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Thermal conductivity of AmO_{2-x}

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Abstract

The thermal diffusivity of americium oxide was determined in the temperature range from 299 to 1473 K by a laser flash method. The thermal diffusivity of AmO_{2-x} decreased with increasing temperature. The thermal conductivity of AmO_{2-x} was estimated from the measured thermal diffusivity, the specific heat capacity and the bulk density. It was found that the thermal conductivity of AmO_{2-x} decreased with increasing temperature in the temperature range investigated. It was also found that the decrease in O/Am ratio during the thermal diffusivity measurements under vacuum resulted in a slight decrease in thermal conductivity of AmO_{2-x}.

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1. Introduction

Minor actinides (MAs: Np, Am, Cm) are accumulated in the irradiated nuclear fuels. Especially, americium (Am) has high and lasting radiotoxicity. To reduce the environmental burden and to use the repository efficiently, burning or transmutation of MAs is an option for the future nuclear fuel cycle. Therefore, various MAs containing fuels have been developed as advanced nuclear fuels for the fast reactors or transmutation systems. Among these fuels, MA oxides are used in MA-MOX (mixed oxide containing MAs) fuel, composite fuels of CERCER (ceramic–ceramic), CERMET (ceramic–metal), etc. [1–3]. For these backgrounds, it is important to determine the thermal conductivity of americium oxide as a basic property to design the fuels and evaluate the irradiation behavior.

The thermal conductivity of americium oxide has only been reported by Schmidt [4], who measured the thermal conductivities of AmO_2 and $AmO_{1.5}$ at 333 K by a longitudinal heat flow method. Those of AmO_2 and $AmO_{1.5}$ at 333 K were 0.69 and 0.82 $Wm^{-1} K^{-1}$, respectively. These values are extremely small compared with the other actinide oxides [5–7]. The data on the thermal conductivity of Am-based oxides are also very limited, i.e. $(Am,U)O_{2-x}$, $(Am,Np,U)O_{2-x}$ [8]. These data have shown that the addition of Am to the U-based oxides resulted in an extreme decrease of thermal conductivity.

In this study, the thermal diffusivity of americium oxide was measured by the laser flash apparatus, which has been installed in a glove box with a highly-purified argon gas atmosphere, from 299 to 1473 K under vacuum in heating and cooling processes. The thermal conductivity of AmO_{2-x} was estimated by use of the thermal diffusivity, the specific heat capacity and the bulk density.

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2. Experimental

2.1. Sample preparation

A disk sample of americium oxide for the thermal diffusivity measurement was prepared by sintering americium dioxide powder, $^{243}AmO_2$. The purity of the AmO_2 powder was about 99.7 wt% for nonradioactive impurities. The impurity contents have been mentioned in Ref. [9].

The AmO_2 powder was grinded by an agate mortar and then pressed at 400 MPa into a disk. The disk was sintered at 1673 K for 8 h in flowing air at 250 ml/min. The O/Am ratio of the disk could not be analyzed before the thermal diffusivity measurements since a destructive measurement was required. However, considering from the dissociation pressure isotherms in Ref. [10], it could be presumed that the O/Am ratio of the obtained americium oxide sample was about 1.9. A tentative americium–oxygen phase diagram reported by Cordfunke [11] is reproduced in Fig. 1. According to the phase diagram, the sample of $AmO_{1.9}$ could consist of two kinds of phases with bcc and fcc structures.

The characteristics of sintered AmO_{2-x} are summarized in Table 1. The diameter and thickness were measured by a dial gauge and found to be 3.021 mm and 0.583 mm, respectively. The weight was 40.79 mg. The bulk density, which was calculated from the size and the weight of the sintered sample, was 9.76 Mg/m^3. The theoretical density of $AmO_{1.9}$, which was calculated from the molecular weight and the lattice parameter [12], was 11.51 Mg/m^3. The relative density of the sample, which was defined as the bulk density divided by the theoretical density, was 85%TD (TD: theoretical density).

2.2. Thermal diffusivity measurements

The thermal diffusivity of the sintered AmO_{2-x} sample was measured by the laser flash method. The detailed information of the thermal diffusivity measurement apparatus was mentioned in Ref. [9,13]. The uncertainty of the thermal diffusivities obtained with this system was estimated to be less than 5% [13]. 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 [14,15].

