

SANG-GYU PARK^{1*}, SEUNG UK MUN², KI HWAN KIM¹, HOON SONG¹, JUN HWAN KIM¹**DEVELOPMENT OF NdYO₃ POWDER FABRICATION AS A REACTION PREVENTING RAW MATERIAL FOR METAL FUEL CASTING**

Metal fuel is a promising candidate for fast reactor, but the problem of loss of nuclear material due to the high reactivity of the metal fuel and the melting crucible in the fuel casting process must be solved for loss control and waste reduction. To this end, it is necessary to develop a new coating material that can minimize high reactivity in order to develop new material casting parts capable of reducing reaction loss. In this study, research was conducted to develop a new material to improve the degree of anti-reactivity of the crucible. Research was conducted to develop a new material from Nd-Y-oxide based materials, which has shown good anti-reactivity previously. YAG(Y₃Al₅O₁₂), YNdLa, YZrNd, YNdCe oxide materials were selected as a candidate material. This study identifies NdYO₃-based materials as the most promising candidates for high-temperature applications due to their superior reaction resistance.

Keywords: Metal fuel; Reaction prevention; Y₂O₃; NdYO₃; Sintering

1. Introduction

Nuclear systems are an important and attractive energy source [1,2], but the spent nuclear fuel contains long-lived radioisotopes that emit strong radiation and high heat. Therefore, securing technology to safely manage spent nuclear fuel, whose radioactive toxicity persists for hundreds of thousands of years or more, is one of the most important issues at the national level. To this end, dry processing technology (pyroprocessing) and sodium-cooled fast reactor (SFR) technology development, which are currently part of spent nuclear fuel processing, are being conducted [3,4]. U-transuranics (TRU) nuclear fuel is produced through this pyroprocessing, and the problem of decreased nuclear fuel recycling rate due to increased nuclear material loss rate is an essential element to be resolved in order to secure the legitimacy of reusing spent nuclear fuel. In the TRU nuclear fuel casting process, the reaction between the cast parts and the metal fuel induces a decrease in the metal fuel yield and an increase in the nuclear material loss rate. To solve this problem, it is necessary to develop a new material that can prevent the reaction between the metal fuel casting melt and the cast parts.

In this study, various candidate materials were selected to discover new materials with superior reactivity reduction

compared to the commercial material 8-YSZ material, and the manufacturing process conditions for these materials were optimized to verify the reactivity reduction. Research was conducted to develop a new material from NdYO₃-based materials, which has shown good anti-reactivity previously. YAG(Y₃Al₅O₁₂), (La/Nd)YO₃, (Zr/Nd)YO₃, and (Ce/Nd)YO₃ were selected as candidate materials, and the pellets were manufactured by CIP (cold isostatic pressing) and then sintered. The sintering process was performed at 1550°C to 1620°C for 3 hours in an Ar atmosphere. The porosity and phase change were analyzed based on the density and XRD analyses for each condition, and the reactivity reduction was verified using the sessile drop test.

2. Experimental

As for raw material powder specifications, the Nd₂O₃ powder had a purity of 99.999% and an average particle size of 2.5 μm (Inner Mongolia CAMO), and the Y₂O₃ (QUANNAN), ZrO₂ (Qingdao terio Corp.), CeO₂ (Solvay) powders had purity of 99.9% and an average particle size of 0.5 μm. Five types of molar composition ratios for the powders were shown in TABLE 1.

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TABLE 1

Composition of the materials

Name	Composition (molar ratio)					
	Y ₂ O ₃	Nd ₂ O ₃	La ₂ O ₃	CeO ₂	ZrO ₂	Al ₂ O ₃
YAG	37.5					62.5
(La ₁₅ /Nd ₂₅)YO ₃	60	25	15			
(La ₅ /Nd ₃₀)YO ₃	65	30	5			
(Zr/Nd)YO ₃	20	50			80	
(Ce/Nd)YO ₃	60	25		15		

