A study on the passive film of Alloy600 and Alloy 690 formed in the high temperature aqueous solution with additives

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1. Introduction

Alloy 690 and Alloy600 are used as a material for the steam generator tubing in the pressurized water reactor(PWR) of nuclear power plants due to its high corrosion resistance. Although those are a highly corrosion resistance material, their stress corrosion cracking(SCC) have been found on occasion , which are deeply related to a surface oxide film on a base material which have occurred on the primary side as well as the secondary side of a tubing[1,2]. And The SCC is accelerated in the existing Pb which is the impurity of secondary steam generator components. The Oxide on a steel surface in an aqueous solution above 100℃ is composed of a duplex film structure[3,4]. 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. The outer layer of the oxide is less adhesive, which is formed by a dissolution and precipitation mechanism. Growth processes of the inner layer and the outer layer occur at the metal/oxide and oxide/electrolyte interfaces, respectively and the growth rates 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.

These works deal with an electrochemical investigation of the passive films formed on Alloy 600 and Alloy 690 with additives in the high pressurized water environments. Passive films were formed on Alloy 600 and Alloy 690 by an immersion method for 336 hrs. The passive films were investigated by as-impedance spectrum, SEM and EDX.

2. Experimental

The chemical compositions of the Alloy 600 plate and Alloy 690 plate are given in Table 1 and Table 2.
The Alloy 600 plate was thermal treatment and Alloy 690 plate was high temperature mill-annealed(HTMA) at 1025℃ for 3 min.

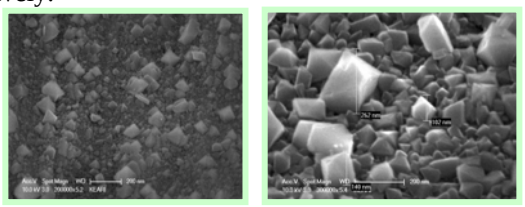
These specimens of a 1 cm X 1 cm area were used as a working electrode, which was mechanically ground with silicon carbide paper up to #1500 successively. And these specimens were finished by using a 1um diamond suspension solution. To remove the impurity on the specimens are treated by Ultra sonic treatment for the 5 minutes at last. A platinum wire and Li electrode were used as the counter and the reference, respectively. The 0.1M NaOH aqueous solution are used by the electrolyte. PbO and PbO + NiB were used to investigate effect as the additives.
To form the passive film, the specimens were immersed for the 336 hrs.

After a passive film was formed, ac-impedance measurement was conducted in the frequency range of 10^{6}-10^{-1} Hz by using a 10mV amplitude perturbation to analyze the characteristics of the oxide resistance.

In order to identify the surface morphology and chemical composition, the Scanning Electron Microscope(SEM) and Energy Dispersive X-ray spectroscopy(EDX).

3. Results and discussion

Fig. 1 shows the morphology obtained from the Alloy 600(a) and 690(b) in the 0.1M NaOH aqueous solution. Because the particles of the Alloy 600 are smaller than the particles of the Alloy 690, the passive films formed on the Alloy 600 are denser than those of the Alloy 690 relatively.



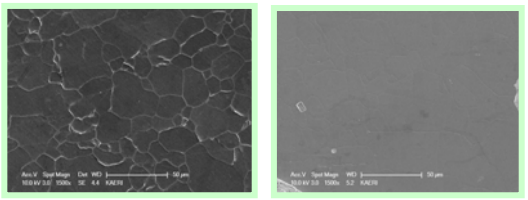
(a) (b)

Fig. 1. The particles of the passive films formed on the Alloy 600(a) and Alloy 690 in the 0.1M NaOH aqueous solution.

Fig. 2 shows the passive film of the Alloy 600 and Alloy 690 in the PbO additive into the 0.1M NaOH solution. The passive film formed on the Alloy 600 is like an ichthyotic shape. The surface of the Alloy 690 corrodes along grain boundary. But the surface of the Alloy 690 is likely safer than that of the Alloy 600. As the results, the passive films of the Alloy 600 are weaker than those of the Alloy 690 in the PbO additive into the 0.1M NaOH aqueous solution.
The PbO additive affects the form of the passive film on the Alloy 600 seriously.

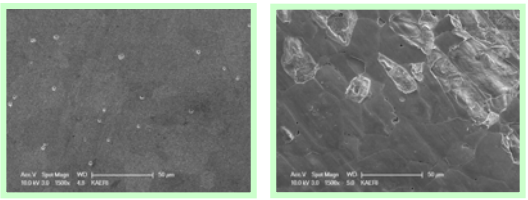
Fig. 3 shows the surface of the Alloy 600 and the Alloy 690 in the PbO and NiB additives into the 0.1M NaOH solution
The surface of the Alloy 600 in the NiB+PbO solution is less corroded than that in the PbO solution. But the surface of the Alloy 690 is deteriorated more by the NiB additive.

Fig. 4 was analyzed the surface of the Alloy 600 by the EDX. The Pb composition is enriched along grain boundary.



(a) (b)

Fig. 2. The surface of the Alloy 600(a) and Alloy 690(b) in the 0.1M NaOH into PbO additive aqueous solution.



(a) (b)

Fig. 3. The morphology of the Alloy 600 and Alloy 690 in the 0.1M NaOH into the PbO and NiB attivitives

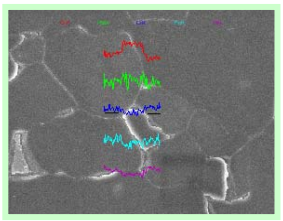


Fig. 4. The line scanning of the surface of the Alloy 600 in the 0.1M NaOH into the PbO additive solution.

4. Conclusion

The surface oxide films on Alloy 600 and the Alloy 690 have been investigated with additives. The passive films were characterized by analyzing the ac-impedance spectrum. And the surface and the particles of the specimens were analyzed by SEM and EDX. The PbO additive affects the passive film formed on the Alloy 600 and Alloy 690. The NiB inhibitor affected the passive film of the Alloy 600 more than that of the Alloy 690.

5. Reference

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Table 1. Chemical compositions of the Alloy 600(wt%)

C	Ni	Cr	Fe	Ti	Al	Mn	Si	Co	Cu	N	B	P	S
0.026	72.4	16.81	9.01	0.36	0.16	0.83	0.33	0.01	0.01	0.018	0.001	0.007	0.001

Table 2. Chemical compositions of the Alloy 690(wt%)

C	Ni	Cr	Fe	Ti	Al	Mn	Si	Cu	P	S
0.05 max	58	27-31	7 - 11	0.04 max	0.4 max	0.5 max	0.5 max	0.5 max	0.015 max	0.015 max