Electrochemical Investigation of Passive Film Formed on Alloy 600

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1. Introduction

Alloy 600 is used as a material for steam generator tubing in pressurized water reactors(PWR) due to its high corrosion resistance under PWR environment. In spite of its corrosion resistance, stress corrosion cracking(SCC) has occurred on the primary side as well as the secondary side of the tubing[1,2].

Oxide on steel surfaces in aqueous solution above 100^oC is composed of duplex film structure. Inner layer of the oxide is dense and less porous, which is formed by growth of oxide layer on metal surface. Outer layer of the oxide is loose adhesive, which is formed by dissolution precipitation mechanism. Growth processes occur at the metal/oxide and oxide/electrolyte interfaces and are controlled by 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].

Understanding of basic electrochemical behaviors about anodic dissolution and passivation of bare surface of metals and alloys provides important information about localized corrosions like SCC and pitting. However, the passive properties of Alloy 600 which is widely used in the nuclear industry have received relatively less attention than those of the stainless steels.

This work deals with electrochemical investigation of passive films formed on Alloy 600 as a function of aqueous solution temperature and solution pH. Passive films were formed on Alloy 600 as potentiostatic or immersion method. The passive films were characterized by analyzing potentiodynamic curve, cyclic voltammogram, ac-impedance spectrum and depth profiling. In addition, semiconductor property of passive film was assessed using Mott-Schottky plot.

2. Experimental

Alloy 600 of 1cm x 1cm area as a working electrode was mechanically polished with silicon carbide paper up to #1200 successively. A platinum wire and Ag/AgCl electrode were used as a counter and reference electrodes, respectively. For the electrolyte, aqueous 0.5M H_3BO_3 solutions of 30, 60 and 90^oC were prepared. And aqueous 0.5M Na_2SO_4 and 0.5M NaOH solution of 30^oC were also used as electrolyte.

Passive films with potential application were obtained during application of 0.4V(Ag/AgCl) for 2hrs and passive films without potential application(immersion) were also formed during 10 days immersion in aqueous solution.

Potentiodynamic polarization experiment was performed in the potential range of -0.6 to 1.5V(Ag/AgCl) with a scan rate of 0.5mV/s by using a potentiostat/galvanostat(EG&G Model 263A) interfaced with a personal computer. Cyclic voltammetry was carried out in the potential range of of -0.5 to 1.5V(Ag/AgCl) with a scan rate of 100mV/s. Ac-impedance measurement was performed from 10^6 Hz down to 10^{-1} Hz using 10mV amplitude perturbation at the potential ranged from -0.5 to 0.5V(Ag/AgCl) or open circuit potential. Cyclic voltammetry, ac-impedance measurement and potential application during passive film formation were carried out with a Solartron 1255 frequency response analyzer connected with Solartron 1287 electrochemical interface.

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 potentiodynamic curves obtained from Alloy 600 in 0.5M H_3BO_3 aqueous solution as a function of solution temperature. As temperature increased, passive current and corrosion potential increased, indicating that the passivity of the surface film formed at lower temperature is more protective.

Fig. 2 presents cyclic voltammograms obtained from Alloy 600 in 0.5M H_3BO_3 aqueous solution of (a) 30^oC and (b) 60^oC with a scan rate of 100mV/s. Above 0.65V(Ag/AgCl), the current related with oxygen evolution reaction was measured. The cathodic peak related to oxygen reduction appeared in the applied potential range of about 0.1~0.2V(Ag/AgCl), followed by the cathodic current due to hydrogen evolution reaction below -0.5V(Ag/Ag/Cl). It should be noted that the first cycle is distinguished from other cycles. One would expect that the anodic current corresponding to passive film formation on Alloy 600(passive current) is measured during anodic scan of first cycle. The anodic current measured in the range of potential above corrosion potential during the first cycle or early cycles is composed of the passive current and oxygen evolution current. After several early cycles, oxygen evolution reaction, oxygen reduction reaction and hydrogen evolution reaction currents approach to certain values, respectively. From the change of cyclic voltammogram with cycling, it is revealed that steady state passive film is completely formed during early cycles and the formed film is stable not to be dissolved in the applied potential range of this work.

