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Dissolution of Oxide Layer on Alloy 600 by HYBRID Solution

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1. Introduction

Alloy 600 is a polycrystalline nickel-based alloy (72 % Ni minimum, 14-17% Cr, 6-10% Fe) that has been widely used in pressurized water reactors (PWR). In PWR plants, Alloy 600 has been used for steam generator tubes. The high nickel content of alloy enables it to retain considerable resistance under reducing conditions at high temperature and makes it resistant in corrosion by a number of inorganic compounds. As the increase of the operation age, radioactive oxide layer on Alloy 600 surface becomes to form. To reduce radiation exposure of workers, the oxide layer should be dissolved out by decontamination agent. The decontamination agent developed in KAERI is called HBRID (HYdrazine Base Reductive metal Ion Decontamination). The objective of the study is to evaluate the dissolution performance of Cu^+-N_2H_4-HNO_3 system on the simulated oxide layer formed on Alloy 600.

2. Methods and Results

2.1 Oxide Layer Characterization

Specimens (～7.6 cm^2) of Alloy 600 polished up to 600 grit/P1200 silicon carbide paper on the automatic grinder were used for the formation of oxide film. Corrosion specimen of Alloy 600 was prepared [1]. Alloy 600 specimen was placed in a mixed solution of 0.05 M EDTA and N_2H_4. Then, the solution was maintained at 185 ^{0}C for 70 hours.

Fig. 1 shows TEM image of corrosion specimen of Alloy 600 and line scan profiles of the component elements. It implies that Ni, Cr and O are the main elements in an inner oxide layer. High content of Ni is ascribed to the mixture of Ni metal and nickel chromium oxide. In the outer oxide layer, the content of Ni decreases steeply. From the results, it can be inferred that the elements of the outer oxide layer are Fe, Cr, O and Ni. Fig. 2 shows SAED pattern of the outer oxide layer. Lattice is regularly arranged and has the same spacing. The outer layer oxide has a crystalline phase. Soustelle et al. [2] studied the phase composition and structure of oxide films formed on Alloy 600 in primary water conditions at 360 ^{o}C. Their results showed the presence of $FeCr_2O_4$ in all cases, whereas $NiFe_2O_4$, and $NiCr_2O_4$ and possibly NiO were only observed at the lowest hydrogen partial pressures. Nakagawa et al. [3] characterized the hydrogen effect on the composition of oxide layers grown on Alloy 600 in simulated primary water conditions at 320 ^{o}C. The oxide layers formed at lower hydrogen content were shown to be Ni-rich whereas formed at higher hydrogen content were iron- and chromium- rich.

In this study, it was found that Ni-rich oxide is formed in the inner oxide layer and nickel chromium ferrite is formed in the outer layer.

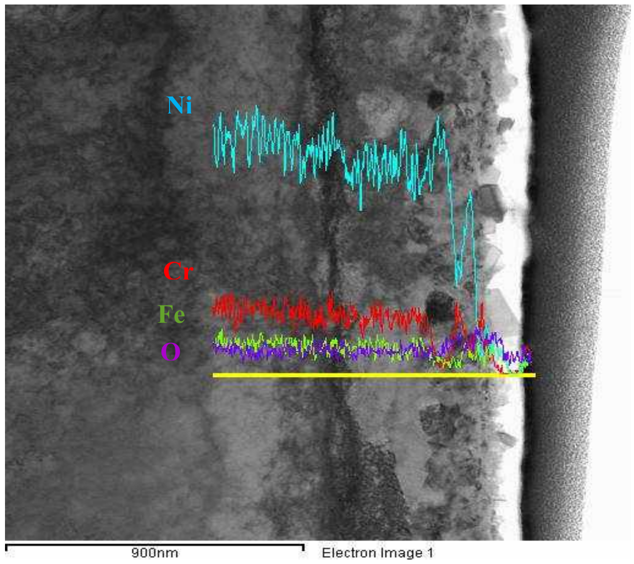


Fig. 1. TEM image of Alloy 600 specimen and line scan profiles of component elements.

Fig. 2. SAED pattern of the simulated oxide layer.

