

# Magnetite-Accelerated Stress Corrosion Cracking of Alloy 600 in 10% NaOH Solution

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## 1. Introduction

The factors affecting stress corrosion cracking (SCC) of Alloy 600 in the secondary coolant environments have systematically been defined in the view point of microstructure, environment, and stress. Nevertheless, the mechanism of rapid stress corrosion cracking of this material is still unresolved.

It should be noted that most steam generator (SG) tubes and heated crevices in the secondary side of operating SGs are covered with porous magnetite deposits. Examination result of deposit flakes taken from an operating SG tubes clearly shows that numerous pores were present within the magnetite deposits [1,2]. These pores are boiling chimneys that are formed when the secondary water boils and the vapor bubbles escape from the heated outer surface of the tubing through the deposits. Therefore, most of the tube surface is covered with magnetite, except for the open pores, and thus only the local tube surface surrounded by the open pores is exposed to the bulk water. This means that actual corrosion phenomena occur under conditions which the local surface of the tube is in contact with the porous magnetite deposits.

Magnetite is well known as a conductive material, and its electrical conductivity indicates almost metallic behavior [3]. Consequently, a galvanic cell can be activated on the tube surface in contact with magnetite. Therefore, if the tube surface behaves as an anodic member in the coupling system with magnetite, this may become a potential factor that accelerates SCC. Therefore, the goal of this work is to investigate SCC and electrochemical behaviors of Alloy 600, coupled to magnetite under a simulated crevice environment. For this, SCC tests were conducted using specially designed magnetite-deposited U-bend specimens and the effect of magnetite on the electrochemical behavior was investigated.

## 2. Experimental

All specimens were prepared from Alloy 600 plates, which were annealed at 1060 °C for 2.5 min, followed by water quenching. Fig. 1 shows the dimensions of the U-bend specimens for the SCC tests. Before bending, the specimens were ground using silicon carbide paper of up to 1000 grit, and ultrasonically cleaned in acetone for 3 min and then in distilled water for 3 min. The U-bend specimens were fabricated according to the guideline provided by ASTM G30-97.

To make a galvanic couple between Alloy 600 and

magnetite, a magnetite layer was electrodeposited over the whole surface of the assembled U-bend specimen except for a width of approximately 0.8 mm at the apex area. The electrodeposition process of the magnetite layer is given in detail elsewhere [4,5]. Fig. 2 shows the electrodeposition process and the magnetite-deposited SCC specimen.

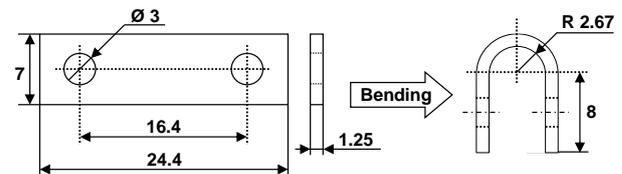


Fig. 1. Electrodeposition process of a magnetite layer on a U-bend SCC specimen and the magnetite-deposited SCC specimen.

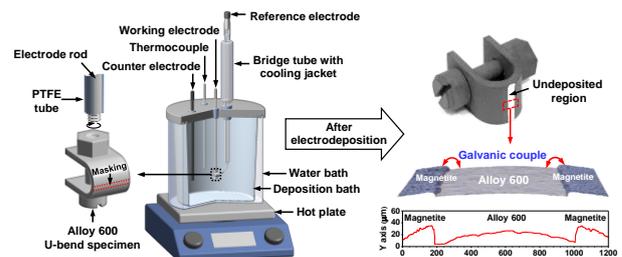


Fig. 2. Electrodeposition process of a magnetite layer on a U-bend SCC specimen and the magnetite-deposited SCC specimen.

SCC tests for the magnetite-free and magnetite-deposited specimens were carried out separately in deaerated 10 wt% NaOH solutions at 315 °C for 300 h by using a static Ni-autoclave with a capacity of 2 L. This test condition was chosen to simulate the crevice environment of the secondary side in SGs of PWRs. After the SCC test was completed, specimens were cut along the center lengthwise to examine the stress corrosion cracks. These samples were embedded in a cold mounting resin, polished with 0.3 μm Al<sub>2</sub>O<sub>3</sub> powder, and observed using an optical microscope (OM).

Potentiodynamic polarization tests were performed at 280 °C in the same solution used for the SCC tests using a static Ni-autoclave with a capacity of 1 L. An external Ag/AgCl electrode with 0.01 N KCl was used as the reference electrode, and a platinum wire was used as the counter electrode. After the open-circuit potential (OCP) was stabilized at 280 °C, polarization scans were performed from the OCP toward the positive or negative

direction at a scan rate of 30 mV/min.

