Potential Utilization of Laser Flash Analysis for On-Site Measurement of UO_2 Stoichiometry

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1. Introduction

Oxide fuel stoichiometry often comes at a great importance during IAEA and SSAC inspection for nuclear material accountancy. By and large, thermogravimetric analysis (TGA) has been used for that matter ever since its first introduction about 60 years ago [1]. One shortcoming of the TGA method is the lack of decent hand-carry device for on-site inspection due to the nature of the methodology. To address this issue, we suggest the utilization of thermal conductivity profile up to lower temperatures (~ 300 °C) and measured the thermal conductivity of stoichiometry-specific CeO_{2-x} pellets, as a surrogate material for non-stoichiometric UO_2, using laser flash analyzer (LFA) to demonstrate the feasibility of the method.

2. Experimental Methodology

2.1 Sample preparation

As-received CeO_2 powder (99.9%, 1-μm, Avention) was pressed into green pellets (9.8 mmD × 2 mmL) under 250 MPa using hydraulic press (KSHM-010P, Kumsung). The green pellets were then heated at 5 °C/min rate up to 1500 °C and held for 1 h ~ 20 h under low oxygen partial pressure (~0.01 %) argon gas atmosphere. Oxygen partial pressure (p_{O_2}) in argon gas was monitored using oxygen sensor (C-100, Nano-ionics Korea) throughout the sintering process.

Various hypo-stoichiometric CeO_{2-x} pellets ($0 < x < 0.05$) were fabricated referring to the constitutional Ce-O phase diagram [2] with equilibrium oxygen partial pressure at 1500 °C. The non-stoichiometric equilibrium reached over 10 h sintering time.

The sample density was measured at room temperature using the Archimedes method.

2.2 Thermogravimetric analysis (TGA)

The stoichiometry of sintered pellets were reaffirmed using TGA (STA 449 F5, NETZSCH).

2.3 Laser flash analysis (LFA)

The thermal diffusivity of stoichiometry-specific CeO_{2-x} pellets were measured from 25 °C to 300 °C using LFA (LFA 467 HT, NETZSCH).

3. Results & Discussion

3.1. Density

The measured density of sintered CeO_2 were ranging from 96.3 to 97.6 %TD, which are well matched with density of fresh UO_2 fuel for LWR (95 % ~ 97 %TD).

Table 1. Measured density of sintered non-stoichiometric CeO_2 pellets

Sintering time	Measured density (g/cm^3)	% TD
1 h	6.98	96.68
5 h	6.96	96.39
10 h	7.02	97.18
20 h	7.04	97.56

3.2. Stoichiometry

Fig. 1 shows a TGA mass gain of non-stoichiometric CeO_2 sample sintered 20 h. Subtle mass drop through the second isothermal step was regarded as balance drift error. Measured mass changes were calibrated by adding average mass drop.

Mass gain from oxidation of non-stoichiometric CeO_2 to stoichiometric CeO_2 is converted into O/Ce ratio as follows:

$$\mathrm{O/Ce} = \frac{(1-w_{Ce})/A_O}{w_{Ce}/A_{Ce}} \tag{1}$$

$$w_{Ce} = \left(\frac{A_{Ce}}{A_{Ce}+2A_O}\right)\left(\frac{m_2}{m_1}\right) \tag{2}$$

where m_1 and m_2 are mass of non-stoichiometric and stoichiometric CeO_2 respectively, A_{Ce} is atomic mass of cerium, A_O is atomic mass of oxygen, and W_{Ce} is mass fraction of cerium in CeO_2.

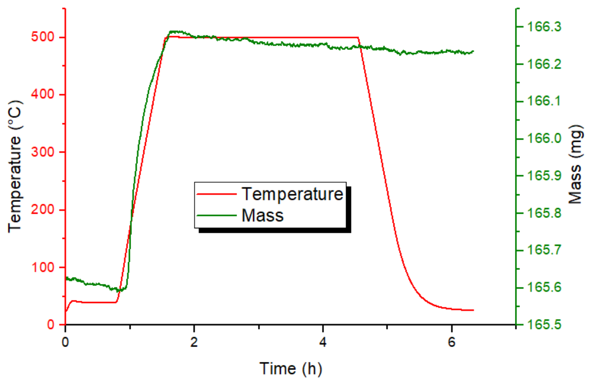

Fig. 1. TGA curve of non-stoichiometric CeO_2.

Calculated from measured mass gains of the heating curve up to 500 °C showed agreement with intended stoichiometry within ± 0.005.

3.3. Thermal conductivity

Using measured density and diffusivity data of in this study and heat capacity data of Nelson et al.[3], thermal conductivity of sample was calculated as follows:

$$k = \alpha \cdot \rho \cdot C_p \tag{3}$$

where α is thermal diffusivity, ρ is density, and C_p is heat capacity.

Thermal conductivity of samples with different density was adjusted to independently evaluate the stoichiometry effect on thermal conductivity using the following equation:

$$k_2 = k_1 \frac{\rho_2}{\rho_1} \tag{4}$$

where k_1 and ρ_1 are the thermal conductivity and measured density, and k_2 and ρ_2 are the same variables for the density of interest (96 % TD).

Fig. 2 shows measured thermal conductivity of non-stoichiometric CeO_2, which drastically lowered with small stoichiometry deviation at low temperature. Hence, a portable LFA device can be designed by adopting reduced size furnace and insulator for low temperature operation only.

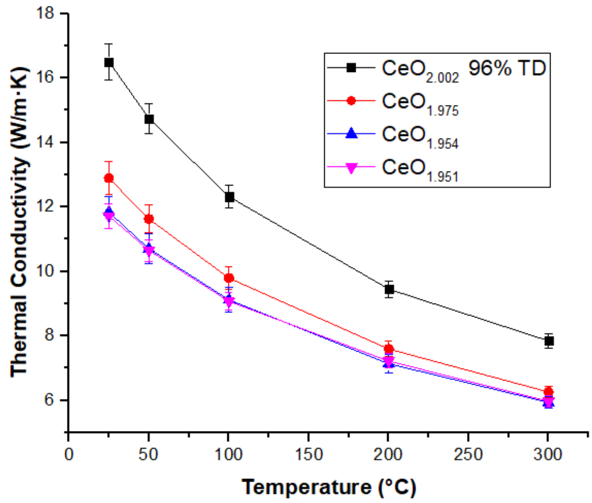

Fig. 2. Thermal conductivity of non-stoichiometric CeO_2.

4. Conclusions

Various stoichiometric specific CeO_{2-x} pellets were fabricated as the surrogate of non-stoichiometric UO_2 pellets. Collected thermal conductivity profiles indicate clear potential of LFA method to be used for on-site measurement of UO_2 fuel stoichiometry.

ACKNOWLEDGEMENT

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