Stress Corrosion Cracking Behavior and Surface Oxidation Properties of Alloy 600 and 690 in Secondary Environment with Impurities

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1. Introduction

Steam generator (SG) of a nuclear power plant is a heat exchanger that generates steam for driving turbines on the secondary side. Reactor coolants of the primary side are used as a heat source by SG and it occupies a large area of 50% or more of the primary side pressure boundary. If SG is damaged due to corrosion, radioactive materials leak from the primary system to the secondary system, affecting stability. Simultaneously, the operation rate may be reduced due to maintenance and repair after shutdown. The maintenance activity of SG may be hindered and its life may be shortened[1].

Alloy 600 (Ni-15Cr-9Fe) has been used until now as a material for SG tubes due to its slow corrosion rate and excellent resistance to stress corrosion cracking in primary and secondary cooling water environments of pressurized water reactors(PWR). However, issues such as pitting corrosion, stress corrosion cracking, and intergranular attack (IGA) have occurred over long-term use [2,3].

To solve this problem, Alloy 690 whose Cr content is higher by about twice than that of Alloy 600 is used. The increase in Cr content of Alloy 690 is believed to inhibit Cr depletion of crystal grain boundaries and accelerate the formation of chromium oxides, which are problematic in the precipitation of carbides, in turn, increasing corrosion resistance[4].

The secondary system of a nuclear power plant may have a small number of impurities (S, Pb, and Cl etc.) that are introduced during the initial construction, maintenance, and normal operation. The concentrations of these impurities are very low. The movement of cooling water, however, is limited. Therefore, impurities can be concentrated in the gap between the top of tubesheet and the tube where sludge accumulates. The environment is chemically complicated and has a wide range of pH values from acidic to alkaline[5].

In this study, we aimed to analyze the characteristics of the film after corrosion experiment using existing heat transfer tube material in an aqueous solution containing Pb, Cl,and S to identify mechanisms of stress corrosion cracking

2. Experimental

Alloy 600MA, 600TT, and 690TT were used as SG tubings in this work. Chemical compositions are listed in Table 1. A tube was machined for reverse U-bend (RUB) sample preparation. RUB samples were fabricated using mandrel, bolts, nuts, and ZrO washers. Radius of RUB was 12.975 mm. According to a previous report[6], ultimate tensile stress (UTS) is applied to the apex of a RUB specimen in a radius (9–13mm).

The test specimens were immersed in 3.78L C276 autoclaves. The test matrix is shown in Table2. The pH(T) of the solution was adjusted to be 9.5 at 310℃ using NaOH concentration.

Hydrogen concentration of 6ppm and deoxygenation for all autoclave tests were achieved.

An optical microscope was used to observe the crack formation of the specimen. TEM was used to observe the surface of the oxide film.

Table 1. Chemical Compositions of Alloy 600 and 690

Material	C	Si	Mn	P	Cr	Ni	Fe	Co	Ti	Cu	Al	B	S	N	Nb
Alloy 600	0.025	0.05	0.22	0.07	15.67	75.21	8.24	0.005	0.39	0.011	0.15	0.0014	0.001	0.0103	-
Alloy 690	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

Table 2. Chemical Compositions of Test Solution

	Chemical Composition of Test Solutions	Remark
Without	0.022 NaOH	Alkaline
	3m NaCl + 0.45m NaOH	Cl
	0.31m Na_2SO_4 + 0.05m NaOH	S
	0.45m NaOH + 0.31m Na_2SO_4 + 3m NaCl	Cl + S
With	0.022 NaOH + 500 ppm Pb	Pb
	3m NaCl + 0.45m NaOH + 500 ppm Pb	Pb + Cl
	0.31m Na_2SO_4 + 0.05m NaOH + 500 ppm Pb	Pb + S
	0.45m NaOH + 0.31m Na_2SO_4 + 3m NaCl + 500 ppm Pb	Pb + Cl +S

3. Results and discussion

Fig. 1 displays the results of experiments that were conducted in different environments. The cracks in Alloy 690 in the solution containing Pb were the longest. Cracks were found in Alloy 600 regardless of the content of Pb. Alloy 690 without Pb presented negligible cracks. Chloride had a greater effect on the stress corrosion cracking (SCC) than sulfur under the influence of the remaining impurities. When sulfur and chlorine were added together SCC was the weakest.

Optical microscope observation results are shown in Fig. 2 Representative results from experiments were observed for Pb + Cl + S group and without Pb groups. As shown in Fig. 1, the largest cracks were found in Alloy690 containing Pb and no cracks were found in the specimens without Pb. The shape of the cracks was complex and most cracks were observed to be transgranular. For Alloy 600, cracks were found under all conditions. The crack length increased with increase in different impurities. The difference, however, was not evident. The cracks were intergranular. It is considered that the shape and existence of surface oxide film affected SCC in Alloy 690.

Fig. 3 shows the results of TEM observation of the surface oxide layer of Alloy 690, which showed a large difference from the results of optical microscopy. Alloy 690 in the solution containing no Pb had a uniform oxide film on the surface, but in the solution containing Pb, an oxide containing Pb was found on the surface of Alloy 690. It is considered that the shape and existence of surface oxide film affects SCC in Alloy 690.

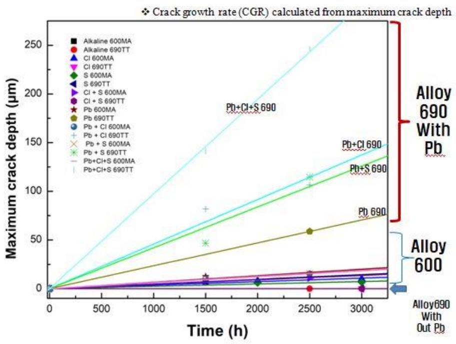

Fig. 1. Crack depth with immersion time for Alloy 600 and 690 in an experimental solution

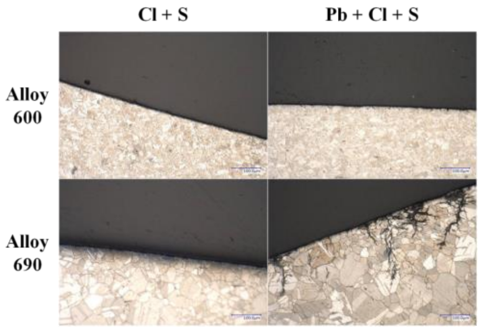

Fig. 2. Optical microscope images of Alloy 600 and 690 in Cl + S and Pb + Cl + S solutions.

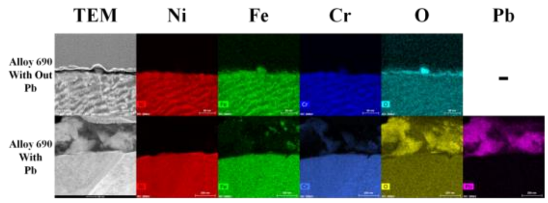

Fig. 3. STEM-HAADF images and EDX elemental maps obtained from APEX in Alloy 690 with and without Pb

4. Conclusions

The SCC of Alloy 690 showed a large susceptibility in the Pb-added environment and was not affected by other impurities (Cl, S). Although Alloy 600 was able to detect cracks in all impurities, it did not show any rapid change with certain impurities. TEM results of Alloy 690 as to the Pb-containing solution showed a non-uniform oxide film on the surface, which was considered to affect SCC.

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