

SUSCEPTIBILITY OF ALLOY 690 TO STRESS CORROSION CRACKING IN CAUSTIC AQUEOUS SOLUTIONS

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Stress corrosion cracking (SCC) behaviors of Alloy 690 were studied in lead-containing aqueous alkaline solutions using the slow strain rate tension (SSRT) tests in 0.1M and 2.5M NaOH with and without PbO at 315°C. The side and fracture surfaces of the alloy were then examined using scanning electron microscopy after the SSRT test. Microstructure and composition of the surface oxide layer were analyzed by using a field emission transmission electron microscopy, equipped with an energy dispersive X-ray spectroscopy. Even though Alloy 690 was almost immune to SCC in 0.1M NaOH solution, irrespective of PbO addition, the SCC resistance of Alloy 690 decreased in a 2.5M NaOH solution and further decreased by the addition of PbO. Based on thermodynamic stability and solubility of oxide, high Cr of 30wt% in the Alloy 690 is favorable to SCC in mild alkaline and acidic solutions whereas the SCC resistance of high Cr Alloy 690 is weakened drastically in the strong alkaline solution where the oxide is not stable any longer and solubility is too high to form a passive oxide locally.

KEYWORDS : Stress Corrosion Cracking, Alloy 690, Lead Oxide, Passive Film

1. INTRODUCTION

Nuclear power plants (NPPs) that use Alloy 600 as a heat exchanger tube in a steam generator (SG) have experienced a variety of corrosion problems such as pitting, intergranular attacks (IGA) and stress corrosion cracking (SCC). In spite of considerable efforts to reduce the material degradation, SCC remains an important problem to be overcome leading to substantial maintenance and thus electric generation unit costs. Recently, ODS-SCC (outer diameter SCC) on Alloy 600TT occurred due to the long-term operation of NPPs. It was predicted that residual stress and incorporated Pb accelerated ODS-SCC [1].

On the other hand, Alloy 690 as an alternative of steam generator tubing material for Alloy 600 shows an excellent SCC resistance in most environments, compared to Alloy 600. Alloy 690 is now being selected as a steam generator (SG) tubing material in newly constructed NPPs and in replaced SG of existing NPPs.

Generally, secondary water pH (T) levels in the crevice of steam generators in NPPs varies widely from 4 to 9.5 depending on the water chemistry control, the water chemistry in crevices, plant-specific condition, etc and then affect SCC behavior [2]. The pH(T) in crevice is predicted to be 10.4 when tested in feedwater containing only NaOH of 40ppm [2]. Chloride and sodium ions can concentrate up to 10^7 - 10^8 times in the crevice than the bulk solution increasing acidity and alkalinity, respectively [3]. Accord-

ing to pH prediction using MRI (molar ratio index) value, pH (T) can attain above 10.5 in some plants [2].

Moreover, 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 [4-7]. It is reported that a threshold level is as low as 0.1ppm for Alloy 600 [7]. Typical concentrations of lead are 100 to 500 ppm but in some plants, concentrations as high as 2,000 to 10,000ppm have been detected [8]. Water chemistry considering such as harmful elements and concentration in the crevice should be controlled in order to minimize the damage caused by corrosion.

The incorporation of lead in oxide degraded the oxide passivity and increased SCC susceptibility. A relatively passive duplex oxide layer of a porous Ni-rich outer layer and a dense Cr-rich inner layer formed in the unleaded solution, but a duplex oxide layer was not observed and cations were depleted when lead was incorporated in the oxide layer that formed in the lead solution. From the thermodynamic considerations and experimental results of the high temperature lead solution, it was shown that the major alloying element Ni of Alloy 600 was depleted in both metallic and Ni oxide states 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 [9].

Apart from Alloy 600, it was found that the Cr-rich oxide played an important role in SCC resistance from the fact that the SCC resistance of Alloy 690 with the passive Cr-rich oxide in the surface is much higher than that of Alloy 600 without Cr-rich oxide in the surface in leaded 0.1M NaOH solution [10]. However it was also reported that even Alloy 690 is also susceptible to lead induced SCC in strong alkaline solutions [11,12]. Therefore recognizing that SCC for Alloy 600 occurred increasingly with the long time operation of nuclear power plants, an investigation of SCC resistance of Alloy 690 needed to be conducted to thoroughly understand how Alloy 690 behaves and reacts in alkaline concentrations with/without lead.

