Effect of the Molar Ratio Index on the Electrochemical Corrosion Behavior of Alloy 600 and SA508Cl.3

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1. Introduction

The laboratory and field experience data indicated that both intergranular attack and intergranular stress corrosion cracking of Alloy 600 steam generator tube material are minimized at a near neutral pH of the range between $5 \sim 9[1]$. Therefore, it is expected that maintaining a crevice pH near neutral should reduce the corrosion rate of Alloy 600. Theoretically, the neutral pH can be achieved by controlling the molar ratio of the cation to anion impurities dissolved in the crevice to be near one.

Based on the above backgrounds, a molar ratio index (MRI) for managing the secondary water chemistry was proposed[2] as the following equation(1):

$$MRI = \frac{Na + K}{Cl + excessSO_4} \tag{1}$$

To date, in order to maintain the desired MRI, several methods are being implemented such as sodium source reduction, chloride injection and ion exchange resin manipulation[2].

This index was derived from the view point of the corrosion behavior of the tube material. Because the tube sheet and the tubes are galvanically coupled in a steam generator, the corrosion behavior of the tube sheet should also be considered in an application of a molar ratio control. In addition, since the MRI is a simple ratio of cations to anions, the total concentration of soluble impurities is not considered.

In this paper, the electrochemical corrosion behaviors of tube and tube sheet material were examined by a polarization method in the solutions with the various MRIs at room temperature. The effect of the impurity concentration at a constant MRI was also evaluated.

2. Experiments

Mill-annealed Alloy 600 and SA508Cl.3 were used as a tube material and tube sheet material, respectively.

The MRIs of the test solutions were controlled to be 0.1, 1 and 10 by an addition of HCl and NaOH. Any other species were not included. The total ion concentrations were 0.011 and 0.11M at each MRI. Regardless of the concentrations, the measured pH at the MRI 0.1, 1, and 10 was about 2, 7 and 12, respectively. All the tests were conducted at room-temperature.

Polarization tests were performed at a scan rate of 20mV/min under continuous deaeration of 300ml/min by extra pure N₂ gas. A saturated Calomel electrode and

a Pt electrode were used as a reference and counter electrode, respectively.

3. Results and Discussion

3.1 Effect of MRI

Figure 1 shows the potentio-dynamic polarization behavior of Alloy 600 and SA508Cl.3 in a solution of MRI 0.1, 1 and 10 at a total ion concentration of 0.011M. In the case of Alloy 600, the active-passive transition appeared at the MRI 0.1, but it was not observed at the MRI 1 and 10. Transpassivity at the MRI 1 and 10 was due to pitting and oxygen evolution, respectively.

SA508Cl.3 showed a high corrosion rate at the MRI 0.1, while a passive behavior was observed at the MRI 10. Polarization behavior of SA508Cl.3 was similar to that of Alloy 600 at the MRI 10. Corrosion rate at the corrosion potential decreased in the order: MRI 0.1, 1 and 10. Especially, the current density at the MRI 0.1 was highest as $1.7\text{E-}6\text{A/cm}^2$ in Alloy 600 and $2.0\text{E-}4\text{A/cm}^2$ in SA508Cl.3.



Figure 1. The potentio-dynamic polarization behavior of Alloy 600 and SA508Cl.3 in a solution of MRI 0.1, 1 and 10 at 0.011M concentration.

3.2 Effect of ion concentration

Figure 2 shows the potentio-dynamic polarization behavior of Alloy 600 and SA508Cl.3 in a solution of 0.011M and 0.11M at a constant MRI 1. The corrosion potentials of Alloy 600 and SA508Cl.3 were about -452mV and -740mV, respectively, not affected by a change in the impurity concentration. The passive current density of Alloy 600 at the MRI 1 was not affected by an increase of ion concentration from 0.011M to 0.11M. However, the pitting potentials decreased from 348mV in 0.011M to 118mV in 0.11M.

In the case of SA508Cl.3 at the MRI 1, the Tafel slopes in anodic and cathodic region decreased as the concentration was increased.

The current density of Alloy 600 in the active region at the MRI 0.1 increased about 10 times and the Tafel slopes of SA508Cl.3 decreased as the concentration was increased.

The corrosion potential and the corrosion rate of both materials at the MRI 10 were little affected by an increase of concentration from 0.011M to 0.11M.



Figure 2. The potentio-dynamic polarization behavior of Alloy 600 and SA508Cl.3 in 0.011 and 0.11M solution at a constant MRI 1.

3.3 Galvanic Corrosion

Figure 3 shows the effect of the MRIs on the galvanic corrosion between Alloy 600 and SA508Cl.3, based on the potentio-dynamic polarization behavior.

The tube sheet material of SA508Cl.3 acted as an anode. The corrosion rate of SA508Cl.3 alone was $2E-4A/cm^2$ at the MRI 0.1, $1E-6A/cm^2$ at the MRI 1 and $1E-7A/cm^2$ at the MRI 10, respectively. By galvanic coupling with Alloy 600, it was increased to $1E-3A/cm^2$ at the MRI 0.1, $5.2E-6A/cm^2$ at the MRI 1 and $1.6E-7A/cm^2$ at the MRI 10, respectively.



Figure 3. Effect of the MRIs on the galvanic corrosion rate between Alloy 600 and SA508Cl.3. **4. Conclusions**

- 1. Both the corrosion potentials and corrosion rates of Alloy 600 and SA508Cl.3 were significantly decreased as the MRI increased from 0.1 to 10.
- 2. The corrosion potential and corrosion rate were not affected by a change of impurity concentration from 0.011M to 0.11M at a constant MRI.
- The corrosion rate of SA508Cl.3, acting as an anode, was increased by about 2~6 times by galvanic coupling with Alloy 600.

REFERENCES

[1] PWR Secondary Water Chemistry Guidlines, Electric Power Research Institute, TR-102134, p.2-7, 1993.

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