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FABRICATION AND CHARACTERIZATION OF REACTION-RESISTANT $LaYO_3$ MATERIAL FOR THE MELTING CRUCIBLE OF METAL FUELS

$LaYO_3$ which has phase stability at high temperature is introduced as a promising candidate for reaction-preventing crucible materials with Uranium-Zirconium (U-Zr) melt containing rare-earth elements (RE). RE is composed of rare-earth elements such as Nd, Ce, Pr and La. The $LaYO_3$ material was synthesized by a solid-state reaction method at elevated temperature according to a pseudo-phase diagram of $LaYO_3$ and Y_2O_3. Green compacts blended with La_2O_3 and Y_2O_3 powder were made by the Cold Isostatic Pressing (CIP) method, with La_2O_3 and Y_2O_3 powders varying with molar ratios from 1.0 to 1:2. $LaYO_3$ synthetics were fabricated at sintering temperatures ranging from 1450°C to 1600°C. $LaYO_3$ pellets sintered at below 1550°C showed a highly dense orthorhombic phase with a perovskite structure, resulting in an enhancing reaction-resistant effect with RE.

Keywords: Metal fuel; Melting crucible; Reaction-resistant; $LaYO_3$; Perovskite structure

1. Introduction

The transuranic (TRU) element, which is obtained through pyro-electrochemical processing of the spent fuels of pressurized water reactors (PWRs), is used to fabricate metal fuels for Sodium-cooled Fast Reactors (SFRs) [1-4]. U-TRU-Zr-RE metal fuels generally have a low centerline temperature and a fuel cycle economy [5-7]. RE is composed of rare-earth elements consisting of 53wt.% Nd, 25wt.% Ce, 16wt.% Pr, and 6wt.% La. Metal fuel slugs are fabricated with an injection casting process operating under atmospheric pressure [8-10]. The metal fuel is melted in a graphite crucible slurry-coated or plasma-spray coated with Y_2O_3 to prevent melt/material interactions [11,12]. Since highly reactive RE is included during the pyro-processing process, even the plasma-spray coated Y_2O_3 layer on the melting crucible reacts with RE in the metal fuel and forms the reaction products of the RE-Y-O system, which produces a considerable amount of fuel loss and a large amount of radioactive crucible waste. Therefore, it is necessary to develop an alternative reaction-resistant crucible material that prevents high reactivity with fuel melt to control the fuel loss and reduce the radioactive waste. The requirements for the reaction-preventing crucible material are thermal shock resistance at an elevated temperature, thermal compatibility with U-Zr-RE fuel material, and phase stability at casting temperatures ranging from 1400°C to 1500°C.

Interlanthanide $LaYO_3$ material, as a RE-Y-O compound, is of interest as a potential candidate for thermal barrier coating in highly refractory materials due to its chemical and thermal stability [13]. The $LaYO_3$ material has a stable orthorhombic perovskite structure which is almost 50 mol.% for each La_2O_3 and Y_2O_3 in the phase diagram of the La_2O_3-Y_2O_3 system [14-16]. The perovskite structure can improve the performance of the reaction-resistant material due to its chemical and thermal stability [17]. Hence, in this study we introduced the perovskite $LaYO_3$ as an alternative reaction-preventing crucible material for fabrication feasibility and phase stability. $LaYO_3$ pellets for the metal fuel melting crucible were prepared and characterized by a sintering method according to the pseudo-phase diagram of La_2O_3 and Y_2O_3.

2. Experimental

In this experiment we used La_2O_3 powder with an irregular shape and a purity of 99.999% and a particle size of approximately 2.5 μm and Y_2O_3 powder with an angular shape and

