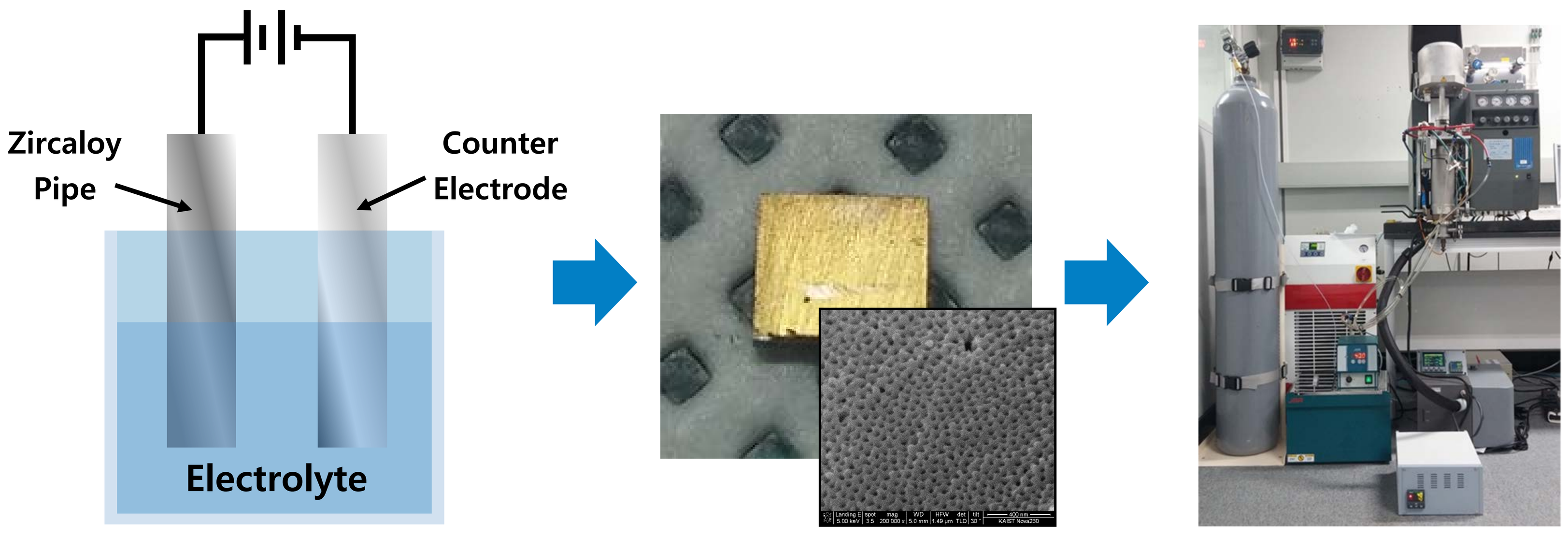
Oxidation Behavior of Zirconium Alloys with Nanostructured Oxide Films in High Temperature Steam Environments

Yang Jeong Park, Jung Woo Kim, Sung Oh Cho
Department of Nuclear and Quantum Engineering, KAIST
yjeong3506@kaist.ac.kr

Abstract

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.

Experiment



Scheme 1. Anodization system, Zr-Nb-Sn alloy with nanostructured oxide layer and TG Analyzer

