

Electrochemical Investigation of Passivity for Alloy 600 and Alloy 690 in Caustic Solutions

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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.

Alloy 690 (Ni 60wt%, Cr 30wt%, Fe 10wt%) is used and planned to be used as a heat exchanger tube of the steam generator (SG) and an alternative of Alloy 600 due to a relatively high stress corrosion cracking (SCC) susceptibility of Alloy 600 under operating conditions of nuclear power plants (NPP).

Secondary water pH which affects SCC behavior substantially spans widely from acid to alkaline in crevice depending on water chemistry control, water chemistry in crevice, plant specific condition, etc. In particular, specific chemical species are accumulated in the crevice of the sludge leading to a specific condition of crevice chemistry. Among these chemical species, 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 is not strong in alkaline solution with lead [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 have been detected [7].

The best method to prevent lead induced SCC (PbSCC) is to eliminate the harmful lead from the NPP chemistry, which is not possible and most NPPs are already contaminated by lead. Moreover only a very low level of sub ppm affects PbSCC. Therefore a mechanistic understanding of PbSCC is very crucial to control and mitigate PbSCC.

It is expected that an addition of lead into a solution modifies the oxide property considering that a passivity of oxide is directly related to SCC behavior. A discovery of the way to avoid this modification can give us a key to control PbSCC such as an inhibitor.

In the present work, an SCC susceptibility was investigated in the presence/absence of lead by using a slow strain rate tensile (SSRT) test. Moreover potentiodynamic experiment and electrochemical impedance measurement were performed for Alloy 600 and Alloy 690 in aqueous solutions with and without lead.

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°C for 15 hours following solution annealing at 975°C for 20 minutes or high temperature mill annealed (HTMA) at 1024°C for 3 minutes. High-purity water (18MΩ·cm at RT) was used as the reference solution. High-purity water (18MΩ·cm at RT) was used as the reference solution. Reagent grade PbO was added to the reference solution at an amount of 5,000 or 10,000 ppm as a source of lead. Deaeration was performed by a high purity nitrogen gas for 20 hours before the tests commenced.

The SSRT tests were performed for uniaxial tension specimens fabricated from Alloy 600 and Alloy 690 tubings in unleaded, and leaded solutions. 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 $2 \times 10^{-7} \text{ s}^{-1}$.

The potentiodynamic experiment and electrochemical impedance test were performed for rectangular plate specimens. 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°C for 14 days. The potentiodynamic experiment was performed as a scan rate of 5mV/s. The impedance measurements were carried out in a frequency range of 10^6 to 10^{-3} Hz at an OCP with a 10 mV perturbation.

3. Results and discussion

Table 1 shows SSRT results for Alloy 600 and Alloy 690 in 0.1M NaOH solution with/without PbO at 315°C. In deaerated 0.1M NaOH solution, Alloy 600 was resistant to SCC while Alloy 690 was very susceptible to PbSCC by adding PbO. PbSCC susceptibility was larger in deaerated solution than non-deaerated solution.

In Fig. 1 showing potentiodynamic curves obtained for Alloy 600 and Alloy 690 in 0.1M NaOH solution with/without PbO at 315°C, passive current increased with PbO addition in the solution indicating that PbO degraded oxide passivity. Oxide degradation by PbO would be greatly related with the PbSCC. However corrosion potential of Alloy 600 was increased to 600mV by non-deaeration of solution, which would lessen Pb incorporation into the oxide leading to better PbSCC resistance, compared to that in deaerated solution.

In deaerated 0.1M NaOH solution, Alloy 690 was resistant to SCC irrespective of PbO addition.

Potentiodynamic curve shows similar trend with that for Alloy 600 whereas SCC susceptibility trend is different from that for Alloy 600. Kinetics of Cr oxide formation as well as passivity should be considered during crack growth. Potentiodynamic curve and impedance spectroscopy don't give us a crack growth information.

Table 2 shows SSRT results for Alloy 600 and Alloy 690 in strong caustic solutions with/without PbO at 315°C.

