Proton Irradiation Induced Mechanical Damage to Nano-Porous Oxide Layer Fabricated by Anodization Technique

Jung Woo Kim [a*], Yang Jeong Park [a] and Sung Oh Cho [a]
[a] *Department of Nuclear and Quantum Engineering, KAIST, Daejeon306701, Republic of Korea*
* *wjddn3703@kaist.ac.kr*

1. Introduction

In the nuclear reactor, zirconium alloys are selected as a material for nuclear fuel cladding because of its properties which are not only excellent in mechanical properties, but also have a small thermal neutron absorption cross section. However, since the Fukushima accident (Japan 2011), the oxidation resistance of nuclear fuel cladding in high temperature accident environment has recently been emphasized. Anodization technique can be suggested as a method to increase oxidation resistance in high temperature accident environment. The fabricated surface has a porous structure, which can play a role in mitigating the high pilling-bedworth ratio of zirconium. The anodization technique is very simple, cheap, and mass-producible.

However, irradiation damage is inevitable under normal operating conditions. In terms of the neutron irradiation damage observation, many studies have been tried, but its irradiation procedure demands a lot of time, energy, and cost. So, many studies reproduce the effect of the irradiation damage using proton irradiation instead of neutron. As widely known, oxidation resistance and mechanical properties degrade when subjected to irradiation damage[1],[2]. Thus, the irradiation resistance of the fabricated oxide layer should be verified for practical application. The method of fabricating pillars using Focused Ion Beam made it possible to measure mechanical properties in microscale.

In this study, the mechanical properties of the oxide layer fabricated by anodization technique before and after proton irradiation will be compared.

2. Methods and Results

2.1 Methods

2.1.1 Sample preparation

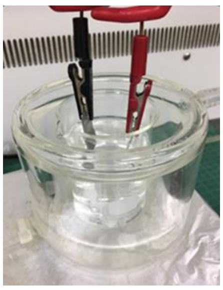

Fig. 1. Anodization system

Zircaloy specimens were cleaned by ultrasonic cleaning for 10 min, 10 min and 20 min in Acetone, Ethanol and D.I water respectively after mechanical polishing. Figure 1 shows the anodization system. Anodization was performed using a Zircaloy specimen as the working electrode and a Pt sheet as the counter electrode. The electrolyte used for the anodization experiment was prepared from ethylene glycol based with NH_4F and H_2O solute. The thickness of the nanoporous structure layer was manipulated by an applied voltage from 30 to 150 V.

2.1.2 Proton irradiation

Anodized specimens were perpendicularly irradiated on 200 keV proton with $1x10^{18}$ H^+/cm^2 fluence condition at the Advanced Radiation Technology Institute. Proton dpa profile was calculated by Stopping and Range of Ions in Matter (SRIM) code.

2.1.3 Pillar fabrication and compassion test

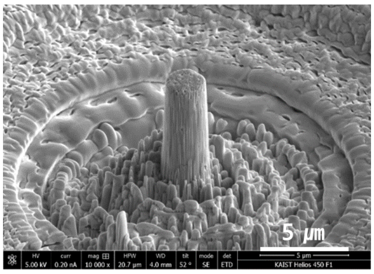

Fig. 2. Micro pillar for compression test

Micro-pillars with diameters of 2 μm and aspect ratio of 3 were fabricated utilizing Focused Ion Beam(Helios 450 F1) using a Ga+ beam at 30 kV. Final milling currents was 0.79 nA.

Each of the unirradiated and irradiated pillars was subjected to a compression test using a Pico-Indenter (PI-87 Hysitron) at a strain rate of 1×10^{-3} s^{-1}.

2.2 Results

2.2.1 Anodization

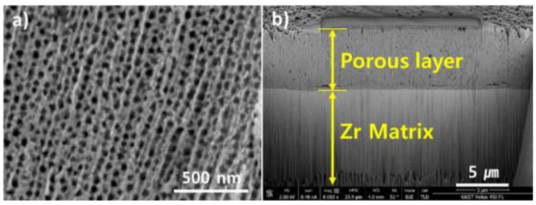

Fig. 3. (a) Top surface SEM and (b) Cross-Sectional BSE images of nano-porous oxide layer fabricated by anodization

Figure 3 shows the surface and cross-sectional images produced by applying anodization. A uniform and well-ordered pore with an average diameter of 50 nm was produced (Fig. 3a). The Zr matrix and the fabricated nanostructured oxide layer are distinguished by contrast (Fig. 3b).

