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An X-ray diffraction study of the Np–Ni system

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Abstract

The neptunium–nickel binary system has been studied by means of powder X-ray diffraction. The previously reported $NpNi_2$ Laves phase was confirmed and a previously unknown intermetallic compound, Np_2Ni_{17}, was identified. The crystal symmetry of Np_2Ni_{17} was determined to be the Th_2Ni_{17} type hexagonal structure which is the same as that of Pu_2Ni_{17}. The lattice parameters of Np_2Ni_{17} were calculated to be: $a_0 = 0.8333 \pm 0.0005$ and $c_0 = 0.8010 \pm 0.0009$ nm. The solubility limit of nickel in Np–Ni solid solutions and the composition range of $NpNi_2$ compound were also discussed. © 1997 Elsevier Science B.V.

1. Introduction

Systematic studies on the alloying behavior between minor actinides and transition metals are being performed [1–5]. In the studies, some phase diagrams have been obtained by combination of experimental and theoretical predictions. Although general shapes for the phase diagrams can be estimated from theoretical models, there is no method which is able to predict the formation of intermetallic compounds in metal alloys. Unlike thorium-, uranium- and plutonium–nickel binary systems, reliable reports were not available in neptunium–nickel system. In the Np–Mn, –Fe and –Co systems, the existence of both Np_6X [6] and NpX_2 [7] (X = Mn, Fe and Co) has been established while for the Np–Ni system, only the existence and lattice parameter of $NpNi_2$ compound have been reported [7]. The existence of $NpNi_5$ was expected based on the existence of Th-, U- and $PuNi_5$ compounds and, recently, we have confirmed the existence and crystal chemistry of $NpNi_5$ compound [8]. The crystal structure of $NpNi_5$ was confirmed to be the same as those of Th- and Pu–Ni_5 compounds, which possess the hexagonal D2d $CaCu_5$ structure. Conversely, UNi_5 compound has the cubic C15b $AuBe_5$ structure. From the similarity of Np–Ni system to Th- or Pu–Ni systems, it could be expected that additional binary compounds such as $NpNi_3$, $NpNi_4$, Np_2Ni_{17} and so on might be formed in the system.

The main purpose of the present study is to elucidate the existence and crystal structure of additional Np–Ni compounds by means of powder X-ray diffraction.

2. Experimental

Three Np–Ni alloys with nominal compositions of Np–14.3, 75.0 and 89.5 at.% Ni were prepared by arc melting mixtures of pure neptunium and nickel metals. The neptunium metal with a purity of 99.99 wt% was obtained from calcium reduction of NpF_4 and electrorefining [9], and the nickel metal was a commercial product with a purity of > 99.9 wt%. After all the metals have been weighed to within 0.01 mg, the metal mixture was charged in a non-consumable arc-melting furnace using a copper hearse, which was installed in a purified-helium atmosphere glove box. The arc-melting were repeated several times to ensure complete homogeneity of the alloy buttons. After the arc-melting, the weight loss of each alloy button was examined to confirm that retention of the components was at least 95%. All the products obtained were very brittle in nature and easily broken into small pieces or powder for microscopic examinations, samples for annealing and X-ray diffraction measurement.

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The arc-melted alloy samples were sealed in partially evacuated (0.1 atm helium for thermal conductance) quartz capillaries for X-ray diffraction analysis. The as-prepared alloy samples were also annealed at 773 and 973 K in the quartz capillaries. Powder X-ray diffraction analyses at room temperature were performed for both the as-prepared and annealed samples using a conventional 114.6 mm Debye–Scherrer camera together with Mo–K radiation. The mounting of X-ray films in the camera was done based on the Straumanis arrangement. The diffraction lines on the X-ray films were indexed and then analyzed with the program POWLES [10] to calculate lattice parameters for each phases observed.

