

Comparison between Alloy 600 and Alloy 690 ODS/SCC behavior

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1. Introduction

Stress corrosion cracking (SCC) has been occurred on Alloy 600 steam generator (SG) tubes frequently in the past and is still being occurred.

Many efforts to reduce SCC degradation were tried and then SCC resistance was improved by applying a heat treatment process from LTMA (low temperature mill annealed) Alloy 600 to HTMA (high temperature mill annealed) Alloy 600, and then TT (thermally treated) Alloy 600.

Intra-granular carbide widely spread in LTMA Alloy 600 dissolves, and inter-granular carbide is then formed during high-temperature mill annealing and cooling, which leads to a great SCC resistance enhancement. Inter-granular carbide is well developed, healing chromium depletion at a grain boundary, and residual stress is removed during additional thermal treatment following mill annealing, which improves the SCC resistance more [1].

In spite of this improvement of Alloy 600TT, Seabrook and Vogtle 1 in the US, using Alloy 600TT, also showed SCC due to a non-optimum microstructure, residual stress, Pb existence, and so on over a 20-year operation of an NPP even though SCC occurs less frequently than LTMA and (or) HTMA Alloy 600s [2,3]. SCC has also occurred for Alloy 600TT tubes in Korea, whose main causes resemble US cases. Hence, SCC on Alloy 600 should overcome because many plants use Alloy 600 as SG tubes.

Contrary to Alloy 600, Alloy 690 as an alternative of steam generator tubing material for Alloy 600 shows an excellent SCC resistance in most environments. Steam generator tubing materials are being selected as Alloy 690 in newly constructed nuclear power plants and replaced steam generators. There is no report about ODS/SCC (outside diameter SCC) for Alloy 690 which was first used in NPP (nuclear power plant) in 1988.

However it was reported [4,5] that Alloy 690 is not resistant to SCC in an alkaline environment including the pH range attainable in the SG crevice and moreover more susceptible to SCC in leaded alkaline solution.

In the present work, SCC resistance of Alloy 690 was compared with that of Alloy 600 in an alkaline solution based on SCC test results, which was discussed in terms of passivity, chemical stability and alloying element. Environment weighted improvement factor for Alloy 690 was also introduced.

2. Experimental

The slow strain rate tension (SSRT) test was performed for uniaxial tension specimens fabricated from the nickel based alloys in the unleaded and leaded solutions. The tests were carried out in half gallon nickel autoclaves at 315 °C and an equilibrium pressure. The test specimens were immersed at an open circuit potential (OCP) without an impressed electrochemical current. The strain rate was $2 \times 10^{-7} \text{ s}^{-1}$. Test procedure was reported elsewhere [5].

RUB (reverse u bend) samples were fabricated using a mandrel, bolt, nut and washer. The radius of RUB was 12.975mm, which was comparable to the previous report of 12.5mm [6]. According to the previous report [7], it was reported that the stress level of UTS (ultimate tensile stress) is applied to the apex of the RUB specimen in a RUB specimen radius range of 9-13mm.

The test specimens were immersed in 3.78 L Ti autoclaves. The pH (T) of the solution is expected to be 9.5 at 310°C by adjusting the NaOH concentration in a solution containing 3m NaCl + 500ppm Pb.

The immersion test was carried out for rectangular plate specimens (10 mm x 10 mm) fabricated from the tubing. The surface of the specimens was polished up to 1 μm using a diamond suspension. A nickel wire was spot welded to the specimen, and the wire was shielded with a heat-shrinkable polytetrafluoroethylene (PTFE) tubing. The immersion test was performed in a 1-gallon nickel autoclave at 315 °C for 28 days.

Materials used for the test were Alloy 600 HTMA, Alloy 600TT and Alloy 690TT, which were mill annealed at 1024°C for 3 min after solution annealing, thermally treated at 704 °C for 15 h after solution annealing at 975 °C for 20 min and thermally treated at 715°C for 10 h after solution annealing at 1105°C for 2 min, respectively.

Various alkaline solutions were made using high-purity water [room temperature resistivity of 18MΩ•cm]. The surface of the specimens for the immersion test was polished up to a 1 μm diamond suspension. Reagent grade PbO was added to the 0.1M NaOH solution as a source of lead.

Deaeration for SSRT and immersion tests was accomplished through high purity nitrogen gas purging for 20 h. For RUB test, the hydrogen concentration of 6ppm and deoxygenation for all autoclave tests was achieved at room temperature by three pressurizing/aspirating cycles from a 100psia to 1000psia overpressure of a 10% hydrogen/90% argon mixture gas and heating with a 200psia overpressure of

5% hydrogen/95% argon mixture gas, based on a previous report [6].

