Effect of Stabilizer on the Behavior of Rare Earth Oxide Based ATCR Absorbers under Coolant and Steam Condition

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1. Introduction

1.1 Background

The conventional neutron absorber material used in control rods, B_4C, undergoes eutectic reactions with the cladding material (Inconel 625) at elevated temperatures, in which elements of the cladding (Ni, Cr, Mo, Fe) form eutectic phases such as the B-Cr eutectic phase (1,630 ℃) and the B-Fe eutectic phase (1,166 ℃). In particular, the B-Ni-Mo eutectic reaction is problematic because it occurs at the relatively low temperature of 1,082 ℃. In addition to these eutectic reactions, B_4C is also vulnerable to oxidation and volatilization once the cladding is breached and it is exposed to steam. It has been reported that when B_4C is exposed to oxygen and steam following cladding damage, oxidation into B_2O_3 begins at approximately 700 ℃ [1], with B_2O_3 simultaneously reacting with H_2O at this same temperature to generate small but measurable amounts of volatile boric acid (HBO_2, H_3BO_3) [2]. Above approximately 1,100 ℃, the weight loss associated with boric acid volatilization outpaces the weight gain from oxidation, leading to a net reduction in specimen mass [3]. This oxidation reaction also generates large amounts of hydrogen ($B_4C + 6H_2O \rightarrow 2B_2O_3 + CH_4 + 4H_2$).

1.2 Objective

Development is underway on materials with superior neutron absorption capability, melting/volatilization temperature, and irradiation swelling stability compared to existing technology materials, capable of maintaining the integrity of the neutron absorber without eutectic reactions or steam reactions during an accident, for use as an Accident Tolerant Control Rod (ATCR) neutron absorber. Rare earth oxide based neutron absorber materials (Sm_2O_3, Gd_2O_3, Eu_2O_3, Dy_2O_3, etc.) have been selected as candidate materials to replace B_4C. However, these rare earth oxide materials are relatively prone to hydration under high-temperature, high-pressure conditions, resulting in a loss of structural integrity when directly exposed to coolant [4,5]. Therefore, to suppress this reaction with coolant water and maintain material stability under accident conditions, it is necessary to evaluate the corrosion resistance of stabilizer-containing neutron absorber materials. To this end, this study conducted washout tests and LOCA (Loss of Coolant Accident) simulation tests on stabilizer-containing rare earth oxide based neutron absorbers to evaluate their corrosion resistance under both coolant and high-temperature steam conditions.

2. Material and Methods

2.1 Specimen fabrication and Analysis

ATCR was based on Eu_2O_3 and Dy_2O_3 with ZrO_2, HfO_2, Ta_2O_5, TiO_2 and Nb_2O_5 added as stabilizers, resulting in the derivation of 12 candidate compositions. Specimens were fabricated by sintering at 1,700 ℃ for 2 hours in air (ambient laboratory atmosphere; no synthetic or inert gas atmosphere was used). The cross sections of the fabricated specimens were polished, and the microstructure was observed by Scanning Electron Microscope(JSM-6510, Jeol, Japan), while elemental distribution was observed by Energy Dispersive X-ray Spectroscopy(X-MaxN on JSM-6510, Jeol, Japan). In addition, phase analysis was performed using X-ray Diffraction(D/Max-2200, Rigaku, Japan) to observe phase changes according to composition.

2.2 Methods

To evaluate corrosion resistance under a scenario in which the ATCR is exposed to coolant during power plants operation, tests were conducted simulating the primary coolant system environment of a nuclear power plants. In accordance with ASTM Standard test method [6], the washout test was performed by exposing specimens to coolant water in a static autoclave at 350 ℃ and 150 bar for up to 10 days (240 hours).

In addition, to simulate the environment in which the ATCR is exposed to a high temperature steam condition due to LOCA, tests were conducted under conditions of 1,200 ℃ at atmospheric pressure with a steam (Ar-94%H_2O) flow rate of 3 cm/s. This was performed using a Simultaneous Thermal Analyzer(STA 449 F5 Jupiter, Netzsch, Japan), exposing the ATCR to this environment for 1 hour. Real time weight changes were measured to evaluate high temperature steam oxidation resistance performance.

3. Results

After the washout test, the specimens largely maintained their structural integrity although some specimens exhibited detachment of parts of the specimen due to corrosion. In all compositions, hydration increased as the stabilizer content decreased, resulting in a tendency toward increased weight loss. For Eu oxide based ATCR, ZrO_2 and HfO_2 were found to be more favorable stabilizer compositions than TiO_2 under coolant corrosion conditions. For Dy based ATCR, TiO_2, ZrO_2 and HfO_2 stabilizers all showed integrity without hydration. In particular, for Dy_2O_3, the stabilizer was found to have a threshold for phase stability with corrosion resistance within a stabilizer molar ratio range of greater than 0.1 and less than 0.33 mol fraction.

