Transactions of the Korean Nuclear Society Spring Meeting
Jeju, Korea, May 12-13, 2016

High Temperature Oxidation Behavior of Zirconium Alloy with Nanostructured Oxide Layer in Air Environment

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

Zirconium (Zr) alloys are being used as a fuel cladding materials because of their low absorption cross-section for thermal neutrons, high mechanical strength (hardness) at high temperature, ductility and corrosion resistance. However, a serious problem related to Zr-based materials has been reported in the Fukushima nuclear accident. If the temperature of the cladding materials increases above 1000℃, which can be caused by a loss of coolant accident (LOCA), Zr becomes an auto-oxidation catalyst and hence produces a huge amount of hydrogen gas from water. Therefore, many investigations are being carried out to prevent (or reduce) the hydrogen production from Zr-based cladding materials in the nuclear reactors. Our team has developed an anodization technique by which nanostructured oxide can be formed on various flat metallic elements such as Al, Ti, and Zr-based alloy. Anodization is a simple electrochemical technique and requires only a power supply and an electrolyte. In this study, Zr-based alloys with nanostructured oxide layers were oxidized by using Thermogravimetry analysis (TGA) and compared with the pristine one. It reveals that the nanostructured oxide layer can prevent oxidation of substrate metal in air.

2. Experimental

2.1. Specimen Preparation

For anodization experiments, Zr-Nb-Sn 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, ethylene glycol (95% purity, Junsei)-based containing 0.3 wt% ammonium fluoride (Sigma-Aldrich) was used and 1% vol. of DI water additions.

2.2. Experimental Procedures

The anodization was performed in a two-electrode electrochemical cell with a platinum sheet as counter electrode and the Zr-Nb-Sn alloy sheet as the working electrode. All the experiment were carried out with DC power source using 90V at a room temperature. After the experiment, the samples were rinsed with DI water, and then dried in air.

2.3. Analysis

The structures of the anodized oxide layer were characterized by field-emission scanning electron microscopy (FE-SEM, Nova230, FEI, USA). TGA (TG 209 F3, NETZSCH) experiments were performed to confirm whether fabricated nanostructured oxide layer can or cannot protect the metal substrate from oxidation.

Figure 1. Thermogravimetry analyzer (TG 209 F3, NETZSCH).

TGA analysis was performed according to the temperature profile as shown in Figure 2. Samples were loaded at room temperature and heated up to 1000℃ at the heating rate of 20K/min. The temperature (1000℃) was maintained 3 - 12 hours. Air in the furnace circulates at the rate of 30ml/min.
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.

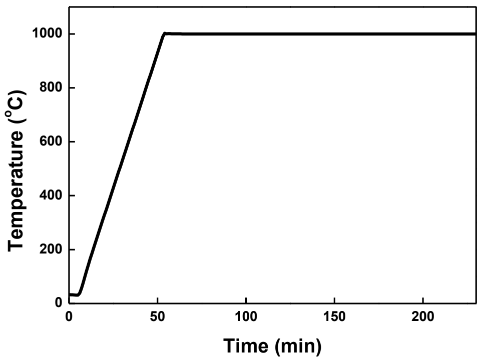

Figure 2. Temperature profile.

3. Results and Discussion

The anodized surface is quite clean and the nanostructure is almost uniform and hexagonal as shown in Figure 3. 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[1].

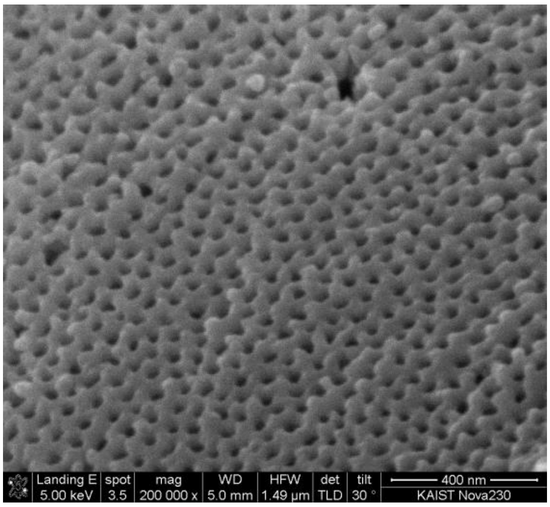

Figure 3. Images of Zr-Nb-Sn alloy with nanostructured oxide layer.

When Zr-based alloy oxidized at high temperature, oxygen atoms in air enter the sample and the mass of the sample increase. If all the zirconium elements oxidized, theoretical maximum weight of oxidized zirconium is 35% heavier then pristine zirconium.

The mass of pristine Zr-Nb-Sn alloy without any treatment reached 135% in just 3 hours (Figure 4.). This result means that all the metal was oxidized. In comparison, the mass of Zr-Nb-Sn alloy with nanostructured oxide layer increase only 5% after experiment.

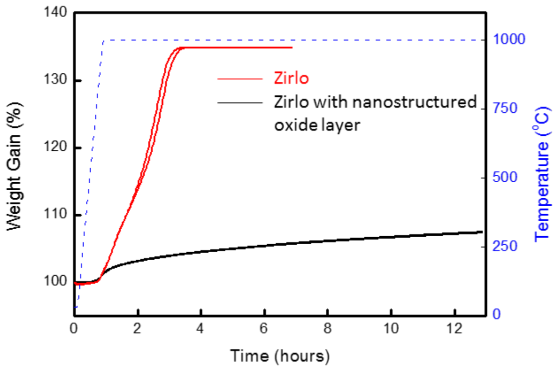

Figure 4. TGA results of anodized Zr-Nb-Sn alloy.

Figure 5.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.

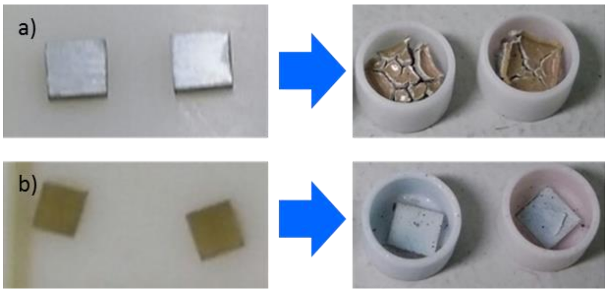

Figure 5. Images of a) Zr-Nb-Sn alloy and b) Zr-Nb-Sn alloy with nanostructured oxide layer before and after TGA experiment.

In contrast, the images of the Zr-Nb-Sn alloy with nanostructured oxide layer before and after TGA experiments described in Figure 5.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 10% even for 12 hours oxidation in air.

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.