

Degradation behavior of Cr coated Zr cladding under 1200°C steam oxidation

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1. Introduction

In 2011, a hydrogen explosion at the Daiichi Nuclear Power Plant in Fukushima, Japan by the tsunami followed by an earthquake off the coast of northeast Tokyo with a magnitude 9.0 led to the exposure of radioactive materials to the atmosphere. This has adversely impacted the nuclear power industry. Rather than abandoning the use of nuclear power to generate electricity, globally, various efforts have focused on making it safer to use, especially since 2011, by developing accident-tolerant fuel (ATF) to prevent the rapid oxidation of zirconium fuel cladding, which is the direct cause of hydrogen explosions [1]. ATF development in the field of cladding materials can be categorized into two: (i) changing cladding materials and (ii) surface coating of cladding material while leaving it unchanged. Several investigations have reported that coatings that only improve the surface material is suitable for rapid commercialization from 2020s for existing commercial nuclear power plants; as a result, most nuclear fuel vendors have advanced technology by applying coating methods used in the existing industry to each company's unique cladding tube [2]. Vendors select chromium as the coating medium because of its superiority with respect to low oxidation rate, excellent adhesion, and so on.

During an accident, zirconium oxidation is inevitable as oxidizing particles penetrate the zirconium base material due to the deterioration of the chromium coating layer under prolonged high-temperature oxidation conditions [3]. Therefore, research has focused on suppressing rapid oxidation reactions during an accident by coating the zirconium cladding with chromium at an appropriate thickness while considering economy and applicability. Based on this, the coating thickness can be fixed; nevertheless, the delay in the passage of oxidizing substances can be further increased by improving the microstructure of chromium comprising the coating. In other words, the amount of zirconium oxidation can be decreased by reducing the chromium grain boundary area through which oxidizing substances migrate at high temperatures, and this change in the coating microstructure depends on the conditions under which the coating is applied.

This study focuses on the evaluation of chromium-coated zirconium cladding samples developed to advance domestic production technology for materials that are currently commercialized by global nuclear fuel vendors. Specifically, a PVD technique, known as AIP, was employed to coat HANA-6TM cladding with chromium. By varying manufacturing parameters, including the bias voltage, we aimed to prepare coatings with diverse microstructural characteristics. The primary objective was to optimize safety margins under accident scenarios, which were assessed by applying the LOCA criteria. Through this approach, we determined the optimal microstructure and manufacturing conditions required for realizing high-temperature steam oxidation resistance. In addition, the microstructures of the as-coated chromium-coated HANA-6TM cladding and their relationship with the oxidation weight gain and microstructural evolution were analyzed, revealing previously unreported suppression mechanisms for chromium grain growth.

2. Experimental

Chromium-coated zirconium claddings were produced at six different bias voltage settings (0, 30, 50, 75, 100, and 125 V). High-temperature oxidation resistance was quantitatively evaluated under a steam environment at 1200°C, where the weight gain of the cladding was measured in real time. The coating microstructures of the claddings fabricated at the six bias voltages exhibited distinct features, including intrinsic defects, bonding quality with the substrate, grain size and shape, and inter-diffusion layer formation.

3. Results and Discussion

At low bias voltages (0–30 V), the reduced kinetic energy of incident particles led to insufficient substrate heating, limiting planar diffusion, and grain structures with cavities and voids along with poor bonding to the substrate. Meanwhile, bias voltages in the range of 50–100 V provided sufficient energy for enhanced diffusion, forming columnar grains with high atomic density, wide grain widths, and excellent bonding with the substrate. However, at 125 V, the excessive kinetic energy of incident particles disrupted the coating crystalline

structure, increasing lattice energy and generating defects at a level comparable to high-energy ion bombardment. Although this high energy improved bonding, it damaged the ZrCr_2 intermetallic layer, promoting the early diffusion of zirconium into the chromium layer. This abnormal early zirconium diffusion induced by excessive ion bombardment hindered chromium grain growth during high-temperature oxidation.

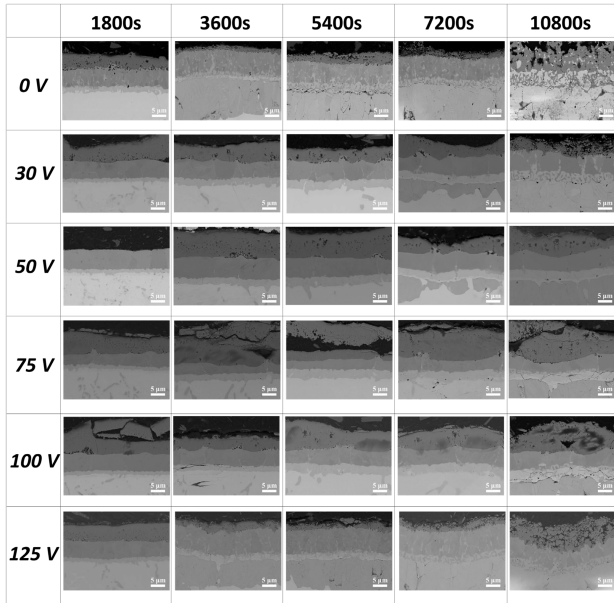


Fig. 1. SEM-BSE image showing the changes in microstructure at the interface between the chromium coating and zirconium cladding chromium coating and zirconium cladding prepared at six bias voltages under 1200 °C steam oxidation [1].