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 10^6 to 10^{-3} Hz using a Solartron 1260 frequency response analyser connected with a Solartron 1287 electrochemical interface for a 3 electrode system. A Nickel wire was spot welded to the specimen as the working electrode, and the wire was shielded with PTFE tubing. The nickel and Pt wires were used as a reference electrode and counter electrode, respectively.

After the immersion test, the surface oxide morphology was observed using SEM (JEOL JSM-6300). The surface oxide layer and its composition for the TEM samples prepared by FIB were examined using a FE TEM-EDS.

3. Results and discussion

SCC susceptibility for Alloy 690TT was increased with the pH(T) higher than 10.2 and aggravated by adding PbO. However SCC susceptibility was decreased in highly caustic solution of 10.9 of pH(T) as shown in Fig.1(a).

Unlike Alloy 690TT, SCC resistance of Alloy 600MA was stronger than Alloy 690TT in highly caustic solution. Rather, Alloy 600MA showed SCC susceptibility in mild alkaline solution and aggravated susceptibility by adding PbO. (Fig. 1(b))

Based on SSRT test results, factor of improvement (FOI) for Alloy 690, compared with Alloy 600 can be determined as follows. The results were shown in Table 1.

- $SCC\ rate = length / time$
- $Time\ to\ a\ certain\ length, t = 1 / SCC\ rate$
- $FOI\ of\ Alloy\ 690 = t(Alloy\ 690) / t(Alloy\ 600)$
 $= SCC\ rate\ (Alloy\ 600) / SCC\ rate\ (Alloy\ 690)$

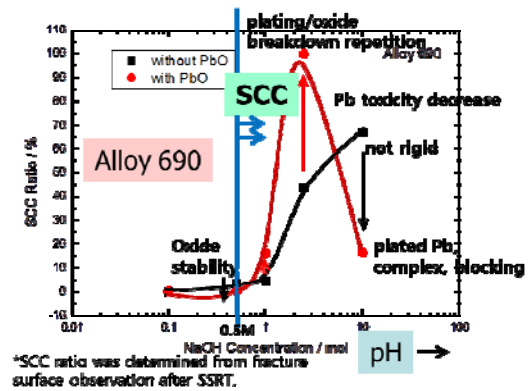
According to the RUB test in a caustic solution including PbO and chloride of pH(T) of 9.5, Alloy 690TT showed significant SCC susceptibility while Alloy 600MA and Alloy 600TT showed better SCC resistance as shown in Table 2.

Fig. 2 shows environment weighted improvement factor for Alloy 690 versus Alloy 600MA which was first proposed by EPRI [8]. They considered weight factors of oxidizing environment, lead contamination, chloride, sulfur and caustic condition. From this curve, integrity or weakness of Alloy 690 can be assessed, compared with Alloy 600 exposed to the same environment. Unfortunately, very limited experimental data were used to establish environment weighted FOI because of insufficient data base under various environments.

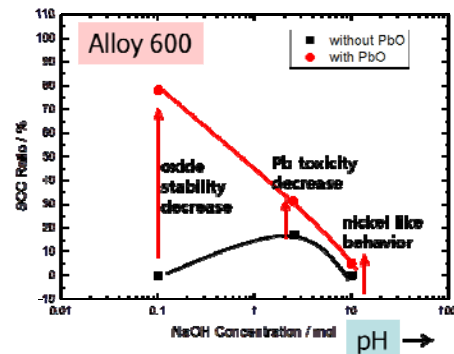
It is found that chloride shows synergic effect on SCC susceptibility with lead according to recent result at this

laboratory while the chloride effect on SCC in caustic solution was ignored determining the original environment weighted FOI. The same FOI for chloride as the FOI in alkaline solution without chloride was used in the alkaline pH range to determine overall environment weighted FOI curve, which seems to cause over estimation of FOI.

Based on additional experimental results under various conditions such as the effect of the only chloride on SCC, FOI curve needs to be modified to apply to SG tubing material integrity assessment.



(a)



(b)

Fig. 1. SCC ratio of (a) Alloy 690TT and (b) Alloy 600MA as a function of the pH.

Table 1. SSRT results and FOI of Alloy 690.

