

## Oxide on Steam Generator Tube Materials in Alkaline Solutions

Dong-Jin Kim, Hyun Wook Kim and Hong Pyo Kim

Nuclear Materials Division, Korea Atomic Energy Research Institute(KAERI), Yuseong, Daejeon, Korea, 305-353

\*Corresponding author: djink@kaeri.re.kr

### 1. Introduction

In spite of much effort to reduce the material degradations, stress corrosion cracking (SCC) is still one of important problems to overcome. Cracks can initiate and propagate through unavoidable breakdowns and alterations of the surface oxide that forms naturally on Alloy 600 in an aqueous solution. Characterisation of the surface oxide properties would therefore be helpful for elucidating PbSCC mechanism.

Secondary water pH levels that reveal a shift from acidic to alkaline states can affect SCC behavior to spread extensively in crevices. The pH depends on the water chemistry control, the water chemistry in crevices, plant-specific condition and so on. Specific chemical species accumulate in crevices leading to a specific condition of crevice chemistry. One of these chemical species is lead. It is one of the most deleterious species in reactor coolants that cause SCC in alloys [1-4].

The lead in a solution is presumed to modify the oxide property and hence induce SCC susceptibility. However the PbSCC phenomenon could be reduced if this type of modification can be avoided through the discovery of a suitable inhibitor.

In the present work, the oxides were investigated in alkaline solutions in the presence/absence of lead at 315°C using TEM, EDS and XPS. Moreover SCC behavior was compared in aqueous solutions with and without lead.

### 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 immersion and potentiodynamic tests and high temperature mill annealed (HTMA) at 1024 °C for 3 min for SSRT test, respectively. The TT Alloy 690 was thermally treated at 715°C for 10 h after solution annealing at 1105°C for 2 min.

Reagent grade PbO was added as a lead source to a solution in amounts of 5,000 ppm or 10,000 ppm. The performance of an NiB inhibitor was evaluated by adding 4 g/L of NiB to the lead solution. 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. 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 a field emission TEM, equipped with an EDS (JEM-2100F, JEOL). The information on the chemical binding was obtained from an XPS (AXIS-NOVA, KRATOS Analytical). The spectra for Ni 2p, Cr 2p, O 1s and Pb 4f were recorded with AlK $\alpha$  radiation ( $h\nu = 1486.6$  eV), at a pass energy of 20 eV. The take-off angle, the base pressure and the sputter rate for a depth profiling were 45°, 6.7x10<sup>-7</sup> Pa and 0.04 nm/s in SiO<sub>2</sub>, respectively. An online database was used for analysis of the XPS results [5].

The SSRT tests were performed on uniaxial tension specimens fabricated from HTMA tubing in unleaded and leaded solutions, and in a leaded solution supplemented with NiB. The tests were carried out in 1.89 L 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 x 10<sup>-7</sup> s<sup>-1</sup>. After the SSRT tests, the surfaces were observed by means of a SEM (JSM6360) for the purpose of determining the SCC ratio.

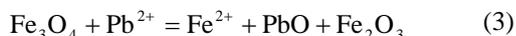
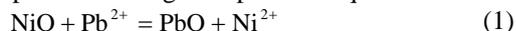
### 3. Results and discussion

Fig. 1 presents the TEM-EDS results for the Alloy 690 immersed in the unleaded 0.1 M NaOH solution (Fig. 1 (a)) and in the leaded solution (Fig. 1 (b)). The outer and inner oxides are Ni-rich oxide and relatively Cr-rich oxide (up to 70wt%), respectively, in the unleaded 0.1 M NaOH solution while a single layer was observed in the leaded 0.1M NaOH solution in spite of chemical compositional variation with the distance, which is similar with the results of Alloy 600. In the leaded solution, a large amount of lead was observed up to 35 % on the surface leading to the Ni depletion in the oxide layer. The Cr concentration in the oxide formed in the leaded 0.1M NaOH solution was higher ( $\geq 30$ wt%) than the concentration of Alloy 690 matrix. It should be noted that the Cr content for Alloy 690 is higher than that for Alloy 600 in leaded 0.1M NaOH solution. The Cr is effectively used as an alloying element of Ni- and Fe-based alloys because of the superior corrosion resistance of Cr oxide [6,7].

