Thermal expansion of neptunium–uranium mixed oxides

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Abstract

Thermal expansions of $Np_yU_{1-y}O_2$ solid solutions were investigated between room temperature and 1273 K by a high temperature X-ray diffraction technique. The lattice parameters of $Np_yU_{1-y}O_2$ solid solutions at high temperatures were given in polynomial expressions of temperature. High temperature heat capacities, C_p, of $Np_yU_{1-y}O_2$ solid solutions were estimated from the thermodynamic relation using the measured thermal expansions and literature data. The estimated errors in the calculated C_p of UO_2 were less than $\pm 5\%$. © 1997 Elsevier Science B.V.

1. Introduction

During the burn-up of nuclear fuels, long-lived lighter actinides (Np, Am and Cm) are accumulated in the fuel; neptunium thus produced amounts to about 60% of these elements. It is necessary to understand the fundamental thermodynamic properties of neptunium–uranium mixed oxides, in order to clarify the behavior of Np in the fuel and/or to develop new fuels containing lighter actinides. Little is, however, known about basic thermodynamic properties of these mixed oxides. The authors have established the phase diagram of the ternary UO_2–U_3O_8–NpO_2 system where a wide and homogeneous solid solution phase of $(Np, U)O_{2+x}$ exists in the range of UO_2–U_4O_9–$U_{0.4}Np_{0.6}O_{2.27}$–NpO_2 [1]. It was also found that lattice parameters of the $(Np, U)O_2$ solid solutions at room temperature decreased linearly with Np content from 547.04 pm for UO_2 to 543.36 pm for NpO_2, indicating that the $(Np, U)O_2$ solid solutions were almost ideal.

In the present study, thermal expansions of $(Np, U)O_2$ solid solutions have been measured by means of high temperature powder X-ray diffraction. An attempt was made to estimate specific heat capacities of these solid solutions from the measured linear thermal expansion coefficients using the thermodynamic relation, $C_p = \beta V / \kappa_a \gamma$, where C_p is the specific heat capacity at constant pressure,

β is the coefficient of isobaric volumetric expansion, V is the molar volume, κ_a is the adiabatic compressibility and γ is the Grüneisen constant.

2. Experimental details

2.1. Materials

Uranium dioxide was prepared by reducing U_3O_8 in a stream of purified hydrogen gas at 1273 K for 10 h. The U_3O_8 was prepared by oxidizing high purity uranium metal blocks with metallic impurities of less than 20 ppm [2] in air at about 1000 K. Neptunium dioxide powder was provided from Fontenay auch Roses, France. The main impurities were Na(50 ppm), Si(50 ppm) and Fe(200 ppm). The NpO_2 powder was heated in air at 1273 K before use.

The weighed amounts of NpO_2 and UO_2 powders were thoroughly mixed and pressed into pellets. These pellets were heated at 1700 K in vacuum. Products were ground in an agate mortar and were 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.

2.2. X-ray diffraction study

High temperature X-ray diffraction study was carried out using a Rigaku RAD-3C diffractometer system attached a furnace unit. Furnace temperature was measured

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by an R-type (Pt/Pt 13% Rh) thermocouple and was controlled by a PID-type temperature controller within ± 1 K during X-ray measurements. Sample temperature was determined by the lattice parameter of the Pt sample holder and the thermal expansion data of platinum [3]. The estimated error in temperature was ± 10 K, most of which came from uncertainties in determination of the lattice parameter of platinum.

Each specimen was annealed first at 1273 K in He–8 vol.% H$_2$ atmosphere for 2 h in order to recover any lattice distortions in crystallites by self-radiation damage, before X-ray measurements were made. Then the furnace temperature was lowered by 50 or 100 K and kept at that temperature for 1 h and the X-ray measurements were carried out in an atmosphere of He–8 vol.% H$_2$ at high temperatures to ensure that the specimen was at the stoichiometric composition. The peak positions of X-ray diffraction taken at room temperature before and after heating were almost identical for all specimens.

Lattice parameters were calculated from all reflections (20° < 2θ < 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.

