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Thermal expansion of neptunium–plutonium mixed oxides

Toshiyuki Yamashita[a,*], Hiroshi Muto[a], Toshihide Tsuji[b], Yukinori Nakamura[b]

[a]Department of Chemistry and Fuel Research, Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki 319-11, Japan
[b]Department of Nuclear Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-01, Japan

Abstract

Thermal expansion of $Np_yPu_{1-y}O_{2-x}$ (y=0, 0.05, 0.1, 0.2 and 0.5) solid solutions was studied by high-temperature powder X-ray diffraction method at temperatures between room temperature and 1273 K in air and in He–8%H_2 atmospheres. From the comparison of lattice parameters measured in air and in He–8%H_2, all of these solid solutions appeared to be the stoichiometric composition when heated in air. The specimens heated in He–8%H_2 became slightly hypo-stoichiometric above 1100 K, and the oxygen deficiency was estimated to be about 0.003 at 1273 K. The linear thermal expansion (LTE) of $Np_yPu_{1-y}O_2$ decreased with increasing Np content at high temperatures, which was consistent with the fact that the LTE value of NpO_2 was smaller than that of PuO_2. The specific heat capacities at constant pressure C_p of these solid solutions were calculated from the thermodynamic relation C_p (J K^{-1} mol^{-1})=$\beta V/\kappa_a\gamma$ using the measured thermal expansion data and estimated mechanical properties. Although the calculated C_p yielded about 20% larger values than those of the literature at high temperatures, the calculated C_p curves showed a similar temperature dependence to the literature one as well as a reasonable composition (Np content) dependence.

Keywords: Thermal expansion; Neptunium–plutonium mixed oxides; Heat capacity

1. Introduction

In order to develop new fuels intended to transmute and/or burn the lighter actinides (Np, Am and Cm) in nuclear reactors, it is important to know the basic properties of the lighter actinide elements and their solid solutions with U and/or Pu. Some information was available in the extensive work by Katz et al. [1] for the binary oxides of each element. Little is, however, known for the ternary oxides among these elements.

We began a research program clarifying the basic properties of the U–Pu–Np–O system several years ago. We proposed the phase diagram of UO_2–U_3O_8–NpO_2 system [2] where the extensive solid solution existed in the range of UO_2–$UO_{2.25}$–$U_{0.4}Np_{0.6}O_{2.27}$–NpO_2. We also examined the thermal expansion of actinide dioxides [3] and $(Np,U)O_2$ solid solutions [4]. In the latter paper, we presented the possibility to obtain the specific heat capacities from the thermodynamic relation, C_p (J K^{-1} mol^{-1})= $\beta V/\kappa_a\gamma$, using measured thermal expansion data and the mechanical properties, as well as the linear thermal expansions of the $Np_yU_{1-y}O_2$ (y=0–1) solid solutions.

Because no data have been reported on the thermal expansion nor the specific heat capacity of $Np_yPu_{1-y}O_2$ solid solutions, we examined the thermal expansion of these solid solutions by the high-temperature X-ray diffraction method and made an attempt to obtain the heat capacity of these solid solutions.

2. Experimental details

Plutonium dioxides were dissolved in 7 M HNO_3 at about 350 K. The solution was passed through an ion-exchange column of Dowex 1-X4 to remove ^{241}Am impurity. Plutonium oxalate was precipitated from the solution by adding oxalic acid, and then heated in air at about 1200 K to decompose the oxalate to PuO_2. Neptunium dioxide was provided from Fonteney aux Roses, France, and was heated in air at 1273 K before use.

The weighed amounts of NpO_2 and PuO_2 powders were mixed thoroughly and pressed into pellets. These pellets were heated at 1700 K in vacuum. Products were ground in an agate mortar and subjected to X-ray diffraction analyses. Heating and grinding processes were repeated several times until a sharp X-ray diffraction pattern from a single-phase solid solution was obtained.

A high-temperature X-ray diffraction study was carried out using a Rigaku RAD-3C diffractometer system attached to a furnace unit. The vacuum housing and a Pt

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[*] Corresponding author. Tel.: +81 29 2825496; fax: +81 29 2825935.

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heating element allowed examination in controlled atmospheres of He–8%H_2 gas or in air at high temperatures. Furnace temperature was measured by an R-type thermocouple and was controlled by a PID-type temperature controller within ±1 K during X-ray measurements. Each specimen was annealed first at 1273 K in He–8%H_2 gas or in air for 1 h in order to recover any lattice distortions in crystallites by self-radiation damage, before X-ray measurements were made.

Lattice parameters were calculated from all reflections ($20° < 2\theta < 145°$) employing the least-squares method for the Nelson–Riley extrapolation. The estimated standard errors of the calculated lattice parameters were within ±0.02 pm. More detailed description of the high-temperature X-ray diffraction was given in our previous paper [3].