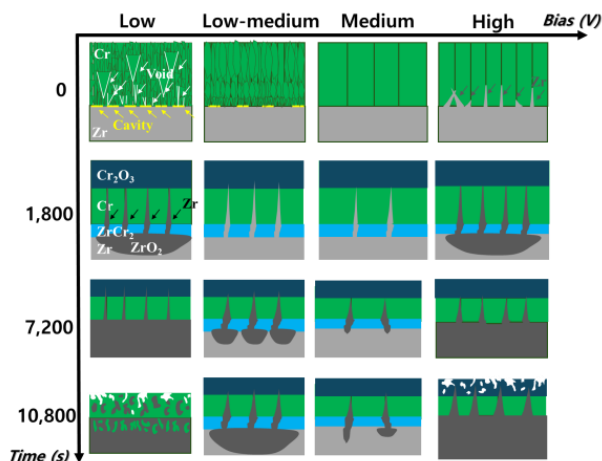


Fig. 2. Extended degradation model of chromium-coated zirconium cladding at high temperature under steam atmosphere: microstructures with various properties can be obtained by controlling bias voltage in the AIP process employed for manufacturing chromium-coated cladding, and the growth rates of chromium grains affected by properties under a steam atmosphere at 1200°C can determine the oxidation rate.

The high-temperature oxidation tests were conducted at 1200°C for up to 10,800 s and those microstructure has been observed as shown in the Figure 1. The oxidation of chromium-coated zirconium claddings was governed by the diffusion of oxidizing species through chromium grain boundaries. The results reveal that the oxidation rate could be controlled by the chromium grain growth rate at the onset of oxidation. Samples fabricated at 50–100 V exhibited rapid grain growth during early oxidation, maintaining low weight gain throughout the experiment. Conversely, samples fabricated at 0 and 30 V exhibited restricted grain growth due to intrinsic defects, resulting in a high weight gain. The 125-V samples, with pre-existing zirconium within chromium grain boundaries, showed limited grain growth during early oxidation and consequently exhibited high weight gain. Figure 2 shows the extended degradation model of chromium-coated zirconium cladding at high temperature under steam condition.

4. Conclusions

One key finding of this study is that the grain width of chromium measured at 1,800 s remained stable until 10,800 s. This suggests that the movement of zirconium and oxygen along grain boundaries during oxidation suppressed further grain growth. Therefore, fabricating chromium coating with favorable microstructures that allow for grain growth is critical during coating processes. We conclude that the precise control of the kinetic energy of chromium particles, achieved by applying an optimal bias voltage in the range of 50–100 V using AIP, is essential for producing coatings with excellent high-temperature oxidation resistance.

Acknowledgments

This research has been carried out as a part of the nuclear R&D program of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) funded by Ministry of Trade, Industry and Energy in Korea. (Grant No. 20224B10200100).

REFERENCES

- [1] J. Carmack, F. Goldner, S.M. Bragg-Sitton, L.L. Snead, Overview of the U.S. DOE Accident Tolerant Fuel Development Program, Idaho National Laboratory (INL), Idaho Falls, IA, USA, 2013. No. INL/CON-13-29288.
- [2] K. Muftuoglu. In: Proceedings of the Annual EPRI/DOE/INL Joint Combined Workshop on Accident Tolerant Fuel and Higher Burup, Palo Alto, CA, EPRI, 2023
- [3] J.C. Brachet, E. Rouesne, J. Ribis, T. Guilber, S. Urvoy, G. Nony, C. Toffolon-Masclet, M.L. Le Saux, N. Chaabane, Palancher, A. David, J. Bischoff, J. Augereau, E. Poulillier, High temperature steam oxidation of chromium-coated zirconium-based alloys: Kinetics and process. *Corrs. Sci.* 167 (2020) 108537.
- [4] T.S. Jung, H. Jang, Y.K. Cho, D.C. Jang, Degradation behavior of chromium-coated zirconium cladding under 1200 °C steam oxidation according to the coating microstructure, *J. Nucl. Mater.* 603 (2025) 155360.