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 2.7×10^{-4} Pa. The measurements were performed from 573 to 1273 K in heating process (Run 1), from 1473 to 573 K in cooling process (Run 2) and from 299 to 673 K in heating process (Run 3).

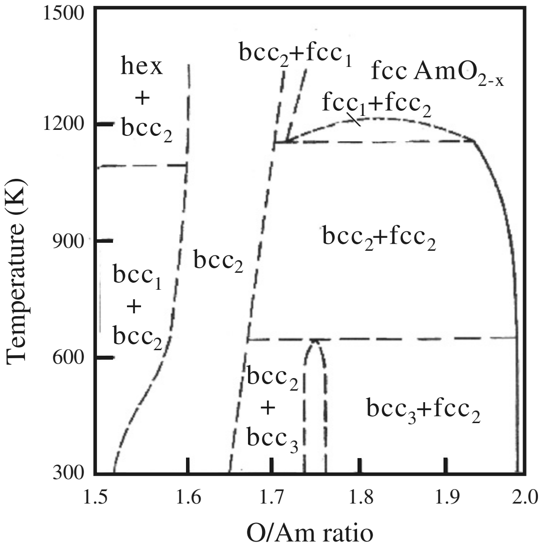

Fig. 1. Tentative americium–oxygen phase diagram [11].

Table 1
Characteristics of sintered americium oxide sample

Diameter (mm)	3.021
Thickness (mm)	0.583
Weight (mg)	40.79
Bulk density (Mg/m^3)	9.76 (85%TD)

After the thermal diffusivity measurements, the contents of oxygen, nitrogen and carbon of the AmO_{2-x} sample were measured to determine the O/Am 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 AmO_{2-x} sample was also examined by powder X-ray diffraction analysis with Cu-Kα radiation to identify the phases and to determine the lattice parameter.

2.3. Estimation of thermal conductivity

The thermal conductivity of the AmO_{2-x} was estimated by the equation:

$$\lambda = \alpha C_p \rho, \qquad (1)$$

where λ, α, C_p and ρ are the thermal conductivity, the thermal diffusivity, the specific heat capacity and the bulk density of the sample, respectively. In this study, the specific heat capacity of AmO_2 [16] was substituted for that of AmO_{2-x}. In order to estimate the thermal conductivity of AmO_{2-x} with 100%TD, the present data were corrected by the analytical equation of Schulz [17]:

$$\lambda = \lambda_{TD}(1 - P)^X, \qquad (2)$$

where λ_{TD} is the thermal conductivity of the sample with 100%TD, P is the porosity of sample and X is the parameter related to the closed pores. When the shape of closed pores is spherical, X is equal to 1.5 [17]. In the present calculation, the value of 1.5 was used. Among a variety of porosity correction formulas, Eq. (2) is in best agreement with the result of the finite element computations in the wide range of the porosity up to 0.3, as reported by Bakker et al. [18].

3. Results and discussion

Fig. 2 shows the thermal diffusivities of the AmO_{2-x} sample. It was found that the thermal diffusivity decreased with increasing temperature. It was also found that the thermal diffusivity from 573 to 773 K obtained in Run 1 was larger than that in Run 2. On the other hand, the thermal diffusivity from 873 to 1273 K obtained in Run 1 was in good agreement with that in Run 2. The thermal diffusivity from 573 to 673 K in Run 2 was in good agreement with that in Run 3. These results showed that the data were reproduced well in three runs except the first half of Run 1. The composition of the sample must have been changed during the first half of Run 1.

After the thermal diffusivity measurement, the content of oxygen was determined to be 10.24 ± 0.18 wt% and the contents of carbon and nitrogen were found to be less than detection limits (0.03 wt%). The O/Am ratio of the AmO_{2-x} sample after the thermal diffusivity measurements was, therefore, determined to be 1.73 ± 0.03. The powder X-ray diffraction analysis revealed that the sample was composed of two bcc phases with the lattice parameters of 1.097 and 1.092 nm, which is consistent with the tentative Am–O phase diagram as shown in Fig. 1. These results suggested that the O/Am ratio decreased from about 1.9 to 1.73 during the measurements. In the case of an oxide, MO_{2-x}, it is known that the decrease in the O/M ratio results in the decrease in the thermal diffusivity [19]. As shown in Fig. 2, it may be safe to say that most part of the decrease in the O/Am ratio occurred during the thermal diffusivity measurement from 573 to 873 K in Run 1. The heating process under vacuum could cause the decrease in the O/Am ratio of the AmO_{2-x} sample.