The powders were milled for 24 hours with alcohol and ceramic balls in a plastic ball mill container to obtain a mixed composite powder. The ceramic balls used were milled using zirconia balls, obtaining a slurry with uniformly mixed powder components. While stirring and heating the slurry in which the composite powder was mixed, the alcohol solvent in the slurry was heated and evaporated. The dried composite powder was heated at 1000°C for 10 hours to remove foreign substances including moisture. The obtained synthetic powder was fabricated in the cold isostatic pressing (CIP) process (KOBELCO). The powder was placed into a rubber mold, sealed, and the pressure was gradually increased to a maximum of 1200 bar over 5 minutes, maintained for 5 minutes, and then the pressure was released. The samples manufactured by the press/CIP process were placed in an electric furnace and sintered by maintaining it at the final temperature (3 types: 1550°C, 1600°C and 1620°C) for 3 hours.

The prepared specimens were subjected to density measurement by the Archimedes method. X-ray diffraction (XRD) patterns of the specimens were recorded using an AXS D8 Advance instrument (Bruker, Billerica, MA, USA), and scanning electron microscopy (SEM Philips, XL series) analysis of the bonded specimens. The sessile drop method was used to investigate the reaction preventing effect of the ceramic materials. An RE alloy coupon having same composition of RE elements in fuel fabrication process (53, 25, 16, and 6 wt.% of Nd, Ce, Pr, and La, respectively) was used as a surrogate. The ceramic samples and RE alloy were contacted and placed in a tube furnace, and the temperature was raised from room temperature to 1500°C at 15°C/min and maintained for 1 h.

3. Results and discussion

In the Y₂O₃-Al₂O₃ binary system, three phases, Yttrium Aluminum Garnet (YAG), Yttrium Aluminum Perovskite (YAP), and Yttrium Aluminum Monoclinic (YAM), are formed depending on the molar ratio of Y₂O₃ and Al₂O₃. The composition used in this experiment was selected as the YAG composition generated when the molar ratio of Y₂O₃ and Al₂O₃ is 3:5. Since the stability of the Nd₂O₃-Y₂O₃ binary system was confirmed in the previous experimental results [5,6], the Y₂O₃-Nd₂O₃-La₂O₃ system was selected as a new material candidate. However, the phase formed in La₂O₃ does not maintain phase stability due to various phase changes depending on the temperature and is too

sensitive to moisture absorption, so the content of La₂O₃ was limited to 15% and 5%, respectively. Since CeNdYO₃ is a material that has not been widely reported in the literature, it was expected to exhibit similar properties to rare earth element La, so a manufacturing test was performed by adding it in the same ratio as La₂O₃ (15%).

The Y₂O₃-ZrO₂-Nd₂O₃ composition system stabilizes ZrO₂ by adding 3 to 8 moles of Y₂O₃, and especially, when 8 moles of Y₂O₃ are added, ZrO₂ is completely stabilized, and the tetragonal phase is maintained until room temperature, so a stable phase can be obtained. In addition, when Y₂O₃ is added further up to 40 moles, two mixed phases are created. On the other hand, when no stabilizer is added, the ZrO₂ single phase undergoes a phase transformation into a monoclinic phase at room temperature, and since this process entails a volume expansion of about 4%, cracks occur when using the parts, so the addition of stabilizers is essential for ZrO₂ parts used for industrial purposes. Thus, the Y₂O₃-ZrO₂-Nd₂O₃ composition system can be viewed as a binary phase diagram between YSZ (Y₂O₃ stabilized ZrO₂) and Nd₂O₃ in a large range. In the composite structure, ZrO₂ has excellent phase stability of YSZ instead of low phase stability, so the above composition was determined.

