A study on a SCC of Alloy 600 in a near neutral solution containing Pb

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1. Introduction

Nickel-based Alloy 600 (Ni 75wt%, Cr 15wt%, Fe 10wt%) has been used for the heat exchanger tubes of the steam generators in nuclear power plants which are operated in a high temperature and a high pressure (300°C, 50bar) [1]. Lead is known to be one of the most deleterious species in the reactor coolants that causes stress corrosion cracking (SCC) of the alloy. It was observed that Pb dissolved in water can produce a lead induced SCC at a concentration of Pb as low as 0.1 ppm in these alloys [2].

During a long exposure time of over 30 years under a high temperature and high pressure water chemical environment, an Alloy 600 surface experiences an oxide formation, breakdown and modification depending on the nature of the grown oxide, combined with a residual stress induced by a tube expansion which is introduced to fix a tube to a tube sheet. Therefore it is strongly expected that an SCC is inevitably related to the oxide property formed on an Alloy 600 surface because a crack initiates and propagates through a breakdown and alteration of a surface oxide, fundamentally speaking.

Generally, an oxide is formed and grown on Alloy 600 in a very complex manner and it is influenced by the temperature, pH, time, chemical species and other environmental conditions [3,4]. Therefore, the characterization of surface oxide properties would be important to elucidate the mechanism of a PbSCC and to develop ameliorating measures such as an inhibitor.

In the present work, the oxides formed on Alloy 600 in aqueous solutions of a mid-range pH with and without lead were examined by using a transmission electron microscopy (TEM), an energy dispersive x-ray spectroscopy (EDXS), an x-ray photoelectron spectroscopy (XPS) and an electrochemical impedance spectroscopy (EIS). Effect of NiB as an inhibitor on the oxide properties was also investigated.

2. Experimental

The test specimens were fabricated from a 19.05 mm (0.75 inches) outside diameter nickel-based Alloy 600 (UNS N06600) steam generator tubing material (Ni 75wt%, Cr 15wt%, Fe 10wt%). The material was solution annealed (SA) at 975°C for 20 minutes, followed by a thermal treatment (TT) at 704°C for 15 hours. High-purity water [room temperature resistivity of 18MΩ·cm] was used as the reference solution. An aqueous solution of ammonia (NH_4OH) was used to adjust the solution to be a pH between 9.5~9.7. Reagent grade PbO was added to the reference solution at an amount of 10,000 ppm as a source of lead. The

performance of a NiB inhibitor was evaluated by adding 4 g/l of NiB into the leaded solution. All the test solutions were purged with a high purity nitrogen gas to remove the dissolved oxygen for 24 hours before the tests commenced.

The slow strain rate tensile (SSRT) tests were performed for uniaxial tension specimens fabricated from a solution annealed tubing in unleaded, and leaded solutions, and a leaded one with a NiB addition. The tests were carried out in 0.5-gallon nickel autoclaves at 315°C and an equilibrium pressure. The test specimens were at an open circuit potential (OCP) without an impressed electrochemical current. The strain rate was 2×10^{-7} s^{-1}. The SSRT tests provide ratings of a materials susceptibility to an SCC in relatively short testing times [5].

The electrochemical tests were performed for rectangular plate specimens (10 mm x 10 mm) fabricated from a thermally treated tubing. The surface of the specimens was polished up to 1 μm using a diamond suspension. An Alloy 600 wire was spot welded to the specimen, and the wire was shielded with a heat-shrinkable PTFE tubing. The test specimens were immersed in a 1-gallon nickel autoclave at 315°C for 14 days. The electrochemical impedance measurements were carried out in a frequency range of 10^6 to 10^{-1} Hz at an OCP with a 10 mV perturbation.

The specimens were examined after the SSRT tests, using their gauge section. The surface oxide layer and its composition was examined by using a field emission TEM, equipped with an EDXS (JEM-2100F). The information on the chemical binding was obtained by using an XPS (AXIS-NOVA, KRATOS Analytical) The spectra for Ni 2p, Cr 2p, O 1s and Pb 4f were recorded with an AlKα radiation (hv = 1486.6 eV), at a pass energy of 20 eV. The take-off angle, the base pressure and the sputter rate for the depth profiling were 45°, 5.0×10^{-9} torr and 0.04nm/s in SiO_2, respectively.

Specimens were washed ultrasonically in acetone for 5 minutes before weighing them and then dried. Corrosion rate was calculated by dividing the weight loss by both the specimen surface area and the immersion period. The surface morphologies of the corroded materials were examined by using SEM equipped with EDS(JSM6360).