3. Results and discussion

3.1. Thermal expansion

Lattice parameters of Np$_y$U$_{1-y}$O$_2$ solid solutions are plotted against temperature in Fig. 1, together with those of NpO$_2$ and UO$_2$. Lattice parameters of every specimen increase smoothly with temperature to about 1300 K,
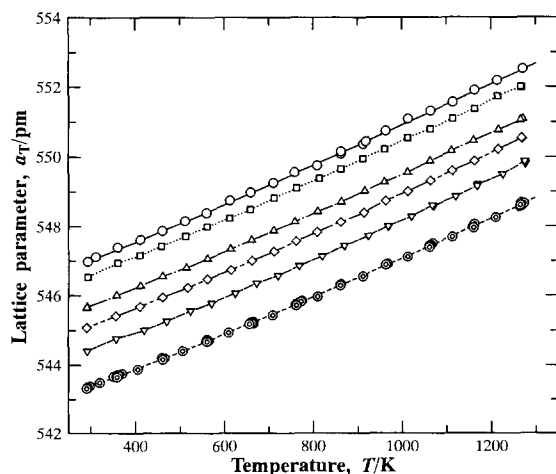
Table 1
Regression data for Np$_y$U$_{1-y}$O$_2$ solid solutions

y value	b_0 (pm)	b_1 (×10^3)	b_2 (×10^6)i	b_3 (×10^{10})	a_{298} (pm)	ESD
0.0	545.567	4.581	1.036	−2.736	547.02	0.041
0.1	545.203	4.193	1.382	−3.872	546.67	0.017
0.3	544.396	3.878	1.615	−4.365	545.68	0.013
0.5	543.903	3.468	2.111	−6.028	545.11	0.014
0.7	543.245	3.462	2.063	−5.925	544.45	0.015
1.0	542.032	4.276	0.9075	−1.362	543.38	0.028

a_T (pm) $= b_0 + b_1 T + b_2 T^2 + b_3 T^3$.

indicating that no phase transitions nor any other orderings occur in the temperature range investigated. Measured lattice parameters were fitted as a commonly used function of temperature in the form of $a_T = b_0 + b_1 T + b_2 T^2 + b_3 T^3$ where a_T is 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.

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

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

where a_T and a_{298} were the lattice parameters at temperature T and 298 K, respectively. The a_{298} values are listed in Table 1. Calculated results are plotted against temperature in Fig. 2. The LTE(T) values of UO$_2$ and NpO$_2$ obtained in the present study showed close agreements with the recommended literature values [4,5] within
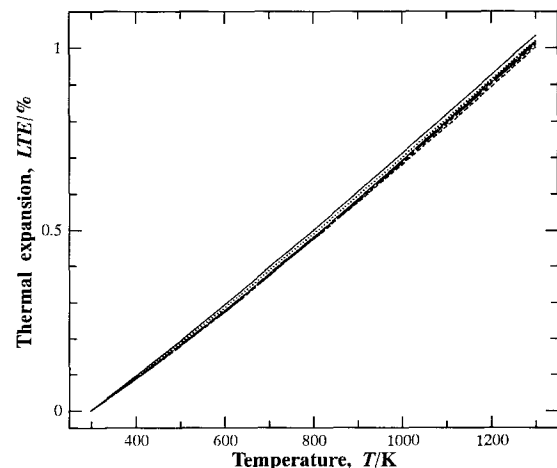

Fig. 1. Thermal expansion of Np$_y$U$_{1-y}$O$_2$ solid solutions plotted as the lattice parameter versus temperature. (○) UO$_2$, (□) y = 0.1, (△) y = 0.3, (◇) y = 0.5, (▽) y = 0.7 and (⊙) NpO$_2$.

Fig. 2. Percent linear thermal expansion of Np$_y$U$_{1-y}$O$_2$ solid solutions plotted against temperature. (————) UO$_2$, (· · ·) y = 0.1, (– – –) y = 0.3, (– · –) y = 0.5, (– · · –) y = 0.7 and (– – –) NpO$_2$.

±0.02%. More detailed comparison and discussion of the LTE(T) for actinide dioxides will be given in our another paper [6]. As can be seen from the figure, the LTE(T) values of $Np_yU_{1-y}O_2$ solid solutions lie between those of UO_2 and NpO_2 and decrease with Np content: 1.034 for UO_2, 1.020 for 10%Np–UO_2, 1.018 for 50%Np–UO_2, 1.008 for 70%Np–UO_2 and 1.001 for NpO_2 at 1300 K.

