Journal of Alloys and Compounds, 213/214 (1994) 402–405
JALCOM 4032

Investigation of the neptunium–zirconium system by X-ray diffraction

Michel M. Gensini, Richard G. Haire and John K. Gibson
Transuranium Research Laboratory, Oak Ridge National Laboratory, PO Box 2008, Oak Ridge, TN 37831-6375 (USA)

Abstract

X-ray powder diffraction analysis at 25 °C has been used to further characterize the Np–Zr phase diagram. We have studied a variety of Np–Zr aggregate compositions obtained by different preparative methods, including arc melting of the components. For the materials at ambient temperature, obtained by either slow cooling or quenching from elevated temperatures, we observed one or more of the following product phases: α-Np, α-Zr, $NpZr_2$ and one new phase. The last was interpreted tentatively to be either Np_4Zr or Np_6Zr. Calculations based on the X-ray data suggested a limited solubility of Np in α-Zr and an even lower solubility of Zr in α-Np. The X-ray data for the $NpZr_2$ phase showed that it possesses hexagonal symmetry and is isostructural with UZr_2 and $PuZr_2$. Annealing of Np–Zr composites at selected temperatures did not enhance the formation of $NpZr_2$.

1. Introduction

Alloys of zirconium with U, Np and Pu are of interest for various technological applications and for fundamental assessments of f-electron bonding behavior. The U–Zr [1] and Pu–Zr [2] systems have been studied extensively, while only limited work has been done on the Np–Zr system. In the U–Zr system, only a UZr_2 intermediate phase forms, while in the Pu–Zr system, two intermediate (Pu_xZr_y) binary phases in addition to $PuZr_2$ have been reported [2]. Since Np is the nearest neighbor of U and Pu, it was of interest to investigate the behavior of the Np–Zr system. We previously initiated studies of the Np–Zr system using differential thermal analysis (DTA) [3]; the major conclusions from these earlier studies were that Np and Zr have limited mutual solubilities and $NpZr_2$ is an intermediate phase which decomposes around 540 °C.

The work presented here is an extension of this earlier effort and concentrated on using X-ray diffraction (XRD) analysis for examining various Np–Zr composites obtained by three preparative routes.

2. Experimental details

The alloys were made from commercial zirconium metal (99.8 wt.%) and neptunium metal (99.9 wt.%). Alloy specimens (about 100 mg quantities) were obtained by (a) DTA [3] (*in situ* preparation), (b) arc melting and (c) DTA after arc melting.

X-ray powder diffraction analyses at 25 °C were performed on portions of these materials using Mo Kα radiation and Debye–Scherrer-type powder cameras. The observed interplanar distances and lattice parameters were refined using the programs POWLES [4] and MICRO-CELLREF [5]. Theoretical powder patterns were calculated with the MICRO-POWD program [6].

3. Results and discussion

Pure Zr and Np, as well as Np–Zr composites of various compositions (10, 25, 50, 67, 75 and 90 at.% Zr), were studied by XRD. The existence of four different phases was indicated by the X-ray data: α-Np, α-Zr, $NpZr_2$ (analogous to the δ phase of the U–Zr system) and an unknown phase believed to be either Np_4Zr or Np_6Zr. We did not obtain evidence for β-Np, γ-Np, β-Zr, NpO_2, NpN or any other additional phase or impurity in the products. The cell parameters obtained for pure α-Zr and pure α-Np were in good agreement with those found in the literature [7, 8].

3.1. *The δ phase ($NpZr_2$)*

Indexing of the X-ray data for the δ phase was based on a hexagonal structure in which the (0, 0, 0) sites are preferentially occupied by Zr atoms and the ($\frac{2}{3}$, $\frac{1}{3}$, $\frac{1}{2}$) and ($\frac{1}{3}$, $\frac{2}{3}$, $\frac{1}{2}$) sites are randomly occupied by Np and Zr atoms. This random distribution means that the significant "compound" composition is not restricted to the exact stoichiometry of 67 at.% Zr but can exist

Elsevier Science S.A.
SSDI 0925-8388(93)04032-Y

over a composition range, since the similarity of the atomic sizes of neptunium and zirconium allows for considerable substitution with little lattice strain. The proposed space group is *P6/mmm* [9] with three atoms per unit cell. Table 1 compares the lattice parameters of UZr_2, $NpZr_2$ and $PuZr_2$.

Although the proper symmetry assignment for UZr_2 is a modified, C32-A1B_2-type, hexagonal structure, it is also possible to index its diffraction lines in terms of a large b.c.c. cell. According to Boyko [10], the transformation of a single crystal of the γ phase of UZr_2 (b.c.c. cell), which is a disordered solid solution, to the ordered δ phase yields a twinned crystal which has four hexagonal cells. This causes the X-ray pattern to have a cubic appearance. This same phenomenon had been observed previously in the Ti–Cr system [11]. However, in the U–Zr system a cubic structure for the δ phase may be rejected, since it does not satisfy the details of the powder diffraction data and is inconsistent with the material's optical activity [12]. A list of our diffraction data for $NpZr_2$ with both cubic and hexagonal indexing is given in Table 2. Assignments for the major lines of α-Zr and α-Np that are coincident with cubic indexing lines of $NpZr_2$ are indicated.

