Journal of Alloys and Compounds, 182 (1992) L9–L14
JALCOM 148

Letter

Phase diagram of the Pu–Zr system in the Zr-rich region

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(Received August 28, 1991)

1. Introduction

The phase relationship of the Pu–Zr system is important for understanding the irradiation behaviour of metallic U–Pu–Zr fuel, which is a candidate as an advanced fast breeder reactor fuel [1]. However, only little information is available on the Pu–Zr phase diagram, especially in the zirconium-rich region. The diagram proposed by Marples [2] agrees with that by Bochvar *et al.* [3] for most parts, but there are some minor differences. Bochvar *et al.* reported a peritectoid reaction, ϵ-Pu + α-Zr = δ-Pu, around 913 K. Lauthier *et al.* [4] pointed out that the peritectoid reaction takes place at 888 K, which differs from the phase diagram of Marples [2], where ϵ-Pu decomposes eutectoidally at 891 K. The phase diagram presented by Ellinger *et al.* [5], which is shown in Fig. 1, is similar to that of Marples, in principle. This work was therefore carried out in order to have a better understanding of the phase relationships in the zirconium-rich region of the Pu–Zr system above 50 at.% Zr.

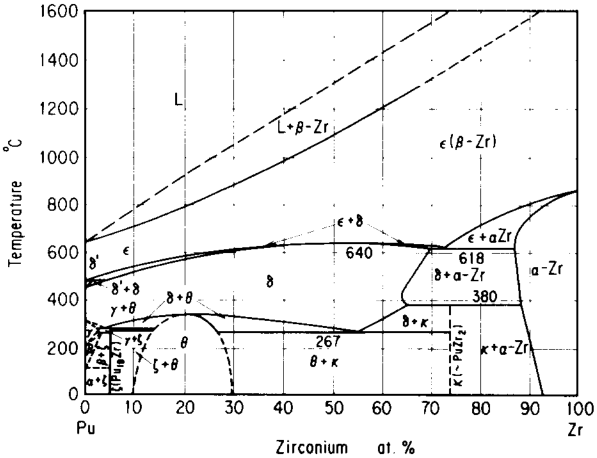

Fig. 1. Pu–Zr phase diagram (after Ellinger *et al.* [5]).

0925-8388/92/$5.00

2. Experimental details

Pu–Zr alloys with various compositions were prepared by a powder metallurgical method using powders of zirconium metal and plutonium hydride as starting materials. Zirconium powder of 99.2% purity and a particle size of less than 40 μm was obtained from Goodfellow Metal Company. The result of a typical analysis of the zirconium powder used is shown in Table 1. Plutonium hydride, a mixture of hexagonal PuH_3 and cubic $PuH_{2.7}$, was synthesized by heating plutonium metal chips in a stream of pure hydrogen gas at about 700 K. The plutonium metal was obtained from Harwell Laboratory. Its isotopic composition and the impurities contained in it are shown in Table 2. A typical X-ray diffraction pattern of plutonium hydride prepared by us is shown in Fig. 2, where no oxide phase is noticeable.

Fine powders of plutonium hydride and zirconium were mixed in an agate mortar after weighing with an accuracy of 0.2 mg. Powder mixtures were compacted into small pellets of 0.5–1.0 g and then kept in a vacuum at about 800 K for at least 2 h after the completion of hydrogen gas release.

TABLE 1

Impurities in the zirconium metal powder used

Elements	Concentration (ppm)	Elements	Concentration (ppm)
Al	28	Cr	320
Cu	24	Fe	2250
Hf	90	Mg	2400
Mn	30	Ni	<20
Si	70	Pb	<20
Ti	<20	V	<20
N	32	Cl	100

TABLE 2

Characteristics of plutonium metal

Isotopic Analysis (wt.%)			
Pu-239	94.33		
Pu-240	5.27		
Pu-241	0.40		
Impurity Analysis (ppm)			
U	50	Ti	5
Fe	70	Si	25
Ni	50	C	220
Cr	15	N	240
Al	45	Mn	5

