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Microstructural Analysis of Zirconium Alloy with Anodic Nanoporous Oxide Film after Oxidation under a High-Temperature Air/Steam Flow

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1. Introduction

With zirconium alloys, which are widely used in the field of nuclear engineering, the explosive generation of hydrogen, a by-product of the reaction between zirconium and steam, has been indicated as the cause of the accident at the Fukushima Nuclear Power Plant in 2011. Therefore, the goal of much research on accident-tolerant fuel-cladding materials (ATFs) has been to increase the safety of zirconium alloy cladding materials in reactors. The main research flow has been an attempt completely to replace zirconium alloy with ceramic materials using SiC or other metal materials such as Mo and FeCrAl. These studies provide improved corrosion resistance instead of abandoning the powerful advantages of zirconium. The authors proposed an anodization method with which to fabricate a nanostructured zirconium oxide film on the surface of the alloy to improve the corrosion resistance at a lower cost. In the present paper, after the anodization of Zr-Nb-Sn alloys to produce nanostructured oxide films, the corrosion resistance of specimens is evaluated using a thermogravimetric analyzer in high-temperature air and steam environments in comparison with pristine Zr-Nb-Sn alloys. As a result, the nanostructured oxide film formed by anodization shows excellent corrosion protection.

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 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 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 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].

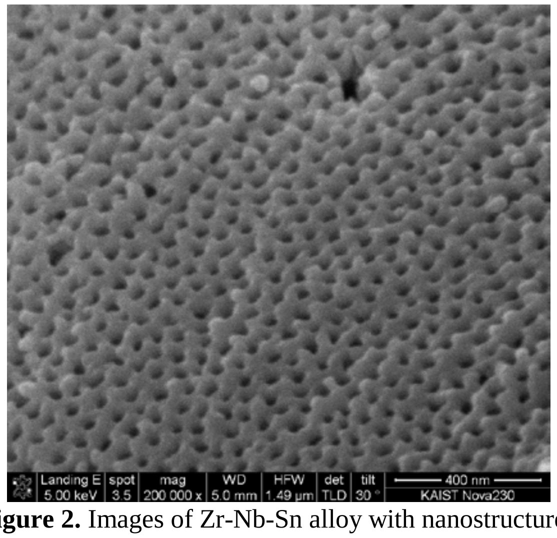

Figure 2. Images of Zr-Nb-Sn alloy with nanostructured oxide layer.

When the Zr-based alloy is oxidized at high temperatures, the oxygen atoms in the water vapor or air enter the sample and the mass of the sample increases. In the graph of the weight gain trend of the alloys, the relationship between the weight gain and the exposure time can be generalized by introducing a generalized rate constant. The kinetics of the oxidation of Zr alloys can be generalized by the following equation,

$$W^n_{oxygen\ absorbed} = K_n t, \qquad (4)$$

where K_n is the oxidation rate constant ($(mg/cm^2)^n/s$), n is the oxidation rate exponent and t is the oxidation time (s).

When the oxidation rate exponent exceeds 1, it indicates that the generated oxide film is thickened and prevents further oxidation. Generally, when it is 2 or more, it is regarded as a protective oxide film. Figure 3 shows the results of the nonlinear fitting of the experimental results under the air and steam oxidation experimental conditions described above. When fitting the results of the pristine Zr alloy, only the region before the transition of the oxidation rate occurred was included. When pristine Zr alloys are oxidized between 800 and 1100 degrees Celsius, linear kinetics can be expected due to breakaway oxidation. As shown in Figures 3a and 3c, the oxidation rate exponent is close to 1, allowing the confirmation that the condition of linear kinetics is realized. However, the oxidation reaction between the Zr alloy and the anodic nanoporous oxide film coincides with the parabolic rate law (Figures 3b and 3d). For the Zr alloy with the anodic nanoporous oxide film, the corresponding oxidation rate exponents showed a value which exceeded 2 regardless of the atmosphere in air or steam at a temperature of 1000 degrees, meaning that the Zr alloy prepared with the anodic nanoporous oxide film has excellent oxidation resistance compared to the pristine Zr alloy and its value of approximately 1, consistent with the experimental results.

