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Thermal expansion of uranium-plutonium dioxides

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Thermal expansions of $Pu_yU_{1-y}O_2$ (y=0-0.1) solid solutions were investigated in the temperature range from room temperature to 1273 K by a high temperature X-ray diffraction method. The lattice parameters of $Pu_yU_{1-y}O_2$ solid solutions for constant y value were given in polynomial expressions of temperature. The lattice parameters at constant temperature decreased linearly with increasing y, followed Vegard's law. High temperature heat capacities, C_p, of $Pu_yU_{1-y}O_2$ solid solutions were estimated from the thermodynamic relation using the measured thermal expansions and heat capacity data of UO_2 and PuO_2 at room temperature. The estimated error in the calculated C_p of $Pu_yU_{1-y}O_2$ solid solutions was less than 7%.

KEYWORDS: thermal expansion, heat capacity, mixed oxide, UO_2-PuO_2 solid solution

I. Introduction

Uranium-plutonium mixed dioxide has been used as nuclear fuels for fast breeder reactor and plutonium thermal reactor. Thermal expansion, heat capacity and thermal conductivity of this mixed dioxide are important fundamental parameters for nuclear fuel designs. Many thermodynamic data have been reported on binary UO_2 and PuO_2, together with ternary $Pu_{0.25}U_{0.75}O_2$ solid solution[1-3]. However, basic thermodynamic properties of these mixed oxides are lacking especially in low plutonium concentrations.

We examined the thermal expansion of actinide dioxides[4] and those of $(Np, U)O_2$[5] and $(Np, Pu)O_2$[6] solid solutions. In these papers, we presented the possibility to obtain the specific heat capacities from thermodynamic relation , C_p (J K^{-1} mol^{-1}) = $\beta V / \kappa_a \gamma$, where C_p is the specific heat capacity at constant pressure, β the coefficient of isobaric volumetric expansion, V the molar volume, κ_a the adiabatic compressibility and γ the Grüneisen constant, using measured thermal expansion data and the mechanical properties.

In the present study, thermal expansions of $Pu_yU_{1-y}O_2$ (y=0-0.1) solid solutions have been measured by means of a high-temperature powder X-ray diffraction method. An attempt was made to estimate specific heat capacities of these solid solutions at high temperatures from the measured linear thermal expansion coefficients and heat capacity of UO_2 and PuO_2 at room temperature by using thermodynamic relation.

II. Experimental

Plutonium dioxide was dissolved in 7M HNO_3 containing a low concentration of fluoride ions. The solution was passed through an ion-exchange column of Dowex 1-X4 to remove ^{241}Am impurities. A portion of the plutonium nitrate solution of 5 and 10 at% concentrations was prepared by mixing purified plutonium nitrate solution with uranium nitrate solution. Uranium nitrate solution was prepared by dissolving high purity uranium metal blocks in dilute nitric acid. The mixed solution was gently evaporated and dried in a mantle heater. Mixed oxide powder was obtained by calcining the solid nitrate at 1073 K in air, and then reacted at 1673 K in vacuum. The obtained powder sample was annealed using a flowing 50% CO - 50% CO_2 gas mixture at 1273 K in order to produce the stoichiometric composition. The $(Pu_{0.05}U_{0.95})O_{2.00}$ or $(Pu_{0.1}U_{0.9})O_{2.00}$ powders obtained were mixed with $UO_{2.00}$ powders in the desired composition of $(Pu_yU_{1-y})O_{2.00}$ (y=0, 0.0198, 0.0301, 0.0500, 0.0775 and 0.1000 in molar fraction of plutonium). The oxide powders were subsequently pressed into a 6 mm diameter pellet in a circular die at about 20 $kgmm^{-2}$. The pellet obtained was then sintered at 1673 K for 3-4 h in vacuum. After pulverizing, mixing, pelletizing and heating procedures had been repeated, the product was then annealed under a flow of 50% CO - 50% CO_2 gas mixture at 1273 K in order to produce a specimen of stoichiometric composition.