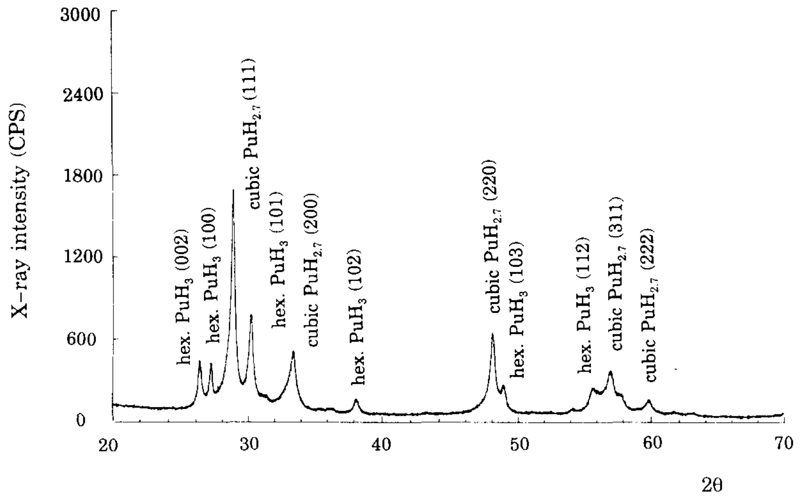

Fig. 2. Typical X-ray diffraction pattern of plutonium hydride.

The oxidation of samples was avoided as far as possible by handling in glove boxes filled with highly purified argon gas. The impurity level of oxygen and moisture in the glove boxes was less than 3 ppm and 5 ppm respectively [6].

The transformations of Pu–Zr alloys were measured with an infrared heating differential thermal analyser (DTA) with two sets of Pt–Rh thermocouples. Cells made of magnesium oxide (MgO) with a density of 99.9% theoretical density (T.D.) and a purity of 99.9% were used in this study. No reaction was observed at the interface between the cell material and the Pu–Zr alloys after the DTA measurement. Sintered rhodium metal was used as a reference material. Alloy samples were heated at a rate of 5 or 10 K min^{-1} in a pure argon gas atmosphere. The temperatures were calibrated by comparing with the melting temperatures of pure metals such as tin, zinc, aluminium, silver and gold. The transformation temperatures of Pu–Zr alloys were estimated from DTA curves by computer analysis. The accuracy of transition temperatures was usually better than 5 K.

Samples, which had been furnace cooled after the DTA measurements, were filed to powder and then examined by X-ray diffraction using a diffractometer with Cu Kα radiation. The procedure of sample preparation for X-ray analysis was described elsewhere [7]. The lattice parameters were estimated from the peaks between 20° and 70° (2θ) with an uncertainty of less than 0.001 nm.

3. Results and analysis

The X-ray analysis of alloys after the DTA measurements indicated the presence of two f.c.c.-structured phases and a hexagonal phase. The lattice parameters of these phases are shown in Fig. 3. The two f.c.c. phases observed were considered to be δ-Pu having different zirconium contents. The phase having the smaller lattice parameter is presumed to be a δ-Pu containing a large quantity of zirconium. Although the results of X-ray analysis did not indicate equilibrium states, it is suggested from the composition dependence of the lattice parameter in Fig. 3 that the maximum solubility of zirconium might exceed at least 70 at.%. The other f.c.c. phase with the larger and constant cell size, which corresponds closely to that of pure δ-Pu, is considered to contain only small amounts of zirconium. The latter δ-Pu phase might form from the decomposition of α-Zr saturated with plutonium during cooling. It is also obvious that the hexagonal phase observed is α-Zr, in which plutonium could dissolve up to more than 10 at.%.

