Investigation of a Lead Induced SCC and Its Mitigation

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1. Introduction

Nuclear power plants (NPP) using Alloy 600 (Ni 75wt%, Cr 15wt%, Fe 10wt%) as a heat exchanger tube of the steam generator (SG) have experienced various corrosion problems such as pitting, intergranular attack (IGA) and stress corrosion cracking (SCC). In spite of much effort to reduce the material degradations, SCC is still one of important problems to overcome. Especially lead is known to be one of the most deleterious species in the reactor coolants that cause SCC of the alloy [1-4]. Even Alloy 690 as an alternative of Alloy 600 because of outstanding superiority to SCC is also susceptible to lead in alkaline solution [5,6].

Lead has been effectively detected in all tubesheet samples, crevice deposits and surface scales removed from SGs. Typical concentrations are 100 to 500 ppm but in some plants, concentrations as high as 2,000 to 10,000ppm has been detected [7].

According to previous reports [2-4,8], lead induced SCC (PbSCC) is more dependent on the crack initiation time than the crack propagation rate. An oxide on Alloy 600 is formed and modified expanding to complex sludge throughout hideout return (HOR) of various impurities including Pb, combined with a residual stress induced by a tube expansion which is introduced to fix a tube to a tube sheet during a long time operation under a high temperature and high pressure water chemical environment. Therefore it is expected that a passivity of an oxide formed on Alloy 600 is deeply related to PbSCC and an inhibitor to hinder oxide modification by lead efficiently can be found.

In the present work, an SCC susceptibility was investigated in the presence of lead and NiB as an inhibitor as well as in the absence of both impurities by using a slow strain rate tensile (SSRT) test. Moreover the oxides formed on Alloy 600 in aqueous solutions with and without lead were examined by using a scanning electron microscopy (SEM), a transmission electron microscopy (TEM), an energy dispersive x-ray spectroscopy (EDXS), an Auger electron spectroscopy (AES), an x-ray photoelectron spectroscopy (XPS) and an electrochemical impedance spectroscopy (EIS). The results were compared with the results obtained in aqueous solutions with NiB.

2. Experimental

The test specimens were fabricated from a 19.05 mm (0.75 inches) outside diameter Alloy 600 steam generator tubing material which was thermally treated (TT) at $704^{o}C$ for 15 hours following solution annealing at $975^{o}C$ for 20 minutes or high temperature mill annealed (HTMA) at $1024^{o}C$ for 3 minutes. High-purity water ($18M\Omega \cdot cm$ at RT) was used as the reference solution. Aqueous solutions used were shown in Fig. 1. Reagent grade PbO was added to the reference solution at an amount of 5,000 or 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. For ammonia and 0.1M NaOH solutions, Alloy 690 steam generator tubing material (Ni 60wt%, Cr 30wt%, Fe 10wt%) which was solution annealed at $1105^{o}C$ for 2 minutes, followed thermal treatment (TT) at $715^{o}C$ for 10 hours was tested. 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 SSRT tests were performed for uniaxial tension specimens fabricated from a HTMA 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 $315^{\circ}C$ 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 electrochemical tests were performed for rectangular plate specimens fabricated from a TT tubing. The surface of the specimens was polished up to 1 μm using a diamond suspension. The test specimens were immersed in a 1-gallon nickel autoclave at $315^{o}C$ for 14 days. The EIS measurements were carried out in a frequency range of 10^{6} to 10^{-3} Hz at an OCP with a 10 mV perturbation.

After the immersion test, the plate specimens were examined. The surface oxide layer and its composition was examined by using a SEM (JSM6360), a field emission TEM, equipped with an EDXS (JEM-2100F, JEOL) and AES (PHI 680 Auger Nanoprobe, Physical Electronics) with the sputter rate of 62Å/min in SiO_2.

3. Results and discussion

As shown in Fig. 1, pH at $315^{o}C$ increases by adding PbO, which seems to be caused by $PbO + H_2O = Pb^{2+} + 2OH^{-}$ reaction.

Fig. 2 presents the elongation to rupture as a function of the high temperature pH of aqueous solutions without/with PbO for HTMA Alloy 600. In spite that pH increases with the PbO addition, addition of PbO into the solution obviously degrades elongation to rupture as well as failure strength (not shown here) except for 40wt% NaOH + PbO. Considering that a neutral pH at $315^{o}C$ is 5.6, HTMA Alloy 600 is susceptible to a PbSCC in a slight alkaline solution. From the result of 40wt% NaOH, there seems to be a pH range susceptible to PbSCC.

