

Effect of Zinc Addition on the General Corrosion of Pre-filmed Alloy 690TT in Simulated PWR Primary Water

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1. Introduction

Nickel-based alloys have widely been used for structural materials in nuclear power plants (NPPs) due to its superior corrosion resistance and high temperature strength. Especially, since Alloy 690TT has a superior resistance to general corrosion and stress corrosion cracking (SCC), the alloy has been used for steam generator (SG) tubes in pressured water reactors (PWRs) [1]. However, a corrosion degradation of the SG tubes in primary water system is inescapable despite its superior corrosion resistance [1-2]. Metallic cations such as Ni, Fe, and Co are released out from the surfaces of SG tubes which are about 65% of the total area exposed to the primary water [3,4]. The released corrosion products are transported into the reactor core by the primary water and deposited on the surfaces of fuel claddings and structural materials. Corrosion products released from the SG tubes cause the serious problems in PWRs, for instance, radiation exposure during maintenance operation, occurrence of axial offset anomaly and power reduction in plant operation [5,6]. Thus, it is important to evaluate and mitigate general corrosion of the SG tubes.

The corrosion behavior of SG tubes will be affected by various water chemistry parameters such as temperature, dissolved hydrogen (DH), dissolved oxygen (DO), and pH value. In addition, zinc injection has also been performed as an important method to minimize the radiation field and general corrosion rate [7-10].

Zinc injection can be adopted in a new PWR or newly replaced SGs. However, most PWRs have implemented the zinc addition technique after a certain period of operation without zinc. Therefore, oxides are already formed on SG tubes before zinc addition. In this context, it is important to evaluate the effect of zinc addition on the corrosion behavior of pre-existing oxides.

In this study, we report the effect of zinc addition on general corrosion of pre-filmed Alloy 690TT tubes in simulated primary water at 330 °C and at 150 bar.

2. Experimental methods

2.1 Specimen and Solution Preparation

Alloy 690TT tubes, which are generally used as a SG tubing material, were used in this study. The chemical composition of the tubes is shown in Table I. The specimen has a diameter of 19.07 mm and a wall thickness of 1.07 mm. Tubular specimens were prepared with a size of 50 mm in length by cutting the long tubing material transversely for corrosion tests. The specimens for the corrosion tests have a hole of 3 mm in diameter to hang on a specimen tree in an autoclave. Some specimens were also cut into 4 mm x 12 mm x 1.07 mm for oxide film analyses.

Table I. Chemical composition of Alloy 690TT (wt. %).

C	Si	Al	Ti	Mn	Fe	Cr	Ni
0.02	0.30	0.14	0.16	0.29	10.1	29.3	59.6

2.2 Corrosion Tests

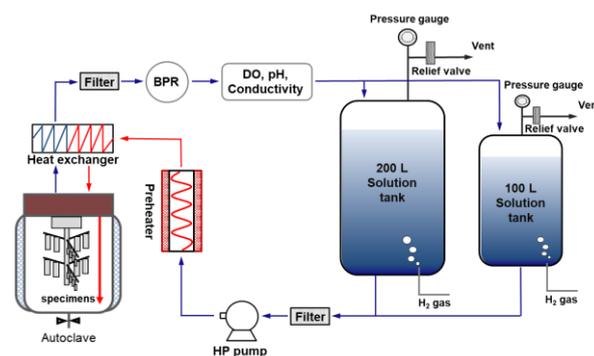


Fig. 1. Schematic of a primary water circulating system for the corrosion test.

A primary water circulating system for the corrosion test was shown schematically in Fig. 1. Simulated primary water was prepared using high purity demineralized water and nuclear-grade lithium hydroxide (LiOH) and boric acid (H₃BO₃). The test solution contained 2 ppm Li, and 1000 ppm B. In addition, depleted zinc acetate was added to the prepared primary water for control zinc concentration. The zinc concentration was controlled to 0, 10, 60 ppb, respectively.