As a result of the high temperature steam oxidation test under simulated LOCA conditions, when all ATCR specimens were exposed to 1,200 ℃ steam conditions for 1 hour, almost no weight change was observed, confirming their integrity.

However, in the case of Dy_2O_3-based ATCR candidate compositions, no change in pore distribution was observed before and after testing, whereas EDS analysis revealed localized elemental segregation.

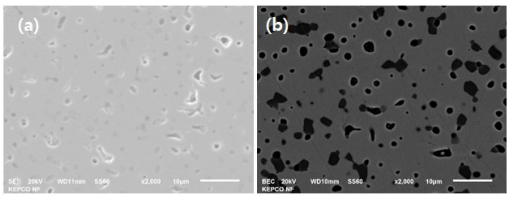


Fig 1. Microstructure images of Dy_2O_3 based ATCR before(a) and after(b) high-temperature steam oxidation testing(×2k)

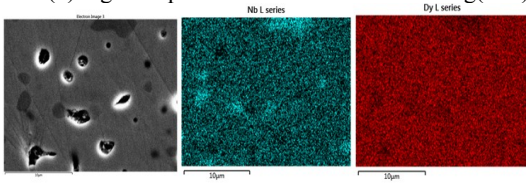


Fig 2. Elemental distribution of Dy_2O3 based ATCR after high-temperature steam oxidation testing

In addition, for all specimens, it was observed that as the stabilizer dissolved into the matrix phase, a distinct secondary phase was clearly formed.

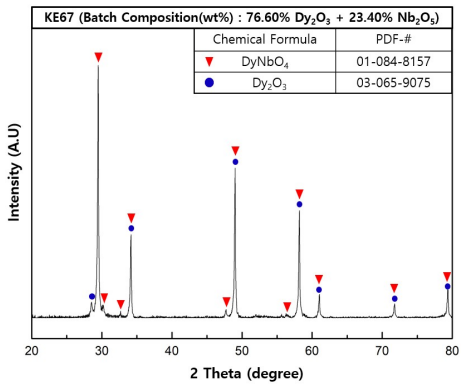


Fig 3. XRD results of Dy_2O_3 based ATCR after high-temperature steam oxidation testing

In contrast, B_4C, tested as a control group under the same conditions, lost 66.6 wt.% due to volatilization.

4. Conclusions

In this study, 12 candidate rare earth oxide based ATCR absorber materials were tested. These materials are currently under development to supplement the safety performance of B_4C, the conventional neutron absorber, addressing its coolant reactivity and material instability under high temperature steam condition in the event of control rod damage under accident conditions.

The test results showed that, in the washout test, hydration occurred as the stabilizer content decreased across all compositions, with a tendency toward increased weight loss. In particular, it was found that the stabilizer added to Dy_2O_3 exhibited a threshold of phase stability with corrosion resistance within a molar fraction range of greater than 0.1 and less than 0.33. In the high temperature oxidation test under simulated LOCA conditions, all compositions showed almost no weight change and maintained integrity even after 1 hour of exposure to a 1,200 ℃ steam condition. In contrast, B_4C, tested under the same conditions, was observed to volatilize by 66.6 wt.%.

Based on these results, ATCR has superior accident tolerance performance compared to the conventional neutron absorber material B_4C, in terms of coolant reactivity and stability in high temperature steam condition.

ACKNOWLEDGEMENT

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REFERENCES

[1] Lawrence M. Litz and R. A. Mercuri, Oxidation of Boron Carbide by Air, Water, and Air-Water Mixtures at Elevated Temperatures, J. Electrochem. Soc., Vol. 110, p. 921-925, 1963

[2] S. P. Randall and J. L. Margrave, Vapour equilibria in the B_2O_3-H_2O system at elevated temperatures, J. Inorg. Nucl. Chem., Vol. 16, p. 29-35, 1960

[3] M. Steinbruck et al., Oxidation of B_4C by steam at high temperatures: New experiments and modelling, Nucl. Eng. Des., Vol. 237, p. 161-181, 2007

[4] Emilie Courcot et al., Stability of rare earth oxides in a moist environment at elevated temperatures-Experimental and thermodynamic studies, J. Eur. Ceram. Soc., Vol. 30, p. 1911-1917, 2010

[5] Mahiko Nagao et al., Hydration Process of Rare-Earth Sesquioxides Having Different Crystal Structures, Langmuir, Vol. 22, p. 9201-9209, 2003

[6] ASTM International, Standard Test Method for Corrosion Testing of Products of Zirconium, Hafnium and Their Alloys

in Water at 680 °F(360 °C) or in Steam at 750 °F(400 °C), ASTM G2/G2M-19, 2025