

Robust Canisters with a Nanoporous Oxide Layer for Spent Nuclear Fuel Storage

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1. Introduction

As wet storage facilities for spent nuclear fuel (SNF) reach saturation, efforts are being made to switch to dry storage. SNF canisters in dry storage are mainly made of austenitic stainless steel, but since most nuclear power plants are located on the shore, they are likely to be exposed to saline environments. It is well known that austenitic stainless steel is very susceptible to chloride-induced stress corrosion cracking (CISCC) [1,2]. Various methods, such as coating and alloying, are being considered to protect stainless steel from CISCC, but there is a limit to the use of another materials.

In this study, a protective nanoporous oxide layer is prepared on the surface of stainless steel using an electrochemical method, anodization. The oxide layer fabricated *via* anodization is self-organized rather than adding new materials. In addition, due to the effect of nanopores present in the oxide layer, it has different properties from general barrier-type oxide layers because it can alleviate the stress that occurs while the oxide layer is formed. Accordingly, the mechanical properties of the fabricated nanoporous oxide layer are evaluated to demonstrate stability.

2. Materials and Methods

2.1 Materials

A type 304 stainless steel sheet (1 mm in thickness) was purchased from Goodfellow, UK and cut into 15 mm × 15 mm. Ethylene glycol was received from Junsei Chemical, Japan. Reagent-grade of ammonium fluoride (NH₄F) was procured from Sigma-Aldrich, USA.

2.2 Anodization

Prior to anodization, all stainless steel specimens were sonicated with ethanol and deionized (DI) water for 5 min each to remove any type of impurities from the surface. As illustrated in Fig. 1, anodization was performed at room temperature with the stainless steel sheet (one side insulated with tape) as an anode and a platinum sheet as a cathode. The two electrodes were dipped together in an ethylene glycol-based electrolyte solution containing NH₄F (0.1 wt.%) and water (0.1 wt.%) and separated by a distance of 20 mm. The anodization voltage was kept constant at 60 V. After anodization, the specimens were rinsed with ethanol carefully and dried in a 50°C oven.

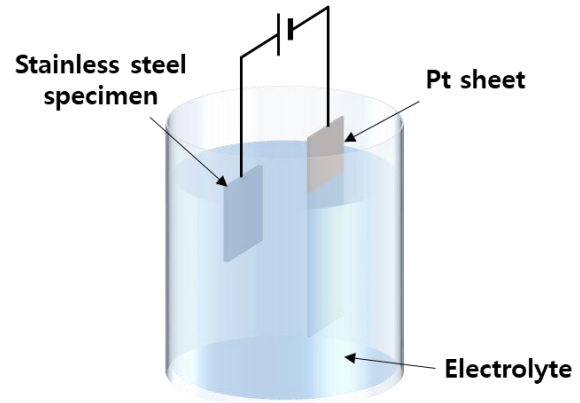


Fig. 1. A schematic view of anodization system for fabricating nanoporous oxide layer on the surface of a stainless steel sheet.

2.3 Characterizations

The surface morphology of anodized stainless steel was investigated with a field emission scanning electron microscope (FESEM, Magellan400, FEI, USA). Energy-dispersive X-ray spectroscopy (EDX) equipped with the FESEM was utilized to analyze the distribution of elements on the surface. The crystallographic structure was examined with an X-ray diffractometer (XRD, SmartLab, RIGAKU, Japan) using Cu K α radiation (wavelength 1.5406 Å) at 40 kV. VDI 3198 test was conducted to measure the adhesion between the oxide layer and substrate using a conical Rockwell C indenter (0.2 mm in radius and 120° of angle), which applies a load of 1,470 N to the specimen. The hardness of the anodized stainless steel was evaluated by Vickers hardness measurement using a load of 200 gf on a tip having a size of 50 μ m in width and length, respectively.

3. Results and Discussion

3.1 Fabrication of Nanoporous Oxide Layer

During the anodization, the surface of the stainless steel was observed to turn yellow. FESEM images in Fig. 2 show the morphology of the pristine and anodized surfaces. There are many pores on the surface when the stainless steel is anodized. The average pore size is approximately 50 nm and the pores are distributed quite uniformly. The elements present of the anodized surface of Fig. 2b are provided as given in Fig. 2c. The oxygen peak is identified, and it is expected that the surface is actually oxidized. Further investigation was performed

to examine the crystal structure of the nanoporous layer. For both pristine and anodized stainless steel in Fig. 3, the diffraction peaks matched the austenite (JCPDS: No. 33-0397) and δ -ferrite (JCPDS: No. 01-087-0722). The anodized one has no significant difference in the crystal structure with the pristine specimen, but it was reported that amorphous iron oxide is contained according to the oxygen observation in the EDX spectrum [3]. Therefore, we confirmed that an amorphous nanoporous oxide layer was formed on the stainless steel surface.

