Fabrication of Zircaloy-4 Fuel Cladding Pipe with Nanostructured Oxide Layer for Prevention of Hydrogen Production

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1. Introduction

Since the Fukushima disaster happened, studies on accident-resistant nuclear fuel has been carried out actively. There has been an attempt to protect zircaloy fuel cladding by coating SiC. Research on producing oxide layer that can block fuel cladding from water on the surface of zircaloy fuel cladding by means of anodizing to reduce the rate of oxidation of fuel cladding at Loss Of Coolant Accident (LOCA) is an significant ongoing study subject. Applying nanostructured oxide layer to the prevention of thermal deformation of oxide layer was already suggested in our research group, the reasons of which is nanoporous structure is better than nanotube structure in terms of corrosion-resistant structure because nanotube structure can be easily peeled off.

In this study, methods which are able to control morphology between nanoporous and nanotube structure were conducted by changing the anodizing conditions. Hence, Using glycerol and ammonium fluoride, Zircaloy-4 was anodized by varying water contents and applied voltage. It reveals that the alloy transition from nanoporous structure to nanotube structure can be changed by varying water contents of anodizing solution and applied voltage.

2. Experimental

2.1. Specimen Preparation

For anodization experiments, Zr-4 alloy pipes were used as a substrate. They were degreased by sonicating in acetone, isopropyl alcohol and deionized water (DI) and dried with air-gun. Specimens for the substrate as cathode, anode as platinum wire was used, respectively. For the electrolyte, ethylene glycol (99.5% purity, Junsei)-based containing ammonium fluoride (Sigma-Aldrich) was used and 1 w% of DI water additions.

2.2. Experimental Procedures

The anodization was performed in a two-electrode electrochemical cell with a platinum wire as counter electrode and the Zr-4 alloy pipe as the working electrode as shown in Fig. 1. All the experiment were carried out with DC power source using high voltage (100V) in a dry glove box at a room temperature. After the experiment, the samples were taken out of the glove box, rinsed with DI water, and then dried in air.

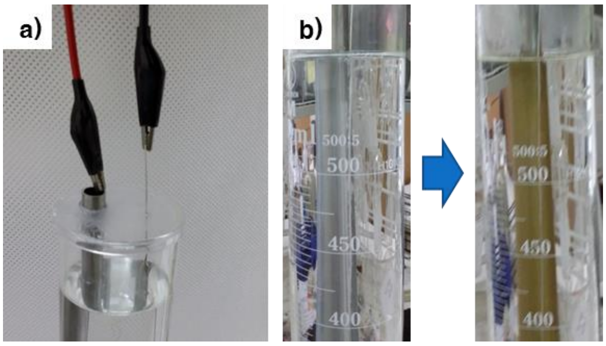

Fig. 1. Pipe anodization performed in a electrochemical cell and color change as anodization proceed.

The structures of the anodized oxide layer were characterized by field-emission scanning electron microscopy (FE-SEM, Nova230, FEI, USA). For the measurement, the samples were mechanically cracked. Characterization of the samples chemical composition was carried out using EDX (EDAX Genesis, fitted to the SEM chamber).

3. Results and Discussion

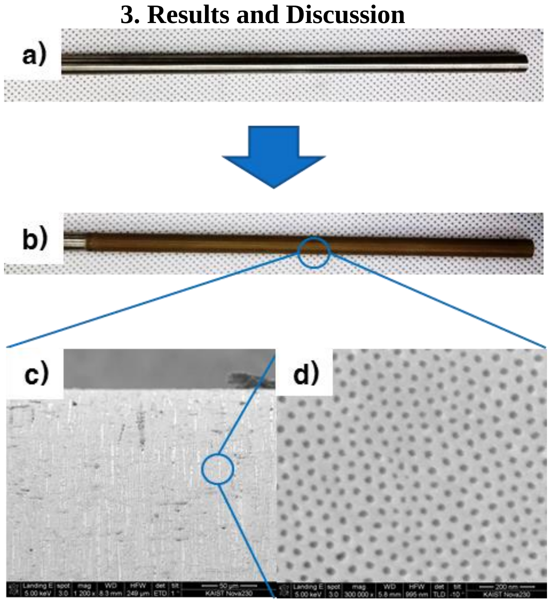

Fig. 2. An example of zircaloy-4 pipe a) before b) after anodization treatment and field-emission scanning electron microscope (FESEM) image of c) the pipe and d) the nano-structured surface of anodized zircaloy-4 pipe.

The formation of anodic oxide layer based on following equation[1].

$$Zr^{4+} + 4OH^{-} \rightarrow Zr(OH)_4 \qquad (1)$$

$$Zr^{4+} + O^{2-} \rightarrow ZrO_2 \qquad (2)$$

The pores on the oxide layer grow by following mechanism.

$$ZrO_2 + 6F^{-} + 4H^{+} \rightarrow ZrF_6^{2-} + 2H_2O \qquad (3)$$

Fig.2 shows the zircaloy-4 pipe before and after anodization treatment. The anodized surface is quite clean and the nanostructure is almost uniform and hexagonal. Recent researches studied by Rahman et al reveal that critical heat flux is dramatically increase on the nanostructured surface since the liquid is easily drawn into the nanostructures in the wetted areas[5].

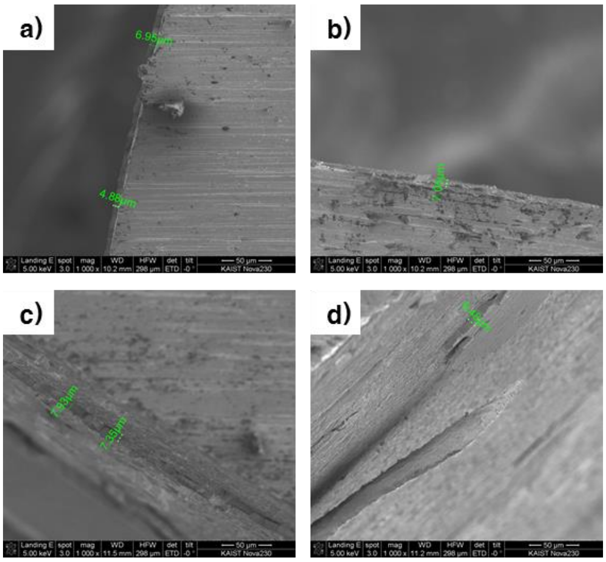

Fig. 3. Cross-sectional field-emission scanning electron microscope (FESEM) images of anodized zircaloy-4 pipe.

Fig.3. is the cross-sectional FESEM images of the anodized zircaloy-4 pipe. The thickness of the nanostructured oxide film is different along the rim. Since the pipe anodized using only one platinum wire, the electric filed was not even. The asymmetry of the electric field make the film not even.

4. Conclusions

Zircaloy-4 pipe with nanostructured surface was fabricated by anodization technique. The produced nanostructure is quite even but the thickness of the oxide layer is not even. The nanostructured surface can increase the thermal characteristics of the zircaloy-4 fuel cladding. The result of this study can be used for the next generation fuel cladding pipe.

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