The results obtained in the present study are shown in Fig. 4, where they are compared with the phase diagram of Ellinger *et al.* [5]. Any indication of a peritectoid reaction as reported by Bochvar *et al.* and Lauthier *et al.* was not noticed from the results of our DTA measurements. Small discrepancies with previous studies are noticeable in some parts of the diagram. The alloys of 75, 82 and 88 at.% Zr showed a eutectoid reaction at about 870 K, which is lower than the values reported previously [2, 5, 8]. The discrepancy might be caused by the different purities of the samples. For example, zirconium bars containing the usual 2% Hf were used in the experiments by Marples [2]. It is also possible that the eutectoid composition is much larger than 73 at.% Zr [2], although the composition could not be clearly determined in this study.

The thermal analysis of the Pr–70 at.% Zr alloy did not reveal a transition due to the eutectoid reaction, but a transition due to the reaction of δ-Pu + α-

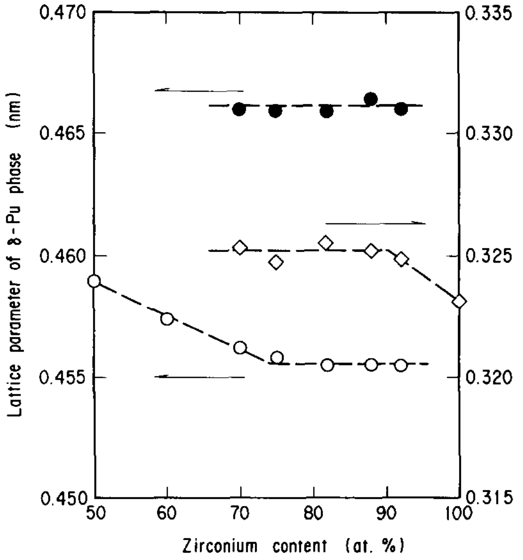

Fig. 3. Lattice parameters of the two f.c.c. phases (●, ○) and the hexagonal phase (◇) in Pu–Zr.

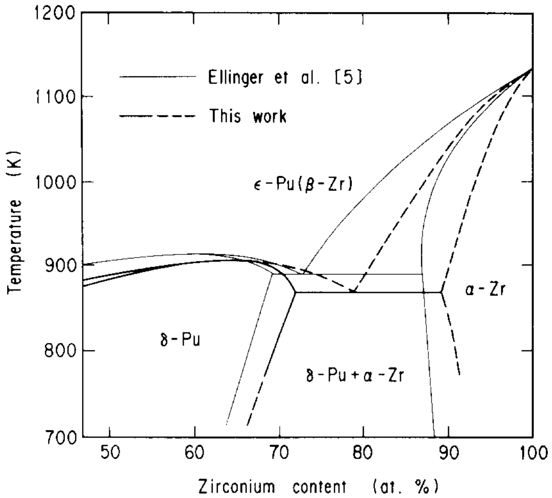

Fig. 4. Comparison of the results of this work (– – – –) with those of Ellinger *et al.* [5] (——).

Zr to δ-Pu at 818 K. It means that the maximum solubility of zirconium in δ-Pu is at least 70 at.% Zr, in agreement with the result from our X-ray analysis. By contrast, Marples reported a maximum solubility of 69 at.% Zr. The discrepancy might be caused by the different sample preparations. In general, alloys for the study of phase diagrams were prepared by arc melting or high-frequency heating. These methods sometimes cause a significant plutonium loss, which results in compositional changes of the alloys. In this study, the loss of plutonium should be negligible, because our alloys were prepared by low temperature heat treatments.

The existence of the intermetallic compound $PuZr_2$ (κ phase), which was reported by Marples [2], was not confirmed even after a heat treatment at 625 K for 700 ks. Lauthier *et al.* questioned the existence of the κ phase, since the compound could be synthesized only in the presence of oxygen [4]. However, more studies are necessary to prove the existence of the κ phase, since the κ phase was reported to be observed after long heat treatments [2].

Acknowledgments

The authors wish to express their thanks to Dr. T. Kondo and Dr. M. Handa for their interest in this work.

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