

Improving Hydration Resistance of Gd_2O_3 by HfO_2 Doping

Isnaini Anissa^a, Ho Jin Ryu^{a*}

^aDepartment of Nuclear and Quantum Engineering, KAIST, Daehak-ro 291, Yuseong-gu, Daejeon, 34141, Korea

*Corresponding author: hojinryu@kaist.ac.kr

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1. Introduction

The concept of soluble-boron-free (SBF) pressurized water reactors (PWRs) requires high-performance burnable absorbers (BAs) to effectively control reactivity. Lumped-gadolinia, in which gadolinia (Gd_2O_3) ceramics are locally placed inside the fuel pellets, such as CSBA and CIMBA, shown good performance of gadolinium-based BAs. However, under high-temperature and high-pressure water conditions, Gd_2O_3 is susceptible to hydration, which may induce volume expansion and mechanical degradation of the absorber material. To overcome this problem, previous studies have explored the addition of CeO_2 has been reported to improve hydration resistance under hydrothermal conditions through cubic phase stabilization and defect chemistry[3].

Based on this approach, the present study investigates HfO_2 as an alternative for improving the hydration resistance of Gd_2O_3 . Hf^{4+} has the same nominal valence as Ce^{4+} , while HfO_2 itself does not react with water, making it a potential candidate for stabilizing Gd_2O_3 under hydrothermal conditions. Scanning electron microscopy (SEM) was used to examine microstructural changes, X-ray Diffraction (XRD) was used for phase evolution, and thermogravimetric analysis (TGA) was performed to evaluate the formation of hydrated phases.

2. Methods and Results

2.1. Fabrication and Hydrothermal Testing of HfO_2 -doped Gadolinia

HfO_2 -doped gadolinia compositions containing 5 and 10 at.% HfO_2 were prepared alongside an undoped Gd_2O_3 reference. Gd_2O_3 and HfO_2 starting powders (purity $\geq 99.9\%$) were weighed according to the target compositions and homogenized by planetary ball milling in ethanol for 20 hours. The mixed powders were dried and compacted into pellets at 180 MPa. The pellets were sintered at 1600°C for 10 hours in air.

Hydrothermal testing was conducted at 200°C and 1.5 MPa for 48 hours. Prior to hydrothermal exposure, all pellets were macroscopically intact, and the as-sintered samples exhibited well-densified microstructures, as shown in Fig. 1. After exposure, the undoped Gd_2O_3 was completely pulverized and exhibited extensive plate-like hydration products with loss of the original grain morphology. The 5 at.% HfO_2 - Gd_2O_3 sample showed fragmentation with localized gadolinium hydroxide

($\text{Gd}(\text{OH})_3$) nanorod after hydrothermal exposure. The 10 at.% HfO_2 - Gd_2O_3 sample retained its overall pellet form and grain morphology, although small cavities were observed. These observations demonstrate that HfO_2 addition improves the resistance of Gd_2O_3 to hydrothermal degradation.

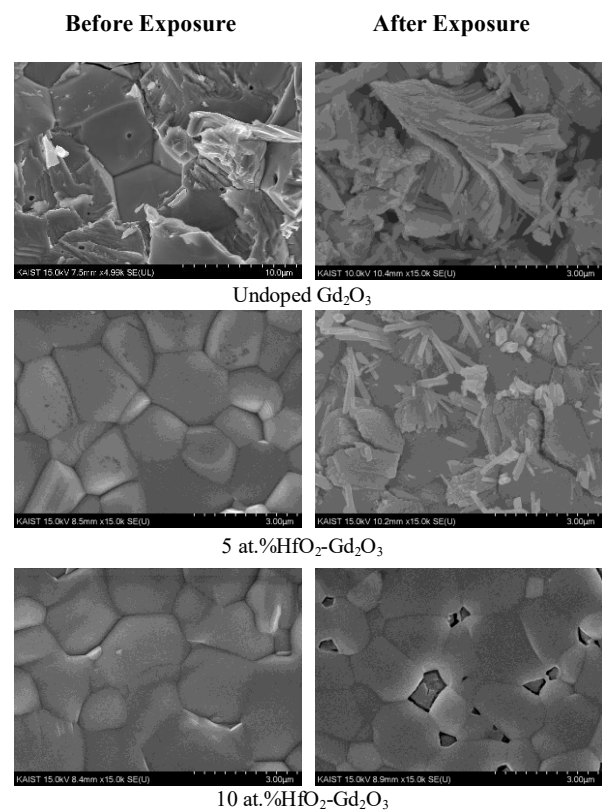


Fig. 1. Microstructure of undoped and HfO_2 -doped Gd_2O_3 before and after hydrothermal exposure.