3. Results and discussion

3.1. Np–14.3 at.% Ni alloys (Np_6Ni)

The alloys were annealed up to 843 K step by step (for 90 h at 673 K and for 213 h at 773 K). After the annealing for 24 h at 843 K, a slight reaction between the alloys and quartz capillary was observed. The diffraction patterns showed that the alloys were composed of αNp and other phases, which are likely to be neptunium oxides (NpO or NpO_2) and $NpNi_2$ compound. Some alloy fragments gave clear diffraction lines of $NpNi_2$ compound with a cubic structure. The lattice parameters of αNp seem to differ slightly from those of pure αNp [11], shown in Table 1. The increase in the lattice parameters is considered to be due to the formation of αNp(Ni) solid solution. However, based on atomic sizes of neptunium and nickel, a decrease in the lattice parameters for the Np–Ni solid solutions can be expected, because the atomic radius of nickel is very small (0.1246 nm) compared with that for α-neptunium (0.1503 nm). It is concluded, therefore, that the increase in the crystal size for the Np(Ni) solid solutions must be due to a decrease in valence for Np in solid solution. The atomic volumes of neptunium in Np(Ni) solid solutions were estimated by assuming that the Np(Ni) solid solution is pure Np metal, as shown in Table 1. By using the relationship between atomic sizes and valences of Zachariasen [12], the valence of neptunium in the Np(Ni) solid solutions was estimated to be about 6.8, which correspond to a reduction of 0.2 from 7 of pure neptunium. If the size effect of nickel with smaller size is taken into consideration, lower valences of neptunium may be expected.

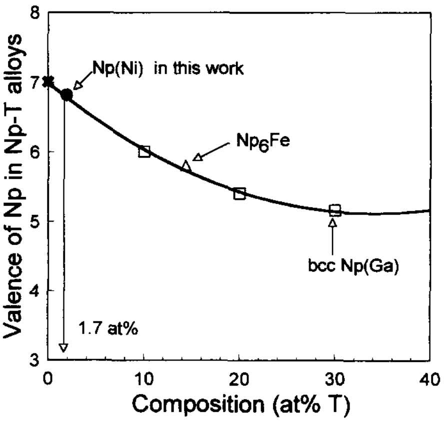

Fig. 1. Np valence and solubility of Ni in the Np(Ni) solid solutions for Np–14.3 at.% Ni alloys, including the data for αNp [12], Np_6Fe [6] and Np(Ga) [13].

Elliot et al. [13] and Giessen et al. [6] have estimated the partial atomic volumes and valences of neptunium in bcc Np(Ga) solid solutions and Np_6Fe compound, respectively, by using a simple technique. Fig. 1 shows the composition dependence of Np valences in the Np alloys, including the valence of pure Np [12]. From the dependence of valences for neptunium on compositions, the solubility of nickel in the Np(Ni) solid solution was determined to be about 1.7 at.%. The solubility seems to be slightly larger than those for U- or Pu–Ni systems, where the solubility of nickel is below about 1 at.% in low temperature phases [14].

The C15-type cubic structure for $NpNi_2$ compound proposed by Lam et al. [7] was also confirmed in this study. The lattice parameter obtained from the alloy annealed at 843 K was $a = 0.7144 \pm 0.0002$ nm. This value is significantly larger than that (0.70981 nm) reported by Lam et al. and is very similar to that for $NpFe_2$. This is considered to be mainly due to a composition region of $NpNi_2$. The composition range will be discussed later.

Table 1
The crystallographic parameters of αNp

Sample	Conditions	Lattice parameters (nm)			Cell vol. (nm^3)	Atomic vol. of Np (nm^3)
		a	b	c		
Pure αNp [a]		0.4722	0.4887	0.6663	0.1538	0.01922
αNp(Ni)	as-prepared	0.475	0.492	0.666	0.1556	0.01945
αNp(Ni)	673 K/90 h	0.476	0.490	0.666	0.1553	0.01941
αNp(Ni)	773 K/213 h	0.477	0.489	0.665	0.1554	0.01943

[a] By Pearson [11].