Result

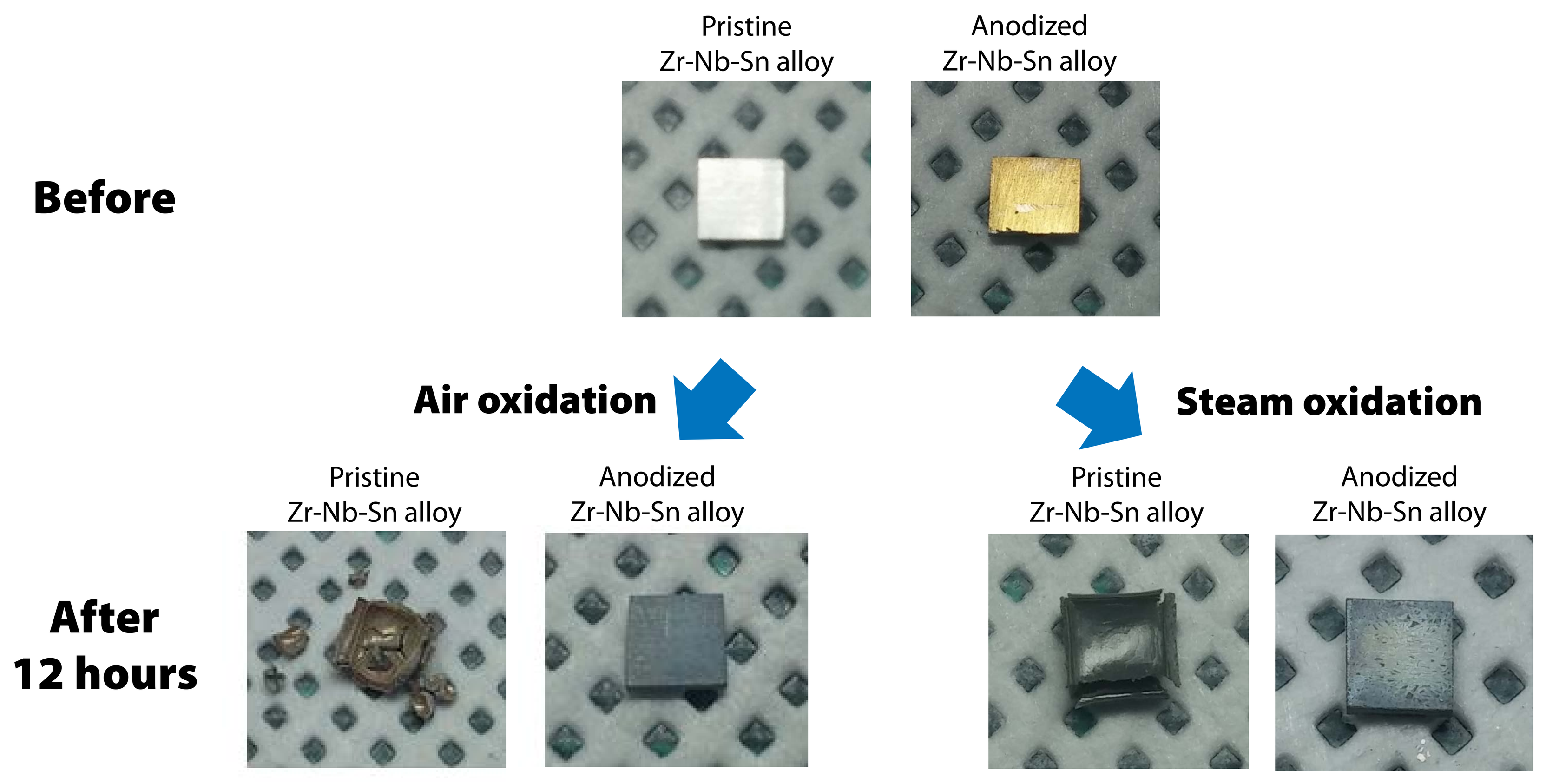


Figure 1. Pristine and Anodized Zr-Nb-Sn alloy before and after oxidation experiment

