Formation of Nanoporous Oxide Layer for SCC Protection on TIG Welded Type 304 Stainless Steel Used in Nuclear Spent Fuel Dry Storage Container

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1. Introduction

SCC, which refers to Stress Corrosion Cracking, occurs when 3 conditions simultaneously action. Corrosive environment, susceptible material, and stress all these 3 factors have to be applied at the same time. That also implies the fact that it is possible to prevent SCC by just eliminating one of those factors.

Nuclear spent fuel dry storage systems are meant to be located near the Nuclear Power Plants which is placed near the seaside. That geographical feature provides a significant environment for corrosion to occur due to excessive Chlorides in the air. Besides, with chloride rich environment, material used for dry storage container, which is Stainless Steel for most , becomes highly susceptible. Plus, weld process is conducted with container which remains the residual stress to the material. From those factors SCC occurs on the weld zone of the Stainless Steel.

To prevent those SCCs, fabricating nanoporous oxide layer on the weld part of Stainless Steel is proposed. Conventionally, thermal sprayed aluminum using high sintering temperature or high temperature heat treatment was used for SCC prevention. Other than that, proposed method uses facile anodization method which is held in relatively low temperature and one step process. In this study, optimization of fabricating highly ordered nanoporous structure on the STS surface and characterization of those structures are conducted. After that, by using electrochemical test, corrosion resistance of as-anodized STS sample was measured to verify its effectiveness.

2. Methods and Results

There are mainly 2 steps for experimental section. First one is to optimize the condition for fabricating highly ordered nanoporous oxide layer on the weld STS substrate, and second one is to verify its function of improving corrosion resistance by electrochemical test. For analysis of test results, FESEM, Potentiodynamic Polarization test equipment was used as characterization tool.

2.1 Specimen Settings

Specimens of Type 304 stainless steel that is composed of 17-20wt% Cr, 8-11wt% Ni, < 2wt% Mn and the remaining Fe were used for the anodization. To reenact the real welding process, after welding, electropolishing was conducted. As you can see from **Fig.1**, specific form of specimen was custom ordered. That stick part was designed to grip the specimen so that only circular part, which is weld zone and heat affected zone, can be immersed to the electrolyte totally. Stick part is designed with 0.2 mm thickness, so it can be cut off easily. Before anodization specimen was sonicated with Acetone for 10 min. , rinsed with DI water, and stored in 60 ℃ oven.

Fig.1 custom ordered specimen

2.2 Experimental conditions

Before the anodization, cooling bath was set to temperature 278K. Target material was custom ordered 304 type STS weld part above. Platinum sheet was used as counter electrode. Electrolyte was composed of 0.1 M H_2O + 0.1 M NH_4F with ethylene glycol balanced. 80 V was applied to the electrodes for 3600 sec. with constant voltage. All the process can be expressed with schematic diagram as shown in **Fig.2**. After anodizing, specimen was rinsed with Ethanol and dry stored in 60 ℃ oven.

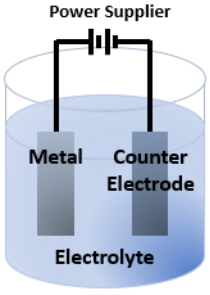


Fig.2 Anodization system

Fig.3 Potentiodynamic polarization test

For electrochemical test conducting to prove its corrosion resistance, Potentiodynamic Polarization test was used as shown in **Fig.3**. By applying voltage through three different electrodes, working / counter / reference electrodes, it is possible to evaluate tendency of corrosion. Anodized sample was used as working electrode, and platinum film was used for counter electrode. Reference electrode was saturated calomel electrode. Open Circuit Potential was achieved before the test, and potential range was -250 ~ 250 mV. For last, artificial seawater was used for electrolyte. **Table1** shows the chemical composition of seawater.