Table 2
The crystallographic parameters for $NpNi_2$ compounds

Sample	Lattice parameter, a (nm)	V_{mol} (nm^3)	d_{Ni} (nm)
$NpNi_2$ [a]	0.70981	0.0447	0.2510
$NpNi_2$ in 14.3 at.% Ni alloy	0.7144	0.0456	0.2526
$NpNi_2$ in 75.0 at.% Ni alloy	0.7057	0.0439	0.2495
Ni [b]			0.2492

[a] For stoichiometric $NpNi_2$ by Lam et al. [7].
[b] For pure Ni [15].

3.2. Np–75.0 at.% Ni alloy ($NpNi_3$)

This alloy was used to examine the composition region between $NpNi_2$ and $NpNi_5$ compounds. The alloys sealed in quartz capillaries were annealed for 100 h at 973–990 K. The X-ray patterns of the cubic $NpNi_2$ including NpO_{2-x} were obtained for both the as-prepared and annealed samples. This result suggests that there would be no additional compounds in the composition region between $NpNi_2$ and $NpNi_5$ compounds, although whether the existence of NpO_{2-x} affects the appearance of Np–Ni compounds or not is not clear. The refinement of X-ray diffraction pattern for $NpNi_2$ observed in the $NpNi_3$ alloy annealed at 973 K for 100 h gave the lattice parameter of $a = 0.7057 \pm 0.0003$ nm. It should be noted that this lattice parameter is smaller than those (0.70891 and 0.7144 nm, respectively) for the stoichiometric $NpNi_2$ [7] and our Np_6Ni alloy. The crystallographic parameters for the $NpNi_2$ compounds are summarized in Table 2. The result suggests that the $NpNi_2$ compound has a composition range over which this phase is stable, and that the lattice parameter decreases significantly as the nickel concentration increases. In other words, the substitutions of Ni by Np or Np by Ni in the $NpNi_2$ compound result in an increase or a decrease of the lattice parameters. This tendency can be easily expected from the fact that even if Np has any valence in the $NpNi_2$ compound, the atomic size of Np must be larger than that of Ni. The random substitution seems more likely than assuming increases of Ni vacancies or interstitials. $ThNi_2$ and $PuNi_2$, which possess the same crystal structure as $NpNi_2$, have narrow composition ranges of 64.75 ± 0.5 [15] and 66.5–68 [16] at.% Ni, respectively, over which these phases are stable. UNi_2 [16] also has a narrow composition range of 66.7–67 at.% Ni, although the crystal structure is the hexagonal C14-type. In this study, the composition range of $NpNi_2$ compound was roughly estimated from a simple method, in which the atomic volumes of Np and Ni in $NpNi_{2+x}$ are assumed to be constant. The molar volume, V_{mol}, of the $NpNi_{2\pm x}$ where V_{Np} and V_{Ni} are the atomic volumes of

Table 3
X-ray powder data for Np_2Ni_{17} annealed at 973 K

$d_{obs.}$ (nm)	$d_{calc.}$ [a] (nm)	hkl	I(obs.)	I/I_0(calc.)
0.5401	0.5362	101	vvw	11
0.4133	0.4167	110	w	6
–	0.4005	002	–	3
0.3608	0.3608	200	vvw	0
0.3490	0.3502	102	vvw	5
0.3284	0.3290	201	vw	4
0.2898	0.2887	112	s	37
0.2690	0.2681	202	vw	3
0.2569	0.2582	211	vw	4
–	0.2504	103	–	14
0.2391	0.2406	300	m	44
0.2251	0.2254	212	vw	4
0.2147	0.2146	203	m	9
–	0.2083	220	–	47
0.2062	0.2062	302	vs	100
0.2000	0.2003	004	w+	26
–	0.1930	104	–	4
0.1907	0.1908	213	w–	13
0.1836	0.1848	222	w–	12
–	0.1790	312	–	2
0.1767	0.1760	401	vw	1
–	0.1751	204	–	2
0.1642	0.1645	402	vvw–	1
–	0.1614	214	–	3
0.1605	0.1602	313	vvw	7
0.1567	0.1575	410	vvw–	2
0.1541	0.1539	304	w+	10
–	0.1495	403	–	3
0.1469	0.1466	412	w–	11
0.1443	0.1444	224	m–	16
0.1406	0.1407	323	vw	5
0.1386	0.1389	330	vw	8
0.1312	0.1312	332	m–	23
0.1273	0.1271	116	vw	5
0.1248	0.1251	315	vvw	2
–	0.1215	423	–	3
0.1208	0.1203	600	w	20
0.1165	0.1167	306	w+	18
0.1145	0.1141	334	vw	4
0.1110	0.1110	522	vw	4
–	0.1084	433	–	2
0.1068	0.1072	505	vvw	1
–	0.1042	440	–	4
0.1034	0.1031	604	w	15
0.1022	0.1021	416	vvw	5
–	0.1001	008	–	3
0.0963	0.0963	336	w–	8
0.0929	0.0924	308	vw	3
0.0907	0.0909	630	vvw	6
0.0873	0.0874	526	vw	3
0.0790	0.0787	820	vvw	5
0.0770	0.0770	608	vvw	6

