Influences of Zn Concentration on the General Corrosion Behavior of Alloy 690TT in Simulated Primary Water of PWRs

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1. Introduction

In the primary system of pressurized water reactors (PWRs), corrosion products containing Fe, Ni, and Co are mainly released from steam generator (SG) tubes exposed to primary water. The corrosion products are transported by the coolant and deposited on the surfaces of fuel claddings [1,2].

Co-58 and Co-60 are formed by a radioactivation of Ni-58 and Co-59, respectively which are originated from the corrosion release of SG tubes. The activated corrosion products in the fuel core are the major source of radiation build-up and occupational radiation exposure of workers during shutdown maintenance period of nuclear power plants [1,2].

To decrease the radiation field of primary system, the corrosion products released from SG tubes must be reduced because the surface of SG tubes are about 65% of the total area exposed to the primary coolant of PWRs. Hence, it is crucial to mitigate the general corrosion release of the SG tubes [3,4].

The general corrosion behavior of SG tubes will be affected by various water chemistry parameters such as Li/B coordination, dissolved hydrogen (DH), pH, temperature, dissolved oxygen (DO), etc [5]. In addition, Zn injection has also been performed as a proper method to decrease the radiation field and corrosion release rate [6].

In many nuclear power plants, trace concentrations of Zn(usually 5 ppb up to 10 ppb) are added to the primary coolant in the form of depleted Zn acetate (DZA) [6]. In previous investigations, higher Zn concentrations (15-40 ppb) were injected when the main purpose was primary water stress corrosion cracking (PWSCC) mitigation, while lower Zn concentrations (5-10 ppb) were added when corrosion release rate reduction was the objective [6,7].

Recently, the research shows that these Zn injection programs should be changed that PWSCC mitigation may be achieved with lower Zn concentrations, while corrosion release rates are likely to be mitigated more considerably by higher Zn concentrations [8]. Higher Zn concentrations may lead to a more rapid increase in cumulative exposure and rapid reduction in corrosion release rates [8]. However, there are still several issues about the proper Zn concentration for corrosion mitigation of SG tube.

Therefore, in this study, the effectiveness of Zn concentration on the general corrosion and release rate of Alloy 690TT was investigated using a primary loop system. By successively switching the two solution tanks, the target Zn concentration was maintained during the general corrosion test for 3000 h. The microstructure of the oxide films of Alloy 690TT was analyzed by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and energy dispersed spectroscopy (EDS). The general corrosion and release rate of Alloy 690TT were evaluated by using chemical descale methodology.

2. Experimental procedure

The tubing material used in this work was commercial Alloy 690TT with an outer diameter of 19.07 mm and a wall thickness of 1.07 mm. The chemical composition of the tube is presented in Table I. Tubular specimens were fabricated with a size of 50 mm in length by cutting the long tubing transversely for general corrosion tests. Some pieces of SG tubes were cut into 4 mm x 12 mm x 1.07 mm for oxide film analyses.

The simulated primary water was prepared from high purity demineralized distilled water with the resistivity above 18 MΩ-cm and nuclear-grade lithium hydroxide (LiOH) and boric acid (H_3BO_3). The test solution contained 2 ppm Li, and 1000 ppm B. In addition, DZA, which is generally used in PWRs, was injected to the primary coolant for control the Zn concentration. The Zn concentration was selected to 0, 5, 10, 60 ppb. DO was controlled to be less than 2 ppb and DH was continuously maintained 35 $cm^3/kg \cdot H_2O$ by controlling the hydrogen overpressure of the solution tank. General corrosion tests were performed at 330 ^oC under 150 bar.

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

C	Si	Al	Ti	Mn	Fe	Cr	Ni
0.02	0.32	0.16	0.33	0.33	10.4	29.3	Bal.

Fig. 1 shows the schematic of the primary water recirculating system used for the general corrosion tests. The loop system consisted of the following main components: solution tank of primary water, high pressure (HP) pump, pre-heater, heat exchanger, back

pressure regulator (BPR), various water chemistry sensors such as DO, pH, and conductivity sensors.
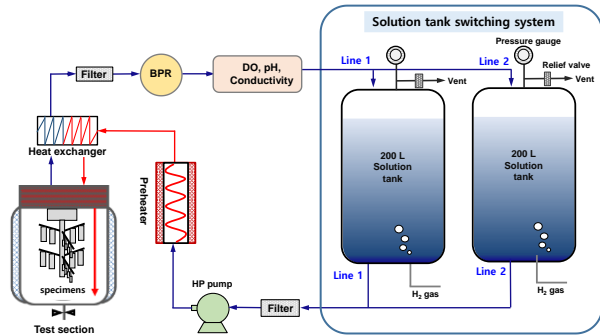

Fig. 1. Schematic of loop system for general corrosion test.