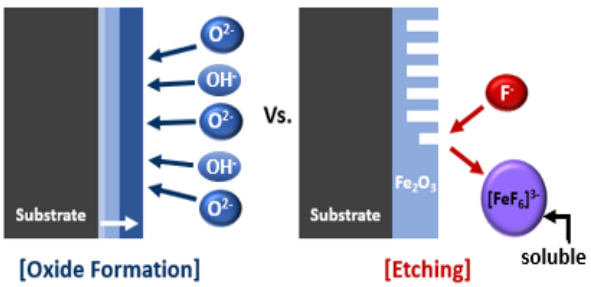
Element	**Composition (g/L)**
Cl	19.00
Na	9.72
Mg	1.30
S	0.81
Ca	0.40
K	0.35
Sr	0.007
B	0.004

Table 1 Chemical composition of artificial seawater

2.3 Nanopores formation on weld stainless steel

After welding, substrate surface is divided into mainly two regions. One is Fusion zone, also called as weld zone, and the other one is Heat Affected Zone. HAZ is composed of sensitized region and grain coarsening region. Due to heat input while welding, grains of HAZ are coarsened, and it becomes relatively more coarser near the fusion boundary. Also from the study of correlation between time to initiate the SCC and applied stress, it is clear that fusion zone and HAZ are less resistant to SCC. Simply saying, by welding stainless steel, no other phase change occurs except grain coarsening at the HAZ.

Stainless steel is mostly composed of Iron. When Iron forms the oxide layer on the surface, its volume expansion stress cracks the layer and flakes off. But with nanopores formed with Iron oxide layer can relieve the volume expansion stress resulting in protective layer. Nanopores formation process is explained with two competing reactions, oxide formation and etching.



$$Fe + H_2O \rightarrow FeO + H_2 \quad (1)$$

$$2Fe + 3H_2O \rightarrow Fe_2O_3 + H_2 \quad (2)$$

$$Fe_2O_3 + 12F^- + 6H^+ \rightarrow 2[FeF_6]^{3-} + 3H_2O \quad (3)$$

Oxygen ions from water contents forms metal oxide. (1,2) On the other side, fluorine ions form electrolyte forms soluble compounds resulting in etching of metal oxide. (3)

To fabricate perfectly ordered nanoporous oxide layer, several factors have to be considered. Considerable factors are electrolyte composition, anodizing duration, applied voltage or current, and cooling temperature. In order to optimize the condition, factors were examined one by one. Firstly, electrolyte composition was tested as following **Fig.4**.

(a) 0.2 M H_2O + 0.1 M NH_4F in E.G.

(b) 0.1 M H_2O + 0.2 M NH_4F in E.G.

(c) 0.1 M H_2O + 0.1 M NH_4F in E.G.

Fig.4 Anodized sample in 3 different conditions

As you can see from **Fig.4 (a)**, due to excessive water contents, soluble compounds in oxide layer were too much dissolved resulting in insignificant change on the STS surface. From **Fig.4 (b)**, due to excessive fluorine ions in the electrolyte, too much etching reactions were present resulting in burned off surface. Lastly for **Fig.4 (c)** fabricated oxide layer was stable all over the surface by sufficient ratio of electrolyte. Secondly, anodizing duration was tested. Although using proper conditions, such as sufficient ratio of electrolyte or voltages, temperature and other factors, with short time of anodization, nanopores were just partially formed on the surface as you can see in **Fig.5**.

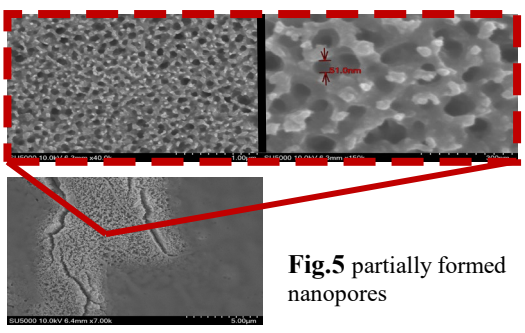


Fig.5 partially formed nanopores

Finally, rest of the remaining factors, voltage, current, and cooling temperature, all these three factors are corelated each other. Most important factor among those is current density. In order to fabricate highly ordered nanopores on the surface, about 100 A/cm^2 of current density is needed. From the study on effect of electropolishing variables on the current density-voltage relationship, current density is proportional to the cooling temperature. For achieving such current density cooling temperature should be around 278 K. It is not just current that forms the pores, to form ordered nanopores also there should be enough potential to draw the fluorine ions to etch the surface. It is examined that at least 80 V is needed for enough etching reaction.