2.2 Dissolution of Oxide Layer on Alloy 600

Fig. 3 shows the amount of dissolved metal ions against time during the application of each step. When the oxidation pretreatment step was omitted, it was observed that the reductive dissolution reaction was slow. Specimens were treated with a solution containing HNO_3 and $KMnO_4$ before the reductive dissolution step. The amount of the dissolved Fe and Ni ions during the oxidation step is negligible. As shown in Fig. 3, Fe and Ni ions are continuously dissolved out from the oxide layer in the reductive dissolution steps. Contrary to the Fe and Cr ions, small amount of Ni ion was dissolved.

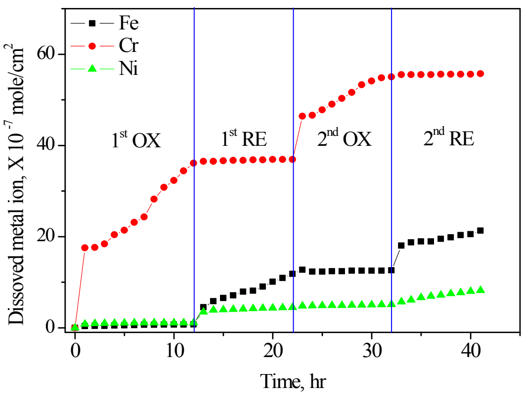
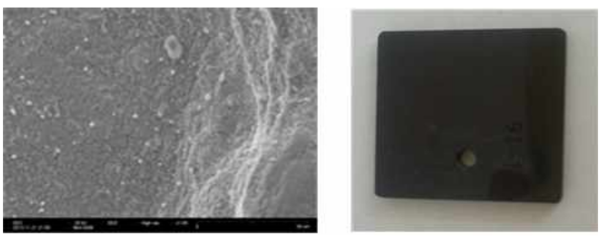


Fig. 3. Dissolved metal ion from Alloy 600 oxide layer against time, oxidation step ([$KMnO_4$] = 1g/L, [HNO_3] = 0.34 g/L, T= 95 ^{0}C), reductive dissolution step ([N_2H_4] = 0.04 M, [Cu^+] = 5 X10 $^{-4}$ M, pH = 3 by HNO_3, T= 120 ^{0}C).

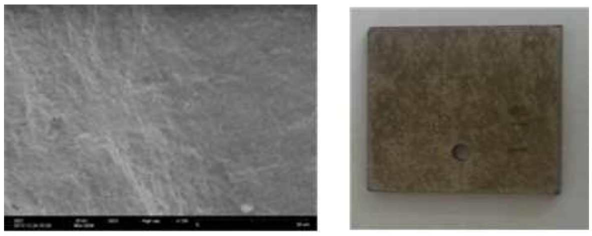
Prior to dissolution, the morphology of oxide layer formed on Alloy 600 was investigated. Fig. 4 shows the SEM image and photograph of the Alloy 600 specimen before the application of the dissolution step. Visual observation shows a black metal oxide completely covering the surface of the specimen. SEM image shows the densely adhered small oxide particles. Larger particles cover the specimen sparsely.



(a) (b)

Fig. 4. (a) SEM image of Alloy 600 surface (X 500) before dissolution test and (b) photograph of Alloy 600 specimen.

Fig. 5 shows the SEM image and photograph of the Alloy 600 specimen after 42 hours' dissolution steps. Visual observation shows a bare metal surface and light brown color oxide coves the specimen. SEM image shows the full dissolution of the densely adhered oxide particles.



(a) (b)

Fig. 5. (a) SEM image of Alloy 600 surface (X 500) after dissolution test and (b) photograph of Alloy 600 specimen.

3. Conclusions

The simulated oxide layer formed on Alloy 600 surface was efficiently dissolved by the successive applications of NP and HYBRID. The total concentration of HYBRID used for the dissolution of simulated oxide layer is below 0.2 wt%. From the test results, we can also infer that HYBRID does not cause any corrosion problem to Alloy 600. The simultaneous destruction of hydrazine and nitrate ion will greatly reduce the generation of the secondary waste. A feasibility study on the reduction of the generation of the secondary waste is performed.

ACKNOWLEDGEMENTS

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