Accelerated Corrosion of Alloy 600 by Magnetite Deposits in Simulated Secondary Water Containing PbO

Geun Dong Song, Won-Ik Choi, Soon-Hyeok Jeon, Do Haeng Hur*
Nuclear Materials Safety Research Division, Korea Atomic Energy Research Institute, 989-111 Daedeok-daero, Yuseong-gu, Daejeon 305-353, Republic of Korea
**Corresponding author: dhhur@kaeri.re.kr*

1. Introduction

Mill annealed Alloy 600, which is used as a steam generator tube material has experienced various corrosion damages such as stress corrosion cracking, intergranular attack, and pitting corrosion in the secondary side of pressurized water reactors. These types of corrosion mainly occur in heated crevices between tubes and their support plate or tube sheet, which are covered by magnetite deposits. This is because the aggressive chemical impurities can be concentrated within these crevices by local boiling, resulting in the formation of a highly corrosive environment [1]. In addition, the concentration of impurities causes the change of pH to acidic or alkaline conditions, and this phenomenon is also well recognized as a contributor [2-3].

The researches related to the corrosion of Alloy 600 have been mainly focused on the crevice water chemistry, and there are many investigations for the effect of water chemistry factors such as impurities, pH, and temperature etc., up to now. However, it should be noted that a real corrosion phenomenon of Alloy 600 occurs in the situation which is connected with the magnetite deposit under operating conditions. Magnetite is an oxide, but it shows almost metallic behavior in electrical properties [4]. For this reason, a galvanic corrosion between the tube surface and magnetite can occur in the heated crevice environments. Therefore, it is necessary to evaluate the effects of not only impurities but also galvanic coupling with magnetite on the corrosion behavior of Alloy 600.

In this paper, the effect of magnetite on the corrosion behavior of Alloy 600 was investigated in a simulated heated crevice environment. Pb was selected as an impurity, the Alloy 600 specimen connected with magnetite was prepared using the electrodeposition method. From the experimental results, the combined effect of magnetite and Pb on the corrosion behavior of Alloy 600 is discussed.

2. Experimental procedures

2.1 Material

Alloy 600 was melted in a high frequency vacuum induction furnace, and hot-rolled in a temperature range of 1150–1250℃. The plates were cold-rolled with a total thickness reduction of about 70%. Alloy 600 corrosion coupons were machined from the cold-worked sheets into a size of 30 mm × 20 mm × 1 mm. These corrosion coupons were annealed at 1060℃ for 2.5 min followed by water quenching. Finally, the corrosion coupons were ground down with 1000 grit silicon carbide papers, and then ultrasonically cleaned in acetone and ethanol for 5 min, respectively. The chemical composition of Alloy 600 is given in Table 1.

Table 1. Chemical composition of Alloy 690 (wt.%).

C	Al	Si	Ti	Cr	Mn	Fe	Ni
0.02	0.06	0.1	0.1	15.7	0.3	10.0	Bal.

2.2 Preparation of magnetite-deposited specimen

To evaluate the effect of magnetite on the corrosion behavior of Alloy 600, it is necessary to continuously maintain the galvanic connection with magnetite in a test solution until the test was over. To make this situation, magnetite layer was electrodeposited on the whole surface of the corrosion coupons except the circular area of 60 mm^2 in the center, as shown in Fig. 1. The area ratio of magnetite to Alloy 600 was controlled to be 20 in the magnetite-deposited corrosion coupon. The details for the electrodeposition process are given in the previous studies [5-6].

The characteristics of the electrodeposited magnetite were analyzed using a scanning electron microscope (SEM).

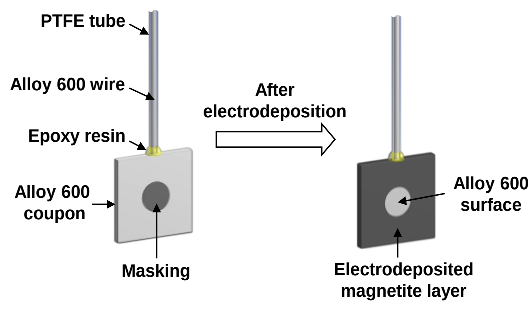

Fig. 1. Schematics for the preparation of magnetite-deposited corrosion coupons.

2.3 Immersion corrosion test

Immersion corrosion tests were conducted in simulated secondary water with and without 100 ppm PbO at 315℃ for 650 h under a deaerated condition using Ni-autoclaves with a capacity of 3.8 L.

Two types of corrosion coupons were used in the immersion corrosion test: magnetite-free and magnetite-deposited Alloy 600. In the case of magnetite-deposited Alloy 600, the magnetite layer was also electrodeposited on a specimen holder made of Alloy 600 material to prevent another galvanic effect. The tests for each condition were conducted in a separated autoclave.

After the immersion test was completed, the properties of oxide layer formed on Alloy 600 were analyzed using a transmission electron microscope (TEM) and an energy dispersive X-ray spectroscopy (EDS).

3. Results and discussion

Fig. 2 shows the SEM images of the electrodeposited magnetite layer on the Alloy 600 corrosion coupon. As shown in Fig. 2(a), the polyhedral-shaped magnetite particles were homogeneously electrodeposited on the surface of the Alloy 600 corrosion coupon. The average thickness was 20 μm, and no defects such as cracks and holes could be observed in the cross section of the magnetite layers, as shown in Fig. 2(b). In addition, there was no gab at the interface between the magnetite layer and Alloy 600 corrosion coupon, indicating that magnetite was tightly bonded to the surface of Alloy 600. Consequently, this magnetite-deposited corrosion coupon is very useful to evaluate the effect of magnetite on the corrosion behavior of Alloy 600.