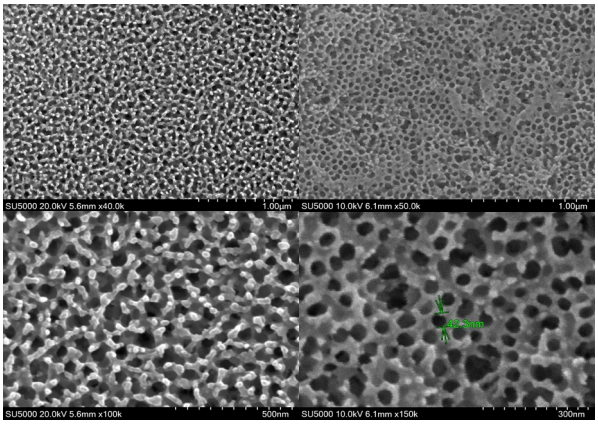
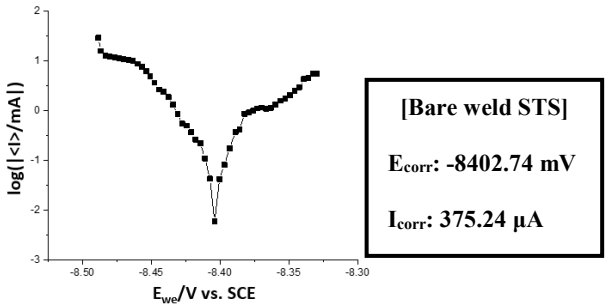


Fig.6 FESEM image of nanoporous oxide layer

Satisfying all the variables above, nanopores as shown in **Fig.6** can be formed. Diameter of pores are about 40nm and it's stably distributed all over the surface.

2.4 Electrochemical test

To verify nanoporous oxide films' effectiveness, corrosion test should be conducted. Among many tests, potentiodynamic polarization test was used. By applying voltage to the electrodes composed of working electrode, counter electrode ,and reference electrode V-log[I] curve can be obtained. Further using Tafel fitting to those graphs, corrosion potential(E_{corr}) and corrosion current(I_{corr}) can be measured. Here, corrosion potential means " how fast corrosion occurs" which is better with higher value. Then corrosion current means " how much corrosion occurs" which is better with lower value.



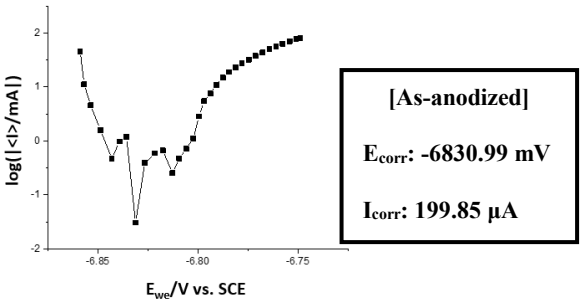


Fig.7 Corrosion test result

As you can see from **Fig.7**, as-anodized sample shows better corrosion resistance feature than bare sample.

3. Conclusions

Anodization is a simple process which can be a better solution for Stress Corrosion Cracking occurring at weld stainless steel used for nuclear spent fuel dry storage canister than conventional heat treatment process. Comparing with older method it is fast, conducted in low temperature, safe, costly efficient, and also application to various fields is possible.

Firstly, by customizing specimen with studies of microstructures and effects of heat input to the stainless steel, experiment was prepared. Then for the anodization condition, various considerable factors were tested to optimize the best condition for fabricating highly ordered nanoporous oxide layer. Optimized condition was using electrolyte composed of 0.1 M H_2O + 0.1 M NH_4F in Ethylene Glycol, applying constant voltage of 80 V for 3600 sec. , and cooling temperature of 278 K. After fabricating highly ordered nanopores, electrochemical test was conducted to testify its effectiveness. Corrosion potential and corrosion current were both better with as-anodized sample meaning more corrosion resistant.

By applicating this technique to various industrial areas, it can be expected that plenty of merits such as cost effectiveness, environment friendly, also simplicity will obtained. There is much more possibility of developing and optimizing this technique which has bright prospect.

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