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Unit Cell of the Zeta Phase of the Plutonium-Zirconium and the Plutonium-Hafnium Systems

by

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ABSTRACT

The unit cell of the isostructural Pu-Zr and Pu-Hf zeta phases (~ 3 at. % Zr or Hf) was found to be body-centered tetragonal with a = 18.19 ± 0.01 Å and c = 7.851 ± 0.003 Å.

INTRODUCTION

The existence of the Pu-Zr zeta phase has been reported by Ellinger[1] and confirmed by Kutaitsev et al.[2] and Taylor.[3] The isostructural Pu-Hf zeta phase has been observed by Kutaitsev et al.[2] and by Ellinger et al.[4] These zeta phases are stable below about 270°C at atmospheric pressure. Their equilibrium concentration of zirconium or hafnium is about 3 at. %, however, the metastable zeta phase containing as little as 2 at. % Zr or Hf is readily prepared. Since attempts to isolate single crystals from polycrystalline alloys were unsuccessful, the unit cell of the zeta phase was determined from x-ray diffraction powder data.

EXPERIMENTAL

Powder data were obtained both with a Norelco diffractometer and with 114.59-mm-diam powder cameras. The diffractometer traces were all made with CuKα radiation, but the most satisfactory photographic patterns were taken with CrKα radiation. Alloy buttons about 1 cm in diameter that had been mounted in epoxy resin and polished for micrographic examination served as diffractometer samples. Alloy filings sealed in evacuated, clear silica capillary tubes were used in the powder cameras.

RESULTS

By the method of searching out relationships in $\sin^2\theta$ values, the x-ray powder data of the zeta phase have been indexed on the basis of a body-centered tetragonal unit cell. Table I lists the low-angle reflections taken from the diffractometer trace of a Pu-2 at. % Hf alloy. The calculated $\sin^2\theta$ values are based on the lattice parameters

$$a = 18.167 \pm 0.003 \text{ Å}$$
$$c = 7.856 \pm 0.001 \text{ Å}.$$

The good agreement between the calculated and observed values, and the small number of missing reflections, support the correctness of the indexing.

Precision unit-cell dimensions were determined by least-squares extrapolation of the measurable high-angle lines on powder patterns taken with CrKα radiation. The computer program of Vogel and Kempter[5] as modified by Roof[6] was used. A typical set of data of a Pu-3 at. % Zr alloy is shown in Table II, which yielded the following lattice parameters

TABLE I

Pu-2 at. % Hf ZETA PHASE DIFFRACTOMETER DATA (CuKa)

BODY-CENTERED TETRAGONAL, a = 18.167 ± 0.003 Å

c = 7.956 ± 0.001 Å

HKL	$10^5 \sin^2\theta$(calc.)	Peak Intensity	$10^5 \sin^2\theta$(obs.)	d, Å(obs.)
600	6471	4	6478	3.029
402	6731			
332	7091			
620	7190	5	7205	2.872
422	7441	15	7450	2.824
611	7612			
541	8331	5	8335	2.670
512	8519	83	8529	2.640
103	8833	10	8863	2.589
710,550	8998			
631	9050	90	9058	2.561
640	9347	37	9350	2.521
213	9552	76	9585	2.490
442	9498			
701	9768	59	9776	2.466
532	9958	3	9963	2.442
303	10270	7	10290	2.403
602	10317			
730	10426			
721	10488	45	10498	2.379
323	10990	16	11016	2.323
622	11036			
800	11504	12	11503	2.273
413	11709			
651	11926	10	11940	2.231
820	12223	7	12225	2.205
811,741	12645	3	12639	2.168
712,552	12835			
660	12942			
503,433	13147	19	13183	2.123
642	13193			

TABLE II

Pu-3 at. % Zr ZETA PHASE, HIGH-ANGLE DIFFRACTION DATA (CrKα)

BCT a = 13.1959 ± 0.0016, c = 7.3511 ± 0.0003 Å

HKL	$10^4 \sin^2\theta$(calc.)	$10^4 \sin^2\theta$(obs.)	Intensity
10·9·3 α_1	9078	9084	S
606 α_1	9079		
12·8·2 α_1	9084		
10·9·3 α_2	9109	9124	S
606 α_2	9110		
12·8·2 α_2	9115		
15·0·1 α_1, 12·9·1 α_1	9119		
15·0·1 α_2, 12·9·1 α_2	9150	9156	MW
945 α_1	9155		
13·4·3 α_1, 11·8·3 α_1	9237	9244	S-
626 α_1	9238		
14·4·2 α_1	9242		
13·8·1 α_1	9436	9442	W
12·7·3 α_1	9553	9556	W
10·3·5 α_1	9630	9634	MW
716 α_1, 556 α_1	9634		
12·10·0 α_1	9658	9667	VW
10·3·5 α_2	9663		
716 α_2, 556 α_2	9667		
14·1·3 α_1	9712	9714	S
646 α_1	9713		
12·4·4 α_1	9735	9741	S-
14·1·3 α_2	9745		
646 α_2	9746		
875 α_1	9788	9790	M
15·1·2 α_1	9796		
875 α_2	9821	9826	W
15·1·2 α_2	9829		

$$a = 18.1959 \pm 0.0016 \text{ Å}$$

$$c = 7.8511 \pm 0.0008 \text{ Å}.$$

We found that the lattice parameters varied in a random manner from film to film evidently owing to the overlapping reflections and the consequent difficulty in accurately measuring their positions. The mean values as determined from eight separate samples of both Pu-Zr and Pu-Hf alloys are

$$a = 18.19 \pm 0.01 \text{ Å}$$

$$c = 7.851 \pm 0.003 \text{ Å}.$$

On the basis of these lattice parameters and a measured density of 17.5 g/cm^3 for the 3 at. % Hf zeta phase, the number of atoms in the unit cell is calculated to be 115.4, hence 116 so as to conform to the equivalent positions of a tetragonal space group. Thus, the ideal composition of zeta is probably $Pu_{28}M$ (3.4 at. % Zr or Hf). With four formula weights per unit cell, the calculated density for $Pu_{28}Zr$ is 17.44 ± 0.04 g/cm^3 and for $Pu_{28}Hf$ 17.57 ± 0.04 g/cm^3.

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