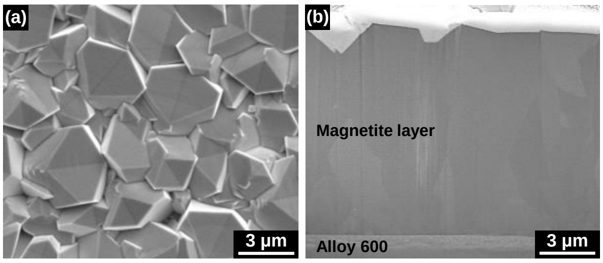

Fig. 2. SEM images of the electrodeposited magnetite layer: (a) surface and (b) cross section.

Fig. 3 shows the cross sectional STEM images and the EDS line profiles for the oxide layer formed on Alloy 600 after the test for 650 h. Only an oxide layer consisting of Ni, Cr and Fe was uniformly formed on the surface of Alloy 600 in PbO-free test solution as shown in Fig 3(a), while the addition of PbO significantly affected the formation of the oxide layer as shown in Fig 3(b). In the test solution with 100 ppm PbO, polyhedral particles were formed on the outer surface of continuous oxide film, and the chemical composition of these particles showed nearly pure nickel oxide (NiO). The inner oxide layer beneath these particles was enriched in Cr and Fe, and the thickness was about 2-times thicker than that formed in PbO-free solutions. Pb was also significantly detected in the outer surface of the inner oxide then gradually decreased towards the matrix. Furthermore, EDS line profile of Pb showed a similar tendency to those of Cr and Fe, but contrary to that of Ni. These results suggest that the presence of Pb accelerates the corrosion of Alloy 600, especially the dissolution of Ni.

In the case of magnetite-deposited Alloy 600 in the test solution with 100 ppm PbO (Fig. 3(c)), relatively large NiO particles were formed on the outer surface, but the number of particles was decreased as compared with that formed on the magnetite-free Alloy 600. However, the inner oxide layer was very thick and complex compared to that of the others. The chemical composition of the inner oxide was basically similar to that formed on magnetite-free Alloy 600 in the test solution with 100 ppm PbO, but metallic Ni or NiO islands were additionally observed. In this inner oxide layer, Pb was detected even at the region adjacent to the matrix. In summary, it is considered that the corrosion of Alloy 600 is more accelerated in the condition which is connected with magnetite and as a result, this phenomenon leads to the formation of the complex inner oxide with less protective nature. Thus, Pb may easily migrate within this complex inner oxide and reach the matrix, consistently promoting the corrosion of the matrix.

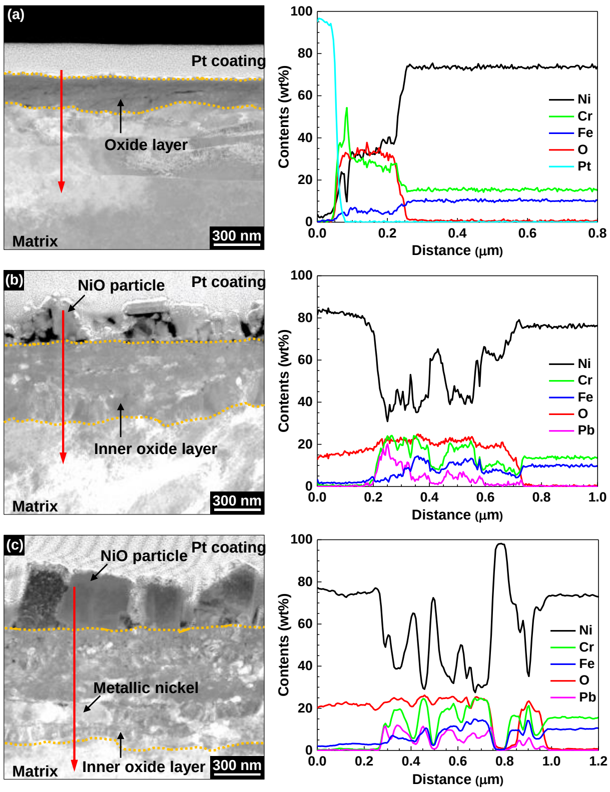

Fig. 3. STEM images and EDS line profiles of Alloy 600 after the immersion test for 650 h: (a) Magnetite-free Alloy 600 in PbO-free test solutions, (b) Magnetite-free Alloy 600 in the test solution with 100 ppm PbO, and (c) Magnetite-deposited Alloy 600 in the test solution with 100 ppm PbO.

4. Conclusions

(1) In PbO-free solution, an oxide layer consisting of Ni, Cr and Fe was homogenously formed on the surface of magnetite-free Alloy 600.

(2) In 100 ppm PbO solution, a double-structured oxide layer was formed on the surface of magnetite-free Alloy 600: Polyhedral NiO particles in the outer layer and Cr- and Fe-enriched oxide in the inner layer.

(3) In the case of magnetite-deposited Alloy 600 in 100 ppm PbO solution, relatively large NiO particles were formed on the outer layer, and the inner oxide layer was very thick and complex.

(4) Based on these significant results, the corrosion of steam generator tubes that occurs in heated crevices covered with magnetite need to be assessed in terms of not only water chemistry factors but also the galvanic corrosion with magnetite.

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