

Effects of the dissolved oxygen and pH on a passivity of the oxide film formed on the Alloy 600

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1. Introduction

Alloy 600 is commonly used in the primary systems of PWR plants because of its excellent resistance to a stress corrosion cracking and pitting. But a stress corrosion cracking and pitting corrosion are occasionally observed under PWR conditions, which may be correlated with the passive film on the Alloy 600 surface[1,2]. There is little information on the composition of films growing on the surface of Alloy 600 at high temperature. Therefore, an understanding of the basic electrochemical behaviors about an anodic dissolution and the passivation of the bare surface of metals and alloys provides important information about localized corrosions like a SCC and pitting. Oxide on the steel surfaces in an aqueous solution above 100°C is composed of a duplex film structure. The inner layer of the oxide is dense and less porous, which is formed by a growth of the oxide layer on the metal surface. Outer layer of the oxide is less adhesive, which is formed by a dissolution precipitation mechanism. Growth processes occur at the metal/oxide and oxide/electrolyte interfaces and are controlled by a transport of the layer forming species through the layer, i.e. by the inward diffusion of oxygen including electrolyte species and the outward diffusion of metal cations[3-5].

This work deals with an electrochemical investigation of the passive films formed on Alloy 600 as a function of pH of the aqueous solution with/without dissolved oxygen. Passive films were formed on Alloy 600 by immersion method for 20 hrs. The passive films were characterized by analyzing the potentiodynamic curve, ac-impedance spectrum and a depth profiling.

2. Experimental

Alloy 600 of 1cm×1cm area as a working electrode was mechanically ground with silicon carbide paper up to #2400 followed by Al₂O₃ polishing and ultra sonic treatment. A platinum wire and Ag/AgCl electrode were used as a counter and reference electrodes, respectively. The aqueous 0.5M H₃BO₃, 0.5M Na₂SO₄ and 0.1M NaOH solutions as the electrolytes were prepared. The concentration of the dissolved oxygen in solution was adjusted by an N₂ purging. Potentiodynamic experiment was performed in the potential range from -0.2 under the ocp to 1.5V(Ag/AgCl) with a scan rate of 0.5mV/s. Ac-impedance measurement was carried out in the frequency range of 10⁶ to 10⁻¹ Hz using a 10mV amplitude perturbation. In order to identify the

composition and depth of the passive film, Auger electron spectroscopy(AES) was used

3. Results and discussion

Fig. 1 shows the potentiodynamic curves obtained from the Alloy 600 in 0.5M H₃BO₃ aqueous solutions with/without dissolved oxygen. Comparing the aerated aqueous solutions with the deaerated aqueous solutions, the passive current and corrosion potential were decreased in deaerated solution, indicating that the passivity of the surface film is more protective.

Fig. 2 presents the ac-impedance obtained from the Alloy 600 in a 0.5M H₃BO₃ aerated and deaerated solutions. The resistance of Alloy 600 in aerated solution decreased compared with the resistance in deaerated solution, consistent with potentiodynamic results.

Fig. 3 is plot of oxide thickness against pH of aqueous solutions with/without dissolved oxygen. The oxide film in the aerated solution is highly thicker than the oxide film in deaerated solution. Judging from the results of Figs. 2 and 3, the dissolved oxygen plays an important role for the passivity of the oxide film formed. When comparing the thickness and the resistance of the oxide films formed in the aqueous solutions with/without the dissolved oxygen, the thickness was increased and the resistance was decreased in the presence of the dissolved oxygen from the results of the depth profiling and the ac-impedance measurement, which was explained in terms of the chemical composition and the passivity of the oxide film. It seems that the passivity of the oxide film formed in aerated solution is lower than that in deaerated solution, because the oxide film formed in the aerated solution is porous and less dense.

Fig.4. is the oxide film resistance and the oxide thickness as function of pH. By increasing the pH of the solution with the dissolved oxygen, the oxide film resistance was decreased in the order of 0.5M H₃BO₃, 0.1M NaOH, 0.5M Na₂SO₄ and the oxide thickness was decreased in the order of 0.5M H₃BO₃, 0.5M Na₂SO₄, 0.1M NaOH.