In the present work, the SCC resistance for Alloy 690 was investigated in alkaline solutions (pH (T) = 9.9 and 10.4 in 0.1M and 2.5M NaOH, respectively) in the absence/presence of the lead, which are achievable in a crevice at 315°C using SSRT (slow strain rate tension) test. The oxide morphology and composition of immersed specimen was observed using SEM (scanning electron microscopy), TEM (transmission electron microscopy) and EDS (energy dispersive x-ray spectroscopy) after immersion test in the alkaline solution.

2. EXPERIMENTAL PROCEDURE

The test specimens were fabricated from 19.05 mm outside diameter Alloy 690 steam generator tubing materials (Sandvik, heat number 766881) which were thermally treated (TT) at 715°C for 10 h after solution annealing at 1105°C for 2 min for SSRT and immersion tests. The chemical composition is shown in table 1.

The 0.1 and 2.5M NaOH solutions were made using high-purity water [room temperature resistivity of 18MΩ·cm]. Reagent grade PbO was added to the caustic solution

at an amount of 10,000 ppm as a source of lead. Deaeration was accomplished by a high purity nitrogen gas purging for 24 h.

As shown in Fig. 1, 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 1 L 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 $2 \times 10^{-7} \text{ s}^{-1}$.

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 PTFE tubing. The immersion test was performed in a 1-gallon nickel autoclave at 315°C for 14 days.

Side and fractured surfaces were observed using scanning electron microscopy after SSRT tests. After the immersion test, the surface oxide layer and its composition was examined by using a field emission transmission electron microscopy (TEM), equipped with an energy dispersive X-ray spectroscopy (EDS) (JEM-2100F).

3. RESULTS AND DISCUSSION

Fig. 2 shows stress strain curves obtained in 0.1M NaOH solution without and with 10,000ppm PbO at 315°C. In 0.1M NaOH solution, UTS (ultimate tensile strength) and elongation to rupture were almost constant to be 600 MPa and above 55%, respectively, irrespective of the addition of PbO into solution.

Fig. 3 illustrates that SEM micrographs for side surface of Alloy 690 specimen obtained after SSRT test in 0.1M

Table 1. Chemical Composition of the Alloy 690 TT

Material	C	Si	Mn	P	Cr	Ni	Fe	Co	Ti	Cu	Al	B	S	N	Nb
Alloy 690 TT	0.02	0.22	0.32	0.009	29.57	58.9	10.54	0.01	0.26	0.01	0.019	0.004	0.001	0.017	0.01

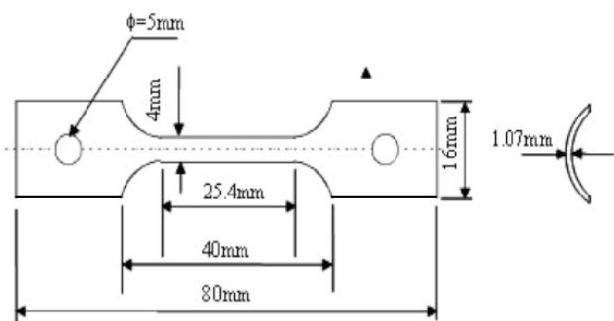


Fig. 1. Design of the Test Specimen Fabricated for SSRT Test.

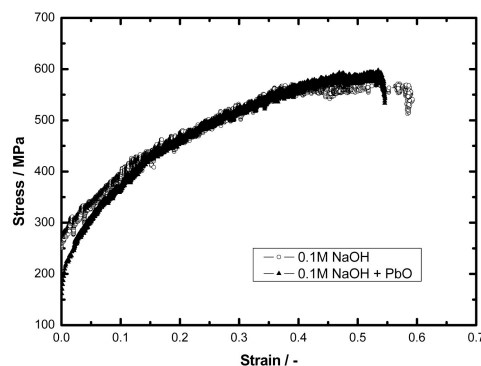


Fig. 2. Stress Strain Curves for Alloy 690 Obtained in 0.1M NaOH Solution without and with 10,000ppm PbO at 315°C