High temperature X-ray diffraction study was carried out using a Rigaku RAD-3C diffractometer attached to a furnace unit. Furnace temperature from room temperature to 1273 K 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 50% CO - 50% CO_2 gas for 1 h in order to recover any lattice distortions in crystallites by self-radiation

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damage, before X-ray measurements were made.

Lattice parameter of $(Pu_yU_{1-y})O_{2.00}$ (y=0-0.10) was calculated from all reflections (20° < 2θ < 145°) employing the least-squares method for the Nelson-Riley extrapolation. Standard deviation of the calculated lattice parameter was estimated to be within ±0.02 pm. More detailed description of the high-temperature X-ray diffraction was given in our previous paper[4].

III. Results and discussion

1. Thermal expansion

Lattice parameters of $(Pu_yU_{1-y})O_{2.00}$ (y=0-0.10) solid solutions are plotted against temperature in Fig. 1. Lattice parameters of every specimen increase smoothly with increasing temperature up to 1273 K, indicating that neither 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 $a_T = b_0 + b_1T + b_2T^2 + b_3T^3$, where a_T is the lattice parameter at temperature T(K). The regression results and a_{298} values are listed in Table 1. The standard deviations of the regression (ESD) are shown in the last column. The values of a_{298} decrease with increasing y contents. Lattice parameters of $(Pu_yU_{1-y})O_{2.00}$ (y=0-0.10) solid solutions at 298 K were in good agreement with those reported by our previous paper[7].

Table 1 Regression data for $(Pu_yU_{1-y})O_2$ solid solutions.

y value	b_0 (pm)	b_1 ($\times10^3$)	b_2 ($\times10^6$)	b_3 ($\times10^{10}$)	a_{298} (pm)	ESD
0	545.67	3.99	1.74	-5.33	546.97	0.04173
0.0198	545.50	4.47	1.04	-2.88	546.90	0.01575
0.0301	545.45	4.38	1.11	-2.69	546.85	0.01223
0.0500	545.34	4.12	1.47	-4.60	546.66	0.00998
0.0775	545.14	4.10	1.43	-3.75	546.48	0.02342
0.1000	545.21	3.15	2.76	-9.66	546.35	0.01298

Lattice parameters for stoichiometric $(Pu_yU_{1-y})O_{2.00}$ (y=0-0.10) solid solutions are shown in Fig. 2 as a function of doped y contents at 298, 500, 800 and 1273 K. The lattice parameters for stoichiometric $(Pu_yU_{1-y})O_{2.00}$ (y=0-0.10) solid solutions at each temperature change linearly with increasing doped y contents. In this study, the deviation from Vegard's law at a particular concentration (y=0.04 for stoichiometric $(Pu_yU_{1-y})O_{2.00}$) which was pointed out by Beauvy[8] was not observed at any temperatures. As seen in Fig. 2, the lattice parameters of solid solutions decrease with increasing y contents, reflecting smaller ionic radius of plutonium than that of uranium.

Linear thermal expansion (LTE) at temperature T is given by the following relation:

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

where a_T and a_{298} are the lattice parameters at temperature T and 298 K, respectively. The LTE(T) of $(Pu_yU_{1-y})O_{2.00}$ (y=0-0.10) solid solutions for constant y value were calculated by applying least square method to the experimental data, and the typical results for y=0, 0.0301

