Evaluation of Phase in Heavy-Ion Irradiated Doped Gadolinia

Hakjun Lee[1], Hyeongjin Kim[1], Ho Jin Ryu[1]*, Seunghyeon Lee[2]
1 Department of Nuclear and Quantum Engineering, KAIST, Daehak-ro 291, Yuseong-gu, Daejeon, 34141, Korea
2 Heavy Ion Irradiation Facility, KAERI, 111 Daedeokdae-ro 989gil, Daejeon, 34057, Korea
Corresponding author: hojinryu@kaist.ac.kr

***Keywords :** Burnable Absorber, Accident-tolerant fuel (ATF), Irradiation Behavior

1. Introduction

For the stable operation of next-generation nuclear reactors, efforts are being made to reduce or eliminate boric acid concentration compared to conventional pressurized water reactors (PWRs). This shift is driven by concerns over the positive Moderator Temperature Coefficient (MTC) induced by boric acid and the delayed response in reactivity control. In 2019, Professor Yonghee Kim's research team in KAIST proposed an alternative approach by incorporating burnable absorber (BA) materials to replace the role of boric acid in reactivity regulation for advanced reactor systems. Among various candidate materials, gadolinia (Gd_2O_3) has been identified as the most promising matrix for burnable absorbers and serves as the key component of the Centered Self-Shielded Burnable Absorber (CSBA) concept.

In this study, argon heavy-ion irradiation was performed on both undoped gadolinia and doped gadolinia compositions designed to mitigate the solubility limitations of pure gadolinia. To assess the effects of irradiation, microstructural analyses were conducted using X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM), and Raman spectroscopy. These analyses aim to evaluate phase transformations induced by irradiation, predict the corresponding volumetric changes, and ultimately determine whether the material retains sufficient mechanical integrity for its intended application.

2. Methods

In this section, experimental techniques and procedures that can assure precise reproduction are described.

2.1 Sample Preparation & Irradiation Experiment

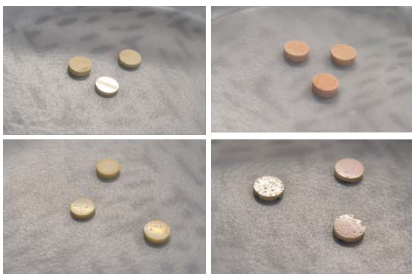

Fig 1. Fabricated Undoped/Doped Gadolinia Samples

Ceramic samples were prepared by powder mixing and sintering to achieve a theoretical density of roughly 95%. Consequently, small coin-shaped gadolinia pellets (sample 1) with diameters of 3-4mm and thicknesses within 1mm were fabricated, with one side finely polished to facilitate the investigation. Doped gadolinia samples (Samples 2–7) were prepared under the same procedures, with their compositions carefully selected based on leaching test results to exhibit improved resistance to dissolution in aqueous environments. For each sample type, 3 samples were prepared for different irradiation periods.

Table I. Sample Basic Properties

Component	Gd_2O_3	Gd_2O_3-90at.%Al_2O_3	Gd_2O_3-5at.%Nb_2O_5, ZrO_2	Gd_2O_3-20at.%Nb_2O_5, ZrO_2	Gd_2O_3-15at.%ZrO_2	Gd_2O_3-5at.%NbO_2
Stoichiometry (%)	Gd – 40% O – 60%	Gd – 4% O – 60% Al – 36%	Gd – 34.95% O – 61.17% Nb – 1.94% Zr – 1.94%	Gd – 21.43% O – 64.29% Nb – 7.14% Zr – 7.14%	Gd – 33.01% O – 61.17% Zr – 5.83%	Gd – 37.25% O – 60.78% Nb– 1.96%
Sample Density (g/cm³)	8.1	5.2	7.0	6.8	7.2	7.3
Atomic Den (#/cm³)	$6.728*10^{22}$	$9.930*10^{22}$	$5.661*10^{22}$	$5.097*10^{22}$	$6.470*10^{22}$	$6.268*10^{22}$
Max. Expect DPA*	42.6	26.5	40.3	38.9	41.0	41.3
Range (um)	2.30	2.00	2.60	2.45	2.50	2.45

Argon ion irradiation experiment was conducted at the KAERI-affiliated KAHIF (KAERI Heavy Ion Irradiation Facility). Ar^{9+} ion beam with an energy of 6.8MeV was irradiated at an elevated temperature of 400 degrees Celsius.

