Evaluation of Corrosion Behavior of Gd_2O_3-MO_X Burnable Absorber in a High-Temperature Steam

Sungwoo Ha *, Yeonsoo Na, Gwangyeong Lim, Minjae Joo, Chaerin Kim, Yoon ho Kim
ATF Development Section of Nuclear Fuel Technology Department,
KEPCO Nuclear Fuel, Daejeon 34057, Republic of Korea
**Corresponding author: swha@knfc.co.kr*

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1. Introduction

The i-SMR has established boron-free operation and a 24-month long-cycle operation as its primary design requirements. To satisfy these top-tier requirements, conventional burnable absorbers are unsuitable, necessitating the development of an innovative burnable absorber. Currently, under the government-funded project "Development of burnable absorber rod for i-SMR application" which is part of the i-SMR Technology Development Program, materials are being developed to control the initial excess reactivity. These materials include high-content Gd_2O_3-doped UO_2 pellets and a metal oxide-based gadolinia absorber for i-SMR application. Specifically, the metal oxide-based gadolinia absorber can effectively control the high initial excess reactivity of the i-SMR core due to the high content of gadolinia (Gd_2O_3) added to its metal oxide matrix.

Therefore, in this study, prototypes of the metal oxide-based gadolinia absorber were fabricated by adding 20–30 vol% of Gd_2O_3 to selected metal oxide matrices (Al_2O_3, TiO_2, and ZrO_2). Subsequently, their corrosion behavior in a high-temperature steam environment was evaluated. The test results indicated a slight weight loss for the candidate compositions, but the rate of loss was negligible, ranging from 0.004% to 0.008%. The microstructure and composition of the post-test specimens were analyzed using SEM/EDS and XRD. Based on these results, it is concluded that the three candidate materials for the metal oxide-based gadolinia absorber exhibit excellent corrosion resistance in a high-temperature steam environment, making them suitable for i-SMR application.

2. Material and Methods

2.1 Material

The metal oxide-based Gd_2O_3 absorber used in this study can be prepared using either a wet or dry mixing process to homogenize the Gd_2O_3, which has a high neutron absorption cross-section, into the Al_2O_3, TiO_2, and ZrO_2 matrices. Based on the preliminary core design results for the i-SMR, the content of the neutron absorber material, Gd_2O_3, was selected to be approximately 20–30 mol% relative to the matrix phase for each batch.

The fabrication of the metal oxide-based gadolinia absorber followed a conventional ceramic manufacturing sequence: mixing → shaping → sintering.

In the mixing step, ball milling was performed for approximately 24 hours to ensure that the Gd_2O_3 was homogeneously mixed within the Al_2O_3, TiO_2, and ZrO_2 matrices. A binder (PEG 1500) at 1 wt.% and ethanol were added during this process. After the completion of ball milling, the resulting powder was dried in an oven for 24 hours. The dried powder was then sieved using a 250 μm mesh. A measured amount of the homogenized powder was placed into a molding die and uniaxially pressed at a pressure of approximately 500–3,000 kgf/cm² (approx. 49–294 MPa) to produce a green body. The fabricated green bodies were then sintered in a laboratory furnace at 1,400–1,700°C for 4–8 hours in either an air or argon atmosphere.

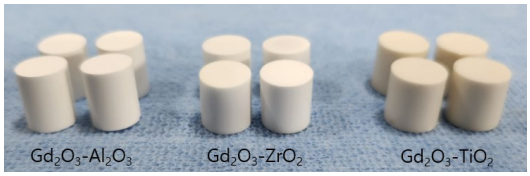

Fig 1. Image of the sintered HIGA specimen

2.2 Methods

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The high-temperature corrosion test was performed using a high-temperature steam oxidation system, as shown in Figure 2. To prevent premature corrosion at lower temperatures—which could occur by reacting with residual oxygen inside the reactor during heat-up in a steam atmosphere and thus affect the corrosion behavior evaluation—the system was purged with Ar gas for at least 2 hours before heating was initiated. Ar gas was also used as a carrier gas to ensure a smooth steam flow. The heating rate was set to 10 K/min to prevent temperature overshoot. Steam was injected at a constant rate of 4 g/h using a steam generator installed in the thermogravimetric analyzer, and the flow rate of the steam-mixed gas was maintained at 1.12 mg/cm²-s.