Material	Test	Environment	Test Method	SCC Rate	Cr	Cl	S	SO ₂	Factor of Improvement (FOI)	Notes
Alloy 690TT	SSRT	Caustic	ASTM G46	0.001	0.001	0.001	0.001	0.001	1.0	Baseline
Alloy 690TT	SSRT	Caustic + PbO	ASTM G46	0.002	0.002	0.002	0.002	0.002	2.0	SCC rate increased with PbO
Alloy 690TT	SSRT	Caustic + Cl	ASTM G46	0.001	0.001	0.001	0.001	0.001	1.0	Baseline
Alloy 690TT	SSRT	Caustic + Cl + PbO	ASTM G46	0.003	0.003	0.003	0.003	0.003	3.0	SCC rate increased with Cl and PbO

Table 2. RUB test results and FOI of Alloy 690.

Material	Test	Environment	Test Method	SCC Rate	Cr	Cl	S	SO ₂	Factor of Improvement (FOI)	Notes
Alloy 690TT	RUB	Caustic	ASTM G46	0.001	0.001	0.001	0.001	0.001	1.0	Baseline
Alloy 690TT	RUB	Caustic + PbO	ASTM G46	0.002	0.002	0.002	0.002	0.002	2.0	SCC rate increased with PbO
Alloy 690TT	RUB	Caustic + Cl	ASTM G46	0.001	0.001	0.001	0.001	0.001	1.0	Baseline
Alloy 690TT	RUB	Caustic + Cl + PbO	ASTM G46	0.003	0.003	0.003	0.003	0.003	3.0	SCC rate increased with Cl and PbO

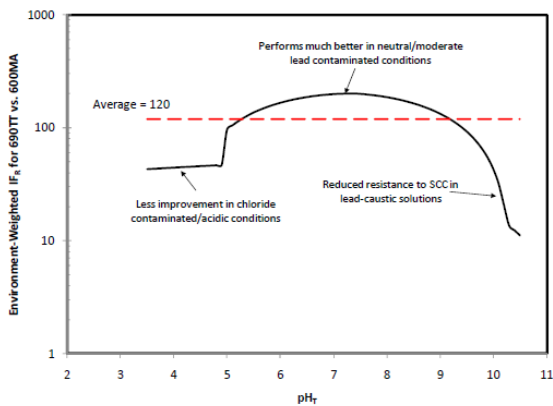


Fig. 2. Environment weighted improvement factor for Alloy 690TT versus Alloy 600MA.

Thick Oxygen Affected Layer (OAL) was observed after immersion test for Alloy 690 unlike Alloy 600 as shown in Fig. 3, which is similar to penetrative oxide observed in primary side. The OAL was increased in thickness with the immersion time. It was revealed that this layer was distributed as alternative oxide and metallic layer.

This indicates that electrolyte can penetrate into deep inside. It is also presumed that fast oxidation of Cr induces Cr depletion within very narrow region (Ni enrichment). This layer can be potential threat to brittle cracking of Alloy 690. The OAL was discussed in view of oxidation kinetics and thermodynamics.

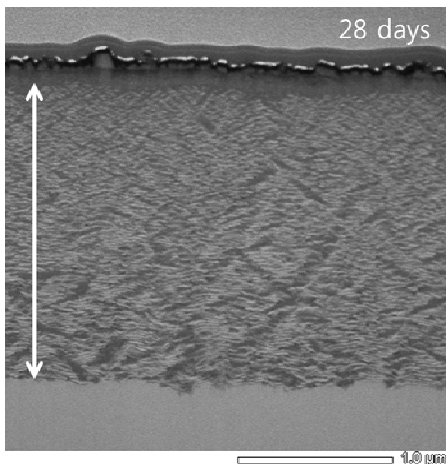


Fig. 3. TEM image for Alloy 690TT cross section after immersion test in 0.1M NaOH + 1,000 ppm PbO during 28 days.

4. Conclusion

ODSCC behavior of Alloy 690 and Alloy 600 as a SG tubing material was compared using SSRT and RUB test results performed at 310 and 315°C in various alkaline solutions with and without PbO.

SCC susceptibility for Alloy 690TT was increased with the pH(T) higher than 10.2 and aggravated by adding PbO. However SCC susceptibility was decreased in highly caustic solution of 10.9 of pH(T).

Alloy 690TT showed significant SCC susceptibility in combined caustic solution including PbO and chloride of pH(T) of 9.5. Unlike Alloy 690TT, SCC resistance of Alloy 600MA was stronger than Alloy 690TT in highly caustic solution. The difference in SCC behavior was expressed in terms of passivity, chemical stability and alloying element.

Environment weighted FOI for Alloy 690 versus Alloy 600 need to be revised based on accurate and wide data base.

Oxygen affected layer was observed and its thickness was increased with the immersion time for Alloy 690TT, which was discussed in view of oxidation kinetics and thermodynamics. This layer can be threat to brittle cracking.

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