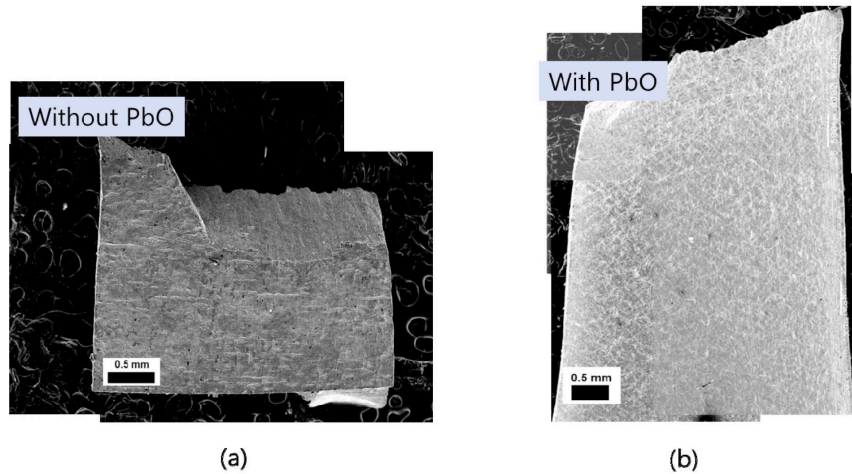


Fig. 3. SEM Micrographs for Side Surface of Alloy 690 Specimen Obtained After SSRT Test in 0.1M NaOH Solution (a) without and (b) with 10,000ppm PbO at 315°C

NaOH solution (a) without and (b) with 10,000ppm PbO at 315°C. It is easy to judge whether SCC occurred or not from the side view of SCC tested surface [13]. SCC did not occur and very slight SCC occurred in 0.1M NaOH solution without and with PbO, respectively. From the results of Figs. 2 and 3, it is indicated that Alloy 690 is resistant to SCC and indifferent to PbO in 0.1M NaOH solution.

Fig. 4 shows stress strain curves obtained in 2.5M NaOH solution without and with 10,000ppm PbO at 315°C. However, it is surprised that UTS and elongation to rupture of Alloy 690 decreased to 500MPa and 30% in 2.5M NaOH solution and 250MPa and 5% in 2.5M NaOH solution with PbO, respectively.

Fig. 5 illustrates that SEM micrographs for side surface of Alloy 690 specimen obtained after SSRT test in 2.5M

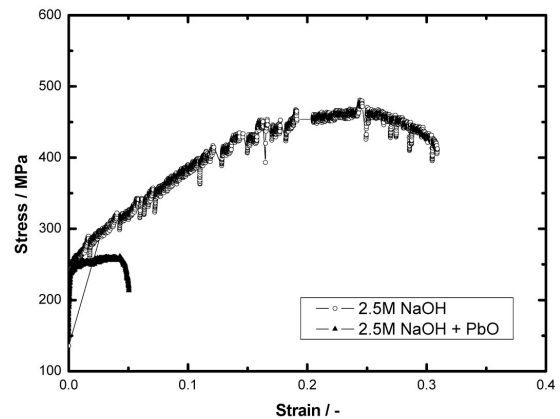


Fig. 4. Stress Strain Curves for Alloy 690 Obtained in 2.5M NaOH Solution without and with 10,000ppm PbO at 315°C

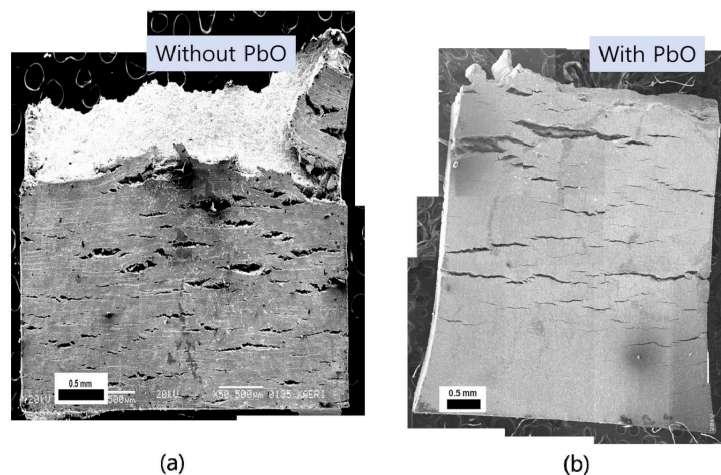


Fig. 5. SEM Micrographs for Side Surface of Alloy 690 Specimen Obtained After SSRT Test in 2.5M NaOH Solution (a) without and (b) with 10,000ppm PbO at 315°C.