4. Conclusion

Passive films formed on Alloy 600 as the aqueous solution with/without dissolved oxygen and pH are investigated electrochemically. Properties of the passive

films were analyzed by a potentiodynamic curve, ac-impedance spectrum and a depth profiling. Dissolved oxygen in the corrosion environment significantly influences passivity of the oxide film formed on the Alloy 600 based on the test results of this study.

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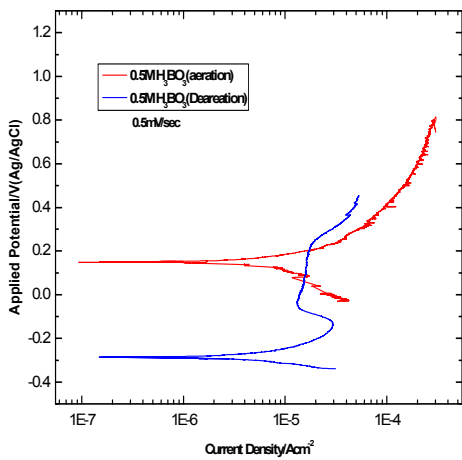


Fig. 1. Potentiodynamic curves for Alloy 600 in the aerated and deaerated 0.5M H₃BO₃ aqueous solutions with a scan rate of 0.5mV/s.

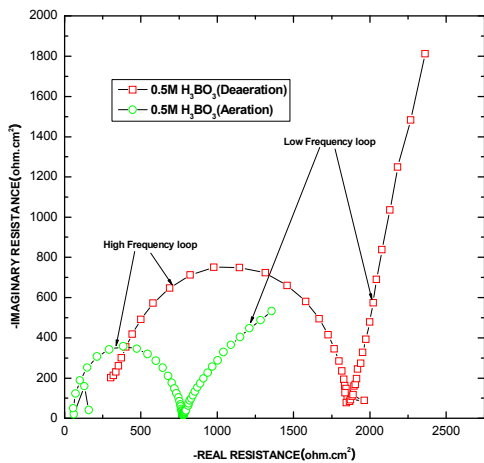


Fig. 2. Ac-impedance for Alloy 600 in the aerated and deaerated 0.5M H₃BO₃ aqueous solutions.

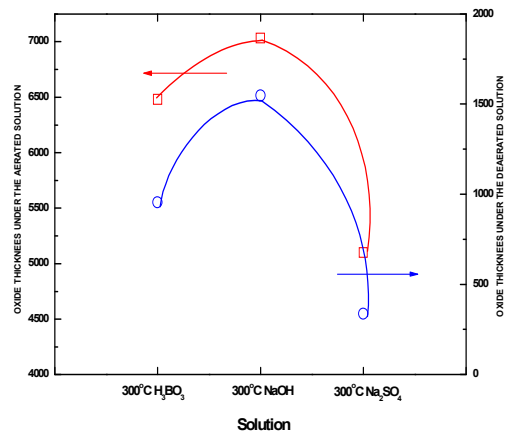


Fig. 3. Plots of oxide thickness against pH of aqueous solutions with/without dissolved oxygen.

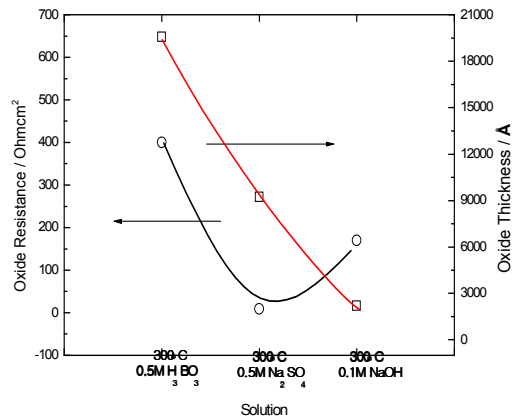


Fig. 4. Oxide thickness and oxide film resistances of the passive films formed on Alloy 600 in the solutions of various pHs with dissolved oxygen.