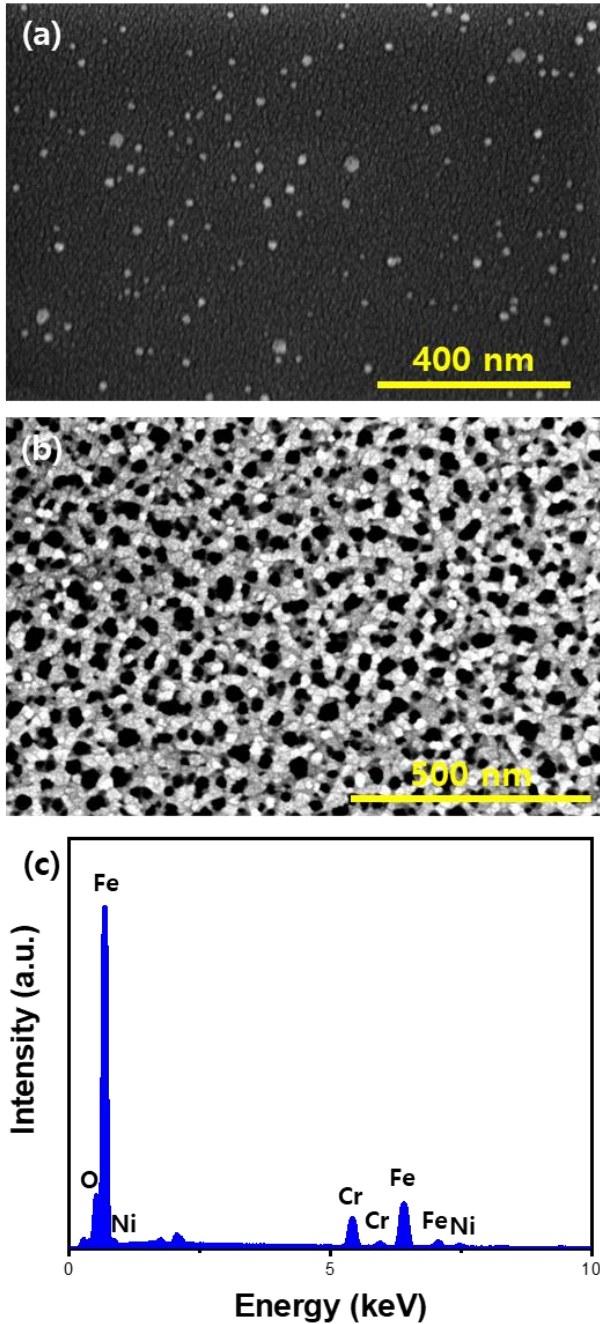


Fig. 2. FESEM images of (a) the pristine stainless steel and (b) anodized stainless steel surface, and (c) EDX spectrum of the anodized one.

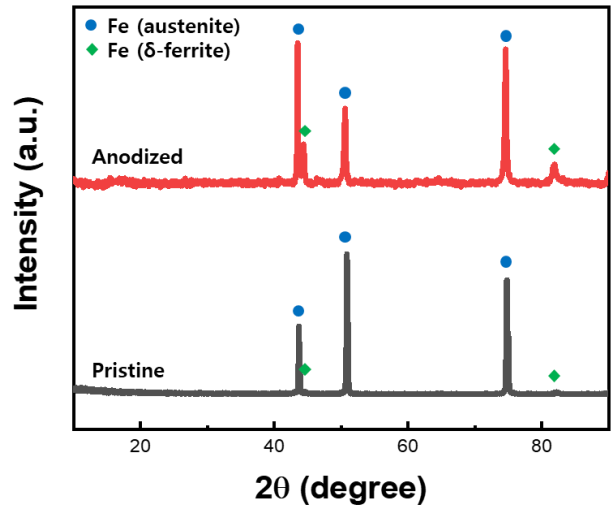


Fig. 3. XRD patterns of the pristine and anodized stainless steel.

3.2 Mechanical Properties of Nanoporous Oxide Layer

It was investigated whether the nanoporous oxide layer formed on the surface of stainless steel had sufficient adhesion to the substrate. Fig. 4 shows the anodized stainless steel surface after the VDI 3198 test. A load of 1,470 N caused damage to the surface and several cracks were observed. According to the classification of the degree of adhesion of the Daimler-Benz method [4], such a form corresponds to the level of HF 2. For HF 2, it is considered that the oxide layer has excellent adhesion.

The oxide layer is a kind of ceramic material, and in general, ceramics show high hardness. The hardness of the anodized stainless steel was measured to be 159.98 HV, which is almost the same as that of typical stainless steel (~158 HV). Although the nanoporous oxide layer formed on the surface after anodization is ceramic, it can be considered to have a lower hardness than general ceramic materials because it is in an amorphous phase as shown in the XRD result of Fig. 3. Fortunately, it is expected that there will be no significant limitations in terms of mechanical stability due to the hardness comparable to that of the substrate. These results demonstrate that stainless steel with a nanoporous oxide layer remains robust.

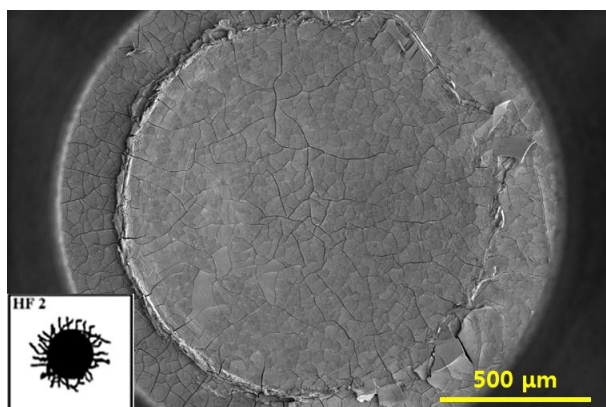


Fig. 4. FESEM image of the anodized stainless steel surface after VDI 3198 test (inset: An example of HF 2 mode from Daimler-Benz method [4]).

4. Conclusions

A facile approach has been proposed to protect austenitic stainless steel from CISCC as a material for canisters for the storage of SNFs. The nanoporous oxide layer on the surface of stainless steel produced by anodization showed much better adhesion to the substrate than the typical coating layer. Despite the low hardness due to the amorphous oxide layer, the anodized stainless steel is mechanically stable and can avoid damage to the substrate. Additionally, it is expected that the nanopores on the surface will relieve stress acting in the material and block aggressive substances such as chlorine to prevent SCC. Therefore, the amorphous nanoporous oxide layer fabricated through anodization has the potential to ensure the integrity of the SNP canister.

Acknowledgement

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