

SCC Behavior of Alloy 690 in Leaded Aqueous Solution

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1. Introduction

Alloy 690 (Ni 60wt%, Cr 30wt%, Fe 10wt%) is used and planned to use as a heat exchanger tube of the steam generator (SG) and an alternative of Alloy 600 (Ni 75wt%, Cr 15wt%, Fe 10wt%) due to a relatively high stress corrosion cracking (SCC) susceptibility of Alloy 600 under operating condition of nuclear power plant (NPP). Secondary water pH which affects SCC behavior substantially is widely spanned from acid to alkaline in crevice depending on water chemistry control, water chemistry in crevice, plant specific condition, etc. Especially, 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 has 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 the 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 finding 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 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 690 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) and an electrochemical impedance spectroscopy (EIS). The results were compared with the results obtained from Alloy 600.

2. Experimental

Alloy 690 steam generator tubing material (Ni 60wt%, Cr 30wt%, Fe 10wt%) which was solution annealed at 1105°C for 2 minutes, followed thermal

treatment (TT) at 715°C for 10 hours was tested. The test specimens were fabricated from a 19.05 mm (0.75 inches) outside diameter Alloy 690 steam generator 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. The performance of a NiB inhibitor was evaluated by adding 4 g/l of NiB into the leaded solution. 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 a TT 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 $2 \times 10^{-7} \text{ s}^{-1}$.

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°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 SiO₂.

3. Results and discussion

Table 1 shows SSRT results for Alloy 690 in various aqueous solutions at 315°C. 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.

Compared with the results for Alloy 690, Alloy 600 shows a strong PbSCC susceptibility in 0.1M NaOH rather than 10wt% NaOH and 40wt% NaOH solutions as presented in Table 2. The reason of this different pH dependency of Alloy 690 and Alloy 600 should be clarified in the future.

Table 3 presents summary of AES results obtained from Alloy 690 and Alloy 600 in 0.1M NaOH aqueous solution with/without lead at 315°C. There is a compositional difference between oxides formed Alloy

690 and Alloy 600 in 0.1M NaOH with lead where Alloy 690 does not show PbSCC but Alloy 600 is susceptible to PbSCC. It should be noted that a Cr rich oxide is observed in an oxide formed on Alloy 690 in leaded 0.1M NaOH. However Cr rich oxide is not observed in an oxide formed on Alloy 600 in leaded 0.1M NaOH. This indicates that Cr rich oxide is deeply related to PbSCC resistance.

Fig. 3 presents the elongation to rupture as a function of the high temperature pH of leaded solutions without/with NiB for Alloy 690 and Alloy 600. Addition of NiB into the solution obviously enhances elongation to rupture representing a degree of SCC for Alloy 690 as well as Alloy 600. It seems that an oxide modification is retarded by NiB, which may be related to a competition of adsorption with PbO

4. Conclusion

Alloy 690 is very susceptible to PbSCC in a strong alkaline aqueous solution apart from a mild caustic solution, contrary to Alloy 600 which is more susceptible to PbSCC in a mild caustic solution.

It seems that a PbSCC is effectively impeded by a presence of Cr rich oxide.

The NiB inhibitor decreased the susceptibility to a PbSCC Alloy 690 as well as Alloy 600, which may be related to an adsorption competition of NiB and PbO.

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Table 1. SSRT results for Alloy 690 in various aqueous solutions at 315°C.

Environment	Elongation to rupture(%)	SCC ratio	pH(315°C) by MULTEQ	Remark
-0.1M NaOH + 10,000ppm PbO addition (Deaeration)	55	1.4	9.9	Caustic
-0.1M NaOH + 10,000ppm PbO addition (Non-deaeration)	54	1.4	9.9	
-10wt% NaOH + 10,000ppm PbO addition (Deaeration)	6	99.9	10.4	Highly caustic Very susceptible to PbSCC
-10wt% NaOH + 10,000ppm PbO addition (Non-deaeration)	8	96.9	10.4	

Table 2. SSRT results for Alloy 600 in various aqueous solutions at 315°C.

Environment	Elongation to rupture(%)	SCC ratio	pH(315°C) by MULTEQ	Remark
-0.01M Na ₂ SO ₄ + 0.01M NaHSO ₄ -10,000ppm PbO addition	64 40	16 57	5.5 8.7	Acid pH increase
-H ₂ O -10,000ppm PbO addition	56 30	0 83	5.8 7.9	Neutral pH increase
-0.01M Na ₂ SO ₄ -10,000ppm PbO addition	49 26	0 81	7.5 8.6	Slight caustic pH increase
-0.1M NaOH + 10,000ppm PbO addition (Deaeration)	24	78	9.9	Caustic
-0.1M NaOH + 10,000ppm PbO addition (Non-deaeration)	35	48	9.9	
-10wt% NaOH + 10,000ppm PbO addition (Deaeration)	38		10.4	Strong Caustic
-40wt% NaOH -10,000ppm PbO addition	- 63	- 25	10.9 10.9	Strong caustic Relatively less susceptible

Table 3. Summary of AES results obtained from Alloy 690 and Alloy 600 in various aqueous solutions at 315°C.

690TT Deaeration	Oxide Composition	Sputtering Time (min)	Remark
0.1M NaOH	Cr30%Ni70% → Ni90%Cr5% → Ni35-40%Cr55%	35	Inner Cr oxide
0.1M NaOH + PbO	Ni55% → Ni65% → Ni50%Cr40% (Pb incorporation, inner Cr-oxide)	70	No PbSCC Inner Cr oxide

600TT Deaeration	Oxide Composition	Sputtering Time (min)	Remark
0.1M NaOH	Ni100% → Ni90-85% → Ni65%Cr25%	100	Passive NiO stable region, Cr oxide
0.1M NaOH + PbO	Ni70% → Ni85%	75	PbSCC Ni depletion, No Cr oxide

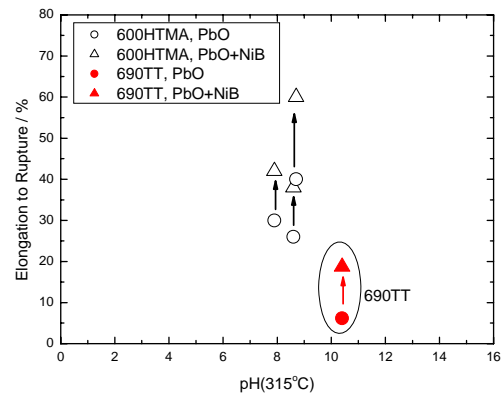


Fig. 1. Elongation to rupture as a function of the pH of leaded solutions without/with NiB for Alloy 690 and Alloy 600.