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The linear thermal expansion and the thermal diffusivity measurements for near-stoichiometric (U, Ce)O_2 solid solutions

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Abstract

The thermal diffusivities of near-stoichiometric (U, Ce)O_2 solid solutions containing CeO_2 up to 22 mol% were investigated in the temperature range of 298–1273 K using the laser flash method. Also, linear thermal expansion measurements were performed in the temperature range of 298–1673 K using a thermomechanical analysis. The thermal conductivities were determined by a calculation of the thermal diffusivity, the density and the specific heat. The thermal conductivities of the tested samples could be expressed as a function of the temperature by the phonon conduction equation $k = (A + BT)^{-1}$. The thermal conductivity decreased gradually with an increasing Ce content. This was attributable to the increasing lattice defect thermal resistance caused by the U^{4+}, Ce^{4+} and O^{2-} ions as phonon scattering centers.

Keywords: Thermal conductivity; Linear thermal expansion; Uranium–cerium oxide; Laser flash method; Thermomechanical analysis

1. Introduction

In the investigation on nuclear reactor materials, the importance of cerium and cerium oxide is emphasized as one of the major fission products produced in a nuclear fuel under nuclear reactor operation. Further, cerium oxide has often been used as a simulating material for plutonium oxide. Although cerium oxide cannot duplicate the behaviors of plutonium oxide exactly, it has been used owing to its similar tendency of the chemical/thermodynamic behaviors and a convenience in handling [1–3].

In the research of mixed oxide fuel (MOX) using cerium oxide, 20–30 mol% CeO_2 contents are mainly used to simulate a fast breeder reactor (FBR) fuel composition, while (U, Ce)O_2 properties data for a low content (below 20 mol%) are required in the relevant research of a MOX fuel for a pressurized water reactor (PWR) [4].

The thermal conductivity of nuclear fuel materials is the most important property to evaluate the fuel performance in a nuclear reactor, because this property affects the fuel centerline temperature, operating power efficiency, safety, release of the fission product, etc. The thermal conductivity of oxide fuel materials decreases with the fission product forming a solid solution, the perturbation of the stoichiometry for the fuel element, increasing burnup, etc. In this regard, the thermal conductivities of UO_2 and various doped-UO_2 have been intensively studied by many investigators [5–15].

In the present work, the thermal diffusivities of near-stoichiometric (U, Ce)O_2 solid solutions containing CeO_2 up to 22 mol% were measured in the temperature range of 298–1273 K using the laser flash method. Also, the linear thermal expansion measurements for the samples were performed in the temperature range of 298–1673 K. The coefficient of the linear thermal expansion (CTE) and the density were calculated from the measured thermal expansion data. The thermal conductivities were determined by a calculation of the density, the thermal diffusivity and the specific heat.

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2. Experimental

Various contents of CeO_2 (Aldrich, 99.9%) powders were added to Integrated Dry-Route UO_2 (IDR-UO_2), supplied by British Nuclear Fuel plc. (BNFL), and mixed using a Turbula^{TM} mixer for 1 h. The powder mixtures were milled using an attrition mill for 4 h. Green pellets for the milled powder mixture were formed by a pressing at about 300 MPa using a small amount of lubricant (Zn stearate). The pellets were sintered at 2023 K for 4 h in a flowing H_2 atmosphere [15]. The sizes of the sintered pellets were about 8.5 mm in diameter and 12–13 mm in height.

For the purpose of an observation on the formation of the solid solution, and a calculation of the theoretical densities, the X-ray diffraction peak of a sample was measured by X-ray diffractometry (XRD, Mac Science, MAC-M03XHF) from $2\theta = 10^\circ$ to 120° at room temperature using a Cu Kα target. The step scanning method was used (counting time = 5 s, step width = 0.05°).

In the temperature range of 298–1673 K, the axial directional length changes of the pellets – initial length was about 12–13 mm – were measured under a flowing argon atmosphere using a Thermo-Mechanical Analyzer (TMA, SETARAM, TMA92), and a heating rate of 5 K/min, according to the ASTM designation [16]. The density was calculated using the measured thermal expansion data.

Samples for the thermal diffusivity measurement were cut to 0.9–1.1 mm in thickness and 6 mm in diameter from a sintered pellet and polished. In the temperature range of 298–1273 K, the thermal diffusivity was measured using a Laser Flash Apparatus (Netzsch, LFA-427). The measurements of the thermal diffusivity were carried out three times at every test temperature step in a vacuum (10^{-4} Pa to 10^{-5} Pa). The thermal conductivities were calculated from the density, the thermal diffusivity and the specific heat which was calculated by the Neumann–Kopp's law using the literature data on UO_2 and CeO_2 [17–22].