Therefore the higher Cr can form more stable oxide in Alloy 690 than Alloy 600. It is presumed that the Cr content preserved at a high level in the oxide is closely related with the superior PbSCC resistance of Alloy 690

(~0% PbSCC), compared with Alloy 600 (78% PbSCC) in the leaded 0.1M NaOH solution.

Thermodynamics can be considered for the experiment in high temperature aqueous solution.



Based on the thermodynamic data and solubility data, a forward reaction is possible for only reaction (1) at 315 °C assuming that concentrations of nickel and lead ions are  $10^{-6}$  M and  $4.5 \times 10^{-3}$  M, respectively while forward reaction for reactions (2) and (3) is not possible. Defect chemistry can be used to rewrite this reaction as follows.



The following summation of reactions (4) and (5) shows that the Ni at the Ni site in the oxide dissolves to leave a Ni vacancy and that the lead ion is oxidised by a reaction with the Ni vacancy in the oxide.



Reaction (6) confirms that Ni as a Ni oxide state can be depleted. A strain field in the oxide which appears to originate from a lattice mismatch as a result of the lead that is incorporated into the oxide degrades the level of passivity.

As expected from the potential difference in the equilibrium oxidation and reduction reactions, the lead electrodeposition are available. Cations in a metallic state such as Ni, Cr and Fe can therefore be depleted in the leaded aqueous solution by lead electrodeposition.

Lead ions in an aqueous solution and electrodeposited lead are oxidised when the pH level at 315 °C is larger than 4.46 and the hydrogen partial pressure is as low as about 5 ppb in the secondary water of an NPP. Thus, the PbO can be detected in the XPS analysis because of three factors: the lead incorporated into the oxide; the oxidation of the electrodeposited lead; and the PbO that is added to the solution.

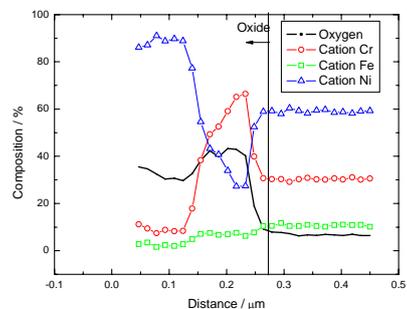
#### 4. Conclusion

The passive duplex oxide layer (a porous Ni-rich outer layer and a dense Cr-rich inner layer) was observed in the 0.1M NaOH solution while the less passive and nickel depleted single oxide layer was obtained in the leaded 0.1M NaOH solution for Alloy 600 and Alloy 690 while Cr content for Alloy 690 is higher than that for Alloy 600 in leaded 0.1M NaOH solution. It is presumed that the Cr content preserved at a high level in the oxide is closely related with the superior PbSCC resistance of Alloy 690 in the leaded 0.1M NaOH solution.

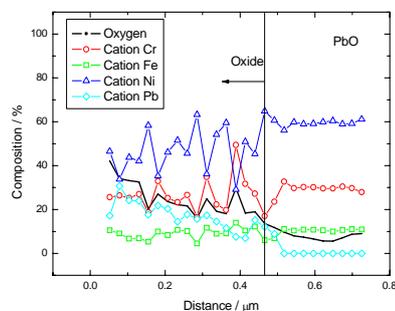
The thermodynamic considerations and experimental results of the high temperature leaded solution indicate that the major element Ni of Alloy 600 can be depleted in a metallic state and in a Ni oxide state unlike Cr. Moreover matrix cations can be depleted by the Pb

electrodeposition. The incorporated Pb prevents the formation of a passive oxide composed of Ni, Cr, Fe and O leading to PbSCC.

PbSCC is significantly reduced when NiB is added as an inhibitor. This result is consistent with the reduction in the amount of incorporated Pb and the increase in electrochemical impedance.



(a)



(b)

Fig. 1. The chemical compositions for the surface oxide layer formed on the Alloy 690 specimens at 315 °C; (a) 0.1M NaOH and (b) 0.1M NaOH + PbO.

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