

Surface analysis of oxide grown on Alloy 600 as a steam generator tube material of a PWR

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1. Introduction

It is well known that stress corrosion cracking (SCC) is still one of important problems to overcome in nuclear power plants (NPP) [1,2]. Recognizing that cracks initiate and propagate through unavoidable breakdowns and alterations of the surface oxide on Alloy 600, the SCC behavior is closely related to the oxide property.

Secondary water pH levels spread from acidic to alkaline states in crevices depending on the water chemistry control, the water chemistry in the crevices, the plant-specific condition and so on. Specific chemical species accumulate in crevices leading to a detrimental effect on SCC. One of these chemical species is lead [3,4].

According to a destructive examination of a pulled tube, a Pb above 5wt% was observed in the crack tip.

Therefore, in the present work, the oxides were investigated in an alkaline solution of pH(T) 9.9 at 315°C as a function of lead content and immersion time using TEM, SEM, EDS and EIS. Moreover SCC behavior was compared in aqueous solutions with various lead contents.

2. Experimental

The test specimens were fabricated from 19.05 mm outside diameter Alloy 600 steam generator tubing materials, which were thermally treated (TT) at 704 °C for 15 h after solution annealing at 975 °C for 20 min for the immersion test, and high temperature mill annealed (HTMA) at 1024 °C for 3 min for the SSRT test, respectively.

Reagent grade PbO was added as a lead source to a solution in amounts of 0 - 5,000 ppm for the immersion test. Deaeration was conducted by purging with a high purity nitrogen gas to remove the dissolved oxygen for 20 h before the tests.

The coupon tests were performed on rectangular plate specimens (10 mm x 10 mm) fabricated from the 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 heat-shrinkable polytetrafluoroethylene (PTFE) tubing. The test specimens were immersed in a 3.78 L nickel autoclave at 315 °C for 14 days. During the immersion test, an electrochemical impedance measurement was performed at the open-circuit potential with a perturbation level of 10mV in the frequency range of 10⁶ to 10⁻³ Hz using a Solartron 1260 frequency response analyzer connected with a Solartron 1287 electrochemical interface. The nickel and Pt wires were

used as a reference electrode and counter electrode, respectively. Separate autoclaves were used for the leaded and unleaded test solutions to avoid any cross contamination.

After the immersion test, the plate specimens were examined. The surface oxide layer and its composition were examined by means of SEM and a field emission TEM, equipped with an EDS (JEM-2100F, JEOL).

The SSRT tests were performed on uniaxial tension specimens fabricated from HTMA tubing in unleaded and leaded solutions. The tests were carried out in 1.89 L nickel autoclaves at 315 °C and equilibrium pressure. The test specimens were at an open circuit potential (OCP) without an impressed electrochemical current. The strain rate was 2 x 10⁻⁷ s⁻¹. After the SSRT tests, the surfaces were observed by means of SEM (JSM6360) for the purpose of determining the SCC ratio.

3. Results and discussion

Fig. 1 shows the results of the TEM-EDS analyses for the specimens tested in the 0.1 M NaOH solution at 315°C as a function of PbO content. Ni-rich oxide in the outer layer and a relatively Cr-rich oxide in the inner layer were formed in the unleaded 0.1 M NaOH solution. This duplex oxide layer was also observed in 0.1M NaOH containing 10 and 100 ppm PbO even though some Pb was detected in the oxide. When the PbO added to solution increased to 1000 ppm, Ni depletion in the outer nickel-rich oxide was observed, and inner Cr-rich oxide was observed less clearly.

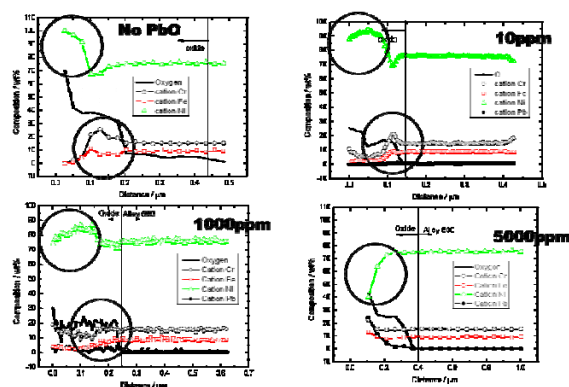


Fig. 1. Chemical compositions obtained from TEM-EDS analyses for the specimens tested in the 0.1 M NaOH solution at 315°C as a function of PbO content.

