

Improvement of Corrosion Resistance of Austenitic Stainless Steel Used in Cooling Water Components by Cathodic Plasma Electrolytic Oxidation

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1. Introduction

Stainless steel is widely used in various fields due to its remarkable properties including high corrosion resistance, good ductility, and being readily formable. Also, it exhibits remarkable mechanical strength, excellent weldability, and high performance at all temperatures. The typical type used in industrial fields is austenitic stainless steel consisting of 304(L) or 316(L). In nuclear power plants, various components are using stainless steel as a base material. Tube support plates in the secondary loop of the steam generator, turbine blade, moisture separator, and seawater lift pumps are the representative components that use stainless steel.

As well known, the secondary and tertiary loop of the nuclear power plant involves corrosive and abrasive environments. With the secondary loop cooling water environment, its relatively high temperature and pressure with dissolved oxygen and pH controlling additives form the corrosive environments for the components using stainless steel. In the case of tertiary loop utilizing seawater as a cooling water exhibits highly corrosive and abrasive environments as well due to the high concentration of salts and abrasive particles in the seawater. Although stainless steel has excellent mechanical strength and high corrosion-resistant properties, with those corrosive and abrasive environments being forced for a long time, it suffers a variety of corrosion and wear problems. Denting, denting problem in the steam generator, cavitation erosion, erosion-corrosion in the turbine blades, general corrosion and pitting corrosion in the seawater lift pump, and Stress Corrosion Cracking (SCC) in the various pipes are the main phenomena occurring.

To improve the corrosion resistance of the stainless steel, previously nanoporous oxide layer formation on the stainless steel surface was studied. It actually improved general corrosion resistance verified with electrochemical characterization showing corrosion potential. But after a long time exposure of the artificial seawater to the nanoporous oxide layer, it was found that corrosion damage penetrated the oxide layer formed. The pores that mitigated volume expansion stress of the growing oxide layer, acted as a corrosive material penetration route so that at a certain point exceeding the threshold concentration of corrosive species induced corrosion failure.

In this study, to supplement those problems, Cathodic Plasma Electrolytic Oxidation (CPEO) method will be discussed. CPEO utilizes extremely high pulsed voltages and temperature to form a protective layer on the substrate. In the presence of certain electrolytes, target metals are placed as a working electrode and the counter electrode is electrically connected. Generally, the CPEO process shows a loose porous layer and inner compact layer with great hardness and adhesion. Due absence of nanopores on the surface corrosive species concentration will be blocked efficiently and additional protection from wear attacks can be achieved with excellent hardness. By changing the electrolyte composition and electrical conditions, contemplating the mechanisms of the compact oxide layer formation process will be the main issue of this paper. For this purpose surface morphologies and composition of the fabricated compact oxide layer will be examined.

2. Methodology

2.1 Materials and characterization

A specially designed stainless steel specimen was used for the CPEO experiment. As shown in Fig. 1, the specimen had a circular part and handle attached for the electrical connection. For stainless steel, type 316 L was used as it's composed of the basic composition of the most widely used stainless steel. In the case of electrolyte, glycerol (ACS reagent, $\geq 99.5\%$) was used as an organic solvent and KCl (ACS reagent, 99.0-100.5%) was used as a conductive material. Deionized (DI) water was also used to dissolve the conductive material into the electrolyte. Before the CEPO process, sonication of the sample in acetone & DI water for 10 min. was conducted and dried in an oven. After the CPEO process, the sample was rinsed with ethanol and dried in an oven.



Figure 1. Type 316 L stainless steel specimen

After the experiments, the morphology characterization of the specimen was conducted using a field emission scanning electron microscope (FESEM, Hitachi SU5000, Japan), and cross-sectional composition was characterized with the SEM attached Energy Dispersive X-ray Spectroscopy (EDX). The crystalline structure and composition of the specimen were examined using an X-ray diffractometer (XRD, D/MAX 2500 V, Rigaku, Japan). Lastly, for the corrosion resistance evaluation, the potentiodynamic polarization (PDP) technique was used utilizing Reference 600 Potentiostat / Galvanostat (Gamry, Warminster, PA, USA).