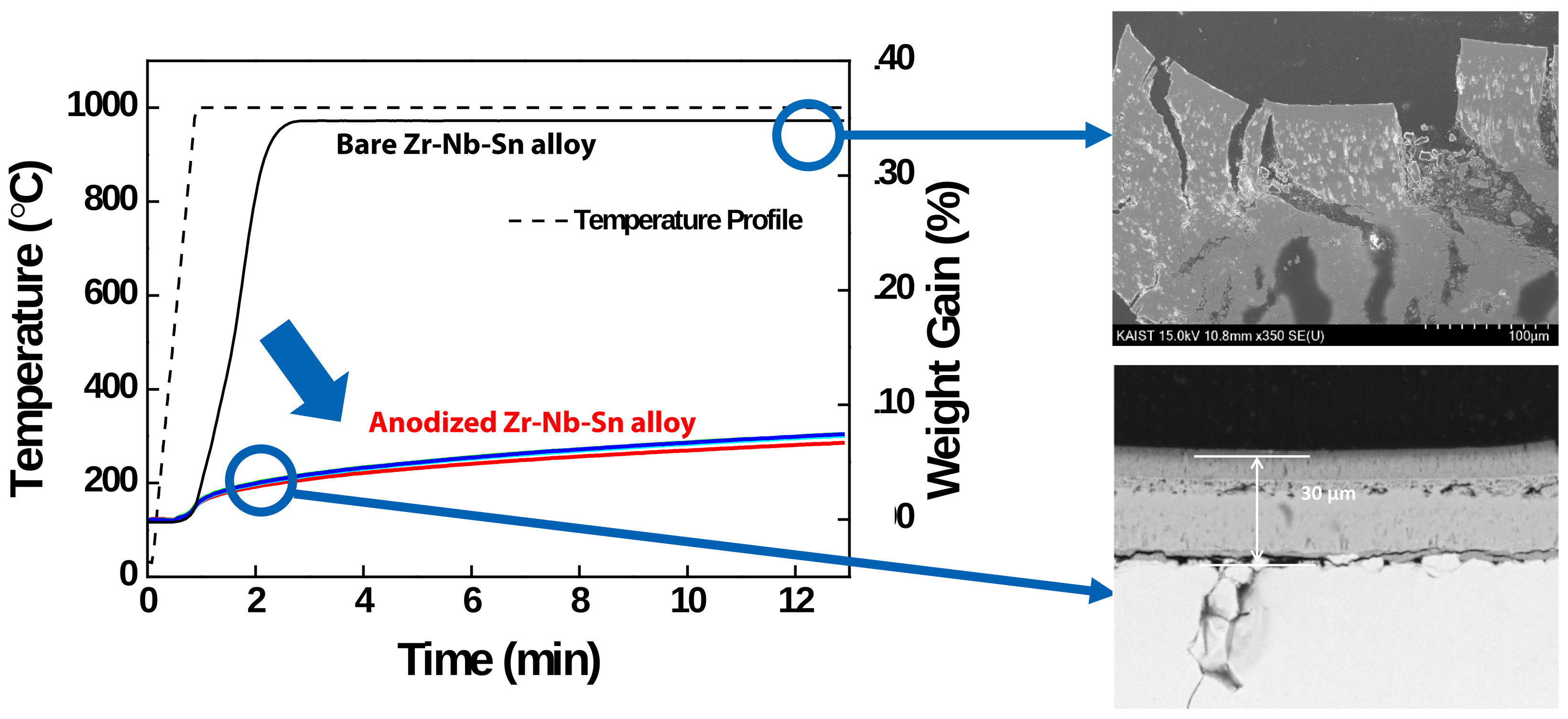


Figure 2. TGA results of pristine and anodized Zr-Nb-Sn alloy and FESEM image of the sample after oxidation experiment in air environment

