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Pitting corrosion of Alloy 690 in thiosulfate-containing chloride solutions

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Abstract

The effects of thiosulfate ion and solution pH on pitting corrosion of Alloy 690 in chloride solution were explored. Potentiodynamic polarization measurements were conducted to evaluate pitting corrosion susceptibility of Alloy 690 in these environments. The results showed that pitting corrosion occurred in the mill-annealed (1050°C/5min) Alloy 690 in 1 wt% NaCl solution but not in 0.1 M $Na_2S_2O_3$ solution. The value of pitting nucleation potential (E_{np}) determined in 1 wt% NaCl solution (without $Na_2S_2O_3$) increased with increasing solution pH value in the range of 2–10. The addition of $Na_2S_2O_3$ to 1 wt% NaCl solution greatly affected the pitting corrosion behavior, which was dependent on concentration. The preformed nickel sulfide surface film due to the presence of $Na_2S_2O_3$ caused Alloy 690 to become more susceptible to pitting corrosion in 1 wt% NaCl solution. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The high chromium content of Alloy 690 results in its excellent corrosion resistance in a broad range of aqueous environments. Consequently, it has been used as a substitute for Alloy 600 as the tubing material for pressurized water reactors (PWRs). However, pitting corrosion of Alloy 690 still occurred in thiosulfate-containing chloride solution [1]. The role of thiosulfate ion on the pitting corrosion of stainless steels in chloride solution has been extensively investigated recently [2,3]. Enhanced pitting corrosion of stainless steels due to the presence of thiosulfate ion in chloride solution was generally observed. It has also been reported that the presence of thiosulfate ion in chloride solution causes a decrease in pitting corrosion potential of Alloy 600 [4], and the critical concentration of NaCl to induce pitting corrosion of Alloy 600 decreases as the concentration of thiosulfate ion increases [5]. Whether thiosulfate ion affecting the pitting corrosion behavior of Alloy 690 in the same manner as of stainless steels and Alloy 600 is of interest. Furthermore, the mechanism of the enhanced pitting corrosion of various stainless steels and Alloy 600 in chloride solution, which caused by the presence of thiosulfate ion, is still not clear yet. Considering the fact that the existence of thiosulfate ion may alter the nature of the surface film formed on the alloy surface, the effect of preformed passive film on the pitting corrosion of Alloy 690 is also explored in this investigation.

2. Experimental

The chemical composition of Alloy 690 is given in Table 1. The alloy provided by Sumitomo Metal Technology was heat treated at 1050°C for 5 min, and then followed by water quench before shipping.

Pitting corrosion of Alloy 690 was evaluated by employing potentiodynamic polarization test in thiosulfate-containing solution. Each specimen with an exposed surface area of 10 mm × 10 mm, cut from the plate, was ground and polished with silicon carbide paper to a 800 grit finish. It was then cleaned with acetone in an ultrasonic cleaner, rinsed with water and dried in air. The electrolytes were plain sodium thiosulfate solutions (0.001, 0.01 and 0.1 M), 1 wt% sodium chloride solutions with or without the addition of sodium thiosulfate of various concentration. The electrolyte

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

Element	Fe	Ni	Cr	C	Si	Mn	P	S	Cu	Mo	Co	Ti
wt%	Bal.	60.65	29.70	0.022	0.35	0.29	0.007	0.001	0.02	0.02	0.01	0.2

pH was adjusted by adding either dilute sulfuric acid, hydrochloric acid, or sodium hydroxide solution depending on the electrolyte and pH required. After polarization curve measurement, the specimen was examined with optical microscope (OM), surface film was analyzed with X-ray photoelectron spectroscopy (XPS).

3. Results and discussion

The potentiodynamic polarization curves of Alloy 690 in plain sodium thiosulfate solution at various concentration at room temperature are shown in Fig. 1. The results showed that Alloy 690 could be passivated in such solutions, and the concentration had no significant influence on the anodic polarization behavior of this material. After polarization test, the specimen surface was examined microscopically. No evidence of pitting corrosion was found which indicates that the rise of current density at high anodic potential was not caused by pitting corrosion, but related to other oxidation reaction. In other words, pitting corrosion would not occur solely by the presence of thiosulfate ion. Similar observations have been reported elsewhere for austenitic stainless steels and duplex stainless steel [6].

Fig. 2 shows the cyclic potentiodynamic polarization curves of Alloy 690 in 1 wt% NaCl solution with and without $Na_2S_2O_3$ additions. As shown in this figure, the polarization behavior of Alloy 690 in 1 wt% NaCl solution was greatly affected by $Na_2S_2O_3$, which was also concentration dependent. A hysteresis loop (curve A) was observed in 1 wt% NaCl solution without the addition of $Na_2S_2O_3$. Post-examination showed that pits were formed on the specimen surface. The shifts of the polarization curves were seen when $Na_2S_2O_3$ was added to 1 wt% NaCl solution. As revealed in Fig. 2, pitting corrosion nucleation potential (E_{np}) decreased with the addition of 0.001 or 0.01 M $Na_2S_2O_3$ to 1 wt% NaCl solution, indicating the decrease in pitting corrosion resistance. The enlarged hysteresis loops were observed with the additions of 0.001 M (curve B) and 0.01 M (curve C) $Na_2S_2O_3$. Interestingly, the enhanced pitting corrosion disappeared as the concentration of $Na_2S_2O_3$ was increased to 0.1 M as manifested by the increase of E_{np} (curve D). As reported elsewhere, inhibition of pitting corrosion even occurred for Alloy 690 in NaCl solution when the concentration of $Na_2S_2O_3$ was much higher [7]. These observations manifested that $S_2O_3^{2-}$ ion could either act as a promoter or an inhibitor for pitting corrosion of Alloy 690 in NaCl solution, depending on its concentration. Although not clearly explained, the dual effect of thiosulfate ion on the pitting corrosion

