Thermal Conductivity of Non-Stoichiometric $(Pu_{0.928}Am_{0.072})O_{2-x}$

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Abstract. The thermal conductivity of non-stoichiometric $(Pu_{0.928}Am_{0.072})O2-x$ (x = 0.000 – 0.058) was evaluated using experimentally measured thermal diffusivity by laser flash method. The obtained thermal conductivity was analyzed using oxygen potential data of $(Pu_{0.928}Am_{0.072})O_{2-x}$ to evaluate the effect of Am on thermal conductivity in the hypo-stoichiometric region. In addition, the theoretical thermal conductivity was calculated using the phonon scattering model and slack model for discussing the effect of O/M ratio and Am on the thermal conductivity.

Key Words: Thermal conductivity, O/M ratio, Oxide

1. Introduction

Am-bearing oxide fuel is considered as the fuel candidate for Fast Reactor to reduce the amount of high level radioactive waste. Thermo-physical properties of oxide fuel such as thermal conductivity and diffusion coefficient are very sensitive to the change of O/M ratio. Am is one of high produced minor actinide in irradiated nuclear fuel and its dioxide (AmO_{2-x}) has higher oxygen potential than PuO_2 [1, 2]. Therefore, in the development of Am-bearing MOX fuel, it is very important to evaluate the effect of Am on thermo-physical properties. In this study, thermal diffusivity of $(Pu_{0.928}Am_{0.072})O_{2-x}$ (x = 0.000 – 0.058) was measured under vacuum with a laser flash apparatus in the temperature range from 750 K to 1250 K. The thermal conductivity was evaluated using the measured thermal diffusivity, bulk density and calculated specific heat capacity. In addition, the effect of O/M ratio on the thermal conductivity of MA bearing oxide fuel was also evaluated.

2. Experimental

2.1. Preparation of $(Pu,Am)O_2$ specimens

In this study, as a raw material powder, the powder of $(Pu_{0.928}Am_{0.072})O_{2-x}$ was prepared and this powder had been stored for 30 years, after separation and purification. Am in this powder had produced by beta-decay of ^{241}Pu. The raw material powder was ground in an agate mortar and the ground powder was pressed into a disk shape. The compacts were sintered at 1873 K for 3h under an Ar-H_2 mixed gas containing moisture. After the sintering, the O/M ratio of these specimens was adjusted from 2.000 to 1.936 by heat treatment under the atmosphere of various oxygen potential [3]. The characteristics of the obtained specimens are shown in the TABLE1.

TABLE 1 THE CHARACTERISTICS OF THE EACH SPECIMENS

	Pu content [mol%]	Am content [mol%]	Theoretical density [%T.D]	O/M ratio [-]
Am7-1	92.8	7.2	97.3	2.000
Am7-2			94.3	1.975
Am7-3			96.6	1.966
Am7-4			96.1	1.936

2.2. Thermal diffusivity measurements

The thermal diffusivity was measured in the temperature range from 750 K to 1250 K in vacuum (about 10^{-3} Pa) with a laser flash apparatus which is installed in the glovebox. The thermal diffusivities were measured three times at each temperature and evaluated as the average. The thermal diffusivities were evaluated by the curve fitting method. Measurements were conducted in both heating and cooling processes to check the change of the O/M ratio during the measurements. After the thermal diffusivity measurements, the specimens were heat-treated at 1123 K for 5h in air to confirm the O/M ratio from the mass difference before and after heat treatment. The results of the change of the O/M ratio are shown in Table2. The average O/M ratio was adopted for the evaluation of O/M ratio dependence on the thermal conductivity.

