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Variation of the thermal conductivity of $(U,Dy)O_2$ solid solutions as a function of the Dy content

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Abstract

The relationship between the lattice parameter (a) and the Dy content (y) in $(U_{1-y}Dy_y)O_2$, $0 \le y \le 0.2$, is expressed as $a = 0.5470 - 0.0215y$ in this study. When the above relation was applied to the Ohmichi's rule, it was suggested that U^{5+} existed in preference to U^{6+} in $(U,Dy)O_2$ solid solutions. The thermal conductivities of UO_2 and $(U,Dy)O_2$ gradually decreased with the temperature, which showed that the temperature dependency of the thermal conductivity up to 1473 K followed the phonon conduction model, $K = (A + BT)^{-1}$. The relationship between the thermal conductivity of UO_2 and $(U,Dy)O_2$ could be expressed as $K(\mathrm{SS}) = K_{UO_2}/(1 + K_{UO_2}(0.9704y - 0.0006yT))$. It was also found that the size effect had a greater influence on the lattice defect thermal resistivity than the mass effect and especially, the size difference between the U^{4+} and U^{5+} ions rather than that between the U^{4+} and Dy^{3+} played a dominant role in the reduction of the thermal conductivity of $(U,Dy)O_2$.
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1. Introduction

The use of an extended cycle and a high burnup nuclear fuel are practical means of improving the economics of a nuclear power generation. A neutron absorber should be used in a reactor core to suppress the initial excess reactivity and to effectively control the power distribution throughout the operation. UO_2–$GdO_{1.5}$ pellets [1,2], as a neutron absorber, have principally been used in BWRs and PWRs. Gadolinia, however, is considered to have some limitations for a use of more than 18 months [3]. So, there has been an increased interest in the development of an advanced nuclear fuel with a new neutron absorber that is capable of an extended fuel cycle, a homogeneous power distribution and maintaining the negative moderator coefficient.

Dysprosium and erbium can be considered as slow neutron absorbers suitable for a high burnup and/or extended cycle operation [4,5]. During the sintering of Dy-doped UO_2 pellets, Dy is known to form a solid solution with uranium dioxide by a substitution of the uranium cations in the fluorite structure [6]. Therefore, the addition of Dy to the UO_2 matrix will influence the thermo-physical properties of nuclear fuels such as the thermal conductivity and thermal expansion. Thermal conductivity is one of the most important properties of nuclear reactor fuel pellets as it affects the fuel performance such as a fission gas release and a swelling.

A number of studies related to the thermo-physical properties of UO_2–$GdO_{1.5}$ pellets have been published [7–12], but there are no reports on the thermal conductivity for a Dy-doped UO_2 pellet. In this study, the thermal conductivities of near-stoichiometric $(U_{1-y}Dy_y)O_2$ solid solutions, $0 \le y \le 0.2$, were measured from room temperature to 1473 K.

2. Experimental

The UO_2 powder was mixed with weighed amounts of $DyO_{1.5}$ powder, at concentrations of 1, 3, 5, 7, 10, 20 mol%, by a Turbula® mixer for 1 h and then successively milled by a dynamic ball mill for 1–6 h to prepare samples with a density of more than 95% T.D. The milled oxide powders were compacted with a compaction pressure of 300 MPa and the green pellet specimens were sintered at 2023 K in flowing H_2 for 6 h. The densities of the samples were measured by the water immersion method.

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The X-ray diffraction patterns were recorded in the range of $20^\circ < 2\theta < 120^\circ$ by using a monochromatic Cu Kα radiation on an X-ray diffractometer (MXP 3A-HF, MacScience). The lattice parameters (a) of the (U,Dy)O_2 solid solutions were obtained from all the reflections by employing the Nelson–Riley extrapolation [13]. The volume (V) of each sample was calculated as a^3 and its weight (W) by the following equation, $\{[4M_U(1-y)] + [4M_{Dy}y] + [8M_O]\}/N_0$, where M_U, M_{Dy} and M_O are the atomic weights of U, Dy and O, respectively, y the mole fraction of Dy and N_0 is the Avogadro's number. From this data, the theoretical densities (ρ_{TD}) were obtained by the equation of $\rho_{TD} = W/V$.

The thermal conductivities were obtained from the heat capacity, and the sample density and the thermal diffusivity were measured by the laser flash method (Netzsch LFA-417). The test temperatures for the thermal diffusivity measurement were set to 1473 K except for pure UO_2, which was measured up to 1673 K. The measurements of the thermal diffusivity were carried out three times at every test temperature at a vacuum pressure of 10^{-4}–10^{-5} Pa. The average value of these three measurements was used and the experimental uncertainty associated with these measurements was within 5%.