3. Results and discussion

Effects of heating atmospheres on the lattice parameter for $Np_yPu_{1-y}O_{2+x}$ ($y=0$, 0.05, 0.1, 0.2 and 0.5) were examined both in He–8%H_2 and in air. In Fig. 1, lattice parameters of $Np_yPu_{1-y}O_{2+x}$ solid solutions are plotted as a function of temperature. Open marks indicate the values obtained in He–8%H_2 gas and closed marks in air. Below 1100 K, lattice parameters of the specimen heated in air are the same as those heated in He–8%H_2, indicating that the specimen heated in air is the stoichiometric composition (O/M=2.00). Above 1100 K, however, lattice parameters obtained in He–8%H_2 are larger than those in air. The differences in lattice parameters are about 0.1 pm at 1273 K. Since PuO_2 has been known to become hypo-stoichiometric at high temperatures under very low oxygen potentials, the larger lattice parameter of the specimen heated in He–8%H_2 is attributed to slight reduction of the specimen. Although no relationship has been established yet between the lattice parameter and the composition x in $Np_yPu_{1-y}O_{2-x}$, some information about the relationship was available for hypo-stoichiometric PuO_{2-x}. Gardner et al. reported the lattice parameter of PuO_{2-x} at high temperatures [5]. The change in lattice parameter with x was estimated to be −39 pm at 1273 K. Sari et al. found a linear change in lattice parameter with x for PuO_{2-x} ($0.38 < x < 0.31$) [6]. The change in lattice parameter with x was estimated to be −35 pm at room temperature. Therefore the x value in $Np_yPu_{1-y}O_{2-x}$ heated in He–8%H_2 was estimated to be about 0.003 by assuming that the dependence of the lattice parameter on the x value for the $Np_yPu_{1-y}O_{2-x}$ solid solutions is the same as that for undoped PuO_{2-x}.

Lattice parameters of $Np_yPu_{1-y}O_2$ ($y=0$, 0.05, 0.1, 0.2 and 0.5) heated in air are plotted against temperature in Fig. 2. Closed marks indicate the values shown in Fig. 1 and open marks are those obtained in the second run. Agreement between them is excellent. Lattice parameters for PuO_2 are represented by a solid line. The lattice parameter of each specimen increases smoothly with increasing temperature to about 1300 K, indicating that no phase transitions nor any other orderings occur in the temperature range investigated. Measured lattice parameters were fitted as a function of temperature in the form of $a_T = b_0 + b_1T + b_2T^2 + b_3T^3$ where a_T was the lattice parameter at temperature T (K). The regression results are listed in Table 1. The standard deviations of the regression (ESD) are shown in the last column. Although the lattice parameter at 298 K (a_{298}) shown in the sixth column in the

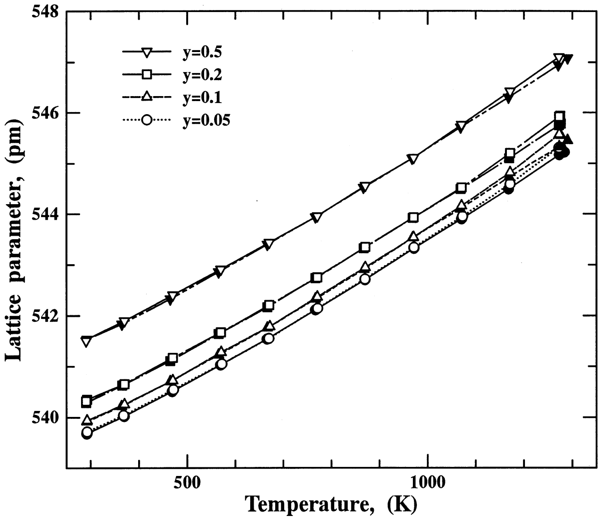

Fig. 1. Lattice parameters of $Np_yPu_{1-y}O_{2-x}$ ($y=0.05$, 0.1, 0.2 and 0.5) obtained in air and He–8%H_2 atmospheres as a function of temperature. (○) $y=0.05$, (△) $y=0.1$, (□) $y=0.2$, (▽) $y=0.5$. Open symbols indicate the values obtained in He–8%H_2, and the closed symbols the values obtained in air.