3.2. Estimation of specific heat capacity at constant pressure

Although many data are available for specific heat capacities at constant pressure (C_p) of UO_2, only a few data have been reported for NpO_2 and none for $(Np, U)O_2$ solid solutions. Westrum et al. [7] measured C_p of NpO_2 at low temperatures in an adiabatic calorimeter and reported that the C_p value at 298 K was 66.22 J K^{-1} mol^{-1}. Arkhipov et al. [8] measured enthalpies of NpO_2 by drop calorimetry in the temperature range of 350 to 1100 K and reported that the C_p value at 298 K was 80.00 J K^{-1} mol^{-1}, which was larger than that obtained by Westrum et al. by about 14 J K^{-1} mol^{-1}. It is, therefore, worthwhile to estimate C_p of NpO_2 and $(Np, U)O_2$ solid solutions from the measured thermal expansion data of these compounds.

Specific heat capacity, C_p, can be derived from the thermodynamic relation, C_p/J K^{-1} mol^{-1} = $\beta V/\kappa_a\gamma$, where β is the coefficient of isobaric volumetric expansion, 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 linear thermal expansion coefficient.

In order to check the validity of C_p estimation from the thermal expansion data, C_p values of UO_2 were calculated. The adiabatic compressibility for UO_2 was calculated from the relation $\kappa_a = 3(1 - 2\sigma)/E_a$ where E_a is the adiabatic Young's modulus and σ is Poisson's ratio. From the literature values of $E_a = 2.28 \times 10^{11}$ Pa [9] and $\sigma = 0.317$ [10], $\kappa_a = 4.82 \times 10^{-12}$ Pa^{-1} was obtained. Momin and Karkhanavala [11] estimated Grüneisen constant, γ, for UO_2 and gave $\gamma = 1.9 \pm 0.1$ as an average value. For the calculation of the C_p value, κ_a and γ values were assumed to be independent of temperature, since no reliable data were available at higher temperatures. The linear thermal expansion coefficient at temperature T, $\alpha(T)$, was obtained by differentiating the expansion curve a_T with T: $\alpha_T = (1/a_{298})(\partial a_T/\partial T)$. Because α_T strongly depends on the functional form of a_T to which observed lattice parameters were fitted, three equation forms were tested:

$$a_T = b_0 + b_1T + b_2T^2 + b_3T^3, \quad (1)$$

$$a_T = b_0 + b_1T + b_2T^2, \quad (2)$$

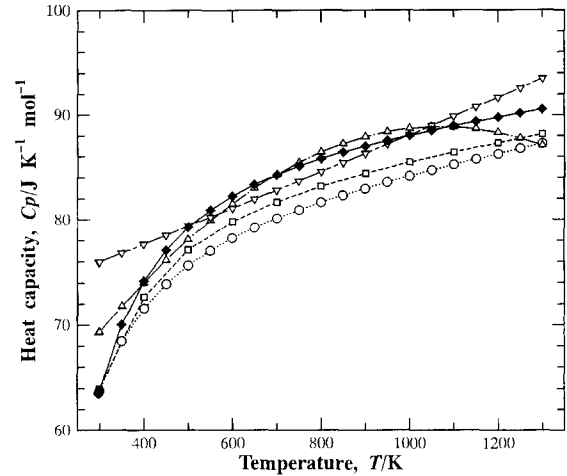$$a_T = b_0 + b_1T + b_2T^2 + b_3/T. \quad (3)$$

Fig. 3. Estimated specific heat capacities of UO_2 plotted against temperature. ($\triangle$) Eq. (1), ($\triangledown$) Eq. (2), ($\blacklozenge$) Eq. (3), ($\square$) Moore and Kelley [12] and ($\bigcirc$) Fredrickson and Chasanov [13].

The standard fitting errors of these three equations were almost identical: 0.040 for Eq. (1), 0.043 for Eq. (2) and 0.041 for Eq. (3).

Calculated C_p values for UO_2 are plotted against temperature in Fig. 3 together with literature data [12,13] for comparison. As seen from Fig. 3, the temperature dependence of C_p is best represented by Eq. (3), although the estimated values are higher than those of the literature values by about 4 J K^{-1} mol^{-1} at high temperatures. The errors in calculated C_p were estimated to be less than $\pm 3\%$ against the data of Moore and Kelley [12] and less than $\pm 5\%$ against more recent values of Fredrickson and Chasanov [13]. It should be noted here that C_p at 298 K by Eq. (3) is calculated to be 63.52 J K^{-1} mol^{-1} which is very close to the commonly accepted value of 63.60 J K^{-1} mol^{-1} [14]. Therefore, Eq. (3) can be employed in the following C_p calculations of $(Np, U)O_2$ solid solutions.