TABLE 2 THE O/M RATIO CHANE BEFORE AND AFTER MEASUREMENTS

	O/M ratio [-]		
	before	after	average
Am7-1	2.000	-	-
Am7-2	1.975	1.968	1.9715
Am7-3	1.966	1.968	1.967
Am7-4	1.936	1.948	1.942

Thermal conductivities, λ, were calculated from the following equation:

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

where α is the thermal diffusivity, ρ is the bulk density and C_p is the heat capacity. The bulk density of each specimen was measured by immersion method at room temperature. The effect of the O/M ratio on the density was corrected using the equation (2).

$$\rho_{2.00-x} = \frac{W_{2.00-x}}{V_{2.00} \times \left(\frac{a_{2.00-x}}{a_{2.00}} \right)^3} \qquad (2)$$

where W_{2-x} and $V_{2.00}$ are the weight of $(Pu_{0.928}Am_{0.072})O_{2-x}$ and the volume of stoichiometric specimen at room temperature, respectively. The $a_{2.00}$ and $a_{2.00-x}$ are the lattice parameter of stoichiometric and hypo-stoichiometric specimen which is predicted by Kato et al[4]. In

addition, the thickness of the specimen during the thermal diffusivity measurement was corrected by using the thermal expansion reviewed by Carbajo et al. [5].

The heat capacity was evaluated by the Kopp-Neumann rule. The effect of the O/M ratio on the heat capacity was taken into account by subtracting heat capacity of oxygen and the heat capacity of hypo-stoichiometry was expressed as the following equation:

$$C_p = (1-y)\times C_p(PuO_2) + y\times C_p(AmO_2) - \frac{x}{2}\times C_p(O_2) \qquad (3)$$

where $C_p(PuO_2)$, $C_p(AmO_2)$ and $C_p(O_2)$ are the heat capacities of PuO_2, AmO_2 and O_2 respectively. In addition, the obtained thermal conductivities were normalized to 100% theoretical density (T.D.) by the Maxwell-Eucken relationship [6, 7, 8].

3. Results and discussion

The Obtained thermal conductivity is shown in *FIG.1* together with the thermal conductivity of $(Pu_{0.972}Am_{0.028})O_{2-x}$ as the function of the temperature [9]. This figure suggests that the thermal conductivity is decreased by the increase of the temperature and decrease of the O/M ratio. In particular, the O/M ratio significantly affect to the thermal conductivity at low temperature.

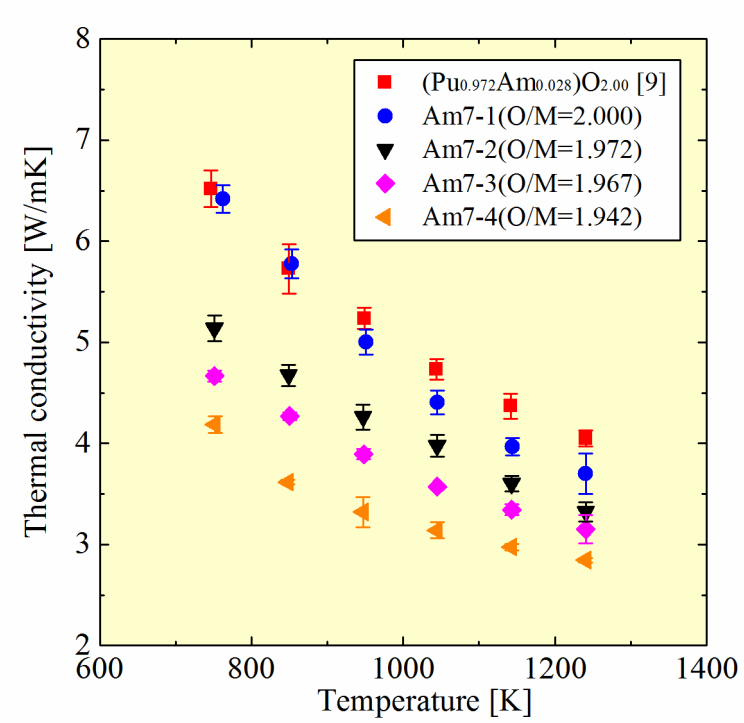

FIG.1. Temperature dependence on the thermal conductivity of $(Pu,Am)O_{2-x}$

In general, thermal conductivity of solid solutions above Debye temperature is represented by the phonon transport model expressed by equation (4) [5].