2.2 Cathodic Plasma Electrolytic Oxidation (CPEO)

Generally, Plasma Electrolytic Oxidation (PEO) process is applied for the valve metals, such as Aluminum, Zirconium, Magnesium, etc. However, in this study, stainless steel should be the target material for plasma electrolytic oxidation. In the case of the PEO process of stainless steel, surface plasma discharges hardly occur because of the absence of the insulating stable oxide layer formed on the surface and the driving force of the iron is lower than that of hydrogen. It means that it is more favorable for oxygens to combine with hydrogen ions to form water rather than forming iron oxides. To solve those problems, the stainless steel sample was placed as a cathode simply. Then at the surface of the cathode, various kinds of gases are formed such as hydrogen gas, the gas phase of water, or even the gas phase of organic electrolyte. Those vapor gas envelopes act as an insulating layer, and a partial anode was formed at the surface of the envelope. Through that high electric field, plasma discharges occur resulting in the generation of various active species. Active ions from the metal cathode and plasma envelope are combined to form an oxide layer in a high temperature and pressure environment. Because it exhibits high temperature and pressure, generated oxide layer shows the strong features of high compactness, hardness, and stability. Fig. 2 is showing those processes of cathodic plasma electrolytic oxidation.

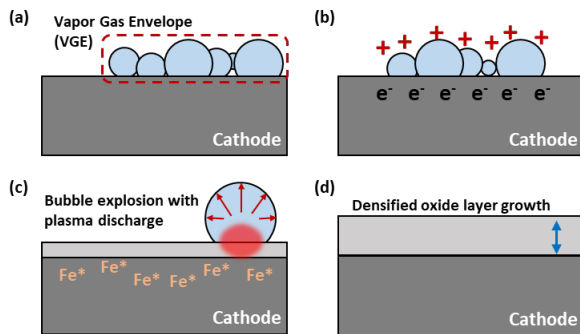


Figure 2. Schematic diagram of CPEO process

For the experiment, an electrolyte consisting of glycerol, DI water, and KCl was used. The composition ratio of the glycerol was 80% and KCl composition was 0.5 M. Voltage was 600 V for the positive bias and 0 V was utilized for the negative bias. The following duty cycle was 20 %. The applied frequency was 100 Hz and the duration was 3 min.

3. Results and Discussion

3.1 Surface morphology and composition

Firstly, after the CPEO process of 316 SS, surface morphology was characterized. Noticeable features were that the surface was highly even and smooth compared to the well-known morphology of the general PEO process. And also, grains were clearly observable. Additionally, at some spots on the surface, the peeled-off oxide layer was characterized as shown in below SEM image in Figure 3. Of course, those peeled-off shapes were occasionally found and the rest of the surface was highly stable.

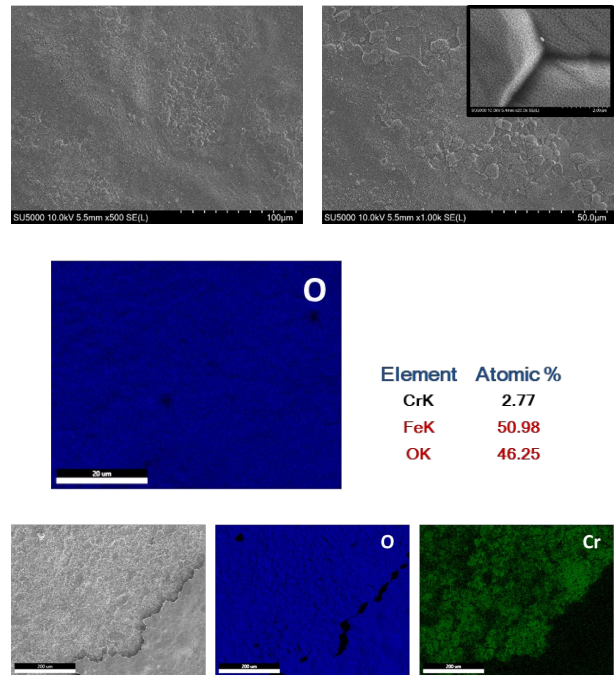


Figure 3. Surface morphologies and composition of CPEOed sample

As shown in the first EDX mapping image in Figure 3, the fabricated oxide layer was obviously composed of iron oxides showing 50.98 and 46.25 atomic % of each iron and oxygen. An interesting part was found in the peeled-off spot. At the revealed layer chromium oxide was mainly fabricated as shown in the last two EDX mapping images in Figure 3. It can be seen that two different layers were fabricated in the shape of layer

