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Thermal conductivity of neptunium dioxide

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Abstract

The thermal diffusivity of neptunium dioxide was measured in the temperature range from 473 to 1473 K by using a laser flash method. The thermal diffusivity slightly decreased with increasing temperature in the temperature range investigated. The heat capacity of NpO_2 was measured in the temperature range from 334 to 1071 K by using a drop calorimetry method. The heat capacity of NpO_2 determined in this study was slightly larger than that of UO_2 and about 7% smaller than that of PuO_2. The thermal conductivity of NpO_2 was determined from the thermal diffusivity, the heat capacity and the bulk density. It was found that the thermal conductivity of NpO_2 from 873 to 1473 K lay between those of UO_2 and PuO_2.

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1. Introduction

Minor actinides (MAs: Np, Am, Cm) are accumulated in the irradiated nuclear fuels. Among MAs, ^{237}Np has a very long life. To reduce the environmental burden and to use the repository efficiently, the partitioning and transmutation of MAs is an option for the future nuclear fuel cycle. Therefore, various MA-containing fuels have been developed as advanced nuclear fuels for fast reactors or transmutation systems. Among these fuels, MA dioxides are included in MA-MOX (MA-containing mixed oxide) fuel, composite fuels of CERCER (ceramic–ceramic) and CERMET (ceramic–metallic), etc. [1–3]. For these backgrounds, it is important to determine the thermal conductivity of NpO_2 as a basic property to design the fuels and evaluate the irradiation behavior.

The thermal conductivity of NpO_2 has only been reported by Kurosaki et al. [4], who calculated the thermal conductivities of NpO_2 by using a molecular dynamics (MD). On the other hand, the data on the thermal conductivity of Np containing mixed oxides are also limited. Schmidt et al. reported the thermal conductivities of $(Am_{0.25}Np_{0.25}U_{0.5})O_{2-x}$ and $(Np_{0.5}U_{0.5})O_2$ [5]. However, there has been no experimental data for the thermal conductivity of NpO_2.

In this study, the thermal diffusivity of NpO_2 was measured by using the laser flash apparatus, which has been installed in a glove box with a highly purified argon gas atmosphere, from 473 to 1473 K under vacuum in heating and cooling processes. The heat capacity of NpO_2 was measured by using the drop calorimeter, which has been installed in a glove box, from 334 to 1071 K. The thermal conductivity of NpO_2 was determined by use of the measured thermal diffusivity, heat capacity and bulk density.

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2. Experimental

2.1. Sample preparation

A disk sample of neptunium oxide for the thermal diffusivity measurement was prepared by sintering neptunium dioxide powder, $^{237}NpO_2$. The $^{237}NpO_2$ powder contained less than 0.5 wt% impurities for ^{237}Np composition.

The NpO_2 powder was ground by using an agate mortar for 50 min and then pressed at 260 MPa into a green disk. The green disk sample was sintered at 1723 K for 7.5 h in flowing air at 300 ml/min. The characteristics of a sintered NpO_2 disk sample are summarized in Table 1. The bulk density of the sample, which was calculated from the size and the weight of the sintered sample, was 10.06 Mg/m^3.

2.2. Thermal diffusivity measurements

The thermal diffusivity of the sintered NpO_2 sample was measured by use of the laser flash method. The detailed information of the thermal diffusivity measurement apparatus was mentioned in Refs. [6,7]. The uncertainty of the thermal diffusivity values was evaluated to be within ±5% [7].

The thermal diffusivity was determined from the temperature rise at the rear surface of the sample measured with an InSb infrared detector after the front surface of the sample was instantaneously irradiated by a pulse of Nd glass laser. The data of the temperature response curve at the rear surface were analyzed by the curve fitting method [8,9]. The graphite powder was sprayed on both the surfaces of the NpO_2 sample before the measurements, as is the case of PuO_2 with partially transparent characteristics [10].