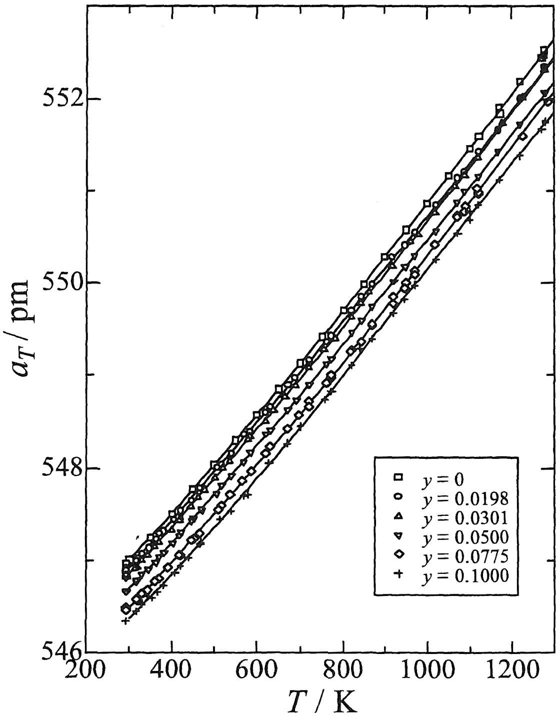

Fig. 1 Thermal expansion of $(Pu_yU_{1-y})O_2$(y=0-0.1) solid solutions plotted as lattice parameter versus temperature.

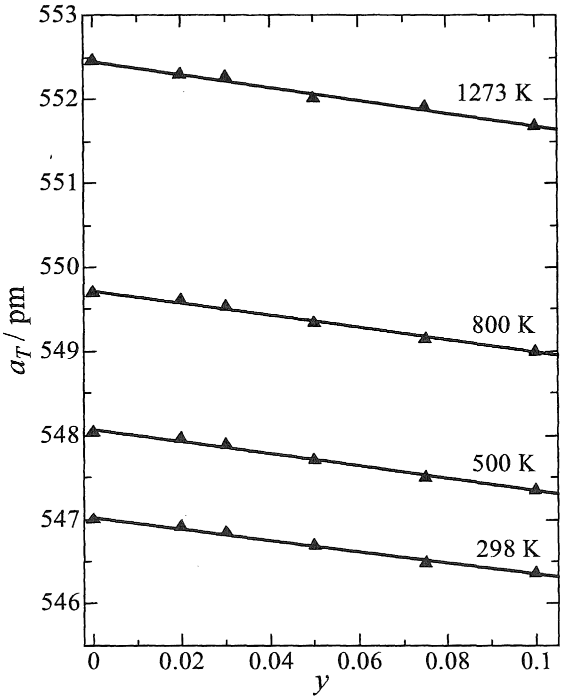

Fig. 2 Lattice parameters for stoichiometric $(Pu_yU_{1-y})O_2$ solid solutions as a function of doped y contents at 298, 500, 800 and 1273 K.

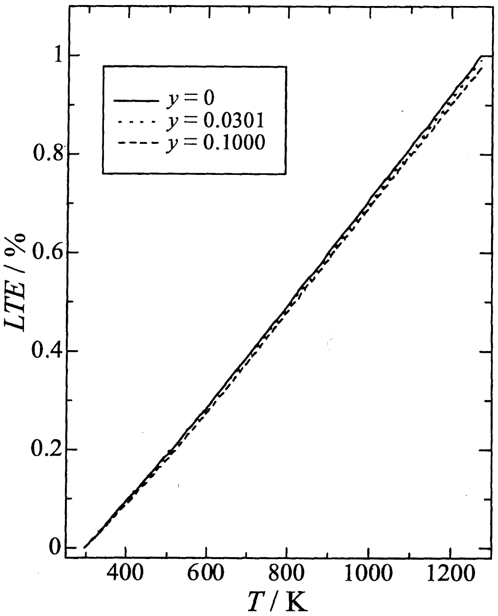

Fig. 3 Linear thermal expansion (LTE) of stoichiometric $(Pu_yU_{1-y})O_2$ (y=0, 0.0301 and 0.1000) solid solutions plotted against temperature.

and 0.1000 are shown in Fig. 3 as a function of temperature. The LTE(T) values of UO_2 obtained in the present study showed close agreements with the recommended literature values[1,3] within ±0.02%. More detailed comparison and discussion of the LTE(T) for actinide dioxides were given in our another paper[4]. As can be seen in the figure, the LTE(T) of $(Pu_yU_{1-y})O_{2.00}$ (y=0, 0.0301 and 0.1000) solid solutions almost do not change for y contents.

