

Oxidation Kinetics of Zirconium Alloy with Nanoporous Oxide Layer at Temperatures of 800-1100°C Air

Y. J. Park*, J. W. Kim, 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

In the case of zirconium alloys, which are widely used in the field of nuclear engineering, the explosive generation of hydrogen, a reaction by-product of zirconium and steam, was pointed out as the cause of the Fukushima nuclear power plant accident in 2011. Therefore, many studies on accident-resistant fuel covering materials (ATF) have been aimed at increasing the safety of zirconium alloy cladding in nuclear reactors. The main research flow was to completely replace zirconium alloys with ceramic materials using SiC or other metallic materials such as Mo and FeCrAl. This study provides improved corrosion resistance without sacrificing the strong advantages of zirconium. The authors have proposed anodizing to fabricate nanostructured zirconium oxide films on alloy surfaces to improve corrosion resistance at low cost. In addition, the oxidation resistance was measured by exposing the specimen to air atmosphere at various temperatures. The antioxidation mechanism was revealed through thermodynamic analysis and microstructure analysis.

2. Methods

2.1. Specimen Preparation

Zr-Nb-Sn alloy plate was used as the substrate for the anodization experiment. They were degreased by ultrasonication with acetone, isopropyl alcohol and deionized water (DI), and dried with an air gun. A sample for a substrate and cathode, and a platinum sheet for an anode were respectively used. In the case of the electrolyte, ethylene glycol (95% purity, Junsei) and 1% by volume DI water addition containing 0.3 wt% ammonium fluoride (Sigma-Aldrich) were used.

2.2. Experimental Procedures

Anodic oxidation treatment was performed in a two-electrode electrochemical cell having a platinum sheet as a counter electrode and a Zr-Nb-Sn alloy sheet as a working electrode. All experiments were performed with DC power at 90V at room temperature. After the experiment, the sample was rinsed with deionized water and dried in air.

2.3. Analysis

The structure of the anodized oxide layer was characterized by field-emission scanning electron microscopy (FE-SEM, Nova 230, FEI, USA).



Figure 1. Thermogravimetry analyzer

A TGA (thermogravimetric analysis) experiment was conducted to confirm whether the prepared nanostructured oxide layer can protect the metal substrate from oxidation. The TGA unit consists of scale and furnace. Measure the mass of the sample according to the temperature change and check the degree of chemical reaction.

To measure the oxidation of the sample with the prepared nanostructured oxide film in an environment such as a LOCA accident, our team designed the TGA device as Fig 1.

We installed argon as a carrier gas to install the steam generator module and create a high temperature steam environment. In order to expose the cladding material having the fabricated nanostructured oxide film to the high temperature steam environment, the fabricated

sample was supported by connecting the platinum wire to the alumina crucible. In order to measure the oxidation of the sample with the prepared nanostructured oxide film in the high temperature water vapor environment, the balance was connected to the alumina crucible. The measurement results of the scales were transmitted to the computer in real time and recorded. The bare Zr-Nb-Sn alloy or anodized Zr-Nb-Sn alloy samples for TGA experiments were cut into 3.5 X 3.5 X 0.58 mm³. This samples were analyzed using TGA device after they were putted in alumina crucible.

3. Results and Discussion

The anodized surface is very clean and the nanostructure is almost uniform and hexagonal as shown in Fig 2. Recent studies by Rahman et al. Show that the critical heat flux rapidly increases on the nanostructured surface because the liquid is easily drawn into the nanostructures of wetted areas [1].

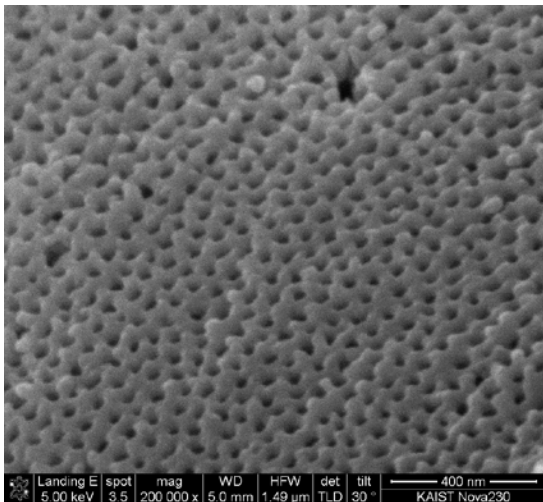


Figure 2. Images of Zr-Nb-Sn alloy with nanostructured oxide layer.

The anodized specimens were less oxidized than the pristine Zr alloys between 800 and 1100 degrees Celsius.