Table II shows the various zinc concentration conditions for the corrosion tests. In Case 1, zinc was not injected to the primary water during 3000 h. However, in the Case 2 and Case 3, zinc was not injected to the primary water first for 1500 h, but the corrosion test was further conducted with 10, 60 ppb zinc injection for 1500 h.

DO was controlled to be less than 5 ppb and DH maintained 35 cc/kg. The corrosion test was performed at 330 °C and 150 bar for 3000 h in total. During the corrosion test, two primary water tanks (200 L and 100 L capacity) were used and switched each other to maintain the target zinc concentration. 200 L and 100 L tanks were used for 10 and 5 days, respectively.

After the corrosion tests, oxide films on the specimens were removed to measure the base metal corrosion using the two-step descaling process. The first step was conducted in an aqueous solution containing 1% KMnO₄ and 5% NaOH at 90°C for 1 min. The second step was performed in a 5% ammonium citrate solution at 90 °C for 1 min. The descaling process was repeated until the oxide films were completely removed. All weight changes were measured using the calibrated microbalance with ±10 µg accuracy.

Table II. Various zinc concentration conditions for the corrosion test.

	Zn concentration conditions	
	Stage 1 (1500 h)	Stage 2 (1500 h)
Case 1	X	X
Case 2	X	10 ppb Zn
Case 3	X	60 ppb Zn

X: no Zn injection

3. Results and Discussion

Fig. 2 shows the SEM micrographs of the oxide films formed on Alloy 690TT under the conditions of Case 1, 2, and 3. All specimens were mainly covered with extremely small polyhedral particles. However, large polyhedral particles were observed more frequently in the following order: Case 1 > Case 2 > Case 3. In addition, the large particles of Case 1 were relatively larger than that of Cases 2 and 3. These features of surface oxides indicate that general corrosion of Alloy 690TT was mitigated by zinc addition even after the pre-filmed alloy was exposed to the zinc water chemistry.

Fig. 3 shows the TEM images and point EDS analysis of the cross sections of oxide films formed on Alloy 690TT. As shown in Fig. 3(a), the outmost particles were composed of Fe-rich oxide with Ni. The inner layer was composed of Cr-rich oxide containing Ni and Fe. In Fig. 3(b), the large polyhedral particles were composed of Fe-rich oxide with Ni. Also, the small

polyhedral particles were composed of Fe, Cr, Ni, Zn oxide and the inner layer was composed of Cr-rich oxide containing Ni, Fe, and Zn. As shown in Fig 3(c) point 3, the small polyhedral particles were composed of Zn-rich oxide with Fe, Cr, and Ni. At all the conditions, a double-layered oxide structure was formed: an outmost layer with Fe-rich oxide and inner layer with Cr-rich oxide.

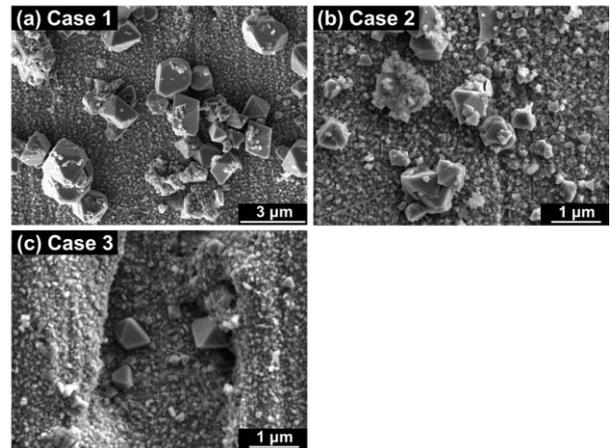


Fig. 2. SEM images of the oxide films formed on Alloy 690TT after corrosion tests for 3000 h under the various zinc concentration conditions: (a) case 1, (b) case 2, and (c) case 3.

