Effect of Pb on the Polarization Behavior of Alloy 600 in a Caustic Solution

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1. Introduction

As one of the most suspect impurities causing the outer diameter stress corrosion cracking (ODSCC) in steam generator tubes, the effect of lead (Pb) on the SCC has been extensively investigated [1]. In spite of numerous studies on the subject, the effects of lead on the polarization behavior and surface oxide formation of Ni base alloys are still debatable. The purpose of this study is to provide basic information about the lead effect. In the measurements of the polarization curves, a cathodic treatment (CT) at a potential below the open circuit potential (OCP) is often performed to remove a surface oxide. To examine the effects of lead and the cathodic treatment on the polarization behavior of Alloy 600, polarization measurements on Alloy 600 samples were performed in 40% NaOH solutions with and without Pb. The results are reported here.

2. Experimental Methods

2.1 Material

The materials used in this study were Alloy 600 HTMA (high-temperature mill annealed) tubing manufactured by SANDVIK. The chemical compositions of the alloy are given in Table 1.

2.2 Polarization

Samples of 5 mm x 10 mm were machined from the alloy 600 tube. Samples were polished up to 0.3μm using alumina powder and spot-welded to an Alloy 600 wire wrapped with a heat-shrink Teflon tubing. The measurements were conducted in 40% NaOH solutions with and without 1000 ppm Pb (as a form of PbO) at 315^{o}C. A nickel wire and an autoclave were used as the reference and counter electrodes, respectively. Before a heating, the solutions were deaerated by bubbling pure nitrogen gas for 2 hours.

Two samples were tested in each solution with or without Pb. One sample was cathodically treated at -1.5 V (vs. OCP) and then polarized from -1.5 V to + 1.5 V (vs.OCP). The other was polarized from the OCP to + 1.5 V without the CT.

Table 1 Chemical compositions of Alloy 600 (wt%)

C	Ni	Cr	Fe	Ti	Al	Mn
0.026	72.4	16.81	9.01	0.36	0.16	0.83
Si	Co	Cu	N	B	P	S
0.33	0.01	0.01	0.018	0.001	0.007	0.001

2.3 Sample preparation for a Surface Analysis

In order to examine the surface states of samples before the polarizations, two samples were exposed to each solution for about 4 hours and then only one of them was cathodically treated at -1.5 V vs. OCP for 30 min. While the vessel was cooled down, the applied potential to one sample was held at -1.5 V vs. OCP. The surfaces of four samples prepared in the two solutions with and without Pb were analyzed by Auger Electron Spectroscopy (AES).

3. Results and Discussion

3.1 Polarization Characteristics

Fig. 1 shows the polarization curves of Alloy 600 in the 40% NaOH solutions with and without 1000 ppm Pb. First, no significant difference was observed on the two curves of the samples polarized without the CT in the solutions with and without Pb. This implies that, in this

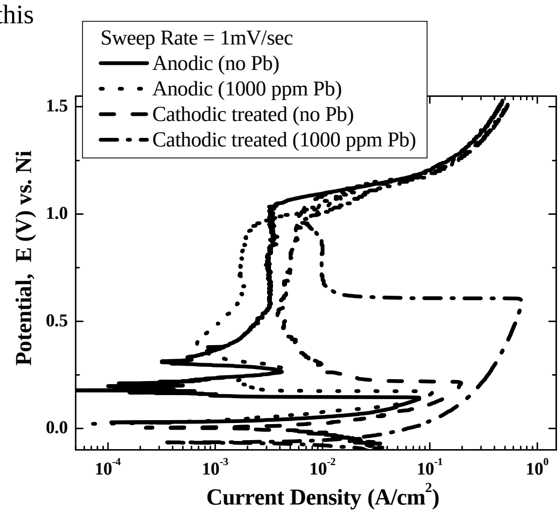

Figure 1. Polarization curves of Alloy 600 in 40% NaOH solutions with and without 1000 ppm Pb at 315^{o}C.

condition (40% NaOH), Pb has little effect on the polarization behavior of Alloy 600. Psailia-Dombrowski has reported that the width of the active peak of Alloy 600 decreased by a PbO addition in a 0.05 M NaOH solution at 300°C [2]. On the other hand, there is another paper reporting that Pb increased the active peak of Alloy 800 in a simulated secondary water condition [3]. It seems that the effect of Pb on the polarization behavior depends on other conditions such as the concentration of NaOH.