2.2.2 Induced damage calculation

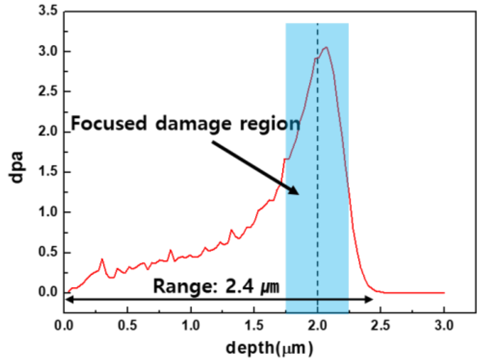

Fig. 4. SRIM code calculation of proton beam

From the fabricated oxide layer surface, the range and damage of the proton irradiation were calculated in Fig. 4. The dpa profile implies significant irradiation damage occurs at a depth of 2 micrometers.

2.2.3 Pillar compression test

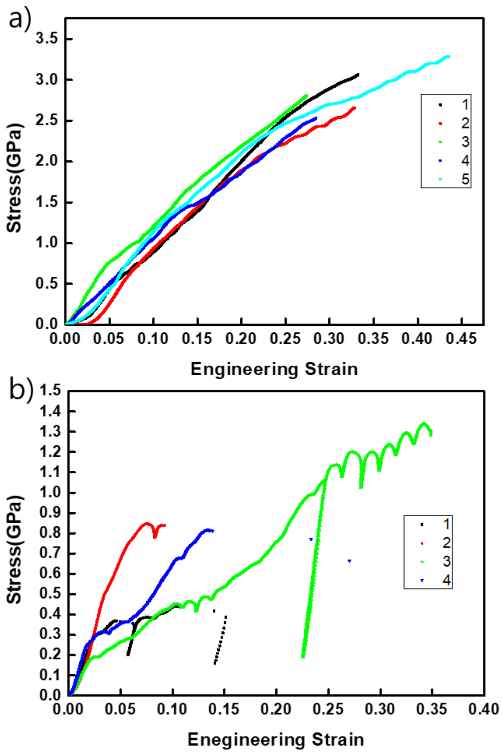

Fig. 5. Compression test results of unirradiated (a) and irradiated pillars (b)

As a result of the compression test of the unirradiated pillar, the fracture stress and strain were measured about 3 GPa and strain 0.3 respectively (Fig. 5a). where the stress is retained but the strain increases area exists intermittently apart from strain/stress slope. This is because compressed pillar has discontinuous porous structure not monolithic. This behavior is believed to be caused by the breakage of individual pores before stress is applied to the entire pillar. Fig. 5b shows results of the compression test of the irradiated pillar. There was no reproducibility of mechanical behavior for each pillar. While there is pillar with strain values similar to pillar before proton irradiation, such as pillar 3, the pillar 1 demonstrate complete mechanical degradation of material. Fracture stress was commonly decreased at least twice times compared in the case of unirradiated pillar. The presence of focused damage region induced proton irradiation provided a prefer location for stress concentration when applying compressive stress.

3. Conclusions

Mechanical properties of nano-porous oxide layer fabricated by anodization technique to zirconium alloy were investigated on micro scale before and after proton irradiation condition. In unirradiated case, the fracture stress and strain were measured about 3 GPa and 0.3 respectively. Nano-porous ceramic structure played a major role in producing high strain values. On the other hand, in the case of the irradiated pillar, the presence of the focused damage region confirmed by the dpa calculation induced a decrease in the fracture stress due to the stress concentration to the damaged area.

REFERENCES

[1] Peng Wang and Gary S. Was, Oxidation of Zircaloy-4 during in situ proton irradiation and corrosion in PWR primary water, Journal of Materials Research 30, 9, (2015) pp 1335-1348.

[2] P. Mukherjee *et al.* , The study of microstructural defects and mechanical properties in proton-irradiated Zr–1.0%Nb–1.0%Sn–0.1%Fe, Journal of Nuclear Materials 297 (2001) 341-344.