upon layer structure. In the PEO process, it is general to have this double layer oxide film structure, a loose layer on the top and a compact layer at the bottom. Similar to the conventional PEO process, the CPEO process is also showing this same feature of loose iron oxide layer and compact chromium oxide inner layer. A more accurate cross-sectional structure will be discussed in the next section of cross-sectional morphology and composition.

3.2 Cross-sectional morphology and composition

Cross-sectional morphology and composition were characterized by mounting and polishing the CPEOed sample. At first, the thickness of the oxide layer was measured as approximately 30 μm . And in the left image of the figure 4, it can be seen that the oxide layer formed was largely even and uniform. In a closer look at the oxide layer, it was composed of a loose layer on the top and a compact layer on the bottom. This kind of structure proved the supposition from the previous section. As already mentioned and supposed in the peeled-off part, after the PEO and CPEO process, an oxide layer is formed in a layer upon layer structure. The loose and comparatively porous layer at the top act as a stress relief layer to compensate for the volume expansion stress of the oxide layer and also can act as a corrosion protective layer by physically cutting off the corrosive species. But, of course, it exhibits a lot of pores and routes for the corrosive species to penetrate through, compact inner layer perfectly blocks the corrosive species resulting in high corrosion resistant coating. And from the EDX line spectrum, it was found and proved again that the outer loose layer was composed of iron oxides and the inner layer was composed of chromium oxides.

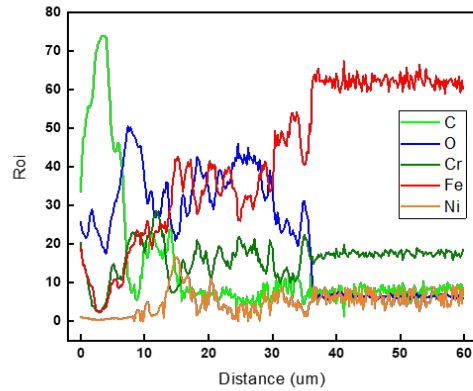


Figure 4. Cross-sectional morphology and composition in the line spectrum

3.3 Crystalline structure

XRD patterns were characterized to figure out the crystalline structure of the oxide layer formed. It was characterized as shown in Figure 5. Mainly Magnetite (Fe_3O_4) and Wustite (FeO) were characterized. And also austenite phase was observed. Austenite peak occurrence is highly adequate owing to the austenitic stainless steel substrate itself. Generally, iron oxides were known to be harmful to corrosion attacks. But it is the Hematite (Fe_2O_3) phase that is harmful resulting in the formation of rust in the presence of water. Magnetite and Wustite can act as stable corrosion inhibitors in an aqueous environment. But surprisingly, chromium oxide was not observed through XRD characterization, perhaps due to its deeper position than the iron oxides affecting the X-ray hard to penetrate.

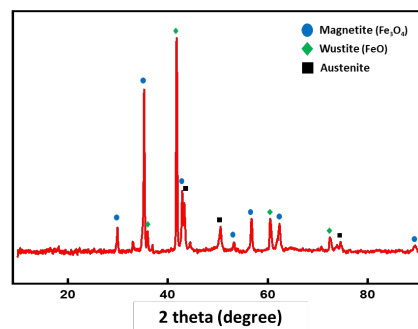
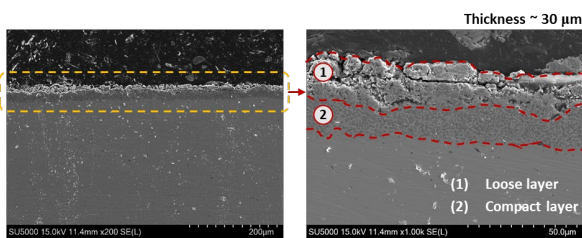