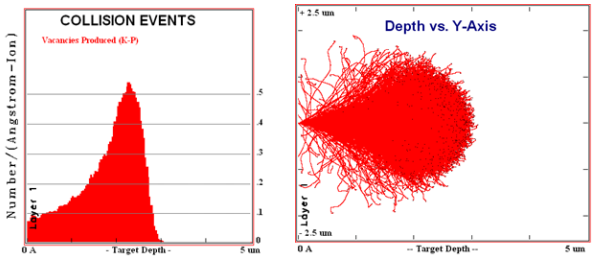

Fig 2. SRIM Simulation Result of Ar Ion Irradiated in Gadolinia. (a) Calculated dpa peaks around 2.0-2.6 μm (b) which can be seen on the trajectory of each simulated Ar ion

As a pre-assessment for actual ion irradiation, assessment of the depth-damage profile from the irradiation is simulated by SRIM 2008, a Monte Carlo code capable of calculating collision-induced displacements per atom (dpa) caused by radiation particles. Expected DPA and maximum-DPA depth (Range) for 5-hour irradiation (Table I) were calculated with parameters of 3.7cm² beam Area, and an average

current of 15μA. Finally, while running the actual irradiation experiment, electricity is measured and irradiation time is controlled so that each sample can reach 10%, 30% and 100% of the maximum expected DPA of 5-hr irradiation.

2.2 X-Ray Diffraction Specifications

For this work, the microstructure of irradiated samples was observed using various analyzing equipment in KARA(KAIST Analysis Center for Research Advancement).

Theta-2theta XRD and Grazing-Incidence XRD(GIXRD) were executed using SmartLab™ High Resolution Thin-film X-Ray Diffractometer (RIGAKU), which utilizes Cu-Kα X-ray source. The scan range was set to be 10-80 ° with a scan speed of 4°/sec applied. GIXRD is a powerful tool to study the phase structure of thin films, such as surface irradiation of given ceramic samples.[2]

3. Results and Discussions

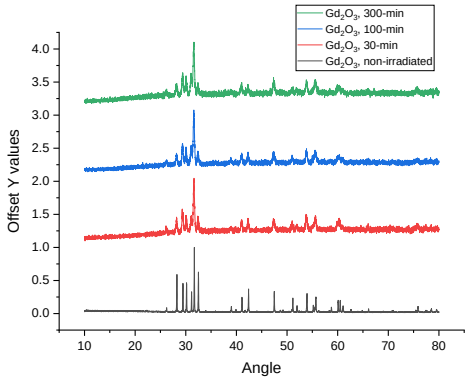

Fig 3. t-to-2t XRD pattern of Irradiated Gd_2O_3

As illustrated in Fig 3, XRD patterns of the undoped Gd_2O_3 samples are presented. PDF Card No.00-042-1465 (Quality : S) matches perfectly with the non-irradiated XRD result (black line), indicating the bulk of gadolinia is in the monoclinic phase. That phase, is kept after 4~40 dpas of irradiation, as shown in colored diffraction patterns. In comparison of 30-min irradiation (red-colored line) and 300-min irradiation (green-colored line), the position of each peak is not shifted, and broadening has not significantly occurred as the calculated dpa level was increased. This indicates that pure gadolinia shows outstanding signs of its anti-irradiation properties, which will be further proved on other kinds of microstructural analyses such as TEM or Raman Spectroscopy.

However, considering the practical application of pure gadolinia in nuclear reactors, its solubility in water presents a non-negligible issue. Therefore, it was necessary to investigate the irradiation resistance of doped gadolinia samples, which were selected based on leaching test results that showed enhanced stability in aqueous environments.

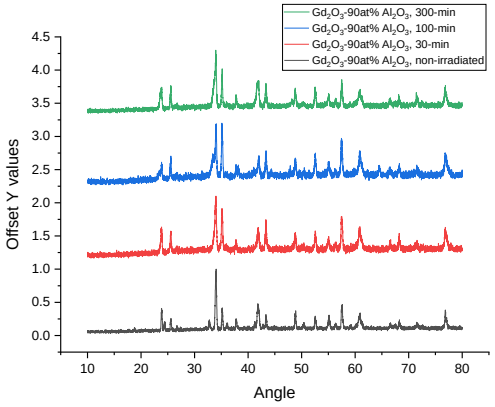

Fig 4. t-to-2t XRD pattern of Irradiated Gd_2O_3-90at% Al_2O_3

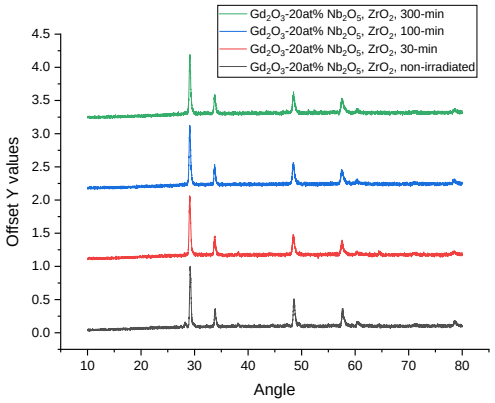

Fig 5. t-to-2t XRD pattern of Irradiated Gd_2O_3-20at% Nb_2O_5, ZrO_2

In several cases: Gd_2O_3-90at% Al_2O_3 (a.k.a. HIGA composition), Gd_2O_3-20at% Nb_2O_5, ZrO_2, Gd_2O_3-15at% ZrO_2, and Gd_2O_3-20at% CeO_2 have shown very stable features in the diffraction patterns along the several tens of dpa irradiation. As shown in Fig 4-5, there was no observable indication that those compositions have modifications compared to the non-irradiated sample, in terms of phase analysis by diffraction pattern. On the other hand, several samples with different compositions exhibited transitions of phases observed in XRD patterns.