2.2. XRD characterization

Sintered pellets and hydration products were ground into powders for X-ray Diffraction (XRD) characterization. The samples were analyzed over a 2θ range from 15° - 80° using $\text{Cu K}\alpha$ radiation.

Fig. 2 shows the XRD patterns of the undoped and HfO_2 -doped Gd_2O_3 samples before and after hydrothermal exposure. XRD analysis shows that the undoped Gd_2O_3 exhibited a monoclinic phase after sintering and $\text{Gd}(\text{OH})_3$ hexagonal phase after exposure. The 5 at.% HfO_2 - Gd_2O_3 sample consisted of approximately 63.8% monoclinic and 36.2% cubic

phases. The phase composition remained nearly unchanged after hydrothermal exposure, despite the macroscopic fragmentation and morphological changes observed by SEM. In contrast, the 10 at.% HfO₂-Gd₂O₃ sample retained the cubic phase after sintering and hydrothermal exposure. No distinct crystalline hydration products were detected in the HfO₂-containing samples after exposure.

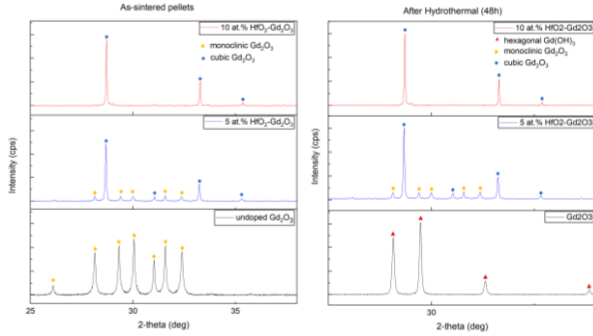


Fig. 2. Magnified XRD patterns of undoped and doped Gd₂O₃ before and after hydrothermal exposure in the 2θ range of 25–38°.

2.3. TGA Characterization

Thermogravimetric analysis (TGA) was performed to evaluate the weight changes associated with hydration products formed during hydrothermal exposure. As shown in Fig. 3, the undoped Gd₂O₃ sample after 48 hours of hydrothermal exposure exhibited a weight loss of approximately 13%, with distinct decomposition events at around 287°C and 430°C associated with hydrated gadolinium species, such as Gd(OH)₃ and GdOOH. In contrast, the HfO₂-doped samples only exhibited a weight loss of 0.1–0.3% without any distinct hydrate-related decomposition peaks. These results confirm that the addition of HfO₂ suppresses the hydration reaction under the present hydrothermal conditions, consistent with the XRD and SEM observations.

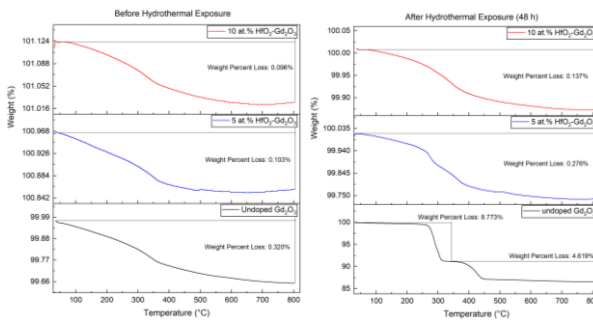


Fig. 3. TGA graphs of undoped and doped Gd₂O₃ before and after hydrothermal exposure.

3. Conclusion

This study investigating the effect of HfO₂ addition on the hydrothermal stability of Gd₂O₃-based BA. The

addition of HfO₂ increased the retention of the cubic Gd₂O₃ phase and reduced the hydrothermal degradation. The 10 at.% HfO₂-Gd₂O₃ showed the highest resistance, retaining its pellet shape and grain morphology after hydrothermal exposure. The absence of detectable crystalline hydration products and the lower weight loss (0.1-0.3%) compared to undoped Gd₂O₃ (~13%) further confirms the hydration suppression.

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