2. Estimation of specific heat capacity at constant pressure

Many data are available for specific heat capacities at constant pressure (C_p) of UO_2, $(Pu_{0.25}U_{0.75})O_2$ and PuO_2[2], but none for $(Pu_yU_{1-y})O_2$ solid solutions less than y=0.1 contents. It is, therefore, worthwhile to estimate C_p of $(Pu_yU_{1-y})O_2$ solid solutions from the measured thermal expansion data of these compounds.

Specific heat capacity at constant pressure, C_p, for an isotropic material can be given by the following thermodynamic relation:

$$C_p\ (\mathrm{J\ K^{-1}\ mol^{-1}}) = 3\alpha V / \kappa_a \gamma, \tag{1}$$

where α is the coefficient of linear thermal expansion, V the molar volume, κ_a the adiabatic compressibility and γ the Grüneisen constant. In our previous paper[4], it has been shown that the specific heat capacity of UO_2 was estimated from Eq. (1) within the error of ±3% against the data of Moore and Kelley[9] and of ±5% against more recent values of Fredrickson and Chasanov[10] at high temperature. The measured thermal expansion data and estimated mechanical properties, such as the adiabatic compressibility (κ_a = 4.82×10^{-12} Pa^{-1}) and the Grüneisen constant (γ= 1.9±0.1 as an average value) at 298 K[4], were used for the estimation of heat capacity. For the calculation of the C_p value, κ_a and γ were assumed to be independent of temperature, since no reliable data were available at high temperatures. The linear thermal expansion coefficient at temperature T, α_T, in Eq.(1) was obtained by differentiating the thermal expansion curve a_T with T as follows:

$$\alpha_T = (1 / a_{298})(\partial a_T / \partial T). \tag{2}$$

As shown in our previous paper[4], α_T strongly depends on the functional form of a_T to which observed lattice parameters were fitted, although a_T did not depend on the functional form of T. A good temperature dependence of C_p was obtained, when measured lattice parameters were fitted into the following function:

$$a_T = b_0 + b_1 T + b_2 T^2 + b_3 / T. \tag{3}$$

In this study, Eq.(3) was used for the estimation of C_p of $(Pu_yU_{1-y})O_2$ solid solutions. As shown in our previous paper[4], the estimated C_p of UO_2 scattered especially at 298 and 1273 K which were the lowest and highest temperatures, respectively.

In order to estimate more reliable heat capacity data at high temperatures in this study, $C_p(T, Pu_yU_{1-y}O_2)$ values of $(Pu_yU_{1-y})O_2$ solid solutions at temperature T are calculated from $C_p(298, Pu_yU_{1-y}O_2)$ at 298K, α_T and V_T at temperature T, and α_{298} and V_{298} at 298 K using the following relation

$$\begin{aligned} &C_p(T, Pu_yU_{1-y}O_2) \\ &= C_p(298, Pu_yU_{1-y}O_2) \times \{(\alpha_T V_T) / (\alpha_{298} V_{298})\}, \end{aligned} \tag{4}$$

which is derived from Eq.(1) by assuming that κ_a and γ values are independent of temperature. The heat capacity for $Pu_yU_{1-y}O_2$ solid solutions, $C_p(298, Pu_yU_{1-y}O_2)$, at 298 K was calculated from Kopp-Neumann's rule:

$$\begin{aligned} &C_p(298, Pu_yU_{1-y}O_2) \\ &= yC_p(298, PuO_2) + (1-y)C_p(298, UO_2), \end{aligned} \tag{5}$$

