Cation Release Mitigation on the Primary Surface of Alloy 690 Steam Generator Tubes via Electrochemical Surface Modification

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1. Introduction

The managing of radioactive contamination in the primary coolant system of nuclear power plants is a significant issue for both operating plants and new buildings because it can affect human radiation exposure during maintenance as well as material degradation [1]. The Co-60 and Co-58, major contaminations sources, are formed respectively by neutron activation of Co-59 and Ni-58. Co-59 is originated from various constituting materials such as hardfacing parts (Stellite[TM], Haynes), an impurity in steam generator (SG) tubes, and stainless steel pipes. Ni-58 is mainly released out from the SG tube surface which is about 70% of the total area exposed to the primary coolant [2]. Thus, the corrosion release of Ni ion can be a severe problem at the plant using SG tubes of Ni-based alloys such as Alloy 600 and 690 having high Ni contents.

This work provides a mitigation method for the cation corrosion release of commercial Alloy 690 SG tubes in a primary coolant system through electropolishing (EP) surface modification.

2. Methods and Results

2.1 Preparation and Characterization of sample surface

The surface-modified specimens were prepared by an EP process using ElectroMet® 4 (Buehler Co, IL). The electropolisher was specially modified to treat the inside surface of commercial Alloy 690 tubes. The EP electrolyte was optimized by a mixture of 70 vol% phosphoric acid (H_3PO_4), 15 vol% sulfuric acid (H_2SO_4) and 15 vol% methanol (CH_3OH). All specimens were then sequentially cleaned with acetone, methanol, ethanol and deionized water for 10 min in each step. To investigate the mitigation effect for the degree of electropolishing , the EP time was varied with 4, 8, and 12 min under fixed conditions of 9 V potential, 3.8 A current and 50cc/min circulation speed of the electrolyte. To compare the surface morphology and roughness for unelectropolished and electropolished specimens, field-emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM) were used.

Fig. 1 shows the inside surface morphologies of unelectropolished and electropolished tubes. The as-received Alloy 690 displays a lot of scratches toward the rolling direction with a rough surface but the electropolished one exhibits a clear crystal structure having a grain size of 20 to 60 μm. This corresponds with the AFM results of both samples as shown in Fig. 2, in which the surface roughness of the electropolished sample decreased dramatically with 17 nm compared to that of the unelectropolished one with 120 nm. This indicates that the rough surface called as baily layer, which can be weak to corrosion environments, can be removed by an electrochemical polishing process and has a smooth crystal surface.
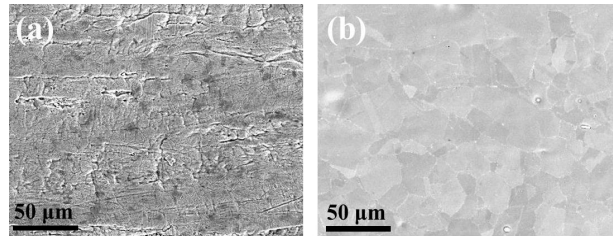

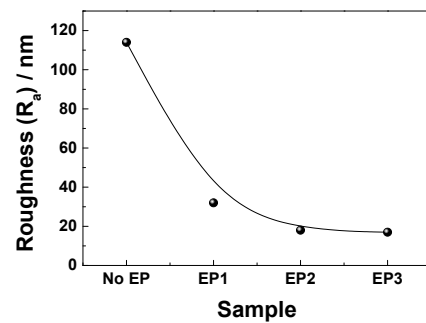Fig. 1. SEM surface images of (a) unelectropolished and (b) electropolished specimens.

Fig. 2. Surface roughness of unelectropolished and electropolished specimens as a function of EP time.

2.2 Corrosion release test

A corrosion release test for the unpolished and electropolished specimens was performed at 330°C under 150 bars in a circulation autoclave loop at a flow rate of $3.8 Lh^{-1}$. A simulated primary coolant was prepared by dissolving the 2 ppm lithium (LiOH) and 1200 ppm boron (H_3BO_4) into deionized water. The dissolved hydrogen concentration was 35 cc/kg (@STP) and low oxygen content of less than 10 ppb. The corrosion test time was varied with 100, 300, 400, 600, 900, and 1000 hours in a simulated primary coolant.