The thermal diffusivity measurements were performed in both heating and cooling processes at intervals of about 100 K in vacuum with background pressure of less than 2.4×10^{-4} Pa. The measurements were performed from 473 to 1473 K in heating process (Run 1), from 1473 to 723 K in cooling process (Run 2) and from 723 to 523 K in cooling process (Run 3).

2.3. Heat capacity measurements

After the thermal diffusivity measurements, the NpO_2 sample (53.89 mg) was loaded in a platinum container (419.12 mg). The container was evacuated and sealed in argon gas atmosphere in the background pressure of about 10 kPa. The enthalpy increment measurement was carried out with the drop calorimetry method using a twin-type drop calorimeter (SETARAM, HT-1000), in which the container was dropped into the calorimeter kept at a given temperature. The differential signal from the thermocouple was amplified and monitored. The heat capacity measurements were carried out in the temperature range from 334 to 1071 K.

Table 1
Characteristics of the sintered NpO_2 disk sample

Diameter (mm)	2.990
Thickness (mm)	0.816
Weight (mg)	57.66
Bulk density (Mg/M^3)	10.06 (90.2%TD)

2.4. Determination of thermal conductivity

The thermal conductivity of the NpO_2 was determined by the equation:

$$\lambda = \alpha C_p \rho, \tag{1}$$

where λ, α, C_p and ρ are the thermal conductivity, the thermal diffusivity, the heat capacity and the bulk density of the sample, respectively. The thermal expansion data [11] were used to calculate bulk density as a function of temperature. The thermal expansion data were also used to determine sample thickness as a function of temperature to calculate the thermal diffusivity. In order to compare the thermal conductivity of NpO_2 with those of actinide oxides in literature, the present data were corrected to 96%TD (TD: theoretical density) using the modified Maxwell–Eucken relationship [12]:

$$\lambda_{96} = \lambda_M \left(\frac{0.96}{1+0.04\beta}\right)\left(\frac{1+\beta P}{1-P}\right), \tag{2}$$

where subscript M and 96 denote the measured value and the value corresponding to 96%TD, respectively. P is the fraction porosity and β is the constant related to the characteristics of pores in the matrix. In the present study, β was taken as 0.5, the value given by Biancheria for the sample with the density higher then 90%TD [13].

3. Results and discussion

3.1. NpO_2 sample

The NpO_2 sample for the thermal diffusivity measurements was characterized by powder X-ray diffraction analysis with Cu Kα radiation. The powder X-ray diffraction analysis revealed that the sample was composed of an fcc single phase with the lattice parameter of 0.5430 nm. The lattice parameter of stoichiometric NpO_2 was 0.5433 nm [11,14,15]. Thus, since this lattice parameter was consistent with that of stoichiometric NpO_2, the NpO_2 sample was regarded as near-stoichiometric composition.

The contents of oxygen, nitrogen and carbon of the NpO_2 samples were also measured to determine the O/Np ratio and the anion impurity contents. The oxygen and nitrogen contents were measured with an apparatus (HORIBA, EMGA-550) based on the inert gas fusion technique. The carbon content was measured with an apparatus (CE Instruments, NC-2500) based on the combustion technique. The content of oxygen was determined to be 12.0 ± 0.2 wt% and the contents of carbon and nitrogen were found to be less than each detection limit (0.03 wt%). The O/Np ratio of the NpO_2 sample was determined to be 2.02 ± 0.04. The results of chemical analyses also suggested that the NpO_2 sample had a stoichiometric composition with high purity.

The theoretical density of NpO_2, which was calculated from the molecular weight and the lattice parameter, was 11.16 Mg/m^3. The relative density of the sample was 90.2%TD.

3.2. Thermal diffusivity of NpO_2

In order to check the accuracy of the thermal diffusivity measurement system for actinide dioxides, the measurements were performed for stoichiometric uranium dioxide ($UO_{2.00}$) sample as a reference. For the thermal diffusivity measurement, a disk-shaped sample of 3.673 mm in diameter, 0.878 mm in thickness and 97.39 mg in weight was prepared. The bulk density, which was calculated from the size and weight of the sintered sample, was 10.47 Mg/m^3. The relative density of the sample was 95.5%TD.

