Oxidation Behavior of Zirconium Alloys with Nanostructured Oxide Films in High Temperature Steam Environments

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1. Introduction

Zirconium (Zr) alloys are used as fuel cladding because of their low cross-sectional area for thermal neutrons, high mechanical strength (hardness) at high temperatures, ductility and corrosion resistance. However, serious problems related to Zr-based materials have been reported in the Fukushima nuclear accident. If the temperature of the coating material rises above 1000 ° C due to loss of coolant accident (LOCA), Zr becomes an automatic oxidation catalyst and generates a large amount of hydrogen gas from water. Therefore, much research has been conducted to prevent (or reduce) the generation of hydrogen from the Zr-based covering material in the reactor. Our team has developed anodizing technology that can form nanostructured oxides on a variety of flat metal elements such as Al, Ti and Zr alloys. Anodizing is a simple electrochemical technique requiring only a power supply and electrolyte. In this study, Zr-based alloys with nanostructured oxide layers were oxidized using thermogravimetric analysis (TGA) and compared with the original ones. This shows that the nanostructured oxide layer can prevent oxidation of the substrate metal in the vapor.

2. Experimental

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 a 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 and the amount of hydrogen generated in the cladding with the prepared nanostructured oxide film in an environment such as a

LOCA accident, our team designed the TGA device as figure 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 having the fabricated nanostructured oxide film to the high temperature steam environment, the cladding fabricated by connecting the platinum wire to the alumina crucible was supported. In order to measure the amount of hydrogen generated in the cladding with the 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 mm^3. 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. 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].

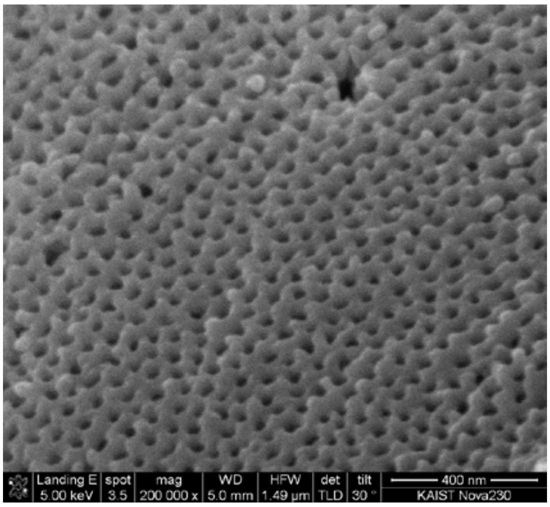

Figure 2. Images of Zr-Nb-Sn alloy with nanostructured oxide layer.

When the Zr-based alloy is oxidized at high temperatures, the oxygen atoms in the water vapor enter the sample and the mass of the sample increases. When all zirconium elements are oxidized, the theoretical maximum weight of zirconium oxide is 35% heavier.

The mass of pristine Zr-Nb-Sn alloy without any treatment reached 135% in just 15 hours (Figure 3.). This result means that all the metal was oxidized. In comparison, the mass of Zr-Nb-Sn alloy with nanostructured oxide layer increase less than 20% after 72 hours experiment.

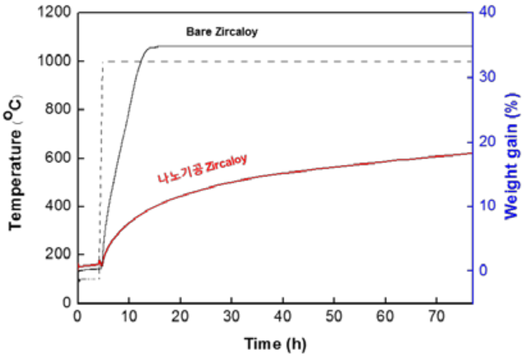

Figure 3. TGA results of anodized Zr-Nb-Sn alloy.

Figure 4.a. shows the images of the bare Zr-Nb-Sn alloy before and after TGA experiments. After experiment, the bare Zr-Nb-Sn alloy sample changed into several pieces of ceramic. Since the volume of metal normally increase during oxidation, the volumetric stress makes the sample broken.

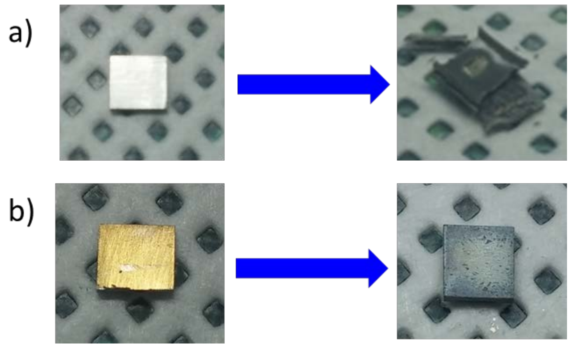

Figure 4. Images of a) Zr-Nb-Sn alloy and b) Zr-Nb-Sn alloy with nanostructured oxide layer before and after TGA experiment.

In contrast, the images of the Zr-Nb-Sn alloy with nanostructured oxide layer before and after TGA experiments described in Figure 4.b. confirm that the sample was only partially oxidized and still maintain its rectangular shape. As a result, nanostructured oxide layer which prepared by our research team can successfully prevent oxidation of substrate metal.

4. Conclusions

Uniform oxide layer with nanoporous structures have been fabricated on the surface of Zr-Nb-Sn alloy. Oxidation behavior of the pristine Zr-Nb-Sn alloy and the Zr-Nb-Sn alloy with nanostructured oxide layer evaluated by measuring weight gain (TGA). In comparison with the pristine Zr-Nb-Sn alloy, weight gain of the Zr-Nb-Sn alloy with nanostructured oxide layer is lower than 20% even for 72 hours oxidation in steam.

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.