$$\lambda = \frac{1}{A + BT} \qquad (4)$$

Here, A and B is the constant. A means the thermal resistivity caused by phonon- defect interaction. On the other hand, BT term represents the intrinsic thermal resistance derived

from the phonon-phonon interaction (Umklapp process). In this study, constant A and B are evaluated by fitting the equation (4) to the obtained results. The evaluated A and B are shown in *FIG.2* as the function of the O/M ratio. This figure indicates that constant A is significantly influenced by the O/M ratio, whereas constant B has almost same value. As expected above, constant A represents the thermal resistivity derived from the phonon-defect interaction. It is considered that the oxygen defect, Am^{3+} and Pu^{3+} are increased with a decrease of the O/M ratio. Therefore, this result suggests that the increase of the oxygen defect, Am^{3+} and Pu^{3+} is attributable mainly to the decrease of the thermal conductivity.

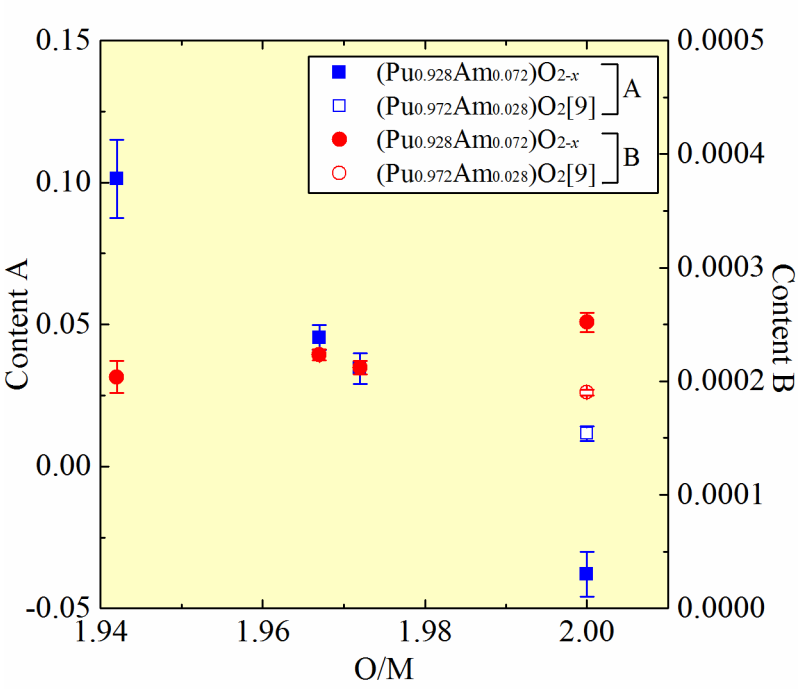

FIG.2. The O/M ratio dependence on the constant A and B

The obtained thermal conductivities are shown in the *FIG.3* as a function of the O/M ratio. In order to evaluate the effect of Am on the thermal conductivity in the hypo-stoichiometric region, the obtained thermal conductivity was analyzed using oxygen potential data of $(Pu_{0.928}Am_{0.072})O_{2-x}$. The oxygen potential data shows that Am and Pu in $(Pu_{0.928}Am_{0.072})O_{2-x}$ is reduced to trivalent over O/M = 1.964 (x = 0.036), and below O/M = 1.964, respectively. The O/M ratio = 1.964 is shown as dash line in the *FIG.3*. It means that the effect of anion on the thermal conductivity switches from Am to Pu, and the thermal conductivity discontinuously decrease at O/M = 1.964. However, the experimental results showed that thermal conductivity continuously decreased with reduction of the O/M ratio. This result indicates that Am has almost comparable effect on the thermal conductivity with Pu in the hypo-stoichiometric region.