The thermal conductivity of UO_2 was calculated from the present experimental thermal diffusivity and bulk density data and the literature values of the heat capacity [16]. Fig. 1 shows thermal conductivity of UO_2 as a function of temperature. The uncertainties of thermal diffusivity, heat capacity and bulk density were evaluated to be within ±5%, ±2% [16] and ±1%, respectively. Thus, a total uncertainty of ±8% in the thermal conductivity of UO_2 is suggested by considering these errors. As shown in Fig. 1, the present result of UO_2 agrees well with reported values [10,17] in the temperature range from 473 to 1473 K. Thus, it was confirmed that the thermal diffusivity measurement system had enough accuracy for actinide dioxides in the temperature range investigated.

The thermal diffusivity measurements of NpO_2 were performed in both heating and cooling processes. The measured thermal diffusivities of NpO_2 are shown in Fig. 2. It was found that good reproducibility of the experimental thermal diffusivity data was confirmed by the consistency of the heating and cooling measurements. From these results, it was suggested that the composition of the sample kept unchanged during the thermal diffusivity measurements. As shown in Fig. 2, the thermal diffusivity of NpO_2 decreased with increasing temperature from 473 to 1473 K.

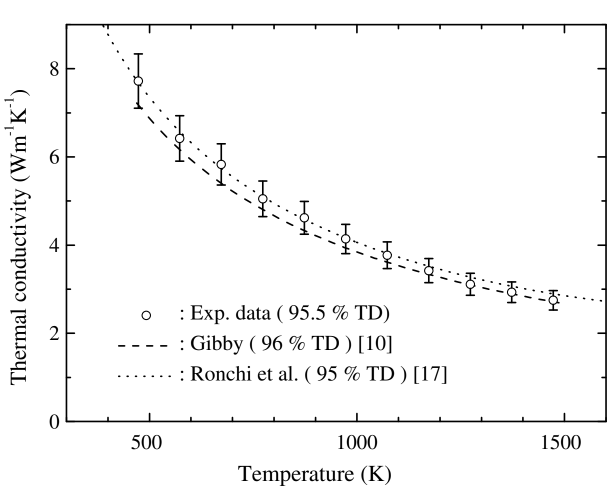

Fig. 1. Thermal conductivity of UO_2 together with those in Refs. [10,17].

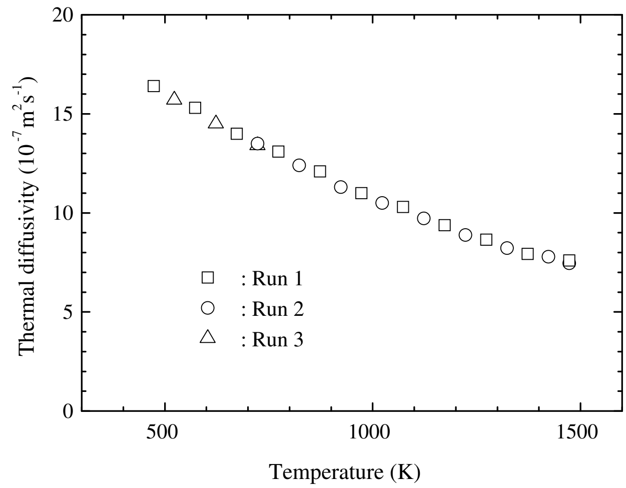

Fig. 2. Thermal diffusivity of sintered NpO_2 sample.