Table 2. SCC Test Results Summarized for Alloy 690 and Alloy 600

Environment	Elongation to rupture(%)	SCC ratio	pH(315°C)by MULTEQ	Remark
- 0.1M NaOH	59	Negligible	9.9	Alloy 690
- 0.1M NaOH + PbO	55	Little	9.9	
- 2.5M NaOH	31	44	10.4	
- 2.5M NaOH + PbO	5	99	10.4	
- 0.1M NaOH	57	Little	9.9	Alloy 600*
- 0.1M NaOH + PbO	24	78	9.9	
- 2.5M NaOH	55	17	10.4	
- 2.5M NaOH + PbO	38	31	10.4	

* Data for Alloy 600 was previously published [9].

NaOH solution (a) without and (b) with 10,000ppm PbO at 315°C. The SCC was shown in 2.5M NaOH solution and got worse adding PbO into the solution.

This indicates that Alloy 690 is susceptible to SCC in 2.5M NaOH without PbO and very susceptible to PbSCC in 2.5M NaOH with PbO, compared with the results of 0.1M NaOH solution with and without PbO.

SCC test results are summarized for Alloy 690 in table 2. For the comparison with Alloy 690, the results of Alloy 600 [9] were also summarized in table 2. The SCC ratio is defined as the SCC area over the cross-sectional area of the specimen, which is obtained from observation of the fracture surface. Fig. 6 is SEM micrograph for fracture surface of Alloy 690 specimen obtained after SSRT test in 2.5M NaOH solution at 315°C. Fracture surface caused by SCC (intergranular and (or) transgranular) in the outside is differentiated from fracture surface caused by ductile fracture in the inside of specimen [14].

The elongation to rupture was determined from the stress-strain curve. Both the elongation to rupture and the SCC ratio can be used as criteria for SCC susceptibility. Their usefulness as criteria is based on the fact that the tensile strength decreases with the SCC leading to the lower elongation to rupture.

According to the previous report [9], the SCC ratio was 78 % in a 0.1 M NaOH solution with PbO but negligible in a 0.1 M NaOH solution without PbO for Alloy 600. The PbO increased the SCC susceptibility to an SCC ratio of 31 % in a highly caustic 2.5M NaOH solution. In this solution without PbO, the sample of Alloy 600 had an SCC ratio of 17 %. Accordingly, the Alloy 600 is more susceptible to a PbSCC in a mild caustic solution such as a 0.1 M NaOH solution rather than a strong caustic solution such as 2.5 M NaOH solution.

It was reported [9] that the major alloying element Ni of Alloy 600 can be depleted in both metallic and Ni oxide states unlike Cr in the high temperature leaded solution. Moreover matrix cations can be depleted by the Pb elec-

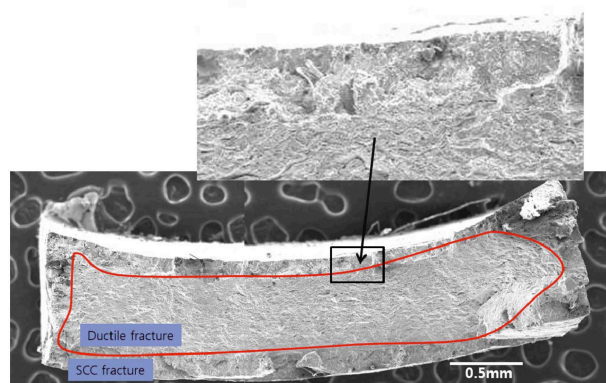


Fig. 6. SEM Micrograph for Fracture Surface of Alloy 690 Specimen Obtained After SSRT Test in 2.5M NaOH Solution at 315°C.