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a purity of 99.9% and a particle size of about 0.5 μm as raw materials for the fabrication of $LaYO_3$. Mixed powder slurries of La_2O_3 and Y_2O_3 powder with molar ratios of 1:1.0, 1:1.05, 1:1.1, 1:1.15, and 1:1.2 were obtained through wet ball milling of La_2O_3 and Y_2O_3 powders for 24 hrs. The powder slurry was then annealed by heating at 1100°C for 10 hrs to remove foreign adhering substances and moisture. Wet ball milling was again performed for 24 hrs to obtain a powder slurry with a uniform composition of the calcined powder. At this time, when the powder slurry was put into the spray-drying apparatus, the inlet and the outlet temperatures were fixed at 130°C and 70°C, and the rotation speed of the disk was in the range of 6000 rpm to 7000 rpm. Spherical mixed powders with particle size ranging from 10 μm to 60 μm were prepared from the slurry of mixed powders through a spray drying and a sieving process. Green compacts using the mixed powders of La_2O_3 and Y_2O_3 were made by cold isostatic pressing (CIP) with a molar fraction in the range of 50% to 54.5% of Y_2O_3. $LaYO_3$ pellets were synthesized by holding the temperature at 1450°C, 1500°C, 1550°C, and 1600°C for 10 hrs, according to the pseudo-phase diagram of La_2O_3–Y_2O_3 system [14-16]. The density of the sintered $LaYO_3$ pellets was determined using an Archimedean immersion method. We investigated the microstructure of the sintered $LaYO_3$ synthetics by scanning electron microscopy (SEM, XL series, Philips) combined with energy dispersive spectroscopy (EDS, 6110, Bruker). The phase structure of the sintered $LaYO_3$ synthetics was examined by X-ray diffraction (XRD, Dmax-2500 pc, Rigaku) using Cu Kα radiation and a Ni filter.

3. Results and discussion

The X-ray diffraction patterns of the $LaYO_3$ synthetic according to sintering temperature and a molar ratio of 1:1.1 (La_2O_3 and Y_2O_3) sintered ranging from 1450°C to 1600°C are shown in Fig. 1. The $LaYO_3$ sintered bodies had a similar X-ray diffraction pattern at sintering temperatures ranging from 1450°C to 1550°C for 10 hrs as shown in Fig. 1(a). The X-ray diffraction patterns of the sintered bodies indicated the formation of a crystallized orthorhombic $LaYO_3$ phase with a perovskite structure *(Pnma)* at a sintering temperature of below 1550°C irrespective of the molar ratio of La_2O_3 and Y_2O_3 [14-16]. The perovskite orthorhombic $LaYO_3$ phase is a thermodynamically stable phase from room temperature to 1585°C based on the pseudo-phase diagram between La_2O_3 and Y_2O_3 [17]. The perovskite structure comprised an orthorhombic atom arrangement of the oxide ions and alternating layers of transition metal ions in the monoclinic coordination [18]. A monoclinic $LaYO_3$ phase was named the B phase in the pseudo-phase diagram between La_2O_3 and Y_2O_3 [13-15]. However, it was confirmed that an ordered monoclinic phase (B phase) was formed partially in the $LaYO_3$ pellet at a sintering temperature of 1600°C, regardless of the molar ratio of La_2O_3 and Y_2O_3 [19]. The $LaYO_3$ formed a stable monoclinic phase (B phase) in the range of 1585°C to 1730°C based on the pseudo-phase diagram between La_2O_3 and Y_2O_3 [17]. The $LaYO_3$ pellets indicated similar X-ray diffraction patterns at a sintering temperature sintered ranging from 1450°C to 1600°C as shown in Fig. 1(b), and the $LaYO_3$ pellets showed a similar X-ray diffraction pattern at 1550°C at the same molar ratio of La_2O_3 and Y_2O_3, as shown in Fig. 1(b). The $LaYO_3$ pellets formed with a stable orthorhombic perovskite structure at the fabrication temperature of metal fuel slugs ranging from 1400°C to 1500°C [10]. Hence, we concluded that the perovskite structure of $LaYO_3$ synthetics with structural phase stability can enhance the performance of the reaction-resistant crucible material for the injection casting of U-TRU-Zr-RE metal fuels.

The bulk density of the $LaYO_3$ synthetics sintered for 10 hrs according to the molar ratio of La_2O_3 and Y_2O_3 is shown in Fig. 2. As the sintering temperature increased, the density of the $LaYO_3$ pellets prominently increased. The density generally shows an indirect indication of the internal defects such as pores in the $LaYO_3$ pellet. The $LaYO_3$ pellets sintered at 1450°C and 1500°C