3.3. Heat capacity of NpO_2

The temperature dependence of enthalpy increment of NpO_2 is shown in Fig. 3(a). The enthalpy increment values $H–H_{298.15}$ at various temperatures were fitted to a polynomial expression in temperature T (K) using Shomate's method [18]:

$$H - H_{298.15} = AT^2 + BT + C + DT^{-1}. \quad (3)$$

The fitted result in the temperature range from 334 to 1071 K is

$$H - H_{298.15} = 3.531 \times 10^{-6}T^2 + 0.08130T - 31.29 + 2117T^{-1} \ (\mathrm{kJ\,mol^{-1}}). \quad (4)$$

The heat capacity was obtained from the first derivative of Eq. (4) with respect to temperature and is given by

$$C_p = 7.062 \times 10^{-3}T + 81.30 - 2.117 \times 10^6 T^{-2} \ (\mathrm{J\,mol^{-1}\,K^{-1}}). \quad (5)$$

The uncertainty of the heat capacity ascribed to the statistical error of the enthalpy increment was evaluated as less than ±3%. The heat capacity values calculated by Eq. (5) are shown in Fig. 3(b). In Fig. 3(b), the results are compared with the literature values of NpO_2 [19,20], UO_2 and PuO_2 [13]. The heat capacity of NpO_2 determined in this study was slightly larger than that of UO_2 and about 7% smaller than that of PuO_2. The heat capacity of NpO_2 in the temperature range higher than 500 K was close to the values reported by Barin and Knacke [19].

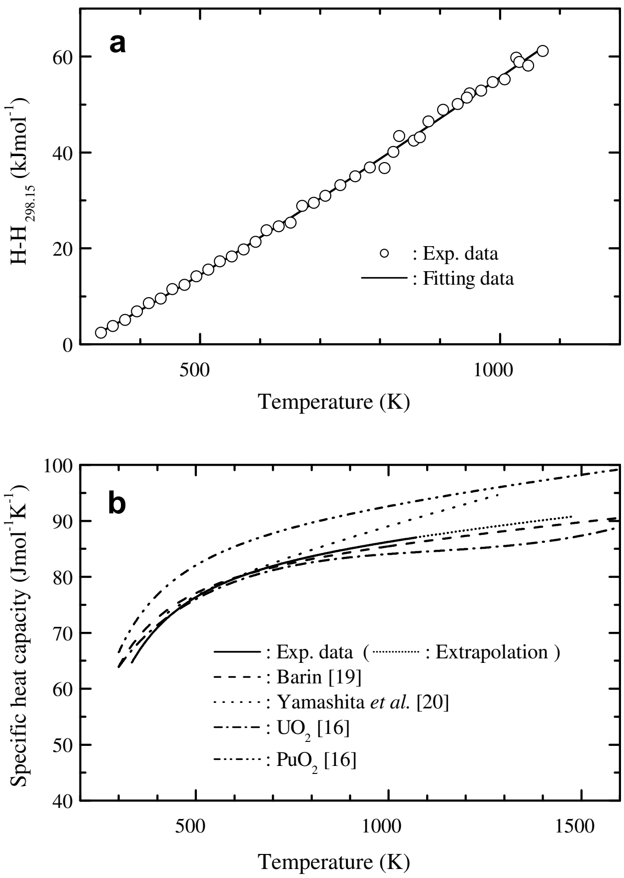

Fig. 3. Results of heat capacity measurement: (a) temperature dependence of enthalpy increment of NpO_2, and (b) heat capacity of NpO_2 sample, together with the literature values of NpO_2 [19,20], UO_2 and PuO_2 [16].

On the other hand, the present result in the temperature range lower than 500 K was smaller than the literature values [19,20], due to the increasing statistical error of the enthalpy increment. Therefore, the present results of heat capacity data fitted by Eq. (5) in the temperature range from 573 to 1473 K were used in the calculation of thermal conductivity of NpO_2. The heat capacity higher than 1071 K was calculated by simply extrapolating Eq. (5).

3.4. Thermal conductivity of NpO_2

The thermal conductivities of NpO_2 with 90.2%TD and corrected to 96%TD are shown in Fig. 4, together with those of UO_2 [17], PuO_2 [10] and $(Np_{0.5}U_{0.5})O_2$ [5]. The uncertainty of the thermal diffusivity, the heat capacity and the bulk density were evaluated to be within ±5%, ±3% and ±1%, respectively. Thus, the total uncertainty was suggested to be less than ±9% by considering these errors.