Fig. 3 presents the elongation to rupture as a function of the high temperature pH of leaded solutions without/with NiB for HTMA Alloy 600. Addition of NiB into the solution obviously enhances elongation to rupture as well as failure strength (not shown here) except for 40wt% NaOH which was not degraded in solution with PbO.

From the TEM-EDXS and AES analyses, a duplex oxide layer was formed at the surface, i.e., porous nickel-rich outer layer and a dense chromium-rich inner layer in the unleaded reference solution. In the leaded solution, a large amount of lead was observed at about 20 %, at the surface leading to nickel depleted single oxide layer. In the leaded solution with the NiB inhibitor, the amount of lead in the oxide layer was significantly reduced and the extent of the cation depletion in the oxide was also decreased. This tendency was consistent with the passivity tendency obtained from the EIS measurement indicating that the oxide passivity is deeply related to PbSCC susceptibility.

The lead ions could have been incorporated into the oxide by an exchange with the metallic cations and hence a possible lattice mismatch might also introduce a strain field in the oxide leading to passivity degradation.

4. Conclusion

Lead species in aqueous solutions cause a PbSCC of a nickel-based Alloy 600 at a high temperature and a high pressure. 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 improving the oxide passivity, and decreasing its susceptibility to a PbSCC.

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Environment	pH(315°C) by MULTEQ	Remark	Experiment
-H_2O -H_2O + 10,000ppm PbO -H_2O + 10,000ppm PbO + 4g/L NiB	5.8 7.9 7.9	Neutral pH increase pH constant	SSRT A600
-0.01M Na_2SO_4 + 0.01M $NaHSO_4$ -0.01M Na_2SO_4 +0.01M $NaHSO_4$ + 10,000ppm PbO -0.01M Na_2SO_4 +0.01M $NaHSO_4$ + 10,000ppm PbO + 4g/L NiB	5.5 8.7 8.7	Acid pH increase pH constant	SSRT A600
-0.01M Na_2SO_4 -0.01M Na_2SO_4 + 10,000ppm PbO -0.01M Na_2SO_4 + 10,000ppm PbO + 4g/L NiB	7.5 8.6 8.6	Slight caustic pH increase pH constant	SSRT A600
-Ammonia -Ammonia + 5,000ppm PbO -Ammonia + 5,000ppm PbO + 4g/L NiB	6.3 7.9 7.9	Slight caustic pH increase pH constant	Immersion A600/A690
-0.1M NaOH -0.1M NaOH + 5,000ppm PbO -0.1M NaOH + 5,000ppm PbO + 4g/L NiB	9.9 9.9 9.9	Caustic pH constant pH constant	SSRT, Immersion A600/A690
-40wt% NaOH + 10,000ppm PbO -40wt% NaOH + 10,000ppm PbO + 4g/L NiB	11.8 11.8	Strong caustic	SSRT A600

Fig. 1. Various aqueous solutions and their pH for SSRT and immersion (electrochemical impedance) tests at 315°C.
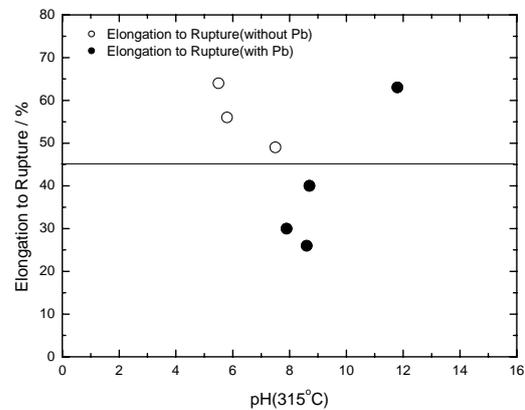
Fig. 2. Elongation to rupture as a function of the pH of aqueous solutions without/with PbO for HTMA Alloy 600.
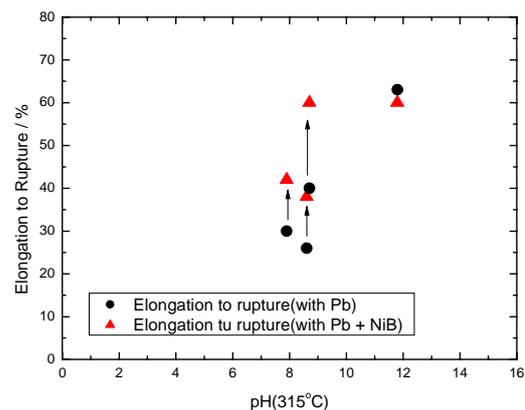
Fig. 3. Elongation to rupture as a function of the pH of leaded solutions without/with NiB for HTMA Alloy 600.