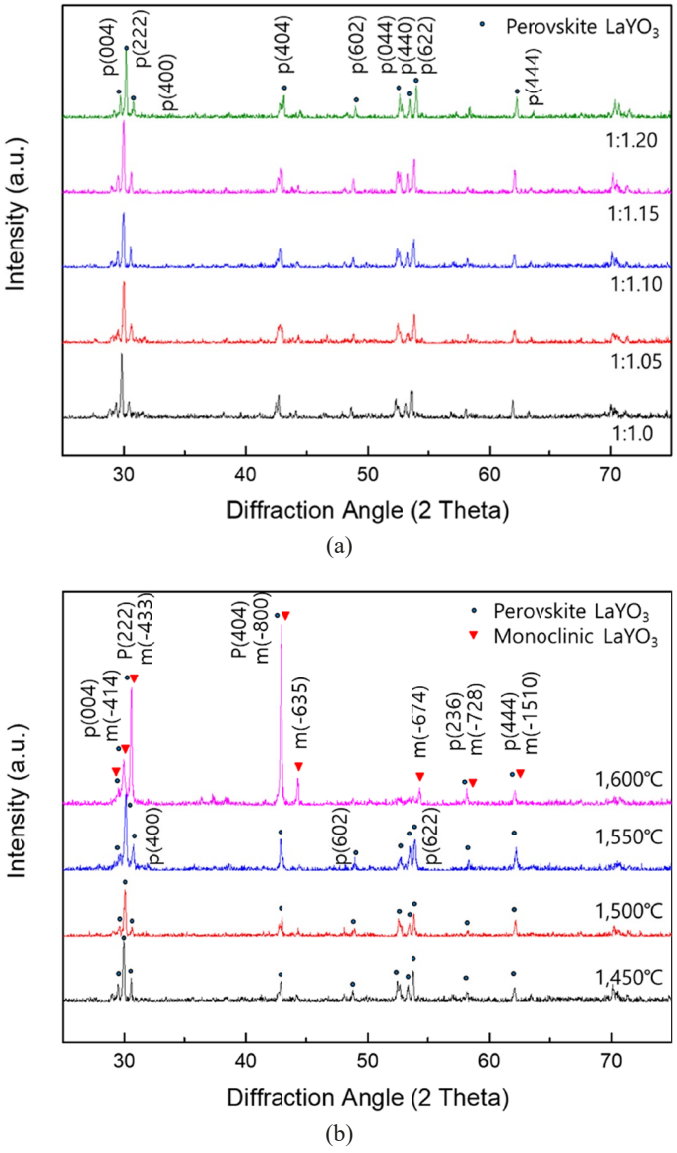

Fig. 1. The X-ray diffraction patterns of the $LaYO_3$ synthetics according to sintering temperature (a) and a molar ratio of 1:1.1 (La_2O_3 and Y_2O_3) sintered ranging from 1450°C to 1600°C (b)

showed insufficient densification with a low relative density of 59.6% and 72.1% due to the lack of consolidation, independently of the molar ratio. When the sintering temperature was raised to 1550°C and 1600°C, the relative density increased greatly up to 89.8% and 97.1% of theoretical density with sufficient consolidation, irrespective of the molar ratio. We think that $LaYO_3$ phase was already formed below the sintering temperatures and then the $LaYO_3$ grains could grow without the consolidation between La_2O_3 and Y_2O_3. The scanning electron micrographs of the $LaYO_3$ pellet according to sintering temperature are shown in Fig. 3. The cross-sectioned micrographs of the $LaYO_3$ pellet showed a similar densification at a constant sintering temperature, independently of the molar ratio. The $LaYO_3$ pellets sintered at 1450°C and 1500°C showed many pores and an insufficient densification due to a lack of consolidation as shown in Fig. 2. The $LaYO_3$ pellets sintered at 1550°C and 1600°C indicated a considerable densification and small pores, resulting in a high relative density of 89.8% and 97.1% with the progress of consolidation as shown in Fig. 2.

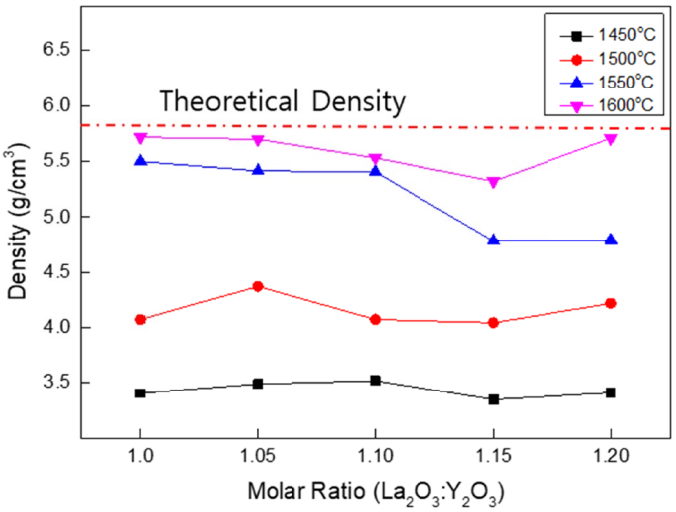

Fig. 2. The bulk density of the $LaYO_3$ pellets sintered for 10 hrs according to molar ratio of La_2O_3 and Y_2O_3