The thermal conductivity of NpO_2 was found to decrease with increasing temperature in the temperature range investigated. This temperature dependence of thermal conductivity showed a similar tendency as those of UO_2, PuO_2 and $(Np_{0.5}U_{0.5})O_2$. The decreases of thermal conductivities with increasing temperature for these oxides are due to the increase in phonon scattering. However, the temperature dependence of thermal conductivity for NpO_2 is smaller than those for UO_2 and PuO_2.

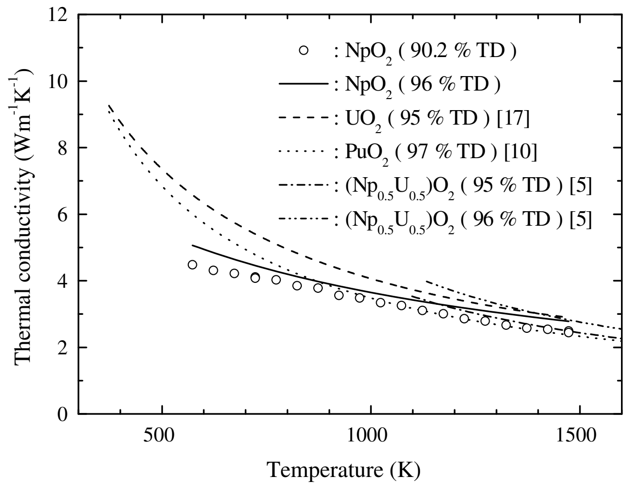

Fig. 4. Thermal conductivity of NpO_2 with 90.2%TD corrected to 96%TD, together with those for UO_2 [17], PuO_2 [10] and $(U_{0.5}Np_{0.5})O_2$ [5].

The fitted results of the thermal conductivity of NpO_2 with 96%TD in the temperature range from 573 to 1473 K was

$$\lambda = \frac{1}{0.09447 + 1.797 \times 10^{-4} T} \ (\mathrm{W\,m^{-1}\,K^{-1}}). \tag{6}$$

The thermal conductivity of NpO_2 with 96%TD from 873 to 1473 K lay between those of UO_2 and PuO_2 with similar densities. However, that of NpO_2 with 96%TD from 573 to 873 K was smaller than those of UO_2 and PuO_2. It is difficult to explain this tendency only from the ionization radius and energy of actinide oxides [21] at the moment.

The thermal conductivity of NpO_2 with 96%TD was close to that of $(Np_{0.5}U_{0.5})O_2$ for above 1098 K [5]. Considering the variation of measured values for $(Np_{0.5}U_{0.5})O_2$, it can be concluded that the thermal conductivity of NpO_2 obtained in this study has a good precision. Mignanelli and Thetford deduced that the thermal conductivity of NpO_2 should be taken as 20% larger than that of $(U,Pu)O_2$ [22]. However, in the present study, such a tendency was not observed.

4. Conclusions

The thermal diffusivity of NpO_2 was measured by using the laser flash method in the temperature range from 473 to 1473 K. The heat capacity of NpO_2 was determined in the temperature range from 334 to 1071 K by using the drop calorimetry method. The following was concluded:

The thermal diffusivity measurements of NpO_2 were performed in both heating and cooling processes. It was found that good reproducibility of the experimental thermal diffusivity data was confirmed by the consistency of the heating and cooling measurements. The thermal diffusivity of

NpO_2 decreased with increasing temperature from 473 to 1473 K.

The heat capacity of NpO_2 in the temperature range from 334 to 1071 K is expressed by $C_p = 7.062 \times 10^{-3}T + 81.30 - 2.117 \times 10^6 T^{-2}$ (J mol^{-1} K^{-1}).

The thermal conductivity of NpO_2 with 96%TD from 873 to 1473 K lay between those of UO_2 and PuO_2 with similar densities and was slightly smaller than that of $(Np_{0.5}U_{0.5})O_2$. The thermal conductivity of NpO_2 with 96%TD in the temperature range from 573 to 1473 K is expressed by $\lambda = \frac{1}{0.09447+1.797\times10^{-4}T}$ (Wm^{-1} K^{-1}).

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