### 3. Results and Discussion

Fig. 3 shows the cross-sectional OM image of the U-bend specimens exposed to 10 wt% NaOH solution for 300 h. No stress corrosion cracks were generated in any of the magnetite-free specimens. However, stress corrosion cracks with a depth of 150-280  $\mu\text{m}$  were generated in all magnetite-deposited specimens. Furthermore, the deepest crack was always observed near the interface between the exposed Alloy 600 surface and magnetite layer, not the apex with the greatest stress in the U-bend specimen. These results indicate that magnetite coupled to Alloy 600 induces the rapid SCC of Alloy 600.

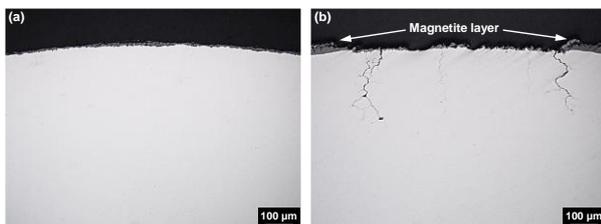


Fig. 3. Cross-sections of the Alloy 600 SCC specimens after the SCC tests: (a) magnetite-free specimen and (b) magnetite-deposited specimen.

Fig. 4 shows the anodic polarization curve of Alloy 600 and cathodic polarization curve of magnetite. The corrosion potential of magnetite was approximately 100 mV higher than that of Alloy 600. This indicates that Alloy 600 behaves as an anodic member of the galvanic couple with magnetite, if these two materials are in electrical contact. In this couple with equal areas of the materials, the corrosion potential of Alloy 600 is expected to be shifted to a more positive value. In addition, the anodic current of Alloy 600 will be increased by galvanic coupling with magnetite. To evaluate the effect of the increased magnetite surface area in the couple, the cathodic curve of magnetite with an area of 50  $\text{cm}^2$  was also presented in Fig. 4, which has been simply estimated from that with an area of 1  $\text{cm}^2$ . The corrosion potential of the coupled Alloy 600 will be more polarized to the active-passive transition region with increasing the magnetite surface area, resulting in the greatly increased anodic current. Therefore, it is considered that these changes in the electrochemical behavior also occur on the exposed Alloy 600 surface in the magnetite-deposited specimen shown in Fig. 3 during the SCC test.

An alloy which exhibits an active-passive behavior in the anodic polarization curve is known to be more susceptible to SCC in its active-passive transition region [6]. In this regard, Pessall et al. and subsequent researchers reported that the caustic SCC of Alloy 600 was significantly accelerated when the electrochemical potential of Alloy 600 was held in the potential range corresponding to the active-passive transition region of

the anodic polarization curve [7-9]. Consequently, the rapid SCC failure in the magnetite-deposited specimen can be attributed to the shift of the electrochemical potential of Alloy 600 to the more susceptible region to SCC by the galvanic coupling with magnetite (shown in Fig. 4).

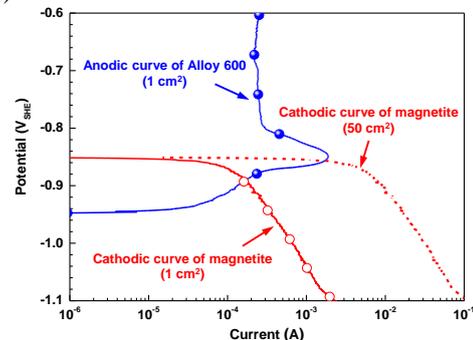


Fig. 4. Electrochemical corrosion behavior of Alloy 600 and magnetite in 10 wt% NaOH solution at 280  $^{\circ}\text{C}$ .

This work confirms that the caustic SCC of Alloy 600 is significantly accelerated when the alloy is in electrical contact with magnetite. From the perspective of the electrochemical behavior, it is demonstrated for the first time that the galvanic coupling with magnetite can shift the electrochemical potential of Alloy 600 into the more susceptible potential region to SCC. Therefore, the magnetite-accelerated stress corrosion cracking (MASCC) mechanism should be considered as a new acceleration factor of SCC in Alloy 600 SG tubes in secondary side conditions, in addition to the impurity concentration within the porous magnetite deposits.

### 4. Conclusions

Magnetite deposited on Alloy 600 induced rapid SCC of Alloy 600. Based on the electrochemical behavior, Alloy 600 and magnetite acted as an anode and a cathode in the galvanic coupling system, respectively. In this couple, the electrochemical potential of Alloy 600 was shifted into the active-passive transition region of the anodic polarization curve, which is the range susceptible to SCC. Therefore, a galvanic corrosion mechanism between magnetite and Alloy 600 is proposed as a new acceleration contributor to a rapid cracking of Alloy 600 in the PWR secondary environment.

### Acknowledgements

This work was supported by the National Research Foundation (NRF) grant funded by the government of the Republic of Korea (NRF-2017M2A8A4015159).

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