During the corrosion tests, two tanks (200 L capacity) were continuously switched each other to maintain the target Zn concentration. Each 200 L tank was used for 10 days.

In order to evaluate the consumed Zn contents in simulated primary water circulated into the loop system for 10 days was analyzed by using the inductively coupled plasma atomic emission spectroscopy (ICP-AES). Fig. 2 shows the consumed Zn concentration in test solution circulated into loop system during the corrosion test. The results shows that Zn concentration in test solution was continuously maintained to be close to the target Zn concentration during the corrosion test.
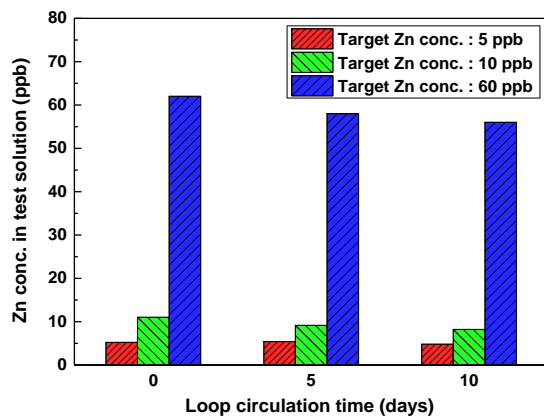

Fig. 2. Zn concentration in simulated primary water circulated into loop system during the corrosion test by using ICP-AES analysis.

After the corrosion tests, the morphology of oxide films formed on Alloy 690 specimens was analyzed using SEM. The focus ion beam (FIB) milling was used to produce TEM samples, allowing us to produce samples of which the oxide film structure could be observed in depth. The microstructure of oxide layers were analyzed using TEM and TEM-EDS.

Chemical descale methodology was used to obtain the corrosion rate of Alloy 690TT. The corrosion products of oxidized specimens were removed by multiple applications of two-step alkaline permanganate (AP) and ammonium citrate (AC) descaling process. First

step was done in 1 wt.% potassium permanganate ($KMnO_4$) and 5 wt.% sodium hydroxide (NaOH) solution. Second step was done in a 5% diammonium citrate solution. Each step was conducted by immersion in a water bath for 2 min at 90 °C. After the steps, the weights of the specimens were measured using a 5-place balance with an accuracy of ±0.01 mg. The two-step descaling process was performed at least three times on each specimen to verify reproducibility.

3. Results and Discussion

Fig. 3 presents the SEM morphologies of the oxide films formed on Alloy 690TT under the Zn concentration range of 0-60 ppb. All specimens were mainly covered with small particles and large polyhedral or round particles. The size of oxide particles formed under 0 ppb Zn condition were much larger than that of oxide particles under 5, 10, and 60 ppb Zn conditions. Based on the SEM results, it is concluded that the surface morphologies of oxide films were similarly formed regardless of Zn concentration. However, the particle size is different depending on the Zn concentration due to the variation of general corrosion rate. The reason for this is that Zn contained oxides are more thermodynamically stable than Zn-free oxides.
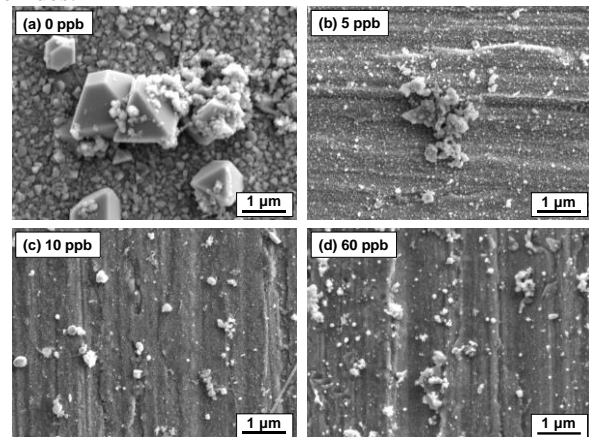

Fig. 3. SEM micrographs of surface of oxide films formed on Alloy 690TT under the four Zn concentrations: (a) 0 ppb, (b) 5 ppb , (c) 10 ppb, and (d) 60 ppb.