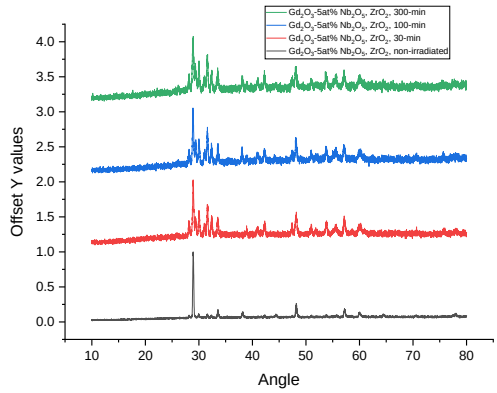

Fig 6. t-to-2t XRD pattern of Irradiated Gd_2O_3-5at% Nb_2O_5, ZrO_2

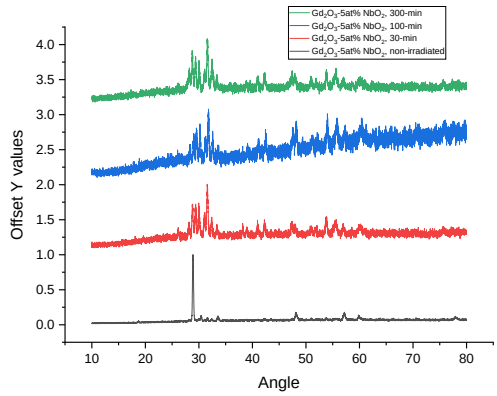

Fig 7. t-to-2t XRD pattern of Irradiated Gd_2O_3-5at% NbO_2

As shown in Fig 6 and Fig 7, in the composition containing Niobium Oxide and Zirconium Oxides, a significant number of peaks were observed around the 30° region compared to the non-irradiated state. This indicates that the monoclinic gadolinia phase was formed due to the irradiation. The PDF card for the monoclinic gadolinia phase is depicted in Fig 7, and no significant difference was observed between relatively low (~4.0) dpa and high (~40) dpa conditions.

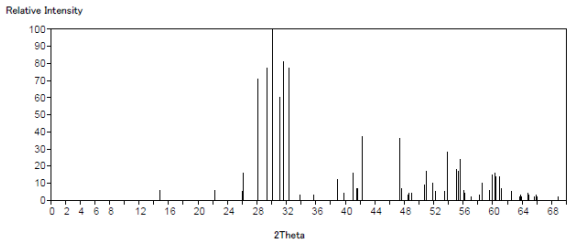

Fig 7.PDF card of Monoclinic Gadolinia Phase

The main peak around 28° is interpreted as an overlap of the primary peak of Gd_3 (NbO_7) at 28°, as identified in PDF Card No.: 01-078-6050 (Quality: S), with the monoclinic gadolinia peak in the same region. The volume fraction of these two phases can be quantitatively determined through subsequent Rietveld refinement analysis.

4. Conclusions

In conclusion, phase transition analysis was conducted using XRD by Ar ion irradiation of doped and undoped gadolinia samples prepared using the KAHIF accelerator. For pure gadolinia, as well as certain compositions containing Ce or Zr, the original phase remained largely intact after irradiation, showing no significant additional phase transition despite increasing dpa levels. This suggests superior radiation resistance from a microstructural perspective.

In contrast, XRD analysis of several compositions, as shown in Fig 6 and Fig 7, revealed the appearance of new diffraction peaks following irradiation, indicating phase transitions induced by radiation exposure. Notably, some compositions containing Nb exhibited the formation of a monoclinic gadolinia phase, which had not been observed in the pre-irradiation state, further suggesting the compositional sensitivity to irradiation-induced structural changes. The next step in this research will involve analyzing how these phase transformations affect mechanical properties, ultimately assessing whether these compositions can be viable for application in reactor environments. Additionally, for compositions that demonstrated relative phase stability, further investigations using TEM or Raman spectroscopy may offer insight into the underlying mechanisms contributing to their radiation resistance.

REFERENCES

[1] Nguyen, Xuan Ha, ChiHyung Kim, and Yonghee Kim. "An advanced core design for a soluble-boron-free small modular reactor ATOM with centrally-shielded burnable absorber." Nuclear Engineering and Technology 51.2 (2019): 369-376.
[2] Oliver Werzer et al. “X-ray diffraction under grazing incidence conditions” nature reviews methods primers (2024) 4:15

ACKNOWLEDGEMENTS

This study was supported by the Ministry of Science, Technology and ICT. (2022M2E9A304619013)