where $C_p(298, UO_2)$ and $C_p(298, PuO_2)$ were heat capacities of UO_2 (63.06 JK^{-1} mol^{-1})[11] and PuO_2 (68.6 JK^{-1} mol^{-1})[12] at 298 K, respectively. $C_p(T, Pu_yU_{1-y}O_2)$ of $Pu_yU_{1-y}O_2$ solid solutions was calculated by substituting Eqs.(2), (3) and (5) to Eq.(4) and the results are shown in Fig. 4 as a function of temperature, together with the experimental C_p values of UO_2[9], $Pu_{0.25}U_{0.75}O_2$[13] and PuO_2[14]. The estimated C_p values of $Pu_yU_{1-y}O_2$ solid solutions show the similar temperature and compositional dependence at low temperature, but are about 7% smaller than those of the experimental values.

This method is worthwhile, because thermal expansion data can be measured by high temperature X-ray diffraction method and heat capacity can be also estimated by using small sample. The estimation of C_p from thermal expansion data at high temperature has a great advantage when samples

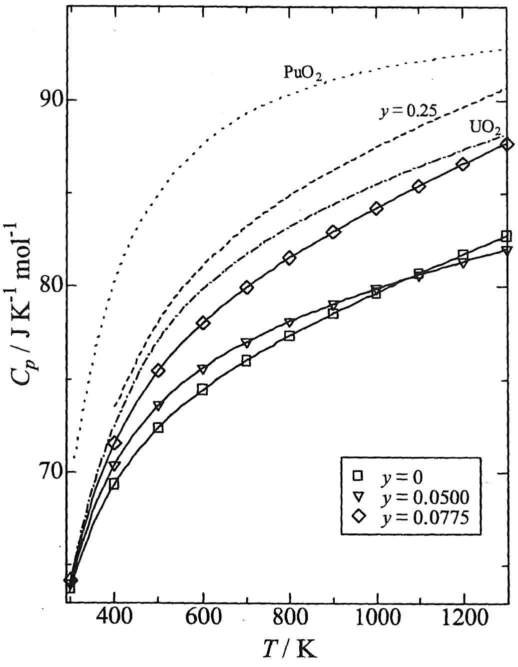

Fig. 4 Estimated specific heat capacities of $(Pu_yU_{1-y})O_2$ solid solutions plotted against temperature. C_p values of UO_2[9], $Pu_{0.25}U_{0.75}O_2$[13] and PuO_2[14] are shown for the comparison.

are radioactive and a gram-order amount of sample is not available. About a gram-order amount of sample is required for usual heat capacity measurements, whereas only some milligram amount is sufficient for the present X-ray diffraction study. It is very fruitful to be able to estimate C_p at higher temperatures from C_p of UO_2 and PuO_2 solid solutions at room temperature which is easier than that at high temperatures. More reliable thermo-physical data such as adiabatic compressibility, adiabatic Young's modulus, Possion's ratio and the Grüneisen constant are required for these actinide compounds in order to improve the accuracy of the estimated C_p of $(Pu_yU_{1-y})O_2$ solid solutions from thermal expansion data.

IV. Conclusions

The lattice parameter of $(Pu_yU_{1-y})O_2$ (y=0-0.1) solid solutions was measured by high temperature X-ray diffraction method as a function of temperature and the following conclusions were obtained.

(1) The lattice parameters of $(Pu_yU_{1-y})O_2$ increased smoothly with increasing temperature, and no thermal anomaly was observed.

(2) Lattice parameters of $(Pu_yU_{1-y})O_2$ decreased with increasing y value, reflecting smaller ionic radii for plutonium ions than those of uranium ions.

(3) Thermal expansion was calculated from the temperature dependence of lattice constant and almost did not change for y contents.

(4) Heat capacities of $(Pu_yU_{1-y})O_2$ at high temperatures were estimated from thermal expansion data in this study and heat capacity data of UO_2 and PuO_2 at room temperature by using the thermodynamic relation.

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