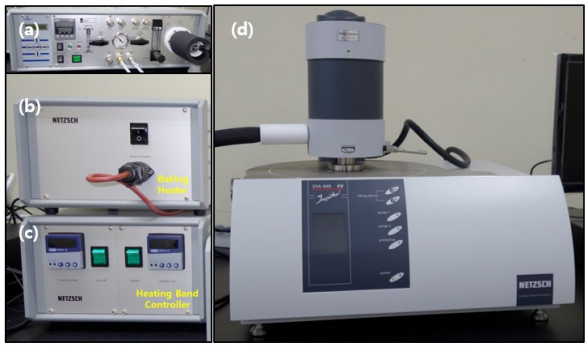


Fig 2. High-temperature steam oxidation system: (a) Steam generator and gas controller, (b) Baking Heater, (c) Heating Band Controller, and (d) Main unit of the Simultaneous Thermal Analyzer (STA).

3. Results

After the high-temperature steam oxidation, all three specimens exhibited weight loss. However, the rate of loss was in the range of 0.004–0.008%, an amount even more negligible than that typically observed in (standard) water chemistry corrosion. Furthermore, considering the standard deviation among the samples, the differences between the three specimens are not considered to be statistically significant.

During steam oxidation, it is possible for oxygen supplied to the specimen surface to fill pre-existing oxygen vacancies, which would lead to a weight gain. However, the observed weight loss in all specimens suggests that the cause can be attributed to phenomena such as hydrate formation or spallation of the surface layer due to a mismatch between the matrix and the reaction products.

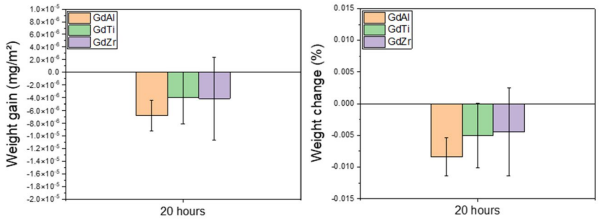
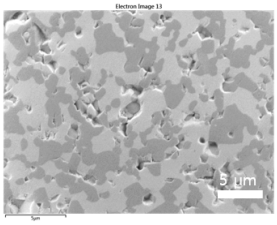


Fig 3. Weight change after the corrosion test (Steam, 1200°C, 20h)

4. Conclusions

In the case of the Gd_2O_3-Al_2O_3 specimen, SEM observation did not reveal any significant spallation on the surface, as shown in Figure 4 below. For unknown reasons, Gd was not detected during the EDS analysis of this specimen. Considering that no EDS peak was detected in the high-energy range, a re-examination is deemed necessary.

Although HSC Chemistry software predicts that the reaction $Al_2O_3 + 3H_2O(g) = 2Al(OH)_3$ is spontaneous below 100°C, it also predicts that Al_2O_3 does not spontaneously form a hydroxide in a high-temperature steam environment. However, a previous study [1] reported that at temperatures exceeding 1,200°C, $Al(OH)_3$ forms and subsequently evaporates, leading to weight loss. Since the specimen used in this study is composed of Al_2O_3 and $GdAlO_3$ in a 3:2 molar ratio, it is concluded that the observed weight loss could be due to the influence of Al_2O_3—specifically, the formation and volatilization of $Al(OH)_3$.

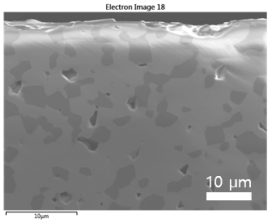


Gd_2O_3-Al_2O_3	Wt%	Atomic%
O	78.72	88.13
Al	15.88	10.54
Ge	5.34	1.32
Gd	0.05	0.00

Fig 4. SEM/EDS analysis of Gd_2O_3-Al_2O_3 after the corrosion test.