Fig. 1 shows the XRD pattern analysis results of the samples. All of the peaks are sharp with high intensity, suggesting good crystallinity. In the case of YAG, the peaks of the sample are in good agreement with the standard diffraction peaks of YAG (JCPDS Card No. 33-0040), indicating the main phase is YAG with the garnet phase. For pattern analysis of Y₂O₃-Nd₂O₃-La₂O₃ system, refer to 41-1105 for Nd₂O₃ with a monoclinic structure and 28-671 for Y₂O₃ with a cubic structure in the JCPDS card. In this study of Y₂O₃-Nd₂O₃ based samples, it was shown that most of the samples had a typical cubic phase through the 28~29° peak (501) and 47° peak (440). However, the pattern of (La₁₅/Nd₂₅)YO₃ sample was similar to that of other samples, but the analysis revealed that the intensity of the 32° peak (020) and 42° peak (004) in the orthorhombic phase became stronger and the orthorhombic and cubic phases began to coexist. As can be seen from the XRD analysis results, the addition of Zr₂O₃ (72° (400)) and Ce₂O₃ (44° (220)) does not significantly deviate from the typical cubic crystal structure of Y₂O₃. Therefore, it is judged that the addition of Zr and Nd does not have a significant effect on the change in the crystal structure. It is also judged that the addition of La does not causes the phase transformation and only coexist independently with NdYO₃.

Fig. 2 shows the density of each sample with increasing temperature. As the sintering temperature increased, the density tended to increase in all compositions. In the case of YAG, densification was insufficient and many pores remained in all temperature ranges. When comparing the (La₁₅/Nd₂₅)YO₃ and (La₅/Nd₃₀)YO₃, the densification characteristics of the (La₁₅/Nd₂₅)YO₃ composition were excellent, so that a completely densified structure could be obtained even at a sintering temperature of 1500°C. In the case of (La₅/Nd₃₀)YO₃, the densification characteristics were somewhat lower than that of (La₁₅/Nd₂₅)YO₃, but when the sintering temperature was increased to 1600°C, a dense structure