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

Unlike SCC behavior of Alloy 600 in alkaline solutions, Alloy 690 is almost immune to SCC in 0.1M NaOH, irrespective of presence/absence of lead. The SCC resistance of Alloy 690 decreased drastically in 2.5M NaOH.

In the previous work [10], the difference of SCC resistance between Alloy 600 and Alloy 690 in 0.1M NaOH was explained from the difference of Cr content in the oxide. Due to the higher Cr in the Alloy 690 than Alloy 600, more stable oxide can be formed leading to the superior SCC resistance of Alloy 690 in the 0.1M NaOH solution without/with PbO.

TEM analysis was performed for the Alloy 690 specimens immersed in 2.5M NaOH. Fig. 7 shows the TEM micrographs and the results of TEM-EDS analyses for the specimens tested in the unleaded 2.5 M NaOH solution (Fig. 7a) and in the leaded solution (Fig. 7b). Unlike 0.1M NaOH solution where duplex layer above 200 nm, i.e. outer nickel rich oxide and inner dense chromium rich oxide was

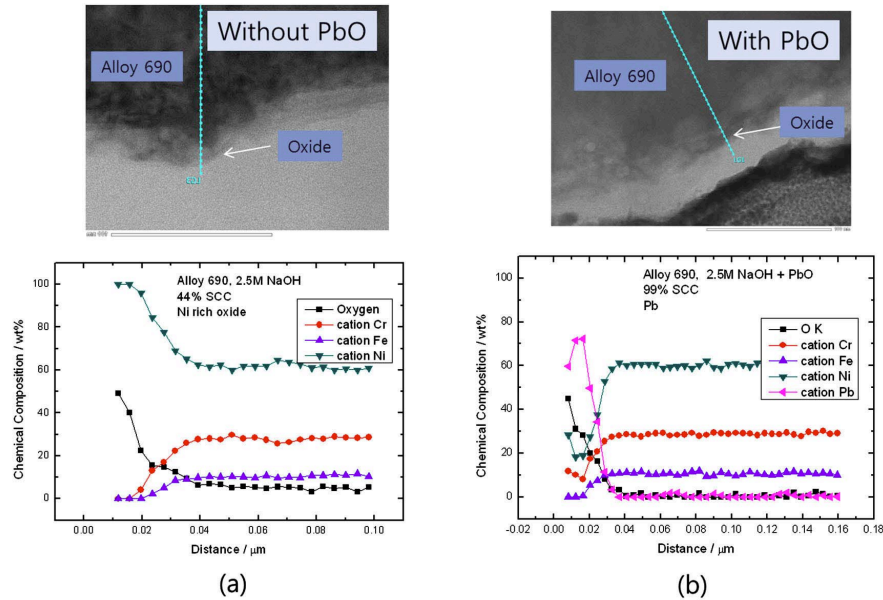


Fig. 7. TEM Micrographs and the Results of TEM-EDS Analyses for the Specimens Tested in (a) the Unleaded 2.5 M NaOH Solution and (b) the Leaded Solution.

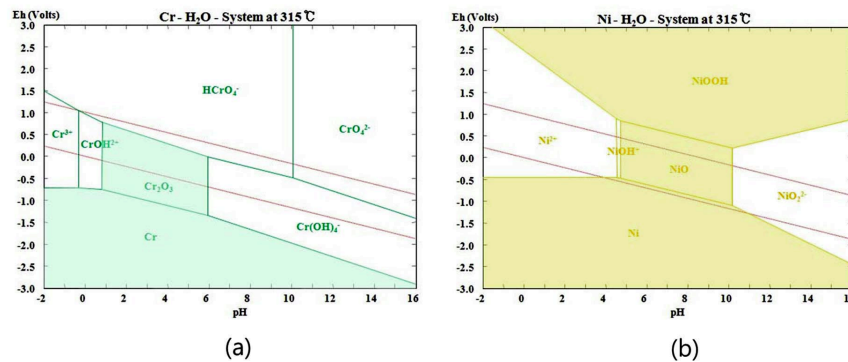


Fig. 8. E-pH Diagrams for (a) Cr-H₂O System and (b) Ni-H₂O System at 315°C.

formed, thin nickel rich oxide of about 30nm thickness was formed, irrespective of the addition of lead into the solution.

