Morphology control of anodic ZrO2 layer for the prevention of H2 production from Zr-4 cladding

Y. J. Park*, J. W. Park, S. O. Cho
Korea Advanced Institute of Science and Technology, 291 Daehakro, Yuseong-gu, Daejeon 305-701, Rep. of Korea
**Corresponding author: yjeong3506@kaist.ac.kr*

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 sheets 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 and cathode, anode and platinum sheet were used, respectively. For the electrolyte, glycerol (95% purity, Junsei)-based containing ammonium fluoride (Sigma-Aldrich)-and the conditions of DI water content (0.4%, 0.2%, 0.1%, 0.05%, 0.0%, vol.) were applied to.

2.2. Experimental Procedures

The anodization was performed in a two-electrode electrochemical cell with a platinum sheet and the Zr-4 alloy sheet, for which the counter electrode and the working electrode, respectively. All the experiment were carried out with DC power source using different voltage (50V, 200V) 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.

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 on purpose. Characterization of the samples chemical composition was carried out using EDX (EDAX Genesis, fitted to the SEM chamber).

3. Results and Discussion

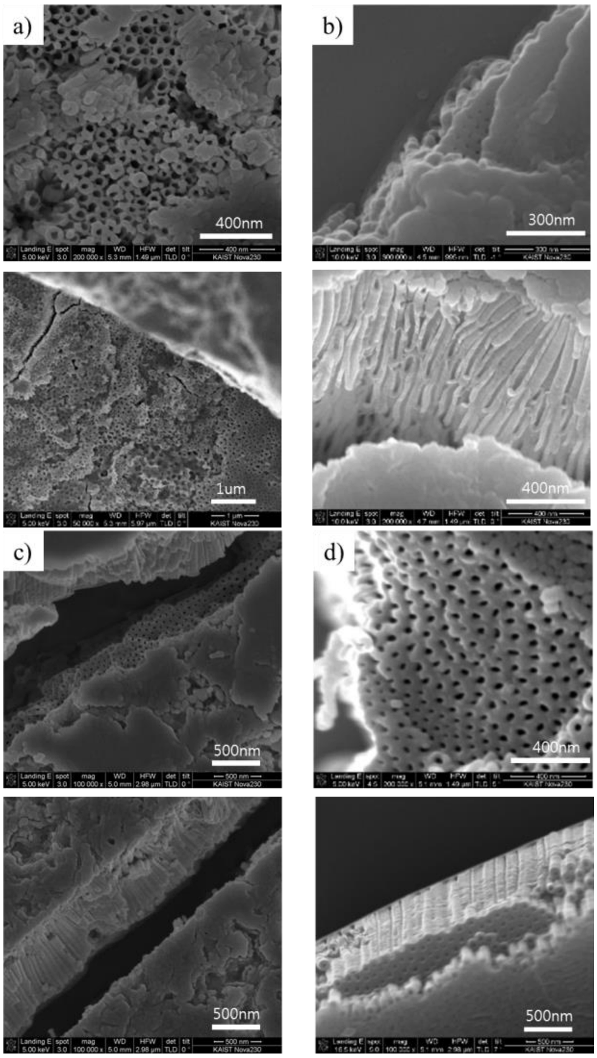

Fig. 1. Field-emission scanning electron microscope (FESEM) images of 1h-anodized Zr-4 alloys formed in glycerol-based electrolyte containing 0.3% NH_4F at 200V with a) 0.4%, b) 0.2%, c) 0.1% and d) 0.05% of water content.

As shown in Fig.1., anodic oxide layer of Zr-4 alloy formed in glycerol-based electrolyte containing 0.3% NH4F at 200V with different water content: 0.4%, 0.2%, 0.1% and 0.05%. When applying 0.4% water content, only nanotube structures are obtained. In this case, water content is enough to dissolve cell boundary which contains a lot of fluoride ions. When applying 0.2% water content, it appears to be changed like porous structure as time goes by at the bottom of the oxide while the structure of the upper part is still nanotube. When applying 0.05% water addition, more solid structure appeared to be formed. Consequently, as the water content decreases, the obtained morphology tends to become nanoporous structure. Ions produced from water have played the role degrading the cell boundary.

Table I: EDX result of 1h-anodized oxide layer formed in glycerol-based electrolyte containing 0.3% NH4F at 200V with 0.05% of water content.

Sample	Part/At%	O K	F K	ZrL	Total
1	Top	50.27	19.81	29.91	100
	Bottom	51.71	25.27	23.01	100
2	Top	39.72	23.33	36.95	100
	Bottom	26.56	42.4	31.04	100
3	Top	35.62	17.74	46.64	100
	Bottom	21.92	27.46	50.62	100

Table I shows the chemical composition of the three anodized samples using EDX. Since the concentration of fluoride ion is not negligible, it seems that the bottom part of the oxide layer is not clearly an oxide but the oxyfluoride (ZrF_xO_y). The zirconium oxyfluoride has the property of both zirconium oxide and zirconium fluoride in microscopic point of view.

