0.25}$  but thereafter, increases rapidly — this is shown in Table 4 and Fig. 3 together with values for the volume of the unit cell.

From the measurements of the metal lattice parameters, the solubility limit of oxygen in  $\alpha$ -zirconium was found to be close to the composition  $ZrO_{0.40}$  (28.6 at % O) and to be independent of the heat-treatment in good agreement with earlier result<sup>1</sup>.

Preparations with oxygen contents below  $ZrO_{0.34}$  give powder patterns substantially identical to that of the pure metal, which indicates that the oxygen atoms are randomly distributed in the octahedral interstices of the metal structure ( $ZrO_{0+x}$ ).

However, the powder photographs of all samples with compositions corresponding to the composition  $ZrO_{0.35}$  and higher contain extra lines independent of the previous heat-treatment. This powder pattern can be hexagonally indexed using a unit cell three times the size of the unit cell of the metal.

This superstructure has been determined from single-crystal data using crystals from samples with the compositions  $ZrO_{0.35}$  and  $ZrO_{0.42}$  which had been heat-treated at 400°C for 1 month.

Table 5 gives the powder pattern of the former sample and Table 6 the observed and calculated intensities of the superstructure reflexions. The following structure, slightly modified during the process of structural refinement from that preliminarily reported<sup>9</sup>, was thus derived for the ideal composition  $ZrO_{0.33}$ :

Table 5. Powder pattern of the sample  $ZrO_{0.362}$  heat-treated at 400°C for 1 month. Dimensions of the hexagonal unit cell:

$a = \sqrt{3} \cdot 3.2503 \text{ \AA} = 5.6295 \text{ \AA}$			$c = 5.1975 \text{ \AA}$	
$I$	$\sin^2\theta_{\text{obs}}$	$hkl$	$(hkl)_{\alpha\text{-Zr}}$	$\sin^2\theta_{\text{calc}}$
vw	0.02508	100		0.02496
w	0.04686	101		0.04692
m	0.07487	110	100	0.07488
m	0.08787	002	002	0.08785
vst	0.09682	111	101	0.09684
vw	0.12170	201		0.12180
m	0.16274	112	102	0.16273
vw	0.19674	211		0.19668
m	0.22466	300	110	0.22463
m	0.27249	113	103	0.27253
w	— *	220	200	0.29951
m	0.31250	302	112	0.31248
m	0.32147	221	201	0.32147

\* Line overlaps line of KCl.

Space group:  $P6_322$  (No. 182)

Unit cell content: 2  $Zr_3O$

2 O in 2(c):  $\frac{1}{3}, \frac{2}{3}, \frac{1}{4}; \frac{2}{3}, \frac{1}{3}, \frac{3}{4}$

6 Zr in 6(g):  $\frac{1}{3}, 0, 0; 0, \frac{1}{3}, 0; \frac{2}{3}, \frac{2}{3}, 0; \frac{2}{3}, 0, \frac{1}{2}; 0, \frac{2}{3}, \frac{1}{2}; \frac{1}{3}, \frac{1}{3}, \frac{1}{2}$

The metal atoms in this structure have the same packing as in the pure metal. The oxygen atoms occupy a certain number of the octahedral interstices of the metal lattice in an ordered way (*cf.* Fig. 4). Thus the superstructure arises from the ordering of the oxygen atoms to give, at this composition, a

Table 6. Observed and calculated intensities of the superstructure reflexions. Guinier Weissenberg

$hkl$	$I_{\text{obs}}$	$I_{\text{calc}}$	$I_{\text{obs}}$	$I_{\text{calc}}$
001	—	0	—	0
100	vw	3	— *	10
101	w	10	26	28
200	—	0.6	— *	4
102	—	0.9	2	3
201	vw	2	11	8
210	—	0.4	—	1
202	—	0.3	—	1
211	vw	2	3	4
003	—	0	—	0
103	—	0.8	3	3
301	—	0	—	0
212	—	0.4	—	0.7
203	—	0.5	—	2
310	—	0.1	—	0.5
311	—	0.9	—	1
213	—	0.7	—	1

\* covered by the  $h00$  continuous radiation streak.

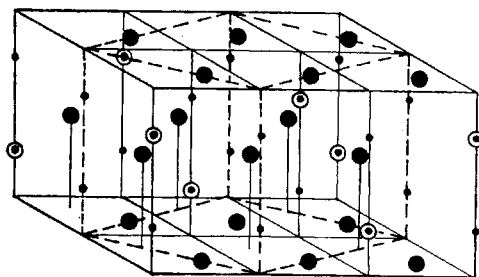


Fig. 4. The structure of  $Zr_3O$ . Large filled circles indicate zirconium atoms, small filled circles the center of the octahedral interstices and open circles oxygen atoms. The unit cell is indicated with dashed lines and the basic  $\alpha$ -Zr with full lines.

completely ordered solid solution, indicated by  $Zr_3O$  and isostructural with the  $Ni_3N$  type.

Preparations richer in oxygen give powder patterns which are entirely analogous to that of  $Zr_3O$ . No intensity differences could be observed for different contents of oxygen. This implies that the excess oxygen atoms are randomly distributed in the empty interstices of the  $Zr_3O$  structure. This region of a partly ordered solid solution ( $Zr_3O_{1+y}$ ) exists up to the solubility limit ( $ZrO_{0.40}$ ).

A discussion of the results obtained for the solid solutions of small non-metal atoms in titanium, zirconium and hafnium will be published elsewhere.

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