3. Results and discussion

It was observed that CeO_2 in the UO_2 matrix was fully formed as a solid solution in this composition range using the X-ray diffraction. The lattice parameters were obtained using the measured peak data [23]. Fig. 1 shows that the lattice parameter linearly decreased with an increasing Ce content. Based on the fact that the data points are on a straight line, i.e. the measured data follow the Vegard's law, it can be considered that the oxygen-to-metal (O/M) ratio for these samples is the stoichiometric or the near-stoichiometric state.

Even if oxygen vacancies were formed at a high temperature, an oxygen pick-up during storage in air could fill the oxygen vacancies since the solid solution containing an oxygen deficiency is very susceptive to oxidation [24]. That is to say, although the samples were sintered in a H_2 atmosphere, the O/M ratio changed to be the near-stoichiometric state (2.00–1.99).

By many investigators [10,13,25–28], hypo-stoichiometric (U, Ln)O_{2-x} has been reported to oxidize easily in air, even at room temperature, to almost a stoichiometric composition.

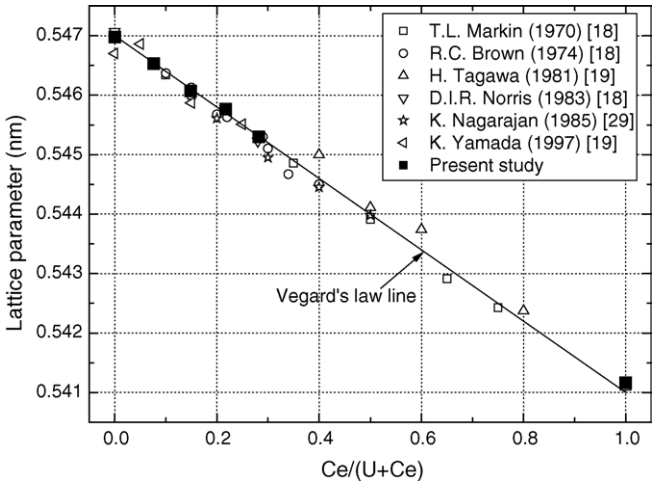

Fig. 1. The measured lattice parameters and literature data of (U, Ce)O_2 as a function of the Ce contents.

So, although the O/M ratio of the samples was not measured in this study, it can be considered that the deviation from stoichiometric in this sample composition range is assumed to be negligible.

3.1. Linear thermal expansion measurements

For the sample of $(U_{1-y}Ce_y)O_2$ ($0 \le y \le 0.22$), the length changes of the sintered pellet were measured using TMA from room temperature to 1673 K in a flowing argon atmosphere. The linear thermal expansions of a sample forming a solid solution increased with an increasing Ce content (Fig. 2). This trend can be correlated with the higher density and melting point of UO_2 (10.96 g/cm^3, 3100 K) as compared to that of CeO_2 (7.65 g/cm^3, 2673 K). The measured linear thermal expansion was fitted as a function of the temperature using a cubic polynomial regression ($\Delta L/L\,(\%) = a + bT + cT^2 + dT^3$), with the fitting parameters given in Table 1, where T is an absolute temperature (K) and T_o is 298 K.

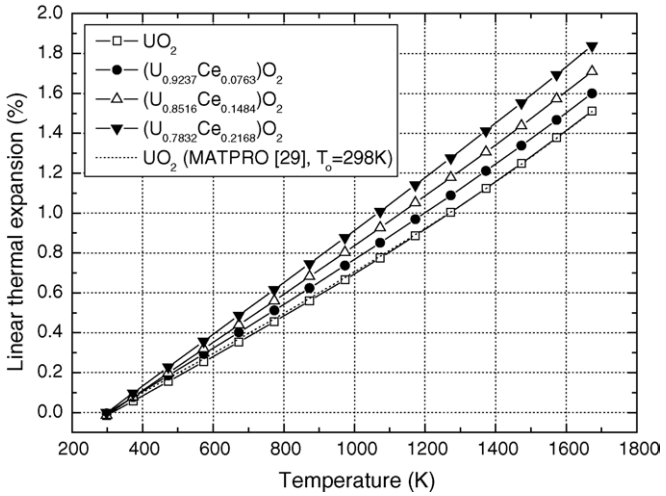

Fig. 2. Measured linear thermal expansion using the TMA method for (U, Ce)O_2 as a function of the Ce content.