3.2. The θ phase (Np_4Zr or Np_6Zr)

In all the alloys specimens studied, we observed diffraction lines which did not correspond to any allotropic phase of Np or Zr, to $NpZr_2$ or to NpO_2 or NpN. The nature and stoichiometry of the unknown phase(s) causing these lines, the analog of which has not been reported for the U–Zr system, may have a counterpart in the Pu–Zr system [2]. Two compounds have been proposed as the θ phase in the Pu–Zr system: Pu_4Zr and Pu_6Zr. Marples [13] reported the existence of a compound with an approximate stoichiometry of Pu_6Zr (orthorhombic structure) and a wide composition range; the structure type and space group were not determined. In contrast, Berndt [14] suggested a compound of the nominal formula Pu_4Zr (space group *P4/ncc* with 16 formula units per unit cell).

In the Np–Zr system our extra diffraction lines for the unknown phase agree well with those suggested for Pu_4Zr and we have tentatively assigned them to Np_4Zr.

TABLE 1. Room temperature cell parameters of UZr_2, $NpZr_2$ and $PuZr_2$

Compound	a_0 (pm)	c_0 (pm)	Reference
UZr_2	503	308	[1]
$NpZr_2$	502.4 (5)	307.5 (3)	This work
$PuZr_2$	505.5	312.3	[13]

TABLE 2. X-ray diffraction data for $NpZr_2$ obtained for a composite with an initial composition 75%Zr–25%Np (major lines of α-Np and α-Zr that are coincident with cubic indexing of $NpZr_2$ are also indicated)

Structural		Theoretical		Observed		Other assignments
Cubic	Hexag.	*d* (pm)	*I*	*d* (pm)	*I*	
211	100	435.1	94	433.7	m+	
222	001	307.5	166	307.4	s	
321	–			281.1	m+	100 α-Zr
400	–			262.7	m+	002 α-Zr
330	110	251.2	1000	250.7	vs	
	101	251.1	753			
332	–			229.4	m	021 α-Np
422	200	217.5	17	216.7	vw	
521	111	194.5	294	194.5	s	
440	–			191.2	s	102 α-Zr
442	201	177.6	279	177.7	s	
541	210	164.4	31		0	
444	002	153.7	79	153.6	w+	213 α-Np
640	–			147.9	m+	103 α-Zr
633	300	145.0	196	144.7	s+	
	211		294			
	102		11			
730	–			138.0	m+	112 α-Zr
732	–			135.9	m+	201 α-Zr
741	301	131.2	86	130.6	w	
	112	131.1	280			
660	220	125.6	121	125.5	m	
	202	125.5	7			
752	310	120.7	12	120.3	vw	
842	221	116.3	57	116.6	w	032, 141 α-Np
930	311	112.3	121	112.2	m	
	212		9			
844	400		0	109.4	m	203 α-Zr
10, 1, 1	302	105.5	128	105.2	w−	
666	401	102.5	43	102.5	w+	
	003		6			
871	320	99.8	6	100.1	vw	
774	103		39			
10, 4, 2	222	97.3	94	97.1	w+	
963	410	94.9	170	94.9	m	
	321		64			
	312		5			
	113		26			
882	203	92.7	29	92.7	vw	342 α-Np
11, 4, 1	411	90.7	44	90.4	w	
–	402	88.8	2	88.3	w+	302 α-Zr
990	330	83.7	44	83.9	w+	
	501		25			
	322		19			
	303		3			

3.3. Np–Zr samples of various compositions

A series of Np–Zr samples of various compositions (10, 25, 50, 67, 75 and 90 at.% Zr) were prepared by arc melting of the individual components. For each of these compositions we were able to observe the presence of α-Np and $NpZr_2$. Excluding the 10%Zr–90%Np composition, it was also possible to detect α-Zr in the samples. These observations suggest that the reaction $Np+2Zr \rightarrow NpZr_2$, did not go to completion under our experimental conditions. This incomplete conversion of the starting materials to $NpZr_2$ (*e.g.* to pure $NpZr_2$ or to $NpZr_2$ plus an excess of α-Zr or α-Np) may have resulted from slow diffusion rates, as was previously concluded in studies of the Pu–Zr system. We found the highest concentration of $NpZr_2$ in a composite having the aggregate composition 25%Np–75%Zr.

A second series of samples consisted of initially arc-melted Np–Zr samples which had been subsequently studied by DTA prior to the XRD analysis. These products represented materials that had been cooled slowly (about 10 °C min^{-1}). Even with this slower cooling rate, the concentration of $NpZr_2$ did not appear to increase. In addition, the cell volumes obtained for α-Np, α-Zr and $NpZr_2$ from data for the arc-melted or the arc-melted–DTA samples were identical.

We have initiated annealing studies using composites containing 33% Np in the initial aggregate for about 72 h at various selected temperatures (300–900 °C). The examination of these samples by X-ray analysis revealed that this short annealing period did not enhance the formation of $NpZr_2$ or alter the cell volume of $NpZr_2$ that was present. Studies involving longer annealing times are in progress.