Figure 5. XRD patterns of CPEOed sample

3.4 Corrosion Resistance

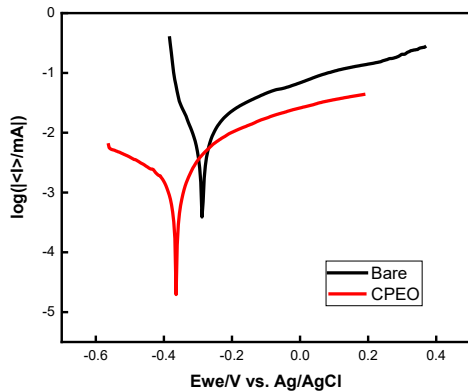


Figure 6. Potentiodynamic polarization curves of Bare and CPEOed samples

Table 1. Polarization curve parameters

	Bare	CPEO
Corrosion potential (E_{corr}) / mV	-287.398	-362.126
Corrosion current (i_{corr}) / μ A	4.119	1.446

Corrosion resistance was evaluated using the potentiodynamic polarization (PDP) method. PDP technique is an electrochemical method to estimate corrosion resistance. It utilized a three-electrode system of working, counter, and reference electrodes. CPEOed sample was placed as working electrode, platinum sheet and Ag/AgCl was used as counter and reference electrode each. By scanning the working electrode with increasing potential, the program reads current outputs resulting in those curve outputs in Figure 6. By Tafel fitting those curves above, basically, corrosion potential and corrosion current density can be derived. Conceptually, corrosion potential is where the net amount of oxidation and reduction coincides. And the corresponding current at that potential is corrosion current. A more simple explanation of those parameters is that corrosion potential possesses the tendency of the sample to be corroded and corrosion current shows the amount of corrosion occurring. But in the case of corrosion potential, it could be changed in various conditions. As corrosion potentials are the result of the oxidation and reduction process, which are the processes of electron movement, microstructure and electrolyte conditions are the important factors in deciding corrosion potential value. For that, corrosion current exhibits a more significant aspect from a corrosion resistance point of view.

As summarized in Table 1, the corrosion current was highly superior for the CPEOed sample, which means that the amount of corrosion happening in the CPEOed sample was way lower. Of course, the corrosion

potential of the bare sample was slightly nobler, but as explained above, corrosion current showed a more important meaning in corrosion resistance.

4. Conclusion

To improve the corrosion resistance of the main material used for the cooling water components in the nuclear power plants, the CPEO process was tested to fabricate the protective oxide layer on the metal surface. Surface morphology showed a smooth structure with grains observable. And iron oxides were mainly observed on the top of the oxide layer by EDX mapping. The interesting part at the peeled-off spot was that the chromium oxides were clearly characterized underneath the outer iron oxide layer. The specific structure of the fabricated oxide layer was characterized by the cross-sectional view. The fabricated oxide film was composed of a loose outer layer and the compact inner layer. EDX line spectrum showed that iron oxides and chromium oxides were mainly formed at the outer and inner layer each. Those layer upon layer structure was expected to further increase the corrosion-resistant property of the protective film by blocking the corrosive species efficiently. By using XRD, it was found that Magnetite and Wustite were mainly formed for the outer layer. However, due to perhaps its deeper position, the crystalline structure of the inner layer was hardly characterized. Finally, by using the electrochemical PDP method, corrosion resistance was evaluated. In the corrosion potential view bare sample showed a slightly better tendency, but in the corrosion current view, which is more significant in estimating the corrosion resistance, the CPEOed sample showed highly improved corrosion resistant property. A slightly inferior value in corrosion potential was perhaps due to occasionally formed peeled-off spots on the oxide layer. Therefore, by optimizing the conditions more to fabricate more stable oxide film, The CPEO process can become a highly promising technique to improve the corrosion resistance of the significant materials used in nuclear power plants resulting in longer life.

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