For the thermal diffusivity measurements, samples were prepared in the shape of discs with 8 mm in diameter and 1 mm in thickness. A pulse from a laser was projected to the front surface of the disc and the temperature rise on the rear side of the disc was obtained by using an infrared detector. The thermal diffusivity (α) was calculated from the following relationship:

$$\alpha = 0.1388\frac{L^2}{t_{1/2}} \tag{1}$$

where $t_{1/2}$ is the time in seconds to one-half of the maximum temperature rise at the rear surface of the disc and L is its thickness in mm.

3. Results and discussion

3.1. Lattice parameter and sample density

The chemical formulae of the UO_2–$DyO_{1.5}$ samples fabricated in this study were expressed as (U,Dy)O_2 because the O/M ratios of these samples were nearly 2.0 [6]. Table 1 shows the disc thicknesses, lattice parameters, sintered densities and theoretical densities of each sample. The lattice parameters of these samples decreased as the Dy content increased. The dependency of the lattice parameter (a, nm) on the Dy content (y) in these near-stoichiometric (U,Dy)O_2 was as follows:

$$a = 0.5470 - 0.0215y \quad (0 \le y \le 0.2) \quad \text{for}\,(U_{1-y}Dy_y)O_2 \tag{2}$$

When Dy^{3+} ions enter the UO_2 lattice and are substituted for the U^{4+} ions in the UO_2 lattice, the neighboring U^{4+} ions must be oxidized to U^{5+} or U^{6+} to maintain electrical neutrality. Ohmichi et al. [14] have shown that the oxidation state of uranium in $(U_{1-y}M_y)O_2$ type solid solutions could be determined from the dependency of the lattice parameter on y, da/dy, by using the ionic radii of Dy^{3+}, U^{4+}, U^{5+} and U^{6+}. If the cation–anion distance in a solid solution is expressed as the sum of the radii of the cation and anion, the lattice parameter of a solid solution is given by the following equation:

$$a = \frac{4}{\sqrt{3}}\left(\sum y_c r_c + \sum y_a r_a\right) \tag{3}$$

where r_c, r_a and y_c, y_a are the radii and the fractions of the cations and anions, respectively. If the oxidation states of the neighboring U^{4+} ions are changed into U^{5+} or U^{6+}, the chemical forms of a solid solution can be given as $U^{4+}_{1-2y}U^{5+}_y Dy^{3+}_y O^{2-}_2$ or $U^{4+}_{1-3y/2}U^{6+}_{y/2}Dy^{3+}_y O^{2-}_2$, respectively. Therefore, in the case of U^{5+}, da/dy can be given as

$$\frac{da}{dy} = \frac{4}{\sqrt{3}}(r_{Dy^{3+}} + r_{U^{5+}} - 2r_{U^{4+}}) \tag{4}$$

If the oxidation state is U^{6+}, da/dy is

$$\frac{da}{dy} = \frac{4}{\sqrt{3}}\left(r_{Dy^{3+}} + \frac{1}{2}r_{U^{6+}} - \frac{3}{2}r_{U^{4+}}\right) \tag{5}$$

The ionic radii of U^{4+}, U^{5+}, U^{6+} and Dy^{3+} with the coordination number of 8 are 0.1001, 0.088, 0.086 and 0.1027, respectively, and that of the O^{2-} ion with the coordination number of 4 is 0.1368 [15]. When these ionic radii were applied to Eqs. (4) and (5), the value of da/dy for the oxidation state of U^{5+} and U^{6+} were, respectively, −0.0219 and −0.0103. The experimentally determined value of da/dy was −0.0215, as shown in Eq. (2) and this indicated that U^{5+} existed in preference to U^{6+} in the (U,Dy)O_2 solid solutions fabricated in this study. Accordingly, the major phonon scattering centers in (U,Dy)O_2 are suggested to be the U^{4+}, U^{5+}, Dy^{3+} and O^{2-} ions.

3.2. Thermal conductivity

The measured thermal diffusivities (α_m) were normalized to 95% T.D. by using the following equation [8,16]:

$$\alpha_{95} = \alpha_m\left[\frac{(1-P)(1-0.05\eta)}{(1-0.05)(1-P\eta)}\right] \tag{6}$$

where α_{95}, η and P are, respectively, the thermal diffusivity normalized to 95% T.D., the experimentally determined fitting parameter including its temperature dependency and the porosity of the samples. Here, for the value of η which is a function

Table 1
Lattice parameters and sintered densities of the pure UO_2 and (U,Dy)O_2 solid solutions at room temperature

Dy (mol%)	Thickness (mm)	Lattice parameter (nm)	Sintered density (g/cm^3)	Theoretical density (g/cm^3)	Relative density (% T.D.)
0	1.104	0.5470	10.66	10.96	97.26
1	1.054	0.5468	10.57	10.94	96.62
3	1.051	0.5464	10.40	10.90	95.41
5	1.008	0.5457	10.34	10.88	95.04
7	1.096	0.5453	10.37	10.85	95.58
10	1.093	0.5448	10.53	10.78	97.68
20	1.062	0.5427	10.48	10.59	98.96

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