In Fig. 1 the variation in the cell volume of α-Zr is presented as a function of the initial aggregate neptunium content. The calculated volumes for α-Zr (25 °C) that had been equilibrated with (10% or more) Np were found to be essentially constant but considerably larger than for pure α-Zr. We therefore conclude that there was an appreciable solubility of Np in the α-Zr; perhaps 10%, based on analogy with the studies done with the Pu–Zr system [15]. Analysis of X-ray data obtained at 25 °C following the annealing of the 33%Np–67%Zr composite suggested that the solubility of Np in α-Zr had decreased (decrease in the cell volume). When the annealing temperatures were higher than 600 °C, this solubility decreased further toward zero and the cell volume became equal to that for pure α-Zr.

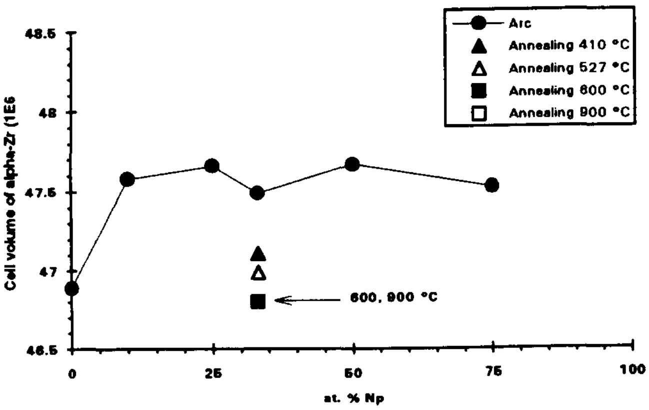

Fig. 1. Variation in cell volume of α-Zr *vs.* aggregate neptunium content.

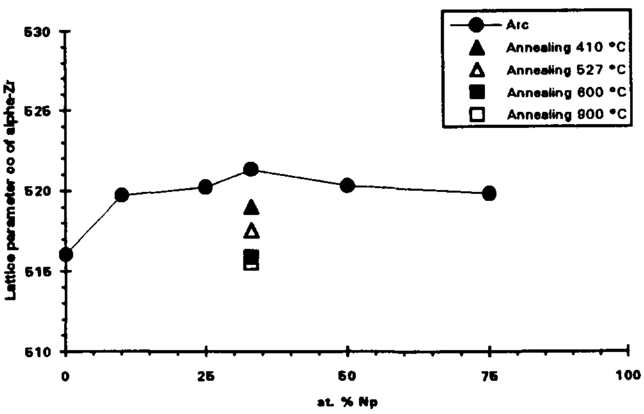

Fig. 2. Variation in lattice parameter c_0, of α-Zr *vs.* aggregate neptunium content.

In contrast, we concluded from the X-ray data that whatever the amount of α-Zr (10% or more) in equilibrium with α-Np, the cell volume of α-Np remains essentially constant. Therefore Zr has negligible solubility in α-Np.

Figure 2 shows the variation in the lattice parameter c_0 of α-Zr as a function of the aggregate neptunium content. The variation between c_0 of pure α-Zr and that of α-Zr saturated with Np ($\Delta c_0=4.0$ pm) is very close to the corresponding difference found in the Pu–Zr system (4.3 pm) [15]. We concluded from the X-ray data that the dissolution of Np in α-Zr only affects the c_0 axis, since we observed that the lattice parameter a_0 remained constant whatever the initial aggregate neptunium content was. This pattern of constant a_0 and variable c_0 is the same as encountered in the Pu–Zr system [15].

4. Conclusions

From our room temperature X-ray studies of Np–Zr composites prepared via different thermal treatments we have concluded that the major products were α-Np, α-Zr $NpZr_2$ and possibly either Np_4Zr or Np_6Zr. The formation of $NpZr_2$ and the values of its lattice parameters are in accord with data published for UZr_2 and $PuZr_2$. We have also shown that $NpZr_2$ has hexagonal symmetry rather than b.c.c. The maximum concentration of $NpZr_2$ was observed in 25%Np–75%Zr composites, although α-Np and α-Zr phases were also present in these samples. The X-ray data support a significant solubility of Np in the α-Zr phase but indicate a low solubility of Zr in α-Np. Annealing of the Np–Zr products at various temperatures (300–900 °C) for periods up to 72 h did not significantly increase the presence of $NpZr_2$ but did apparently alter the solubility of Np in the α-Zr phase. Additional work on the Np–Zr system is under way, but the findings to date contribute to the development of the Np–Zr phase diagram.

Acknowledgments

This work was sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, US Department of Energy under contract DE-AC0584-OR21400 with Martin Marietta Energy Systems, Inc. and by the Japan Atomic Energy Research Institute under the Japan–US Actinide program. This research is supported in part by an appointment to the Oak Ridge National Laboratory Postdoctoral Research Associates Program administered jointly by the Oak Ridge Institute for Science and Education and the Oak Ridge National Laboratory. The authors gratefully acknowledge the interests and efforts of S. Raman (ORNL) and T. Ogawa, T. Mukaiyama and A. Maeda (JAERI).

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