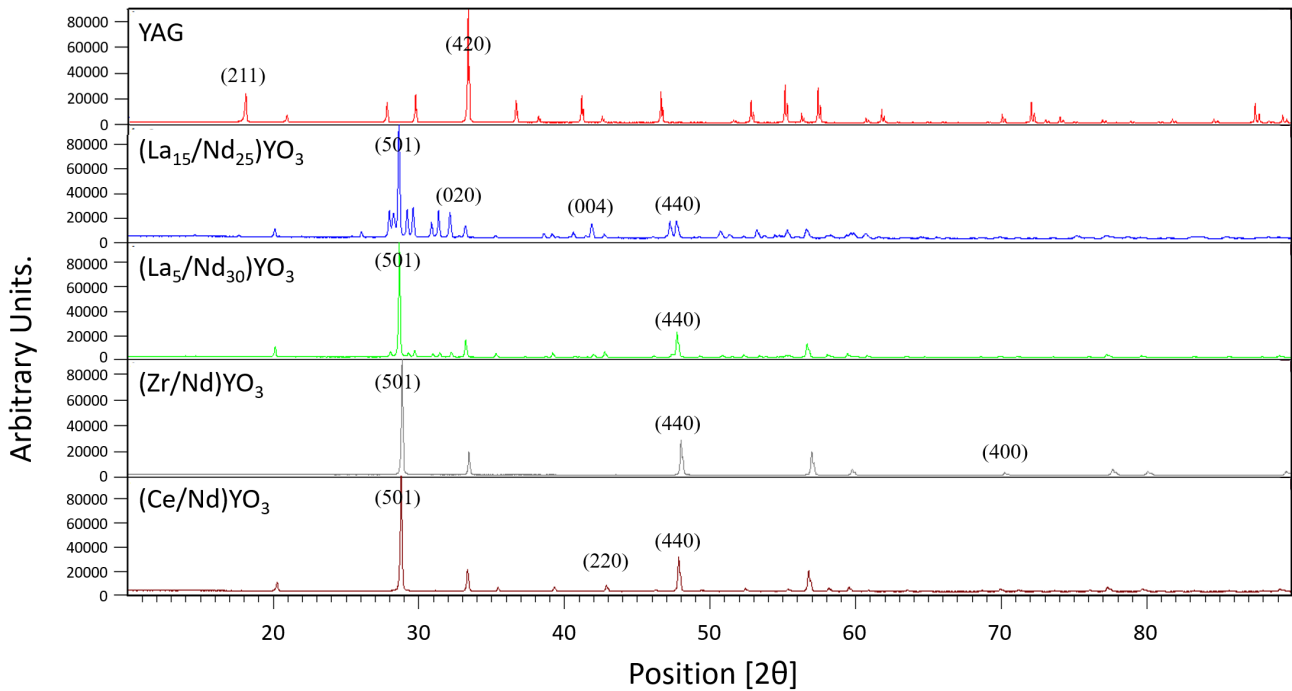


Fig. 1. X-ray diffraction (XRD) patterns of the synthesized samples

with fewer pores could be obtained, and when the sintering temperature was further increased to 1620°C, a completely dense structure could be obtained. Meanwhile, ZrNdY composition and CeNdY composition obtained a relatively dense structure when sintered at 1600°C, and the sintering temperature should be further increased to obtain a denser structure. When the porosity of each material was compared, it could be confirmed that LaNdY oxide had the best densification characteristics. Considering the XRD analysis results and density measurement results comprehensively, it is judged that La-Nd-Y oxide having a

mixed phase of orthorhombic and cubic is the most advantageous for obtaining dense material properties. In the XRD analysis, the coexistence of the orthorhombic crystal structure with increasing La content was confirmed. The rapid densification behavior observed at high temperatures in $(\text{La}_{15}/\text{Nd}_{25})\text{YO}_3$ is believed to be due to the influence of La-Y oxide with an orthorhombic crystal structure. Although there have been few reported studies on LaNdYO_3 , results of high-temperature densification behavior of La-Y oxide series with orthorhombic crystal structure have been reported [7].

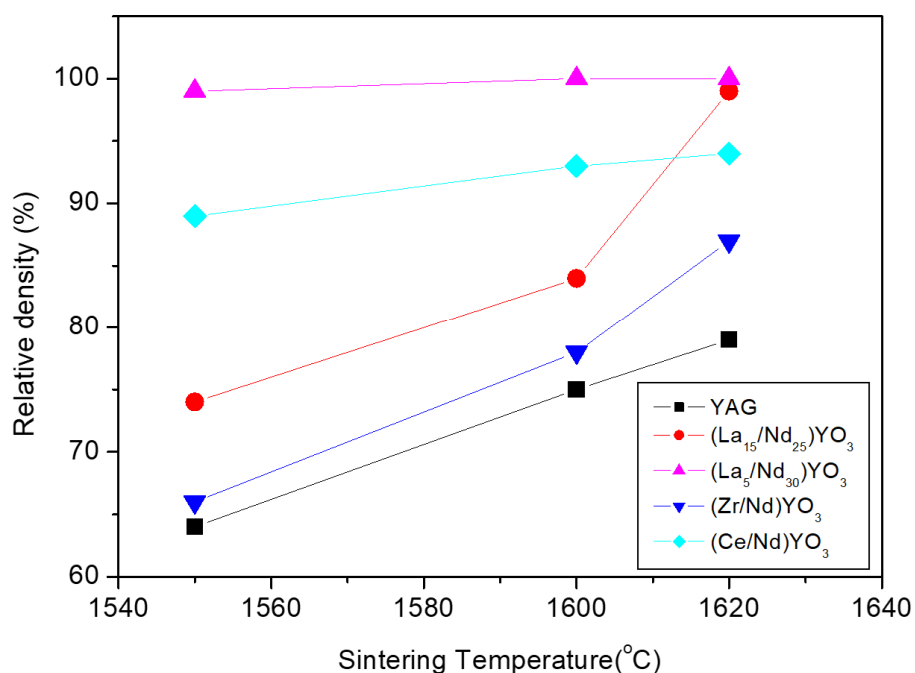


Fig. 2. Variation of the relative density of the samples as a function of sintering temperature