Fig. 4 shows the corrosion and release rate of Alloy 690TT under the various Zn concentration conditions. The corrosion and release rate decreased with the increase of zinc concentration. The corrosion rate of the Alloy 690TT under 0 ppb Zn concentration was 0.041 mg/dm²-day. Compared to 0 ppb Zn concentration, the corrosion rate of Alloy 690TT under 5, 10, and 60 ppb Zn concentration was decreased by about 31 %, 34 %, and 61 %, respectively. In the case of 0 ppb Zn content, the release rate of the Alloy 690TT was 0.008 mg/dm²-day. Compare to 0 ppb Zn concentration, the release rate of Alloy 690TT under 5, 10, and 60 ppb Zn concentration was reduced by about 41 %, 53 %, and

67 %, respectively. Based on the results, in the range of 5-10 ppb Zn, the corrosion rate slightly decreased with increasing Zn concentration. In addition, the general corrosion rate significantly decreased as Zn content increased from 10 to 60 ppb. However, the release rate gradually decreased in accordance with the increase of Zn concentration. It is considered that these results are useful for mitigating the radiation field in the primary water of nuclear power plants.
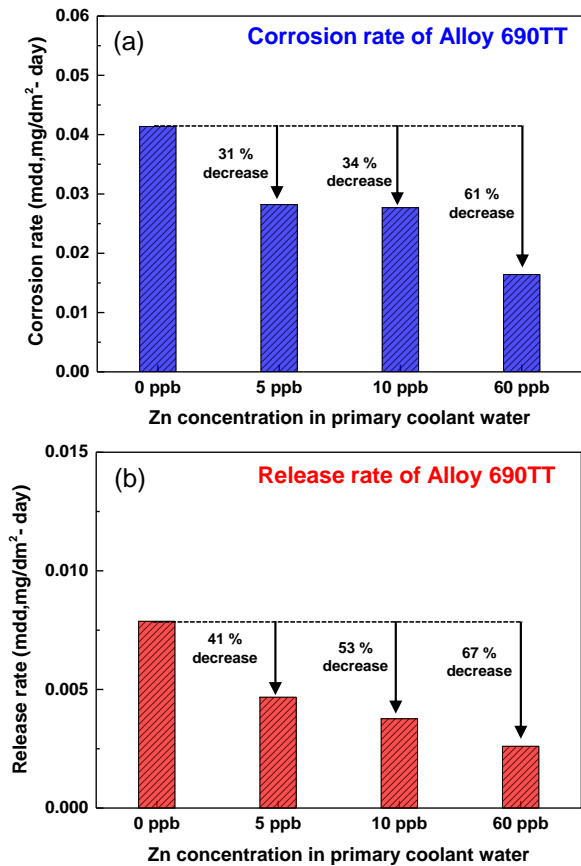

Fig. 4. Corrosion and release rate of Alloy 690TT under various zinc concentrations: (a) corrosion rate and (b) release rate.

Fig. 5 presents the TEM images and point EDS analysis of the cross sections of oxide films formed on Alloy 690TT. In the case of 0 ppb Zn, the outmost particles were composed of Fe-rich oxide with Ni. The inner layer was composed of Cr-rich oxide containing minor Ni and Fe. In the case of 5~60 ppb Zn, the large polyhedral particles were composed of Fe-rich oxide with Ni and Zn. In addition, the small round or 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. Under all Zn concentration conditions, a double-layered oxide structure was formed: an outmost layer with Fe-rich oxide and inner layer with Cr-rich oxide. In the cases of Zn injected conditions, Zn was incorporated in the Cr-rich inner layers. Zn contained oxides are known to be more thermodynamically stable than Zn-free oxides.

Stable oxides indicate 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. Based on the point EDS results, the Zn concentration in the Cr-rich oxide layer increased in the following order: 5 ppb Zn < 10 ppb Zn < 60 ppb Zn. We think that the corrosion resistance of Alloy 690TT under Zn injected conditions was mainly affected on the Zn content incorporated in the Cr-rich inner oxide layer.