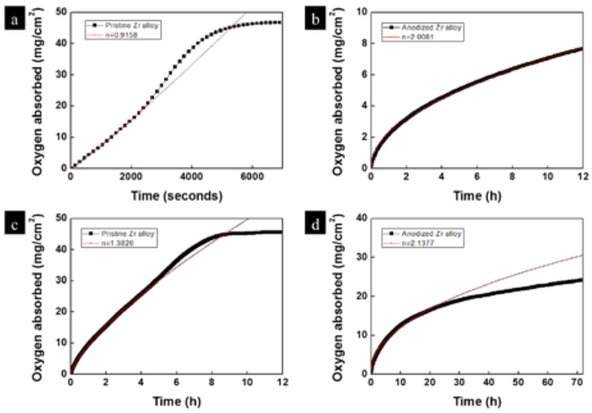

Figure 3. TGA results and nonlinear fitting of pristine and anodized Zr-Nb-Sn alloy.

In the results of our TEM analysis, very large columnar grains were found in the oxides formed during oxidation experiments on the Zr alloys with the nanostructured oxide films. When observing the crystal grains in dark-field images, the areas which appear bright have identical crystal orientations and are therefore likely to be single-crystal grains. The results of these measurements are shown in Figure 4 and 5. An analysis of the diffraction patterns over a wide area of the crystal grains (Figure 4b) also reveals a single diffraction pattern, which is also conducive to the conclusion that it is also a single-crystal grain. The grain size of the crystals in our experimental results is on the order of a few micrometers, which is much larger than the tens of nanometers reported in the literature. This will lead to a shorter diffusion path and will provide more effective corrosion protection. This prediction is also highly consistent with the experimental results.

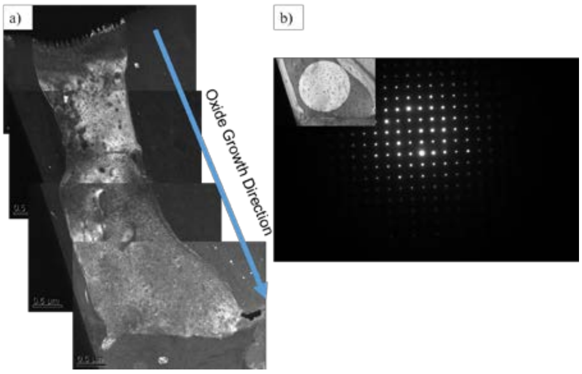

Figure 4. a) Dark-field transmission electron microscopy image showing the oxide structure of Zr-Nb-Sn alloy with anodic nanoporous oxide film after an oxidation experiment in air at 1000℃ and b) electron diffraction pattern identifying a single grain

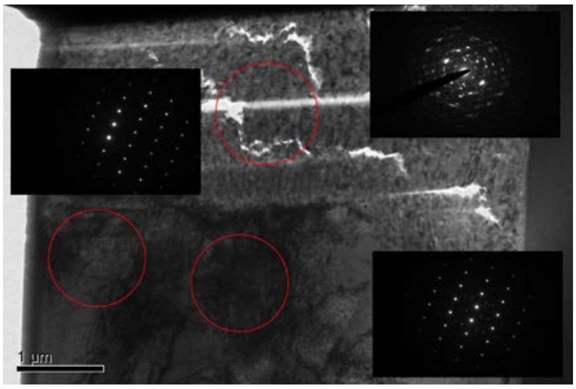

Figure 5. Transmission electron microscopy image showing the oxide structure of pristine Zr-Nb-Sn alloy after an oxidation experiment in air at 1000℃

4. 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.

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