2.3 Evaluation of cation release

The corrosion release rate for unelectropolished and electropolished Alloy 690 tubes was evaluated by a typical gravimetric analysis method using a two-step alkaline permanganate-ammonium citrate (AP/AC) descaling process [3, 4]: (1) 1% $KMnO_4$ and 5% NaOH during 5 min for the outer surface and 3 min for the inner surface, respectively, at 90^oC. This method involves multiple applications and a reverse extrapolation to correct for base metal losses during corrosion oxide removal. A minimum of four and a maximum of five applications were conducted. All weight changes were measured using the calibrated microbalance with ±10 μg accuracy.

Fig. 3 shows the inside surface morphologies for the unelectropolished and electropolished samples after the corrosion test for 400 hr. There is no remarkable difference between both samples and the oxide particles were distributed widely on the surfaces although the particle density on the unelectropolished sample seems to be higher than that of the electropolished one. However, the corrosion release rate, which is calculated by the descaling process, of the electropolished sample for 8 min decreased by a factor of 2.4 compared to that of an unelectropolished sample, as shown in Fig. 4.
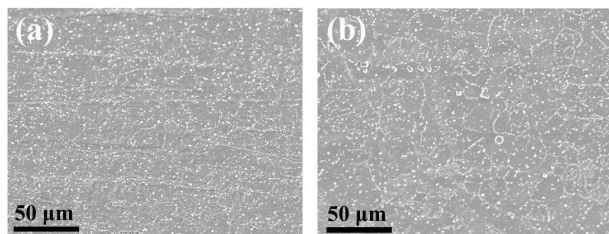

Fig. 3. SEM surface images of (a) unelectropolished and (b) electropolished specimens after corrosion test for 400 hr.
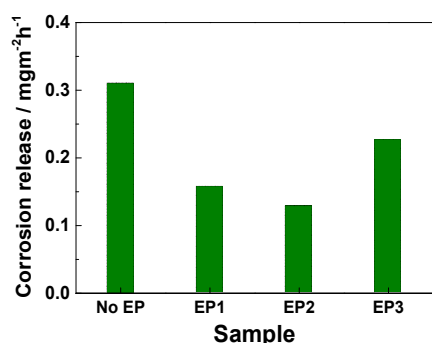

Fig. 4. Corrosion release rate from the inside surfaces of the unelectropolished and electropolished Alloy 690 tubes in high-temperature, hydrogenated water for 400 hours.

3. Conclusions

We modified the inside surface of a commercial Alloy 690 SG tube to investigate the influence of surface condition on the corrosion release rate in the primary coolant system. The change in surface morphologies of corrosion products is negligible, while the corrosion release rate revealed a remarkable improvement by electropolishing of primary surface. In particular, the corrosion release rate is mainly dependent on the surface roughness as a function of EP time. The lowest corrosion release rate was obtained from the sample electropolished for 8 min.

REFERENCES

[1] M. Clauzel, M. Guillodo, and M. Foucault, Correlation Between Ni Base Alloys Surface Conditioning and Cation Release Mitigation in Primary Coolant, NPC2010, pp.1 -12, 2010.
[2] P. Jolivet, A. Tamba, and F. Chahma, Materials Selection According to ALARA during Design Stages of EPR[TM], ISOE Int'l Symp., Nov. 17-19, 2010.
[3] S. Ziemniak, M. Hanson, and P. Sander, Electropolishing effects on corrosion behavior of 304 stainless steel in high temperature, hydrogenated water, Corrosion Science, pp.2465-2477, 2008.
[4] S. Ziemniak, and M. Hanson, Corrosion Behavior of NiCrFe Alloy 600 in High Temperature, Hydrogenated Water, LM-04K143 Report, Nov. 2, 2004.