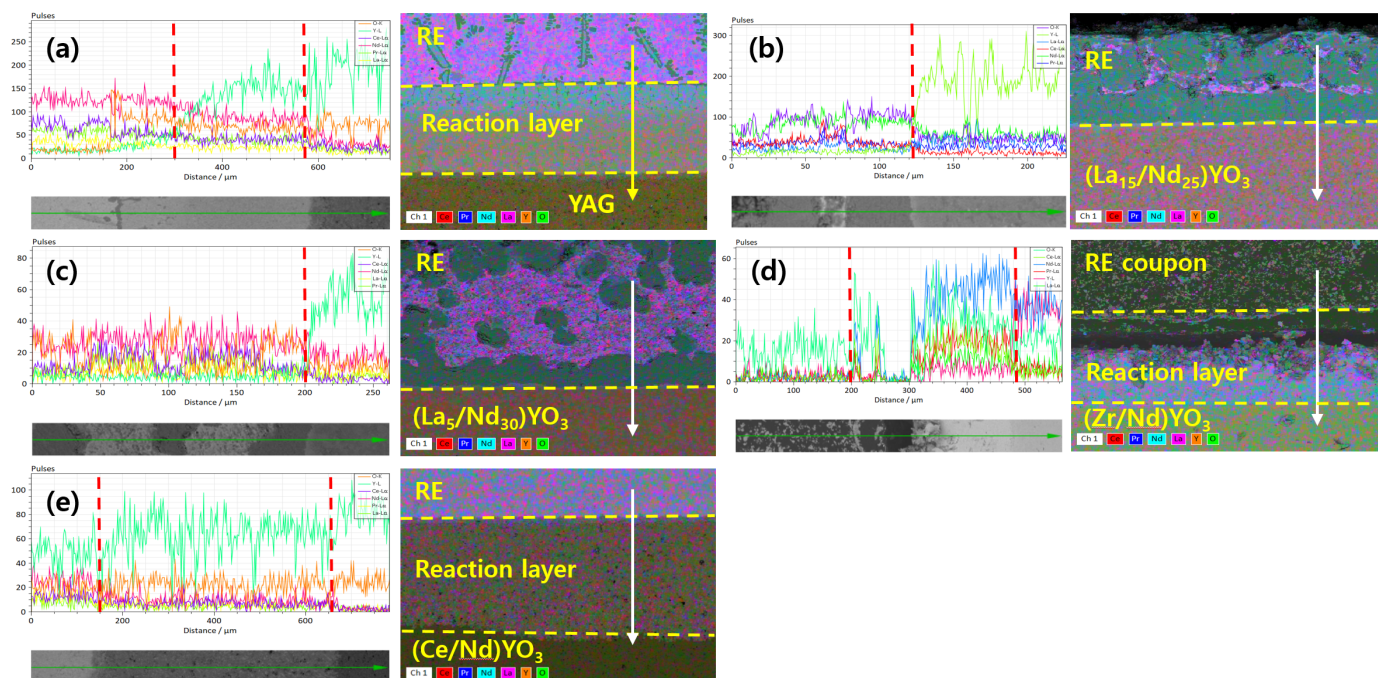


Fig. 3. SEM/EDS results of the samples after sessile drop test

In order to verify the high-temperature reactivity of each material, RE alloy (La, Nd, Ce, Pr) sessile drop test was performed under conditions similar to the nuclear fuel manufacturing process at 1550°C, 10 min. Fig. 3 shows the SEM & EDS analysis results of the samples after sessile drop test. Except for La-Nd-Y oxide, all materials were confirmed to form a reaction layer of about 200 μm thickness at the interface after the sessile drop test. Since rare earth elements were uniformly distributed throughout the reaction layer, it was evaluated that it was not suitable as a material with high reaction resistance, which was the purpose of this study. On the other hand, in the $(\text{La}_{15}/\text{Nd}_{25})\text{YO}_3$ and $(\text{La}_5/\text{Nd}_{30})\text{YO}_3$ samples, no reaction layer was formed and almost no movement of RE elements was observed. Therefore, the La-Nd-Y oxide is judged to have the best reactivity reduction among the candidate materials for the fuel manufacturing process.

4. Conclusions

In this study, we conducted a fabrication test to develop a new material to improve the degree of anti-reactivity of the crucible. YAG($\text{Y}_3\text{Al}_5\text{O}_{12}$), YNdLa, YZrNd, YNdCe oxide materials were selected as a candidate material and successfully fabricated. Most of the samples show cubic structures based on the Nd-Y oxide structure, and the density increased with increasing sintering temperature. The densification characteristics and

reaction prevention characteristics of La-Nd-Y oxide material was evaluated to be the best compared to other materials.

Acknowledgments

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