In both the solutions, the CT increased the height and width of the active peak. Fig. 2 shows the sample cathodically treated in the Pb containing solution. It was identified that the sample was covered by a huge amount of Pb during the CT, which means that Pb ions were deposited to a sample surface. It can be speculated that the polarization curve of the sample cathodically treated in the solution with Pb was obtained on Pb rather than on Alloy 600. In the solution without Pb, the CT increased the peak current density.

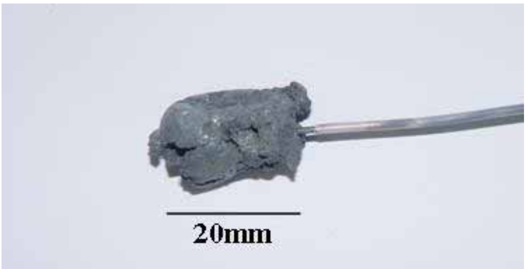

Figure 2. Photograph showing the sample cathodically treated in the Pb containing solution

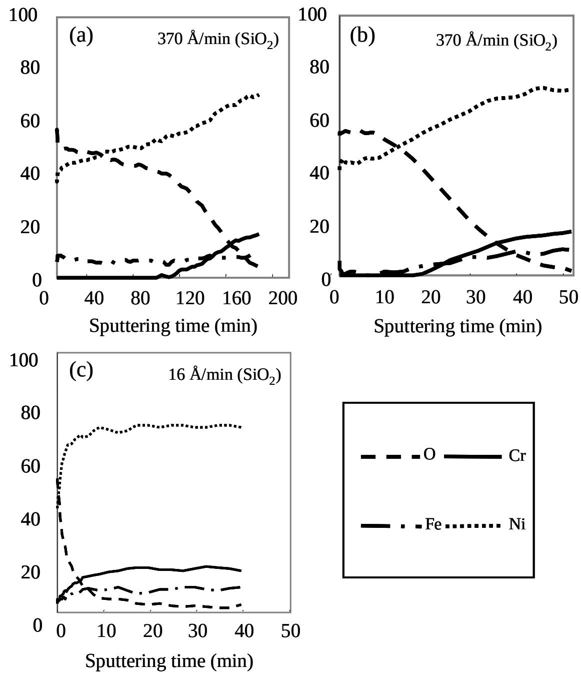

Figure 3. AES depth profiles of Alloy 600 samples exposed to 315°C, 40% NaOH solution for 4h (a) Pb-free condition without cathodic treatment, (b) Pb condition without CT, and (c) Pb-free condition after CT.

3.1 Surface analysis

In Fig 3, the surface oxides of the samples just exposed to the solutions with and without Pb for 4 hours are compared. The oxide formed in the Pb containing solution was thinner. One more thing worth noting is that the Fe was depleted at the surface in the Pb containing solution. This may be one effect of Pb on the oxide formation on Alloy 600. No Pb was detected in the surface oxide. It should be noted that the two samples were immersed in the Pb containing solution at the same time and only one was cathodically treated. Metallic Pb or Pb ions in the sample just exposed to the solution might have dissolved into the solution while the Pb ions in the solution were deposited to the other sample cathodically treated. Generally, Pb is detected in the surface oxide of the pulled tubing from power plants [4]. This should be studied in the future.

Fig. 3(c) shows the AES depth profile of the sample cathodic treated in the solution without Pb. By a 30 min cathodic treatment, a few nm thick oxide was left on the surface, which indicates that the CT could remove very effectively the surface oxide. This can explain the increased peak current density of the sample cathodically treated.

3. Conclusions

In a 40% NaOH solution, Pb has little effect on the polarization behavior of Alloy 600. It seems that the addition of Pb to the caustic solution causes the depletion of the Fe in the surface oxide. The cathodic treatment condition turned out to be very effective in removing the surface oxide in the solution without Pb. However, in the Pb containing solution, Pb ions are precipitated to the Alloy 600 sample surface during the cathodic treatment.

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