Similarly, in the case of the Gd_2O_3-TiO_2 specimen, SEM observation revealed no significant spallation on the surface, as shown in Figure 5 below. However, SEM/EDS analysis indicated a slight increase in oxygen content after the high-temperature steam oxidation.

It has been reported [2] that when TiO_2 is exposed to steam in a high-temperature environment (1,200–1,400°C), the reaction $TiO_2(s) + xO_2(g) + yH_2O(g) = TiO(2+2x+y)H(2y)(g)$ occurs, and the resulting Ti-O-H product is volatile. Therefore, this reaction can be considered a cause of the weight loss in the specimen used in this study. No data could be found for the other constituent phase of the specimen, $Gd_2Ti_2O_7$. Given that the molar ratio of TiO_2 to $Gd_2Ti_2O_7$ is 2:1, it is concluded that the steam reaction involving TiO_2 is the primary cause of the observed weight loss.

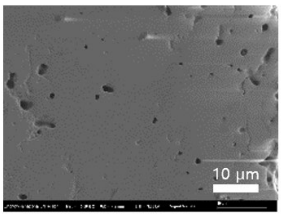


Gd_2O_3-TiO_2	Wt%	Atomic%
O	43.94	82.04
Ti	16.87	10.52
Gd	39.19	7.44

Fig 5. SEM/EDS analysis of Gd_2O_3-TiO_2 after the corrosion test.

Also in the case of the Gd_2O_3-ZrO_2 specimen, SEM observation revealed no significant spallation on the surface, as shown in Figure 6. However, after the high-temperature corrosion test, a tendency was observed near the surface where the Zr content slightly decreased, while the Gd content either increased or decreased. (Note on the analysis: In the SEM/EDS results, the Gd and Ge peaks overlapped in the low-energy region. For an unclear reason, the peak in the high-energy region, where the two elements should be distinct, was weak and consequently identified as Ge; however, it can be regarded as Gd).

Although HSC Chemistry predicts that Zr can react with steam to form a hydrate ($ZrO_2 + 2H_2O(g) = Zr(OH)_4$) at temperatures up to 160°C, and this could be speculated as a contributing factor, a definitive interpretation is complicated. This is because the $Gd_2Zr_2O_7$ phase is more abundant than the ZrO_2 phase in this specimen, and trends of both weight gain and loss were observed depending on the sample. Therefore, it is concluded that for a clear interpretation, the root cause can only be determined by conducting a more precise analysis of specimens after tests with segmented exposure times



Gd_2O_3-ZrO_2	Wt%	Atomic%
O	25.43	72.31
Zr	29.23	14.57
Gd	45.34	13.12

Fig 6. SEM/EDS analysis of Gd_2O_3-ZrO_2 after the corrosion test.

When the crystal structures of all three specimens after the high-temperature steam corrosion test were compared to their as-sintered structures, no changes were observed, as shown in Figure 7. Therefore, it is concluded that the measured weight change is attributed to localized and minute chemical changes that resulted in no, or only a negligible, change to the overall crystal structure. Consequently, all three candidate compositions of the metal oxide-based gadolinia absorber being developed for the i-SMR are determined to be highly resistant to corrosion in a high-temperature steam environment.

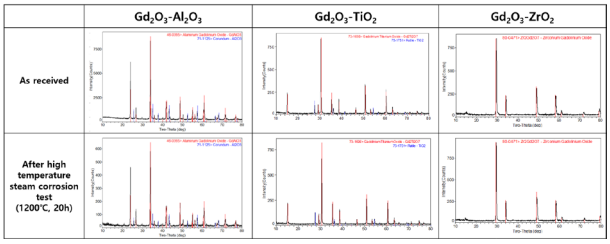


Fig 7. XRD patterns of HIGA candidate materials before and after the corrosion test.

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REFERENCES

[1] Elizabeth J.Opila, Dwight L. Myers, Alumina Volatility in Water Vapor at Elevated Temperatures, J. Am. Ceram. Soc Vol 87[9], p. 1701–1705, 2004

[2] Quynhgiao N. Nguyen, High Temperature Volatility and Oxidation Measurements of Titanium and Silicon Containing Ceramic Materials, MS Thesis, Cleveland State University, 2008