No data of γ and κ_a for NpO_2 and $(Np, U)O_2$ solid solutions were available. Then, γ values for NpO_2 and $(Np, U)O_2$ solid solutions were assumed to be the same as that of UO_2, i.e., $\gamma = 1.9$. κ_a for NpO_2 was calculated from the relation $\kappa_a = 3\alpha V/\gamma C_p$ using the measured α and V values and the reported C_p value of 66.22 J K^{-1} mol^{-1} at 298 K [7]. Although another C_p value of 80.00 J K^{-1} mol^{-1} for NpO_2 at 298 K was reported by Arkhipov et al. [8], this value is apparently higher than those of the other actinide dioxides, 61.7 J K^{-1} mol^{-1} for ThO_2 [15], 63.06 J K^{-1} mol^{-1} for UO_2 [14] and 68.6 J K^{-1} mol^{-1} for PuO_2 [16]. The adiabatic compressibility for $Np_yU_{1-y}O_2$ solid solutions κ_a(ss) was assumed to be calculated from the relation κ_a(ss) = $\kappa_a(UO_2)(1 - y) + \kappa_a(NpO_2)y$ where $\kappa_a(UO_2)$ and $\kappa_a(NpO_2)$ were the adiabatic compressibility of UO_2 and NpO_2, respectively.

Calculated C_p values for NpO_2 and $Np_yU_{1-y}O_2$ solid solutions are plotted against temperature in Fig. 4. Litera-
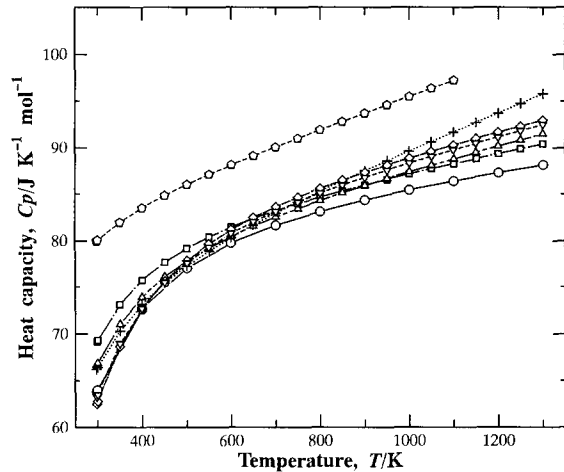
Fig. 4. Estimated specific heat capacities of NpO_2 and $Np_yU_{1-y}O_2$ solid solutions plotted against temperature. ($\square$) $y = 0.1$, ($\triangle$) $y = 0.3$, ($\lozenge$) $y = 0.5$, ($\triangledown$) $y = 0.7$, ($+$) NpO_2, ($\bigcirc$) UO_2 by Moore and Kelley [12] and ($\ominus$) NpO_2 by Arkhipov et al. [8].

ture values of UO_2 [12] and NpO_2 [8] are also shown in the figure for comparison. As seen from Fig. 4, all of the calculated C_p curves are located between the literature data of UO_2 and NpO_2 and show nearly the same values and temperature dependence as that of the literature UO_2. The temperature dependence of calculated C_p values of NpO_2 seems to be consistent with that of measured ones [8], but the former absolute values are lower than the latter ones, probably reflecting the fact that the C_p value at 298 K measured by Westrum et al. [7] is lower than that obtained by Arkhipov et al. [8]. Because of the lack of reliable κ_a and γ values, the accuracy of the estimated C_p for $Np_yU_{1-y}O_2$ solid solutions was not evaluated for the moment.

The estimation of C_p from thermal expansion data has a great advantage when samples are radioactive and toxic materials and a gram-order amount of sample is not avail-

able. About a gram-order amount of sample is required for the usual heat capacity measurements, whereas only some milligram amount is sufficient for the present X-ray diffraction study. More reliable thermo-physical data such as adiabatic compressibility, adiabatic Young's modulus, Poisson's ratio and the Grüneisen constant are required for these actinide compounds in order to improve the accuracy of the estimated C_p from thermal expansion data.

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