[a] Calculated by using the lattice parameters obtained from fitting.

Table 4
The crystallographic parameters for An_2Ni_{17} compounds

Compound	Lattice parameter (nm)		c/a	Cell volume (nm^3)
	a	c		
Th_2Ni_{17}	0.837	0.814	0.973	0.2469
Np_2Ni_{17}	0.833	0.801	0.962	0.2407
Pu_2Ni_{17}	0.829	0.801	0.966	0.2384

Np and Ni atoms in stoichiometric $NpNi_2$ compound [7], respectively. V_{Ni} (0.0112 nm^3) was determined from the interatomic distance of Ni atoms (0.2510 nm) and V_{Np} (0.0224 nm^3) was then calculated from V_{Ni} and V_{mol} (0.0447 nm^3). From the lattice parameters of the Np-rich and Ni-rich $NpNi_2$ compounds, the composition range was found to be 64–69 at.% Ni. This composition range seems to be significantly larger than those for another $AnNi_2$ compound. In this treatment, the valence change of Np with Ni concentrations was neglected, and if it is possible, the composition range would change.

3.3. Np–89.5 at.% Ni alloy (Np_2Ni_{17})

The alloy was used to speculate on whether the Np_2Ni_{17} compound may exist and if so what structure it would have. The refinement of the powder X-ray patterns was performed based on a hexagonal structure similar to those for Th_2Ni_{17} and Pu_2Ni_{17}. Lattice parameters obtained for the alloy annealed at 973 K were

$a = 0.8333 \pm 0.0005$ nm and
$c = 0.8010 \pm 0.0009$ nm.

Table 3 shows the observed and calculated data including d values and intensities. The theoretical data on the powder X-ray diffraction were calculated from the obtained lattice parameters on the basis of the Th_2Ni_{17} structure, with the MICRO-POWD program [17]. Although some weak peaks were missed, the observed data were in good agreement with the calculated ones, suggesting the existence of Np_2Ni_{17} compound with the same structure as for Th_2Ni_{17} and Pu_2Ni_{17}. The $P6_3/mmm$ hexagonal structure for An_2Ni_{17} is closely related with the P6/mmm D2d structure for $AnNi_5$ [18]. The An_2Ni_{17} can be obtained directly from the $AnNi_5$ by substituting one-third of actinide atoms with pairs of nickel atoms whose ligand is oriented along [001]. The lattice parameters and cell volumes of the An_2Ni_{17} are listed in Table 4. The cell height, c, is about two times that of the $AnNi_5$ and its cell volume is equivalent to about six times that of the $AnNi_5$ cells. Just like the compounds $AnNi_5$ (An: Th, Np and Pu) [8], the actinide contraction (5f contraction) with increasing atomic number can be clearly observed. The tendency reflects contractions in bond length/radii. The 5f contraction has not been observed in the actinide-3d transition metal Laves compounds [7]. It should be also noted that the c/a axial ratios of the An_2Ni_{17} compounds are roughly identical to 0.96–0.97.

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