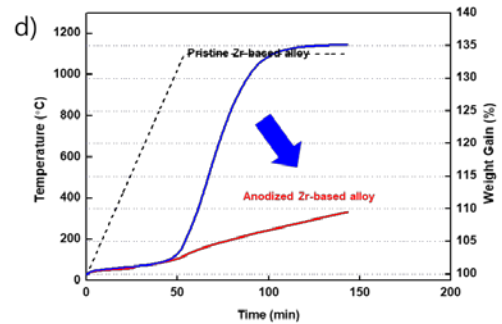
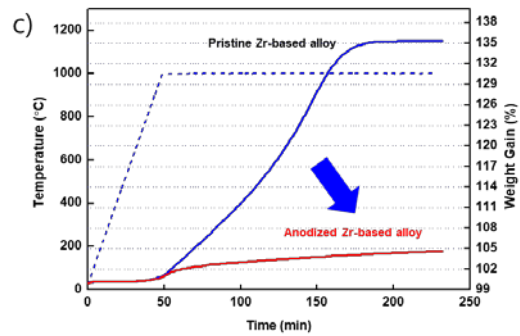
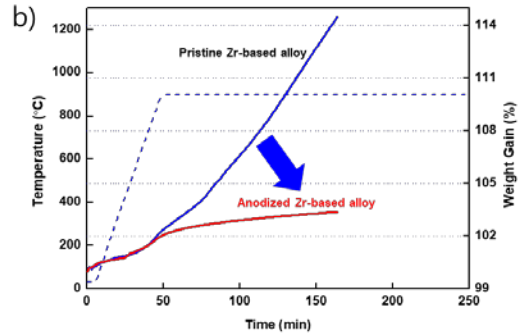
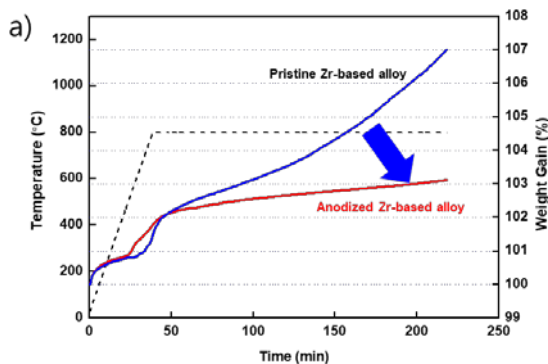


Figure 3. TGA results of pristine and anodized Zr-Nb-Sn alloy in a)800 b)900 c)1000 d)1100.

DSC test was conducted to analyze the reasons for this high resistance to oxidation. A peak that does not appear when oxidizing a pristine specimen appears when oxidizing anodized specimens. It is believed that the chemical reaction occurring at this time will contribute to the antioxidant mechanism.

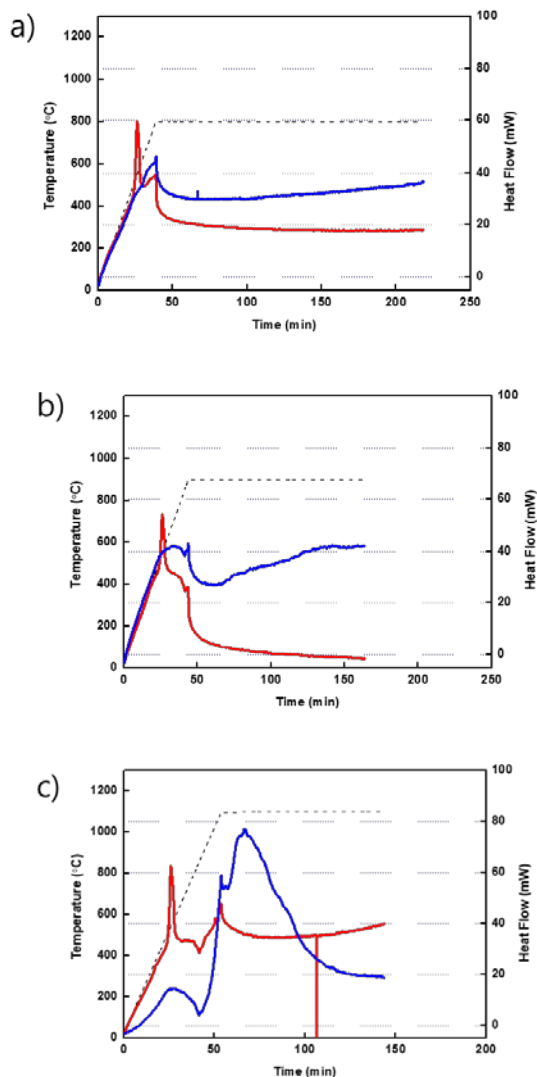


Figure 3. DSC results of pristine and anodized Zr-Nb-Sn alloy a)800 b)900 c)1100.

3. Conclusions

In previous studies, we fabricated nanoporous oxide films on Zr alloy surfaces using anodic oxidation to prevent corrosion of the Zr alloy in light water reactors and to withstand severe accidents such as a LOCA. The oxidation behaviors of Zr alloy with the anodic nanoporous oxide film under a high temperature in air and steam environments were investigated using a thermogravimetric analyzer. As a result, regardless of the anodic oxidation condition, once the nanostructured oxide film is formed, it shows excellent corrosion prevention performance. The results also showed that the oxidation kinetics of the Zr alloy with the anodic nanoporous oxide film follow a parabolic law, indicative of excellent oxidation resistance by the anodic nanoporous oxide film. This was confirmed by

photographs of the sample before and after the oxidation experiment. The large columnar grains shown in the TEM measurement results provide fewer diffusion paths and support the high oxidation resistance of the proposed structure. The tetragonal peak shown in the XRD results is contrary to other findings in the literature, in which the columnar grains are generally in the monoclinic phase, indicating that the tetragonal phase forms a very large columnar grain at a lower temperature despite the fact that it is stable at high temperatures. The results above are meaningful in that they can be expected to assist those involved in the development of ATF materials effective against severe accidents but that also maintain the advantages of zirconium alloys, which have lower manufacturing costs.

REFERENCES

- [1] M. Rahman, E. Olceroglu, and M. McCarthy, *Langmuir* 2014, 30, 11225-11234.
- [2] G. Ali, Y. J. Park, H. J. Kim and S. O. Cho, *J. Alloys Compd.*, vol. 640, p. 205-209S, Aug. 2015.
- [3] G. Ali, C. Chen, S. H. Yoo, J. M. Kum, and S. O. Cho, *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, *Appl. Surf. Sci.*, vol. 258, no. 22, pp. 8724-8731, Sep. 2012.
- [5] Y. J. Park, J. M. Ha, G. Ali, H. J. Kim, Y. Addad and S. O. Cho, *Nanoscale Res. Lett.*, vol. 10, p. 377, Sep. 2015.