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

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

$$Zr^{4+} + O^{2-} \rightarrow ZrO_2 \tag{2}$$

The pores on the oxide layer appeared to be grown by following mechanism.

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

It is well known that the atomic bond between zirconium atom and fluorine atom is somewhat weak so that the OH^- ion can easily break it; zirconium fluoride is water soluble. Since the cell boundary contains a large amount of fluoride ions[2], it can be destroyed by OH^- ion from self-ionization of water.

Fig.2. shows the schematic description of the process forming nanostructure. The difference between dissolving rate for cell boundary and metal/oxide interface is the main factor determining nanostructure. If the dissolving rate of cell boundary is much faster than that of metal/oxide interface, it makes nanotube structure. The reverse is nanoporous structure. Hence, the dissolving rate is highly related to ion mobility of OH^- and O^{2-}.

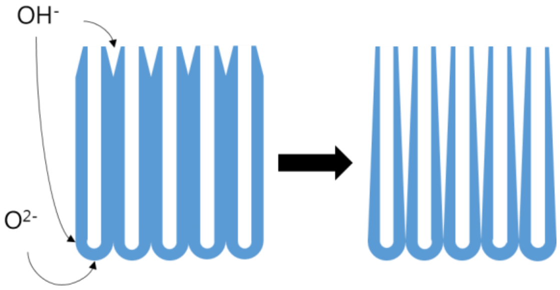

Fig. 2. Schematic illustration of formation of anodic nanostructure by dissolution of cell boundaries and metal/oxide interface.

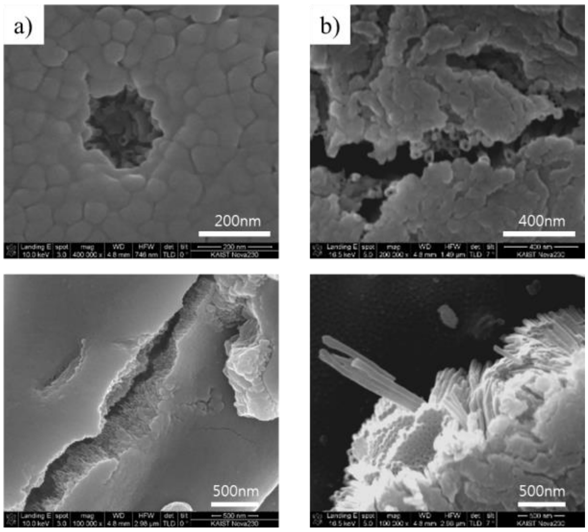

Fig. 3. Field-emission scanning electron microscope (FESEM) images of 1h-anodized Zr-4 alloys formed in glycerol-based electrolyte containing 0.3% NH4F at 50V with a) 0.2% and b) 0.05% of water content.

For lower voltage anodization, OH- ion appeared to dissolve the oxide cell boundary more easily than 200V anodization because low electric field make OH^- exist in the upper part of the oxide layer. Thus, nanotube structure will be formed at low temperature, this prediction of which is shown in Fig.3.

4. Conclusions

Anodizing conditions determining nanoporous structure were obtained. According to the mechanism already suggested, nanoporous oxide layer that can seal the fuel cladding perfectly, and increase critical heat flux (CHF) due to large surface area is easily produced. This results obtained in this paper expected to be facilitated fabrication of accident-resistant nuclear fuel cladding.

REFERENCES

[1] B. Chen, J. Hou, and K. Lu, "Formation mechanism of TiO2 nanotubes and their applications in photoelectrochemical water splitting and supercapacitors.," Langmuir, vol. 29, no. 19, pp. 5911–9, May 2013.

[2] S. Berger, S. P. Albu, F. Schmidt-Stein, H. Hildebrand, P. Schmuki, J. S. Hammond, D. F. Paul, and S. Reichlmaier, "The origin for tubular growth of TiO2 nanotubes: A fluoride rich layer between tube-walls," Surf. Sci., vol. 605, no. 19–20, pp. L57–L60, Oct. 2011.

[3] G. Ali, C. Chen, S. H. Yoo, J. M. Kum, and S. O. Cho, "Fabrication of complete titania nanoporous structures via electrochemical anodization of Ti.," Nanoscale Res. Lett., vol. 6, no. 1, p. 332, Jan. 2011.

[4] C. Lee, H. Kim, H. S. Ahn, M. H. Kim, and J. Kim, "Micro/nanostructure evolution of zircaloy surface using anodization technique: Application to nuclear fuel cladding modification," Appl. Surf. Sci., vol. 258, no. 22, pp. 8724–8731, Sep. 2012.