After early cycles, dissolution current densities at 0.4V(Ag/AgCl) of the passive region were measured as 6.6, 10 and 60μA/cm^2 at 30, 60 and 90°C(not shown here), respectively. Increase in steady state dissolution current with temperature is consistent with the results of potentiodynamic curves, indicating that stability of the surface films on Alloy 600 is degraded with temperature.

It is worthwhile to note that the current related to oxygen evolution reaction increased with temperature. From this, it seems that exchange current density of oxygen evolution reaction increased with temperature leading to increase of corrosion potential in Fig. 1.

Fig. 3 depicts oxide film resistances of the passive films formed on Alloy 600 in 0.5M H$_3$BO$_3$ solutions of various temperatures. Oxide film resistance was obtained, based upon simple Randle circuit for ac-impedance results. Oxide film resistance decreased with temperature, which was consistent with the results of potentiodynamic curve and cyclic voltammogram.

4. Conclusion

Passive films formed on Alloy 600 as a function of aqueous solution temperature and solution pH are investigated electrochemically. Properties of the passive films were analyzed by potentiodynamic curve, cyclic voltammogram, ac-impedance spectrum and depth profiling. Stability of surface films on Alloy 600 was degraded with solution temperature.

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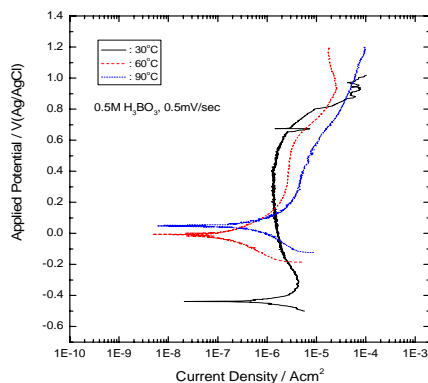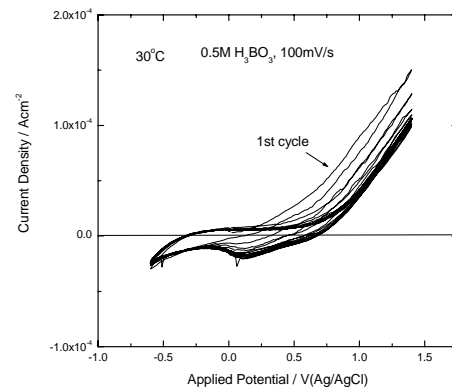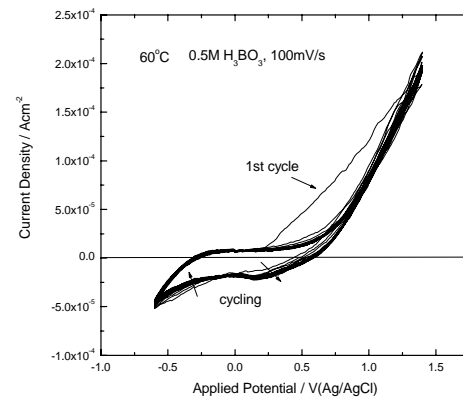[5] J.-J. Park, S.-I. Pyun and S.-B. Lee, Electrochim. Acta 49 (2004) 281.

Fig. 1. Potentiodynamic curves for Alloy 600 in 0.5M H$_3$BO$_3$ aqueous solution of temperature ranging from 30 to 90°C with a scan rate of 0.5mV/s.

(a)

(b)

Fig. 2. Cyclic voltammograms for Alloy 600 in 0.5M H$_3$BO$_3$ aqueous solution of (a) 30°C and (b) 60°C with a scan rate of 100mV/s.

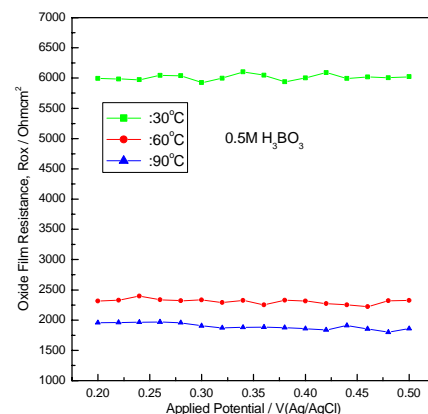Fig. 3. Oxide film resistances of the passive films formed on Alloy 600 in 0.5M H$_3$BO$_3$ solutions of various temperatures.