It was also found that an abrupt drop in thermal diffusivity of AmO_{2-x} by about 16% occurred between 1173 and 1273 K. According to Fig. 1 the AmO_{2-x} sample was transformed from $bcc_2 + fcc_2$ phases to $fcc_1 + fcc_2$ or fcc AmO_{2-x} phase in the temperature range from 1173 to 1273 K. Thus, it may be concluded that this drop in the thermal diffusivity of AmO_{2-x} was attributed to the phase transformation.

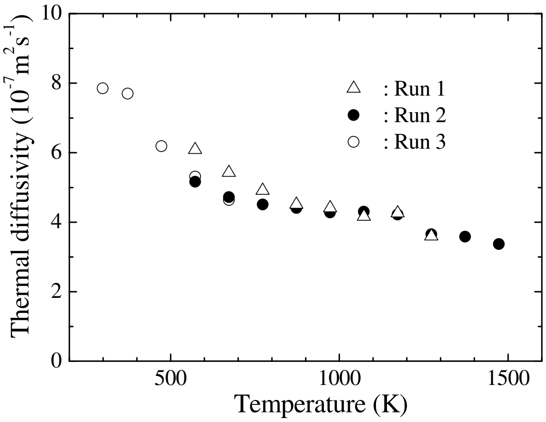

Fig. 2. Thermal diffusivity of sintered AmO_{2-x} sample.

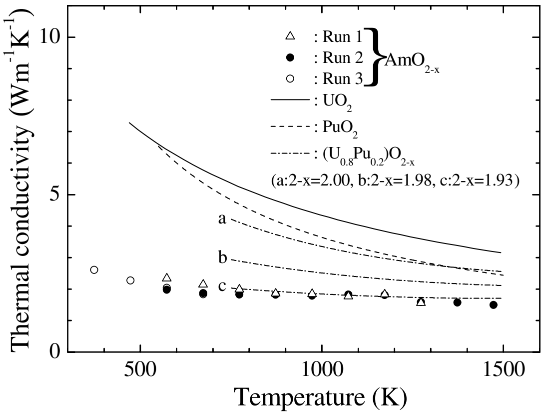

Fig. 3. Thermal conductivity of AmO_{2-x} corrected to 100%TD, together with those for UO_2 (solid line) [5], PuO_2 (broken line) [6] and $(U_{0.8}Pu_{0.2})O_{2-x}$: (a) $2-x = 2.00$, (b) $2-x = 1.98$, (c) $2-x = 1.93$ (dashed line) [7] corrected to 100%TD.

The thermal conductivity values of AmO_{2-x} corrected to 100%TD are shown in Fig. 3, together with those of UO_2 [5], PuO_2 [6] and $(U_{0.8}Pu_{0.2})O_{2-x}$ [7], where the bulk densities were normalized to 100%TD by Eq. (2) for comparison. The O/(0.8U + 0.2Pu) ratios as shown in Fig. 3 are 2.00, 1.98 and 1.93, respectively.

The thermal conductivity of AmO_{2-x} 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 $(U_{0.8}Pu_{0.2})O_{2-x}$ [5–7]. In general, the decreases of thermal conductivities with increasing temperature for these oxides are due to the increase in phonon scattering.

As shown in Fig. 3 the reduction of O/(0.8U + 0.2Pu) ratio caused the decrease of thermal conductivities. According to the literature [19], the most important factor that accounts for the degradation of lattice thermal conductivity is the density of the oxygen vacancies. As with the thermal diffusivity, the degradation of thermal conductivity attributed to the decrease in the O/Am ratio during the thermal diffusivity measurement from 573 to 873 K in Run 1.

4. Conclusions

The thermal diffusivity of the AmO_{2-x} sample was measured by the laser flash method in the temperature range from 299 to 1473 K. The following was concluded:

The thermal diffusivity of AmO_{2-x} decreased with increasing temperature in the temperature range investigated.

The decrease in the O/Am ratio from 1.9 to 1.73 was observed during the thermal diffusivity measurements, which could be attributed to the measurement environment of vacuum.

The thermal conductivities of AmO_{2-x} corrected to 100%TD decreased 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 $(U_{0.8}Pu_{0.2})O_{2-x}$.

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