In deaerated 2.5M NaOH solution (10wt% NaOH) with PbO, SCC susceptibility of Alloy 600 was decreased, compared to that in deaerated 0.1M NaOH solution with PbO. However the Alloy 690 which was almost immune in 0.1M NaOH solution with/without PbO was very susceptible to PbSCC. Alloy 690 showed significant SCC even in 2.5M NaOH in the absence of PbO. Moreover Alloy 690 was more susceptible to SCC in deaerated 40wt% NaOH(~10M NaOH) than that with PbO.

Alloy 690 is very susceptible to SCC in 10wt% NaOH solution with lead, irrespective of deaeration, which is strikingly different from the results in 0.1M NaOH. According to E-pH diagram, there is a difference between two solutions. Stable Ni oxide phases are NiO and NiO₂⁻²(aq) in 0.1M NaOH and 10wt% NaOH, respectively.

The reason for this different pH dependency of Alloy 690 and Alloy 600 should be clarified in the future.

4. Conclusion

In deaerated 0.1M NaOH solution, Alloy 600 and Alloy 690 are resistant to SCC while Alloy 600 is susceptible to PbSCC but Alloy 690 is also resistant adding PbO to 0.1M NaOH solution.

In deaerated 2.5M NaOH solution (10wt% NaOH) with PbO, SCC susceptibility of Alloy 600 was decreased, compared to that in deaerated 0.1M NaOH solution with PbO. However the Alloy 690 which was almost immune in 0.1M NaOH solution with/without PbO was very susceptible to PbSCC. Alloy 690 showed significant SCC even in 2.5M NaOH in the absence of PbO. Moreover Alloy 690 was more susceptible to SCC in deaerated 40wt% NaOH(~10M NaOH) than that with PbO.

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Table 1. SSRT results for Alloy 600 and Alloy 690 in 0.1M NaOH solution with/without PbO at 315°C.

Environment	Elongation to rupture(%)	SCC rate	pH(315°C) by MUREC	Remark
-0.1M NaOH (Deaeration)	57	-0	9.9	Alloy 600
-19,800ppm PbO addition (Deaeration)	26	78	9.9	
-19,800ppm PbO addition (Non-deaeration)	25	48	9.9	
-0.1M NaOH (Deaeration)	58	-0	9.9	Alloy 690
-0.1M NaOH + 19,800ppm PbO addition (Deaeration)	96	1.4	9.9	
-0.1M NaOH + 19,800ppm PbO addition (Non-deaeration)	54	1.4	9.9	

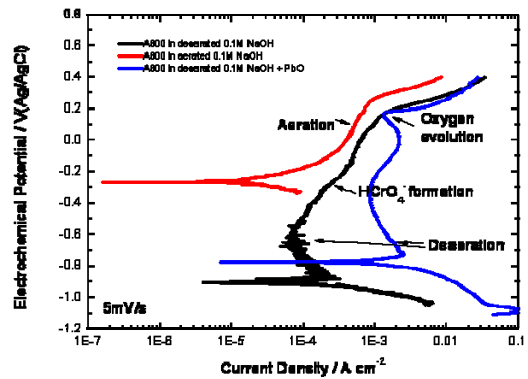


Fig. 1. Potentiodynamic curves obtained for Alloy 600 in 0.1M NaOH solution with/without PbO at 315°C.

Table 2. SSRT results for Alloy 600 and Alloy 690 in strong caustic solutions with/without PbO at 315°C.

Environment	Elongation to rupture(%)	SCC rate	pH(315°C) by MUREC	Remark
-30wt% NaOH (Deaeration)	-	-	10.4	Alloy 600
-19,800ppm PbO addition (Deaeration)	39	31	10.4	
-19,800ppm PbO addition (Deaeration)	65	25	10.9	
-30wt% NaOH (Deaeration)	31	43.5	10.4	Very susceptible Alloy 690 -SCC without Pb
-30wt% NaOH + 19,800ppm PbO addition (Deaeration)	5	98	10.4	
-30wt% NaOH (Non-deaeration)	49	41	10.4	
-30wt% NaOH + 19,800ppm PbO addition (Non-deaeration)	8	87	10.4	-SCC without Pb -Less susceptible with PbO
-30wt% NaOH (Deaeration)	19	67	10.9	
-30wt% NaOH + 19,800ppm PbO addition (Deaeration)	25	98	10.9	