Improvement of alkali silicate heat-resistant coating according to ZIRLO's surface treatment method

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1. Introduction

After the Fukushima Daiichi nuclear disaster in Japan, the importance of research and development of Accident Tolerant Fuel (ATF) to minimize the possibility of hydrogen generation and fusion by breakaway oxidation of nuclear fuel cladding, a vulnerability to nuclear safety, has been highlighted [1, 2]. While zirconium-based alloys are currently used as nuclear fuel cladding, considering various material properties such as reaction cross section and thermochemistry, the coating method on the existing cladding tube is drawing attention to securing the function of ATF in a short period of time so that nuclear fuel integrity can be maintained even in the beyond design basis accident [3].

Alkali silicate is one of the materials widely used as a heat-resistant coating material, which has high heat resistance, oxidation resistance and chemical resistance. In addition, raw materials have the advantage of being cheap and eco-friendly side.

In this research, a nuclear fuel cladding coating material based on alkali silicate was developed. As well as we conducted experiments to enhance the thermal resistance of coating material and maximize the adhesion of coating on ZIRLO's surfaces through surface treatment of ZIRLO, which is currently used as a nuclear fuel cladding material for PWR reactors. In addition, through various analyzes, the difference in energy according to the surface treatment method was measured, and the high-temperature oxidation behavior test was conducted accordingly to derive the optimum surface treatment which can secure high heat resistance even under severe thermal conditions.

2. Experiment

2.1 Surface treatment and Coating

Different surface treatments were conducted on ZIRLO specimen with the surface treatment cases were prepared for bare, heat treatment, plasma treatment and piranha cleaning. Among them, the heat treatment atmosphere was heated by 5 degrees Celsius per minutes to 500℃ and 700℃, respectively, and maintained for 1 hour in argon atmosphere. The treated specimens were observed characterized by X-Ray Diffraction (XRD), on cross-sectional areas through Field Emission Scanning Electron Microscope (FE-SEM) and Energy Dispersive X-ray Spectroscopy (EDS).

Coating material was prepared by mixing aluminum oxide (Al_2O_3) and silicon dioxide (SiO_2) with the idea of a ceramic glaze on mixed silicate made with a blending ratio of sodium, potassium and lithium silicate with the maximum shear strength derived from previous research [4]. To form a thin and uniform coating layer, the coating material was applied several times by spin coating with high rotation.

2.2 Breakaway oxidation behavior of coated ZIRLO

After the silicate coated on ZIRLO undergoes sufficient curing in a high temperature argon atmosphere to pass through the glass transition temperature, we observed what kind of breakaway oxidation behavior of the coated ZIRLO according to the surface treatment. The condition of the high temperature breakaway oxidation behavior test was to be maintained for an hour after reaching 1200 °C by 5 °C min^{-1} in the atmosphere.

3. Results and Discussion

3.1 Case comparison after surface treatment

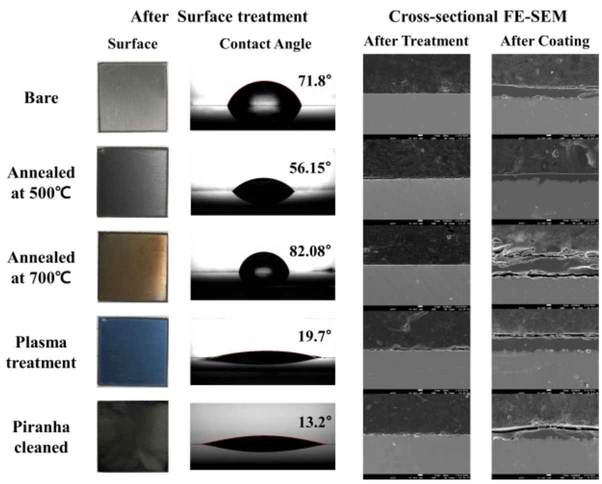


Figure 1. Case comparison after surface modification

Figure 1 show the change in ZIRLO and the contact angle of the surface that can be seen after surface treatment. The contact angle is large in the order of annealed at 700℃, Bare, annealed at 500℃, plasma treatment, and piranha cleaned. When pre-curing at 80 ℃ after applying the coating material, the thickness of coating layer tends to be thicker in the order of the larger contact angle.