0 ppb Zn

Point	Chemical composition (at.%)			
	Ni	Cr	Fe	O
1	20.25	0.27	37.30	42.18
2	16.07	0.53	33.62	49.78
3	2.48	33.94.	2.61	60.97
4	4.31	36.11	2.87	56.71
5	58.16	31.70	10.14	-

■ (Ni, Fe)O   ■ Matrix   ■ Cr-rich oxide

5 ppb Zn

Point	Chemical composition (at.%)				
	Ni	Cr	Fe	O	Zn
1	21.22	8.91	18.03	46.24	5.60
2	14.89	15.57	12.49	51.45	5.60
3	13.41	38.29	1.99	43.54	2.77
4	14.33	32.51	3.19	46.82	3.15

⬤ Zn-containing (Ni, Cr, Fe)O
⬤ Zn containing Cr-rich oxide

10 ppb Zn

Point	Chemical composition (at.%)				
	Ni	Cr	Fe	O	Zn
1	19.40	1.16	27.61	47.40	4.43
2	18.20	1.43	30.29	46.12	3.96
3	19.27	13.10	12.64	51.13	3.86
4	12.16	30.09	5.52	46.23	6.00

⬤ Zn-containing (Ni, Fe)O
⬤ Zn-containing (Ni, Cr, Fe)O
⬤ Zn containing Cr-rich oxide

60 ppb Zn

Point	Chemical composition (at.%)				
	Ni	Cr	Fe	O	Zn
1	11.48	3.32	29.04	46.45	9.71
2	10.75	14.81	12.45	52.05	9.94
3	5.50	30.87	5.57	48.90	9.16
4	62.85	27.24	9.91	-	-

⬤ Zn-containing (Ni, Fe)O   ■ Matrix
⬤ Zn-containing (Ni, Cr, Fe)O
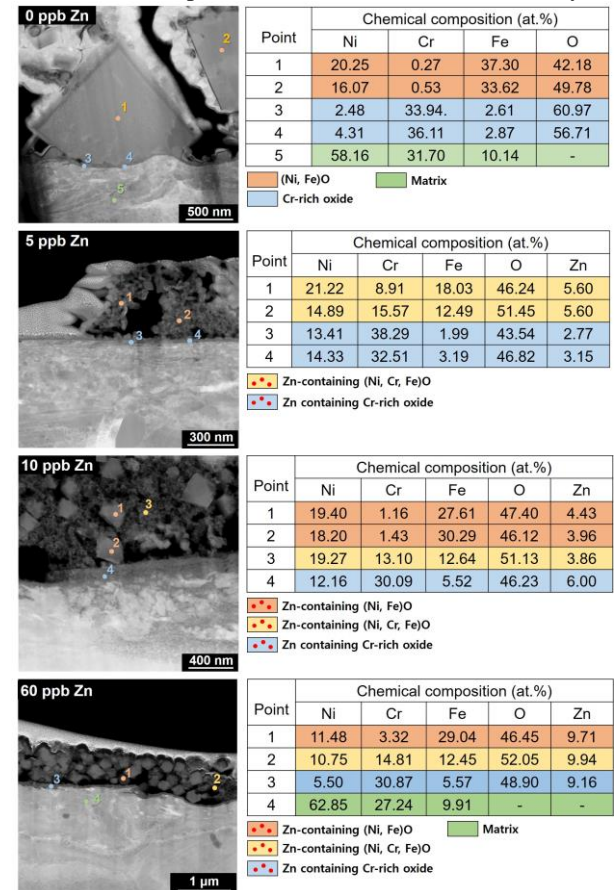⬤ Zn containing Cr-rich oxide

Fig. 5. 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.

4. Conclusions

1) Under the all Zn concentration conditions in the range of 0-60 ppb Zn, the specimens were covered with polyhedral-shaped or round oxide particles. In addition, the size and density of the oxide particles were decreased with the increase of Zn concentration.

2) Corrosion rate decreased by 31 % for 5 ppb Zn, 34 % for 10 ppb Zn and 61 % for 60 ppb Zn compared to that of 0 ppb Zn. Release rate was also reduced by 41 %, 53 %, and 67 % by 5, 10 and 60 ppb Zn addition, respectively, when comparing to that in 0 ppb Zn condition. These results suggests that 60 ppb Zn addition is more effective in mitigating general

corrosion and radiation fields of primary system of PWRs.

3) Based on the TEM-EDS results, the general corrosion resistance of Alloy 690TT in Zn added primary water was mainly affected on the Zn concentration incorporated in the Cr-rich inner oxide layer. The reason for this is that Zn contained oxides are more thermodynamically stable than Zn-free oxides.

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