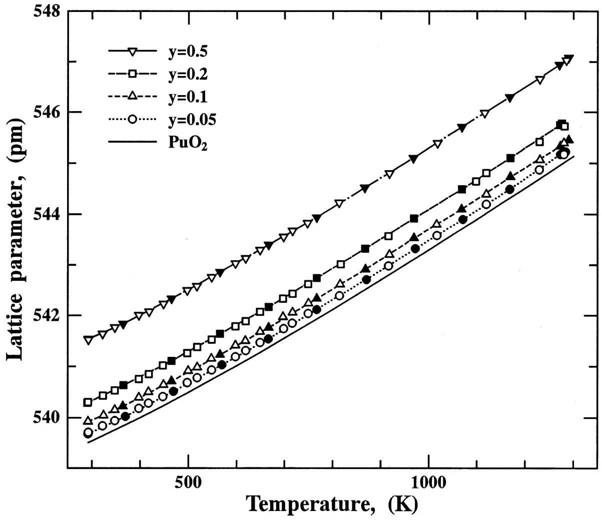

Fig. 2. Thermal expansion of $Np_yPu_{1-y}O_{2.0}$ ($y=0$, 0.05, 0.1, 0.2 and 0.5) obtained in air plotted as the lattice parameter versus temperature. (○) $y=0.05$, (△) $y=0.1$, (□) $y=0.2$, (▽) $y=0.5$. The solid line shows the value of PuO_2. Closed symbols indicate the values plotted in Fig. 1, and open symbols the values obtained in the second run.

Table 1
Regression data for $Np_yPu_{1-y}O_2$ solid solutions

y value	b_0 (pm)	b_1 ($\times10^3$)	b_2 ($\times10^6$)	b_3 ($\times10^{10}$)	a_{298} (pm)	ESD
0.0	538.397	3.169	2.359	−6.265	539.53	0.039
0.05	538.534	3.395	2.067	−5.137	539.72	0.012
0.10	538.793	3.178	2.395	−6.693	539.94	0.013
0.20	539.163	3.202	2.420	−6.993	540.31	0.020
0.50	540.328	3.551	1.854	−4.373	541.54	0.014

a_T (pm)$=b_0+b_1T+b_2T^2+b_3T^3$.

table increases almost linearly with increasing the y value, the experimental a_{298} value for the specimen with $y=0.5$ (541.54 pm) is a little larger than the calculated one (541.43 pm) for the ideal solid solution between PuO_2 and NpO_2, which indicates that some interactions may occur between Np^{4+} and Pu^{4+} in the solid solution. Further investigations, such as vapor pressure measurements will be required for the detailed discussion.

Values of the linear thermal expansion (LTE) at temperature T were calculated by the relation,

$$\mathrm{LTE}(T)\,(\%) = (a_T - a_{298})100/a_{298}.$$

The LTE values of $Np_yPu_{1-y}O_2$ solid solutions at 1300 K were calculated to be 1.037, 1.031 and 1.030% for $y=0$, 0.1 and 0.5, respectively, using the a_{298} value listed in Table 1. The LTE values of the solid solutions decreased with increasing y values, which was good in line with the fact that the LTE value of NpO_2 was lower than that of PuO_2 at high temperature [3].

The specific heat capacity at constant pressure C_p can be derived by using the thermodynamic relation, C_p (J K^{-1} mol^{-1})$=\beta V/\kappa_a\gamma$, where β is the coefficient of isobaric volumetric expansion, V the molar volume, κ_a the adiabatic compressibility and γ the Grüneisen constant. The relation $\beta=3\alpha$ is good for an isotropic cubic material, where α is the coefficient of linear thermal expansion. In our previous paper [4], we have shown that the specific heat capacity was estimated with reasonable accuracy through the thermodynamic relation using the measured thermal expansion data, provided that mechanical properties, such as the adiabatic compressibility, Young's modulus, Poisson's ratio and the Grüneisen constant were available. In the case of UO_2 where the mechanical properties were fairly well known, the estimated C_p values represented the measured ones within the error of about 5% at high temperature. It should be noted here that measured lattice parameters were fitted into the function of $a_T=b_0+b_1T+b_2T^2+b_3/T$, which was used in our previous paper [4], in order to obtain a good temperature dependence of the estimated C_p.

Because no data of the κ_a and γ were available for NpO_2, PuO_2 and (Np,Pu)O_2 solid solutions, these values were estimated as follows. The Grüneisen constant γ for NpO_2, PuO_2 and (Np,Pu)O_2 solid solutions were assumed to be the same as that for UO_2, which was given to be 1.9±0.1 by Momin and Karkhanavala [7]. The adiabatic compressibility κ_a for NpO_2 and PuO_2 were calculated from the relation $\kappa_a=3\alpha V/\gamma C_p$ using the measured α and V values and the reported C_p values, at 298 K, of 66.22 and 68.62 J K^{-1} mol^{-1} for NpO_2 [8] and PuO_2 [9], respectively. These C_p values were obtained by low-temperature heat capacity measurements and were considered to be more accurate than those obtained by high-temperature measurements. Since no measured C_p data were available for (Np,Pu)O_2 solid solutions, the adiabatic compressibility for the solid solutions κ_a(ss) was assumed to be calculated from the relation $\kappa_a(\mathrm{ss})=\kappa_a(\mathrm{NpO_2})y+\kappa_a(\mathrm{PuO_2})(1-y)$ where $\kappa_a(\mathrm{NpO_2})$ and $\kappa_a(\mathrm{PuO_2})$ were the adiabatic compressibility values of NpO_2 and PuO_2, respectively. Although these mechanical properties may be dependent on temperature, they were assumed to be independent of temperature for the zeroth approximation here.

