Electrochemical Corrosion Behavior of Alloy 600 in Chloride-Sulfate Solutions

Do Haeng Hur[*], Myung Sik Choi, Jung Ho Han, Deok Hyun Lee
Korea Atomic Energy Research Institute, 150 Deokjin-dong, Yuseong-gu, Daejeon, 305-353, Korea
[*]*Corresponding author: dhhur@kaeri.re.kr*

1. Introduction

Chloride ions have been known to be one of the main causes for pitting corrosion of Alloy 600 steam generator materials[1-2]. Furthermore, they accelerate the corrosion rates of low alloy steels such as tube sheet and tube support plate, resulting in tube denting[3]. Sulfate ions were also detected on the surface of stress corrosion cracks, intergranular attack and pitting in the secondary side of steam generator tubes[4].

In addition, chloride and sulfate ions are the major cations to determine a molar ratio index for managing the secondary water chemistry[5].

In this work, corrosion behavior of Alloy 600 was studied using a potentiodynamic technique in chloride-sulfate solutions at room temperature.

2. Experimental Methods

2.1 Material

Steam generator tubes of high temperature mill-annealed Alloy 600 with a nominal outer diameter of 19.05mm and a nominal wall thickness of 1.07mm, were used in all tests. For polarization measurements, the tubing was longitudinally sectioned into four pieces, flattened and finally cut into rectangular coupons of 5 mm x 10 mm.

2.2 Test solutions

The solutions were prepared using a reagent sodium chloride and sulfuric acid. By varying SO_4^{2-} and Cl^-, the ratio of sulfate to chloride ranged from 0.11 to 65. In this case, the total molar concentration of NaCl and H_2SO_4 was fixed at 2 M.

Two other test matrix was designed. The one is to vary H_2SO_4 at a constant concentration of 1.0 M NaCl so that the ratio of sulfate to chloride ranged from 0.1 to 1.0. The other is to change NaCl at a constant concentration of 1.0 M H_2SO_4 so that the ratio of sulfate to chloride varied from 1.0 to 33.3.

2.3 Electrochemical test

The specimens were mechanically polished through to 1,200 grit silicon carbide paper and were spot-welded to an Alloy 600 lead wire which was then covered with a polytetrafluoroethylene tube for electrical insulation. A saturated Calomel electrode (SCE) and a platinum wire were used as a reference electrode and counter electrode, respectively. After the open circuit potential (OCP) was stabilized, polarization scan was started from the OCP with a scan rate of 20mV/min. The solution was deaerated by blowing a high purity nitrogen gas during the tests. All tests were conducted at room temperature.

3. Results and Discussion

Fig. 1 shows the potentiodynamic polarization curves of Alloy 600 in solutions of which the molar ratios of sulfate to chloride were larger than 1. The critical current increased with an decreased molar ratio, then finally showed a maximum value at a ratio of 1. The passive ranges and corrosion potentials were decreased. These results indicate the presence of chloride accelerates the corrosion of Alloy 600. In this case, however, no pitting corrosion was observed.
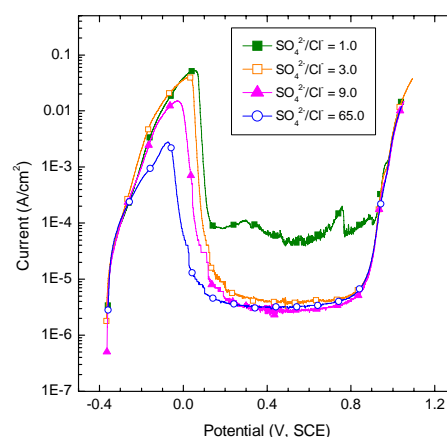

Fig. 1 Potentiodynamic polarization curves of Alloy 600 in solutions of the molar ratios of sulfate to chloride > 1.

Fig. 2 shows the potentiodynamic polarization curves of Alloy 600 in solutions of which the molar ratios of sulfate to chloride were lower than 1. The passivity was not maintained any more, resulting in pitting corrosion. The critical current decreased with a decreased molar ratio.

Similar results were obtained in two other test conditions which were described in Section 2.2.

All these results were summarized in Fig. 3. As the molar ratio of sulfate to chloride increased, the critical current was increased to reach a maximum value at a ratio of 1 and then decreased. Higher cation concentration induced higher critical current density at a constant molar ratio. Pitting corrosion of Alloy 600 occurred only when the molar ratio of sulfate to chloride was below 1, regardless of chloride

concentration. For example, no pitting was observed even in 0.5 M NaCl + 1.5 M H$_2$SO$_4$ solution.

[5] PWR Molar Ratio Control Application Guidelines, Electric Power Research Institute, TR-104811-V1, pp.1-3, 1995.
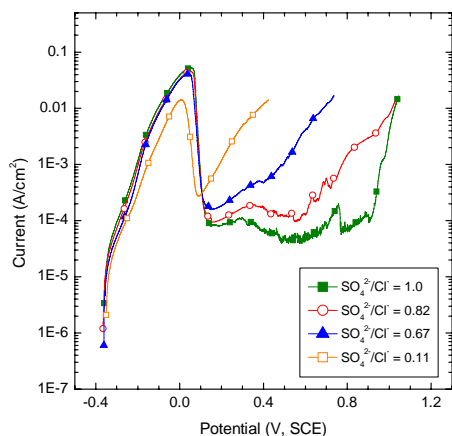

Fig. 2 Potentiodynamic polarization curves of Alloy 600 in solutions of the molar ratios of sulfate to chloride < 1.
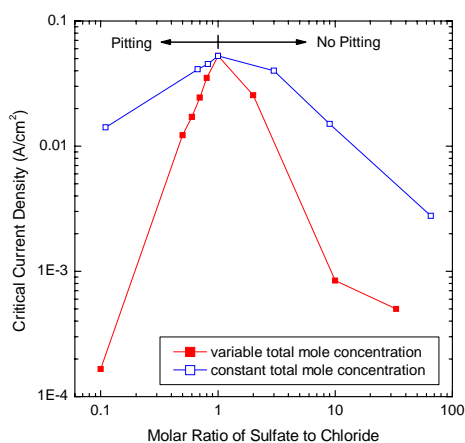

Fig. 3 Variation of critical current density and pitting behavior as a function of the molar ratios of sulfate to chloride.

3. Conclusions

In chloride-sulfate solutions, pitting corrosion of Alloy 600 occurred only when the molar ratio of sulfate to chloride was below 1. This indicates that pitting resulted from a competition of the tendency to pitting by chloride ions and the tendency to general corrosion by sulfate ions. Therefore a high concentration of chloride can not be a sufficient condition to induce pitting corrosion.

REFERENCES

[1] J.R. Park and Z. Szklarska-Smialowska, Corrosion, Vol. 41, p.665, 1985.
[2] D. Choi and G.S. Was, Corrosion, Vol.46, p.100, 1990.
[3] G. Economy and D. Smith-Magowan, Causes of Denting, EPRI NP-3275, Vol. 1, 1984.
[4] Oxide-Film Compositions on Alloy 600 Tubes from Steam Generators, EPRI TR-104066, 1998.