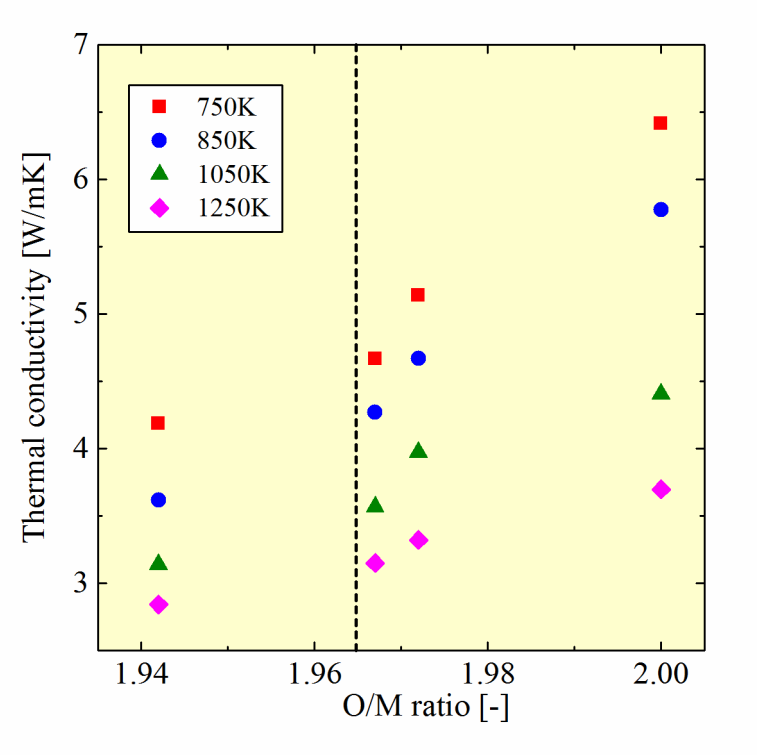

FIG.3. O/M ratio dependence on the thermal conductivity at each temperature

In order to evaluate the effect of the O/M ratio and Am on the thermal conductivity, theoretical thermal conductivity was calculated using the phonon transport model and slack model which is often adopted as the method to evaluate the thermal conductivity of actinide oxides included the hypo-stoichiometric compositions [10,11].

The theoretical constant A was calculated using the thermal conductivity models developed by Abeles [10] and is represented by following equation:

$$A = \frac{\pi^2 V_a T_D}{3 v_p h} \sum_i \Gamma_i \qquad (5)$$

where V_a, T_D, v_p, h, and Γ_i means the average atomic volume, the Debye temperature, the average phonon velocity, Planck constant and scattering cross section parameter of the phonons by a point defect i, respectively [13]. Recently, Debye temperature of PuO_2 was estimated to be 406 K by Kato et al[14]. In this study, Debye temperature of AmO_2 was estimated using the Debye temperature of PuO_2 and melting point of PuO_2 and AmO_2. The average phonon velocity can be calculated using the Debye temperature [11].

The scattering cross section (Γ_i) can be calculated using equation (6) which was proposed by Abeles[10].

$$\Gamma_i = x_i \left[\left(\frac{\overline{M} - M_i}{\overline{M}} \right)^2 + \varepsilon \left(\frac{\bar{r} - r_i}{\bar{r}} \right)^2 \right] \qquad (6)$$

where x_i is the atomic fraction of the point defect i, respectively. Mi and $\overline{M}$ mean the mass of the point defect i and the average atomic mass, respectively. ri and $\bar{r}$ denote the ionic radius of the point defect i and the a ionic radius of the host material, respectively. The ionic

radius of each ion proposed by Shanon et al. and Omichi et al. was applied [15, 16]. The ε parameter means the magnitude of the lattice strain generated by the point defect.

The theoretical constant B was evaluated by Slack and is represented by following equation [15]:

$$B = 3.04\times10^{7}\frac{MT_D^3\delta}{\gamma^2 n^{2/3}} \qquad (7)$$

Here, δ and γ are $(V_a)^{1/3}$ and Grüneisen constant. Kato et al. was estimated the of the Grüneisen constant of PuO_2 to be 2.22 [14]. In this study, it was assumed that the Grüneisen constant of $(Pu,Am)O_{2-x}$ was almost identical to that of PuO_2 because Am content was relatively low.