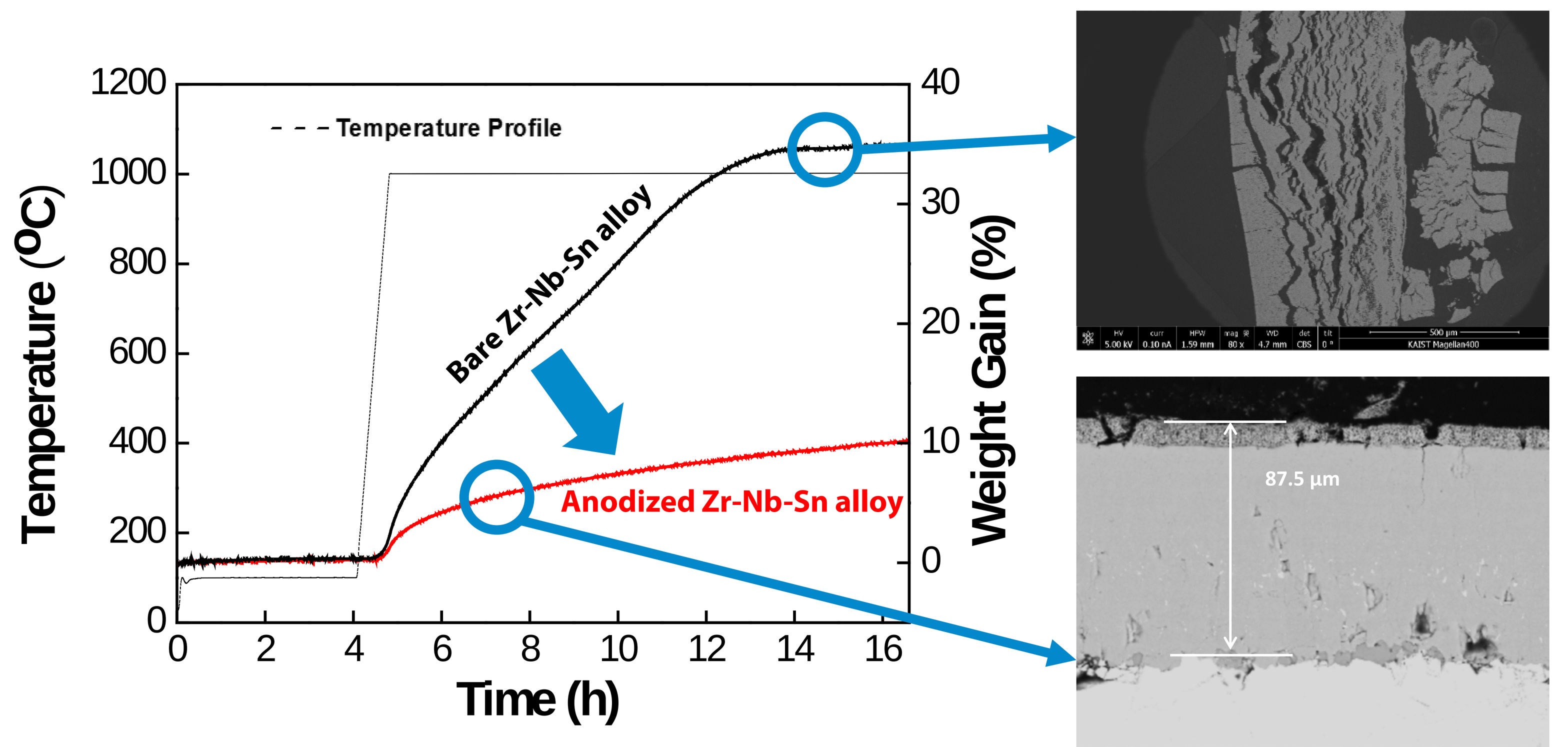


Figure 3. TGA results of pristine and anodized Zr-Nb-Sn alloy and FESEM image of the sample after oxidation experiment in steam environment