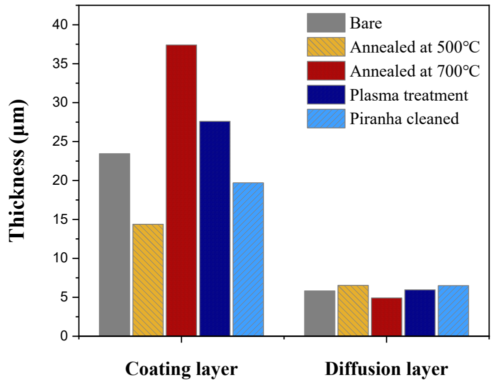


Figure 2. Thickness comparison in each specimen after vitrification

As shown Figure 2, However, after curing at 1200 °C for vitrification, the contact angle showed a different tendency. The thinner the coating layer, the thicker the diffused layer can be observed. The thicken diffusion layer in the annealed at 500°C could be resulted from the applied surface treatment that improved adhesive force between coating material and substrate. Moreover, the annealed at 700°C specimen, which has the thinnest diffusion layer, was fine, but appears to be separated between the coating layer and the ZIRLO, and ZrO_2 was not found on the surface as a result of EDS.

3.2 Surface X-Ray Diffraction

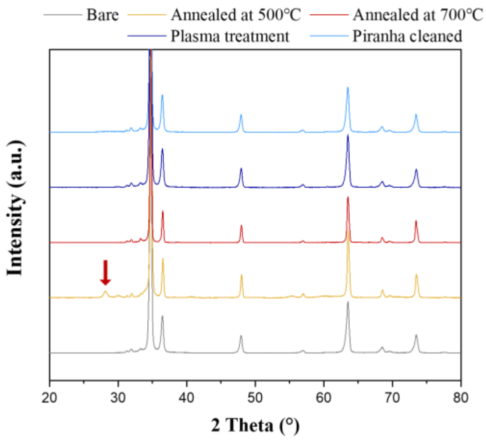
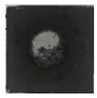
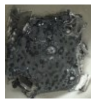
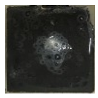
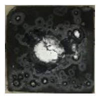


Figure 3. Representative XRD spectra according to surface treatment

The XRD spectra shows the crystalline structure of bare, annealed at 500°C, annealed at 700°C, plasma treatment and piranha cleaned. The intensity of the specimens did not differ significantly. While most of them showed alpha phase, different peaks could be observed in the specimens subjected to heat treatment by pretreatment. In the annealed at 700°C specimen, it was confirmed that the alpha phase and the beta phase coexisted, and in the annealed at 500°C specimen, intermetallic compounds were found together with the alpha phase. In particular, it was confirmed that monoclinic ZrO_2 was formed in the area indicated by the down allow in the specimen of annealed at 500°C [5].

3.3 Breakaway oxidation behavior of coated ZIRLO

Table 1. Breakaway oxidation test after alkali silicate-based coating on the surface treated ZIRLO

	Bare	500°C	700°C	Plasma	Piranha
#1					
#2					

As seen in Table 1, #1 provides figures of each case after sufficient curing in a high-temperature argon atmosphere for the silicate coated on ZIRLO to undergo vitrification. #2 indicates specimes after Breakaway oxidation behavior experiment in the atmospheric environment to verify if the coating material can protect ZIRLO from the brittleness of the coating material due to hydrogen absorption. We observed how the coated ZIRLO exhibits the behavior of breakaway oxidation according to surface treatment.

The specific mass gain was the largest in the Plasma treatment at 917.75 g m^{-2}. Bare and Piranha cases were 259.5 and 35.5 g m^{-2}, respectively, which means that the specific mass gain is the next largest after Plasma. These three cases were not protected and were visually confirmed that the breakaway oxidation occurred. All other cases subjected to annealing by pretreatment showed a tendency to decrease in mass. Annealed at 500°C and 700°C had a change rate of -7.75 and -52.25 g m^{-2}, respectively. It was confirmed that the case where the mass decreased the most was Annealed at 700°C, and the case with the smallest change rate was Annealed at 500°C.

4. Summary and Conclusion

- Experiment to improve heat resistance of alkali silicate-based coating materials according to ZIRLO's surface treatment method and maximize coating adhesion on ZIRLO surface.
- When the alkali silicate-based coating material was coated on the surface treated ZIRLO, the thickness of the coating layer was in the order of annealed at 700°C, plasma treatment, bare, piranha cleaned and annealed at 500°C. This tends to be like the size of the contact angle.

- After curing at 1200 ℃ for vitrification, The thinner the coating layer, the thicker the diffused layer can be observed. The fact that the diffusion layer is thick can be said to have a higher adhesive force.
- Breakaway oxidation behavior test was confirmed by the specific mass gains in high temperature conditions (During 1hr at 1200 ℃ (5 °C min^{-1}), Air.), as a result, the annealed at 500℃ specimen showed the lowest mass change. Which is higher than the bare specimen because the adhesive force between the surface of ZIRLO and the uniformity of coating layer was improved. It is believed that high corrosion resistance in the behavior of high temperature breakaway oxidation can be used as a surface treatment technology to maintain the integrity of nuclear fuel even in case of beyond design basis accident.

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