Thin nickel rich oxide was formed on the dense Alloy 690 matrix. According to the previous results [9,15], outer nickel rich oxide and inner chromium rich oxide formed on the Alloy 690 surface are porous and dense, respectively. It was deduced that inner chromium rich oxide is responsible for SCC resistance. Nickel rich oxide layer on the Alloy 690 shown in Fig. 7 does not appear to be impervious morphologically and compositionally.

Lead was incorporated in the oxide in leaded 2.5M NaOH solution, compared with oxide formed in unleaded 2.5M NaOH solution. Nickel composition decreased in the oxide by lead incorporation in leaded 2.5M NaOH solution, similarly with the results obtained from the Alloy 600 immersed in alkaline solution. Thermodynamically, the major alloying element Ni can be depleted in both metallic and Ni oxide states by reaction with lead in a high temper-

ature aqueous solution, which was observed experimentally using XPS [9]. Nickel oxide and metallic nickel can be changed into nickel ions by reacting with a lead ion. However chromium oxide cannot react with lead ions to become a chromium ion while metallic chromium can be changed to be chromium ion. It is reasonable that the nickel in Alloy 690 behaves like the nickel in Alloy 600 when lead is incorporated into the oxide. The incorporated Pb prevents the formation of a passive oxide composed of Ni, Cr, Fe and O leading to PbSCC.

It is worthwhile to note that Cr rich oxide on the surface of the Alloy 690 is non-existent in the strong caustic solution of 2.5M NaOH.

Figs. 8 (a) and (b) represent E-pH diagrams for (a) Cr-H₂O system and (b) Ni-H₂O system at 315°C obtained from HSC 6.0 [16]. Cr₂O₃ is not stable above pH (T) of 6.0 to be ionic form of Cr(OH)₄⁻ whereas NiO is stable thermodynamically to be pH (T) of 10.2.

Metal dissolves to be metallic ion producing electron ($M = M^{2+} + 2e^-$). Metallic ion reacts with water to make oxide producing proton ($M^{2+} + H_2O = MO + 2H^+$). Cathodic reaction occurs consuming electron and producing hydrogen molecule ($2H^+ + 2e^- = H_2$). Therefore pH does not change by net reaction ($M + H_2O = MO + H_2$). However local pH on specimen surface can decrease in stagnant condition. In doing so, Cr_2O_3 as well as NiO can be formed on the surface of bulk pH (T) of 9.9 (0.1M NaOH) where NiO is stable but Cr_2O_3 is not stable thermodynamically.

However, both Cr_2O_3 and NiO are not stable in the bulk pH (T) of 10.4 (2.5M NaOH) and solubility is too high to form passive and dense oxide on the surface. Consequently, very thin and rather pervious nickel rich oxide is formed on the surface.

High solubility and instability of Cr in strong caustic solution degrades SCC resistance of higher Cr alloy, Alloy 690 rather than that of lower Cr alloy, Alloy 600, as shown in table 2. Lead is incorporated into the surface oxide formed Alloy 690 to be less passive and also facilitates metallic dissolution, which leads to aggravation of SCC resistance of Alloy 690.

4. SUMMARY

- 1) Alloy 690 was almost immune to SCC in 0.1M NaOH solution, irrespective of the addition of PbO, while the Alloy 600 was very susceptible to PbSCC in 0.1M NaOH solution.
- 2) Alloy 690 was very susceptible to SCC in 2.5M NaOH solution without PbO addition and much more susceptible to PbSCC in a leaded 2.5M NaOH solution. The SCC susceptibility of Alloy 690 in 2.5M NaOH solution was larger than that of Alloy 600. Based on thermodynamic stability and solubility of chromium oxide and nickel oxide, high Cr of 30wt% in the Alloy 690 is favorable to SCC in mild alkaline and acidic solutions but the SCC resistance of high Cr Alloy 690 is weakened drastically in the strong alkaline solution where the oxide is not stable any longer and solubility is too high to form a passive oxide locally.
- 3) The SCC resistance of Alloy 690 was degraded by lead oxide in solution. It is plausible that lead is incorporated into the oxide to be less passive oxide

and also facilitates metallic dissolution similar with that for Alloy 600.

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