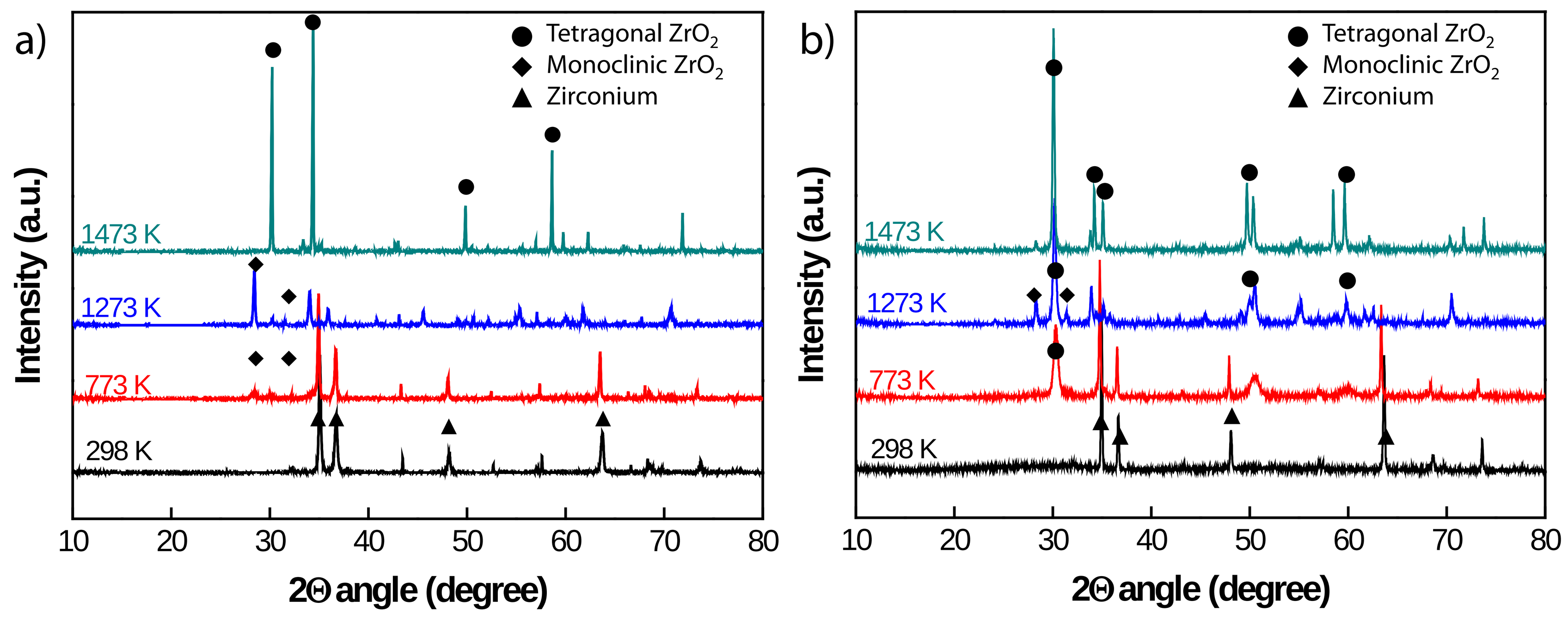
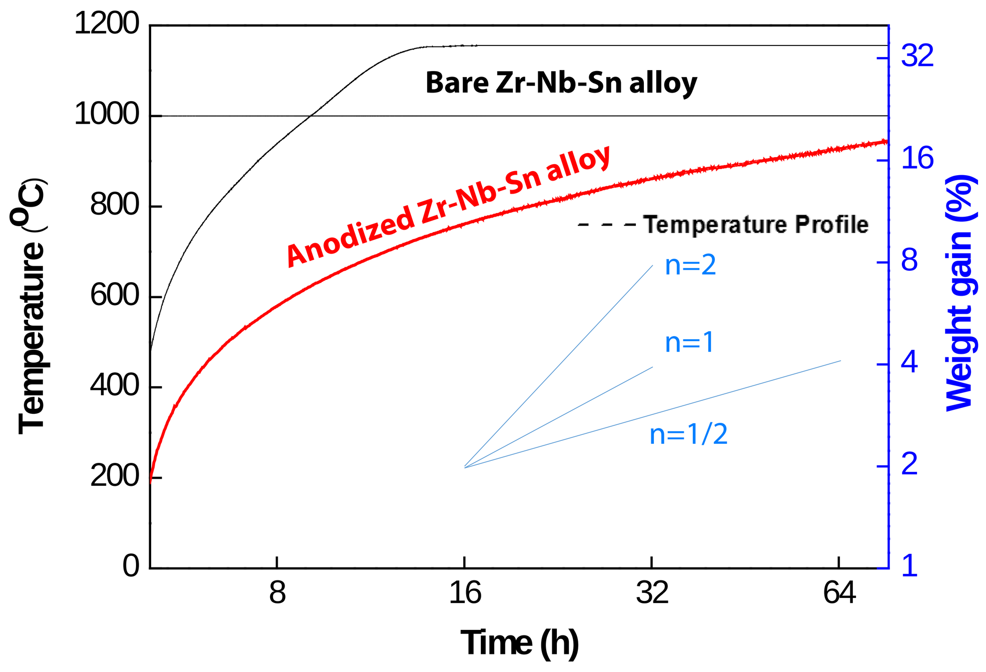


Figure 4. XRD patterns of a) pristine and b) anodized Zr-Nb-Sn alloy after oxidation experiment in air



$$\frac{\Delta m}{S} = k_m(T)t^n$$

$$log\frac{\Delta m}{S} = \log(k_m(T)) + nlogt$$

$n \geq 1$: Non-protective

$n < 1$: Protective

Δm : Weight gain, T : Reaction temperature, S : Surface area, t : Reaction time, k_m: Oxidation rate constant, n : Oxidation rate exponent

Figure 5. Log-scale TGA results of pristine and anodized Zr-Nb-Sn alloy

Conclusion

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.

Reference

[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.