In a 0.1M NaOH + 5000ppm PbO solution, nickel depletion in the oxide was more severe, and the amount

of Pb incorporated into the oxide greatly increased leading to no appearance of inner oxide.

Fig. 2 shows Nyquist plots of the Alloy 600TT specimens in 0.1 M NaOH at 315°C as a function of the PbO content. As the PbO content in the solution increased, the impedance value clearly decreased. At up to 100 ppm content, a capacitive arc composed of the capacitance and resistance appeared, which originates from passive oxide. This impedance was drastically decreased in 0.1M NaOH containing 1000 ppm PbO. The impedance value was more decreased, and an inductive loop was observed in the solution of 5000 ppm PbO. The inductive loop is related to an intermediate phase produced during electrodeposition such as Pb_{ads}^+ [5]. It can be found that the passivity of the surface oxide decreased by adding PbO to a 0.1M NaOH solution. It should also be noted that a PbO increase from 100 to 1000 ppm caused a drastic decrease in oxide passivity.

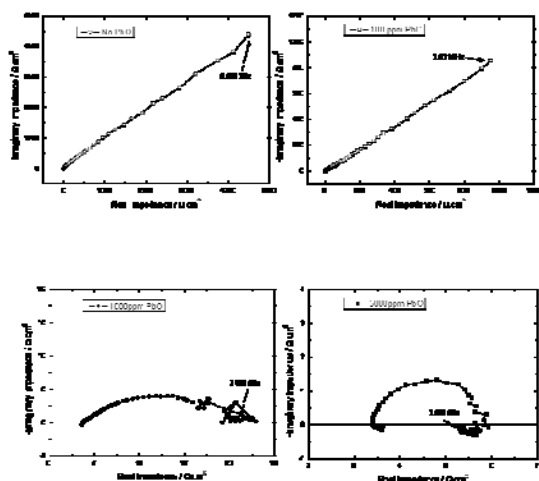


Fig. 2. Nyquist plots of Alloy 600 specimens in 0.1 M NaOH at 315°C as a function of PbO content.

Fig. 3 shows stress-strain curves obtained during the SSRT test for Alloy 600HTMA in 0.1M NaOH at 315°C as a function of the PbO content. The stress-strain curves obtained for the specimens immersed in a solution without PbO and with 10ppm PbO were almost the same, indicating that SCC does not occur in both cases. However, increasing the PbO content to 100-10,000ppm, the ultimate tensile strength and elongation to rupture decreased gradually. This means that only 100ppm PbO could trigger SCC in a 0.1M NaOH, and SCC susceptibility increased with the PbO content. This result shows a consistent tendency with the results of the impedance measurement. It is inferred that the passive oxide is degraded and the chemical composition is changed by the Pb, leading to an increase in Pb-induced SCC susceptibility.

4. Conclusion

When PbO content added to a 0.1M NaOH solution increased at 315°C, the oxide composition was changed

to increase the nickel depletion in the outer oxide and a less clear appearance of the inner chromium rich oxide. This oxide compositional change induced a drastic decrease of oxide passivity. It was found that SCC susceptibility increased when a PbO content of more than 100ppm was introduced to a 0.1M NaOH solution at 315°C, indicating that the oxide properties such as the composition and passivity are directly related to SCC behavior.

With an increase in the immersion time, the outer oxide and inner oxide thicknesses increased and the passivity increased.

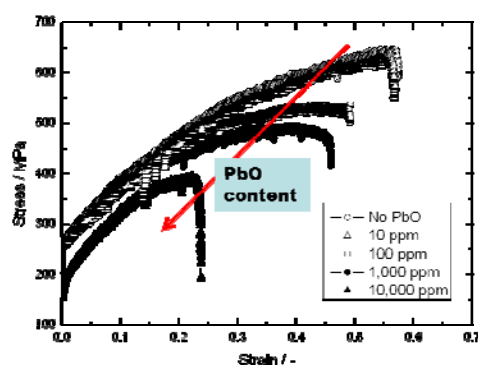


Fig. 3. Stress-strain curves obtained during SSRT test for Alloy 600HTMA in 0.1M NaOH at 315°C as a function of the PbO content.

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