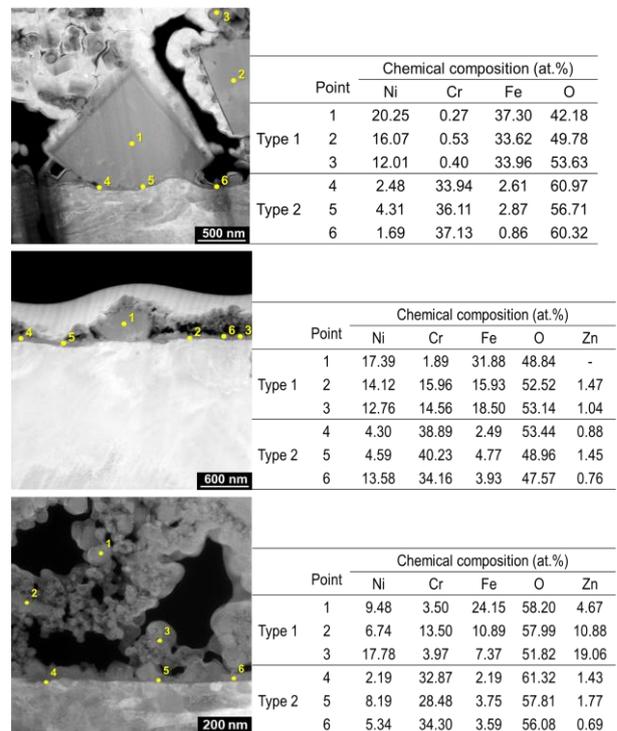


Fig. 3. TEM images and point EDS analyses of cross sections of oxide films formed on Alloy 690TT after corrosion tests for 3000 h under the various zinc concentration conditions: (a) Case 1, (b) Case 2, and (c) Case 3.

In all three Cases, Cr-rich inner oxide layers were observed. However, in both Cases 2 and 3, zinc was

incorporated in the Cr-rich inner layers. Oxides containing zinc are known to be more thermodynamically stable than zinc-free oxides. Stable oxides mean that it is difficult for oxide to dissolve and precipitate. However, the growth of outermost layers of nickel-based alloys is greatly controlled by dissolution and precipitation of Fe or Ni oxides. Consequently, in cases 2 and 3, the stable small oxide containing zinc formed and the growth of the oxide formed on the outermost layer was suppressed.

Fig. 4 shows the corrosion rate which was calculated based on the base metal corrosion. The corrosion rate decreased in accordance with the increase of the added zinc concentration. The lowest corrosion rate (Case 3) was 0.023 mg/dm²-day and the highest corrosion rate (case 1) was 0.041 mg/dm²-day. The corrosion rate of Case 3 specimens decreased approximately 43% compared to that of Case 1.

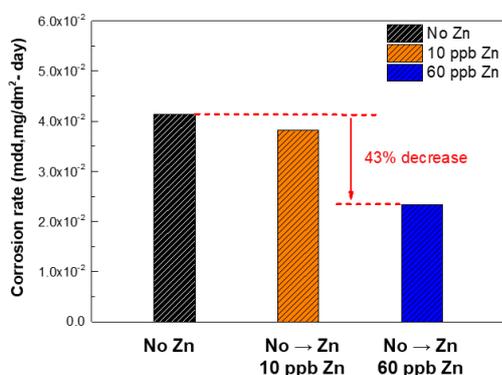


Fig. 4. Corrosion rate of Alloy 690TT in various zinc concentration conditions: (a) Case 1, (b) Case 2, and (c) Case 3.

4. Conclusions

This work has investigated the effect of the zinc addition on corrosion behavior of pre-filmed Alloy 690. The main results can be derived:

- (1) Under the various zinc concentration conditions, all specimens were covered with polyhedral-shaped oxide particles. Also, the size and density of the oxide particles were reduced with the injected zinc concentration.
- (2) Zinc was not detected in the large particles. However, characterization of oxide layer on the surfaces following exposure to zinc confirmed the zinc incorporation of significant concentrations in the small particles and the inner oxide layer.
- (3) The corrosion rate decreased by 8 % for Case 2 and by 43 % for Case 3, compared to Case 1. This result suggests that zinc addition is still effective

in mitigating general corrosion of pre-filmed Alloy 690.

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