3. Results and discussion

The SSRT test results are summarized in Fig. 1. The stress-strain curves are shown for the specimens tested in the leaded solution (10,000 ppm PbO) and in the leaded solution with the NiB inhibitor (10,000 ppm

PbO + 4 g/l NiB), respectively. The failure stress and the elongation in the unleaded reference solution exceed 600 MPa and 47%, respectively. In the leaded solution, the failure stress and elongation were significantly decreased to be 390 MPa and 18 %. The deleterious effect of the lead was substantially reduced by the addition of the NiB inhibitor. The failure stress and the elongation were improved to be 420 MPa and 22 %.

Fig. 2 is a TEM image for a cross-section of the surface oxide layer that was formed in the unleaded solution at 315°C. An oxide layer is observed to be about 400 – 500 nm thick. From the TEM-EDXS analyses for the specimens tested in the unleaded reference solution, the leaded solution, and the leaded one with the NiB inhibitor, a duplex oxide layer was formed at the surface, i.e., porous nickel-rich outer layer and dense chromium-rich inner layer in the unleaded reference solution. It has been reported that metallic ions in a solution are re-deposited to form a porous outer oxide layer [6]. In the leaded solution, a large amount of lead was observed at about 20 %, at the surface. Chromium and nickel were depleted in the oxide layer. The duplex oxide layer observed in the unleaded solution was not discernible in the leaded solution. In the leaded solution with the nickel boride inhibitor, the amount of lead in the oxide layer was significantly reduced to less than 9 %. The extent of the cation depletion in the oxide was also decreased.

Fig. 3 shows the Bode plots obtained from the electrochemical impedance measurements for the Alloy 600 specimens in the test solutions at 315°C: (a) the unleaded reference, (b) the leaded solution without the NiB inhibitor, and (c) the leaded solution with the NiB inhibitor. The total impedance was decreased in the leaded solution by a factor of 30 compared to that in the unleaded solution, over a frequency range of 1 - 10^5 Hz. By the addition of the NiB inhibitor into the leaded solution, the impedance was recovered by a factor of 2. The lead ions could have been incorporated into the oxide by exchange with the metallic cations and hence a possible lattice mismatch might also introduce a strain field in the oxide. These increased charge carrier density and strain field in the oxide might have degraded the passivity of the surface, and caused the susceptibility of the Alloy 600 to a PbSCC.

4. Conclusion

Lead species in aqueous solutions cause a PbSCC of a nickel-based Alloy 600 at a high temperature and a high pressure. Lead can be incorporated into the surface oxide in a metallic state and as PbO. The lead ion in the surface oxide could be oxidized by an exchange at the metallic cation sites, which causes a degradation of the passivity leading to a susceptibility of the Alloy 600 to a PbSCC. The NiB inhibitor, reduced the incorporation level of the lead into the oxide layer, thus substantially improving the oxide passivity, and decreasing its susceptibility to a PbSCC.

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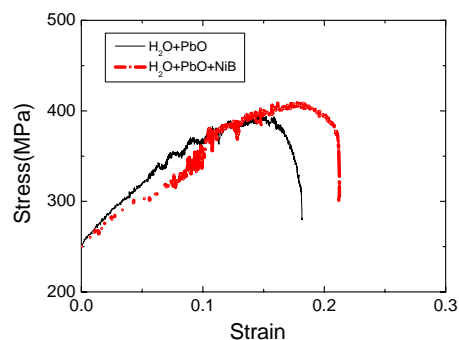[6] J. Robertson: Corrosion Science, Vol. 29 (1989), p. 1275.

Fig. 1. Stress-strain curves in the leaded solutions at 315°C without and with NiB inhibitor.
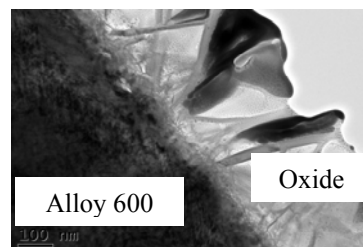

Fig. 2. Image for the surface oxide layer formed in the unleaded solution at 315°C.
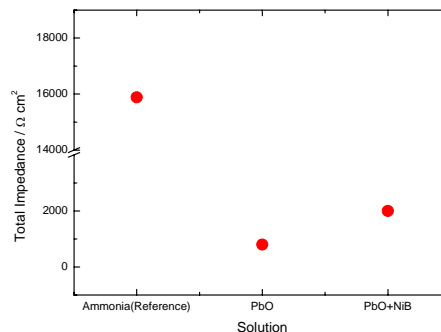

Fig. 3. Total impedance as a function of the test solution for the Alloy 600 test solutions at 315°C: (a) unleaded reference, (b) leaded with PbO, (c) leaded with PbO and addition of NiB inhibitor.