Calculated C_p values for PuO_2, NpO_2 and (Np,Pu)O_2 solid solutions are plotted against temperature in Fig. 3, together with the literature values of NpO_2 [10] and PuO_2 [11]. As seen in Fig. 3, the estimated C_p values are all higher than the literature ones except for those of NpO_2.

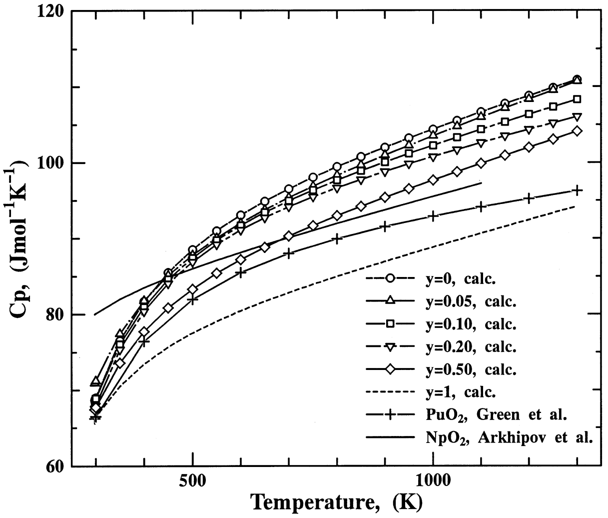

Fig. 3. Estimated specific heat capacities of $Np_yPu_{1-y}O_{2.0}$ ($y=0$, 0.05, 0.1, 0.2 and 0.5) plotted against temperature. (○) $y=0$, (△) $y=0.05$, (□) $y=0.1$, (▽) $y=0.2$, (◇) $y=0.5$ and (+) PuO_2 by Green et al. [11]. The broken line shows the value for NpO_2 estimated earlier [4], and the solid line the value for NpO_2 by Arkhipov et al. [10].

The assumption that the values of κ_a and γ were independent of temperature seems to be the main reason why the estimated C_p values for PuO_2 and solid solutions are higher than those for the literature. According to Padel and De Novion [12], the Young's modulus of UO_2 decreased with temperature and, at 1273 K, it became about 90% of the value at room temperature. Since the specific heat capacity is proportional to the Young's modulus, the difference between the calculated C_p and the literature one would become smaller if the temperature dependence of the Young's modulus of these materials is taken into account. It will be possible to predict more accurate C_p for those materials through the present method when we have a complete set of data for κ_a and γ. Since the C_p value of 80 J K^{-1} mol^{-1} for NpO_2 at 298 K measured by Arkhipov et al. [10] is apparently higher, as discussed elsewhere [4], direct comparison between the measured and the estimated C_p for NpO_2 is not very much fruitful.

Although the estimated C_p curves were about 20% larger than the measured ones, a couple of points are worthy of note. Firstly, all of the calculated C_p curves show nearly the same temperature dependence as those of the literature PuO_2. Secondly, the calculated C_p values for $Np_yPu_{1-y}O_2$ decrease with increasing Np content of y.

4. Conclusions

Lattice parameter of $Np_yPu_{1-y}O_{2-x}$ ($y=0$, 0.05, 0.1, 0.2 and 0.5) was measured by the high-temperature powder X-ray diffraction method at temperatures between room temperature and 1273 K in air and in He–8%H_2 atmospheres.

From the comparison of lattice parameters of the solid solutions obtained in air and in He–8%H_2, the solid solutions were of stoichiometric composition when heated in air, and they became slightly hypo-stoichiometric when heated in He–8%H_2 above 1100 K. The oxygen deficiency at 1273 K was estimated to be about 0.003.

Lattice parameters of the solid solutions at room temperature increased linearly with increasing Np content, and that of $Np_{0.5}Pu_{0.5}O_2$ was slightly larger but beyond experimental error than the calculated value for the ideal solid solution, indicating the existence of some interactions between Pu^{4+} and Np^{4+} ions.

The linear thermal expansion of the solid solutions decreased with increasing Np contents at high temperatures, which was consistent with the fact that the LTE value of NpO_2 was smaller than that of PuO_2.

The specific heat capacities of the solid solutions were calculated from the thermodynamic relation C_p (J K^{-1} mol^{-1})$=\beta V/\kappa_a\gamma$ using measured thermal expansion data and estimated mechanical properties. Although the calculated C_p values were overestimated by about 20% against the literature values, they showed nearly the same temperature dependence as the literature ones, and good composition (Np content) dependence.

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