The theoretical thermal conductivity can be calculated using the equation (5) and (7). However, recently, it was proposed that the heat capacity of Schottoky type is important for the thermal conductivity of PuO_2. Kato et al. proposed the correction formula for theoretical thermal conductivity [14].

$$\lambda = \frac{\left(C_V + C_d + C_{sch}\right)}{\left(C_V + C_d\right)}\lambda_{theoretical}$$

where, $\lambda_{theoretical}$ means the thermal conductivity calculated from the equation (5) and (7). C_V, C_d and C_{sch} are the heat capacity at constant volume, dilatational term and Schottoky term, respectively.

The experimental and calculated thermal conductivities are shown in the *FIG.4*.

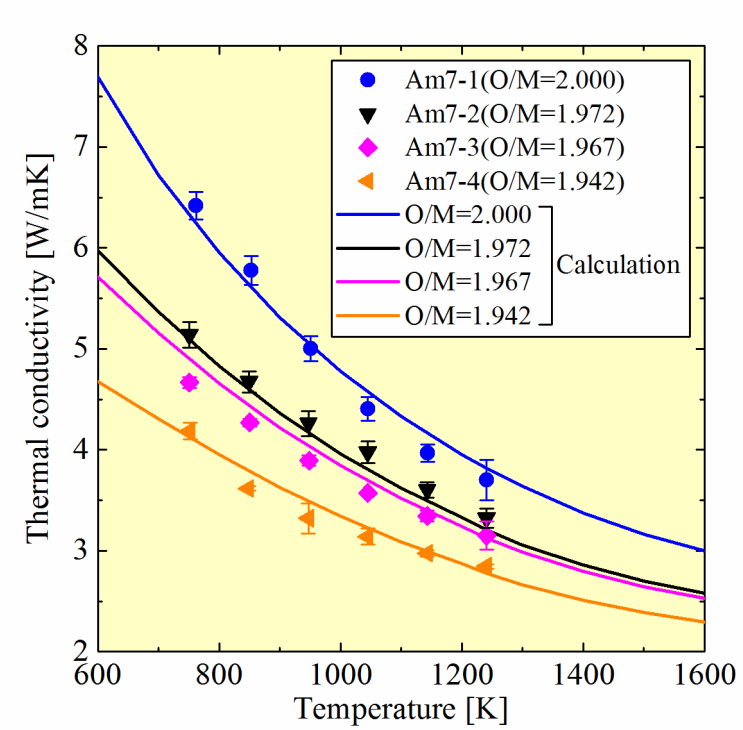

FIG.4. Comparison between the experimental and calculated thermal conductivity

It is clearly shown that the calculated results are good agreement with the calculated results. For the phonon transport model, it is well known that the point defect or the ionic radius

differences has great influence on the thermal conductivity. Hence, this evaluation suggests that the decrease of thermal conductivity of $(Pu,Am)O_{2-x}$ was caused by the increase of oxygen vacancy and ionic radius differences between Pu^{4+} and Pu^{3+} or Am^{4+} and Am^{3+}. In addition, the effect of Am on the thermal conductivity has almost identical with Pu due to the similar ionic radius of Pu^{4+} (0.096 nm) and Am^{4+} (0.095 nm) or Pu^{3+} (0.110 nm) and Am^{3+} (0.109 nm).

4. Conclusion

In this study, the thermal diffusivity of hypo-stoichiometric $(Pu_{0.928}Am_{0.072})O_{2-x}$ with x = 0.00 - 0.058 was measured by the laser flash method in the temperature range from 750K to 1250K, and the effects of the O/M ratio and Am on the thermal conductivity was discussed.

(1) The O/M ratio dependence on thermal conductivity was well represented using the phonon scattering model and slack model. It was clearly shown that the decrease of thermal conductivity was derived from the increase of oxygen vacancy and ionic radius differences between Pu^{4+} and Pu^{3+} or Am^{4+} and Am^{3+}.

(2) The experimental results showed that the thermal conductivity continuously decreased with a decrease of the O/M ratio. This result suggests that Am has almost identical effect on the thermal conductivity with Pu in the hypo-stoichiometric region because of the similar ionic radius of Pu^{4+} and Am^{4+} or Pu^{3+} and Am^{3+}.

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