4. Conclusions

In this study, we synthesized $LaYO_3$ material as an alternative reaction-preventing crucible material by a sintering method based on the pseudo-phase diagram of La_2O_3 and Y_2O_3. The $LaYO_3$ pellets were composed of a perovskite orthorhombic $LaYO_3$ phase with phase stability at sintering ranging from 1450°C to 1550°C, irrespective of the molar ratio of La_2O_3 and Y_2O_3. The $LaYO_3$ pellets sintered at 1550°C and 1600°C indicated a considerable densification and small pores, resulting in a high relative density of 89.8% and 97.1% of the theoretical density with the progress of consolidation, independently of the molar ratio. We propose that the $LaYO_3$ synthetic is a promising candidate for a reaction-preventing crucible material for the injection casting of U-TRU-Zr-RE metal fuels.

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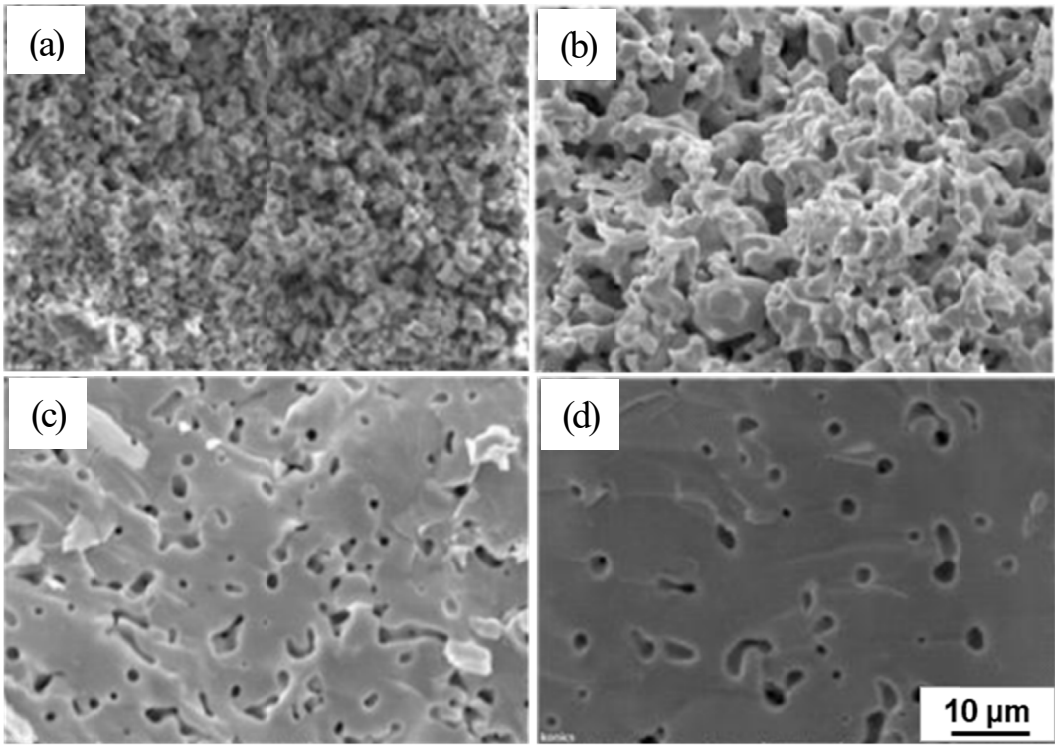

Fig. 3. The scanning electron micrographs of the $LaYO_3$ pellets with a molar ratio of 1:1.1 (La_2O_3 and Y_2O_3) according to sintering temperature: (a) 1450°C, (b) 1500°C, (c) 1550°C, (d) 1600°C

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