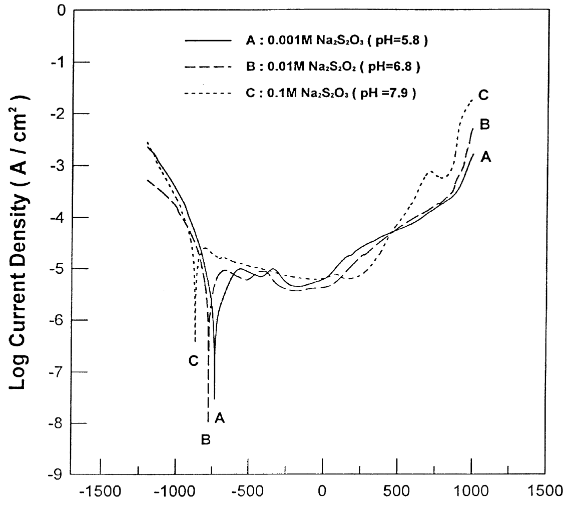


Fig. 1. Potentiodynamic polarization curves of Alloy 690 in $Na_2S_2O_3$ solution of various concentrations.

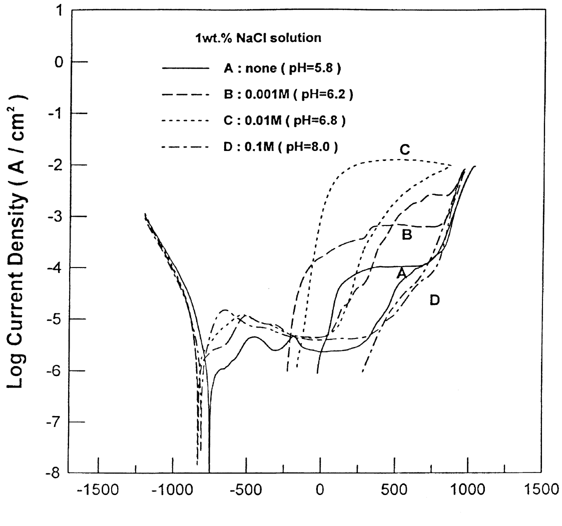


Fig. 2. Cyclic potentiodynamic polarization curves of Alloy 690 in 1 wt% NaCl solution with $Na_2S_2O_3$ additions.

behavior of Alloy 600 in NaCl solutions had also been reported by others [8].

According to the competitive adsorption mechanism proposed by Leckie and Uhlig [9], $S_2O_3^{2-}$ ion might compete for surface site with Cl^-. At low concentration of $S_2O_3^{2-}$, the surface sites were mainly occupied by Cl^- ions, and pitting corrosion was initiated. Under such condition, the formation of S due to the reduction of $S_2O_3^{2-}$ occurred, which was subsequently reduced to form H_2S. The adsorbed H_2S on the metal surface could cause an increase in metal dissolution [10]. If H_2S was adsorbed on the fresh pit surface, enhanced pitting corrosion would be possible. A decrease in E_{np} with the addition of $S_2O_3^{2-}$ was observed. At a high concentration of $Na_2S_2O_3$, on the other hand, the surface sites were almost covered by $S_2O_3^{2-}$ ions, and Cl^- ions were expelled from the surface. This is presumably why pitting corrosion was retarded giving rise to an increase in E_{np}.

After polarization tests, the specimens were examined under OM. The results are demonstrated in Fig. 3. As shown in these micrographs, Alloy 690 was susceptible to pitting corrosion in plain 1 wt% NaCl solution. With the presence of 0.001 and 0.01 M $Na_2S_2O_3$ in 1 wt% NaCl solution, the sizes of the pits were much larger than that in 1 wt% NaCl solution without $S_2O_3^{2-}$, as revealed in Fig. 3(b) and (c). As the concentration of $S_2O_3^{2-}$ increased up to 0.1 M, the pit size as can be seen in Fig. 3(d) decreased and was closed to that shown in Fig. 3(a). These micrographs demonstrated that $S_2O_3^{2-}$ could assist pit nucleation and growth when its concentration was low.

The effects of thiosulfate concentration and pH on the variation of E_{np} for Alloy 690 in 1 wt% NaCl solution are demonstrated in Fig. 4. The results illustrate that E_{np} first decreased and then increased with increasing concentration of $S_2O_3^{2-}$.This figure also shows that E_{np} increased with the increasing pH value (ranging from 2 to 10) in 1 wt% NaCl solution. However, E_{np} became independent of pH when $Na_2S_2O_3$ was added to 1 wt% NaCl solution.

The experimental results indicated that thiosulfate solution itself could not cause the occurrence of pitting corrosion of Alloy 690. However, the addition of thiosulfate ion could enhance pitting corrosion in 1 wt% NaCl solution. Thiosulfate ion seems to influence the passivation behavior in a complicated manner. In NaCl solution, pitting corrosion involves the breakdown of the oxide passive film on the metal surface. In thiosufate-containing NaCl solution, the nature of the surface film was modified by the presence of nickel sulfide as

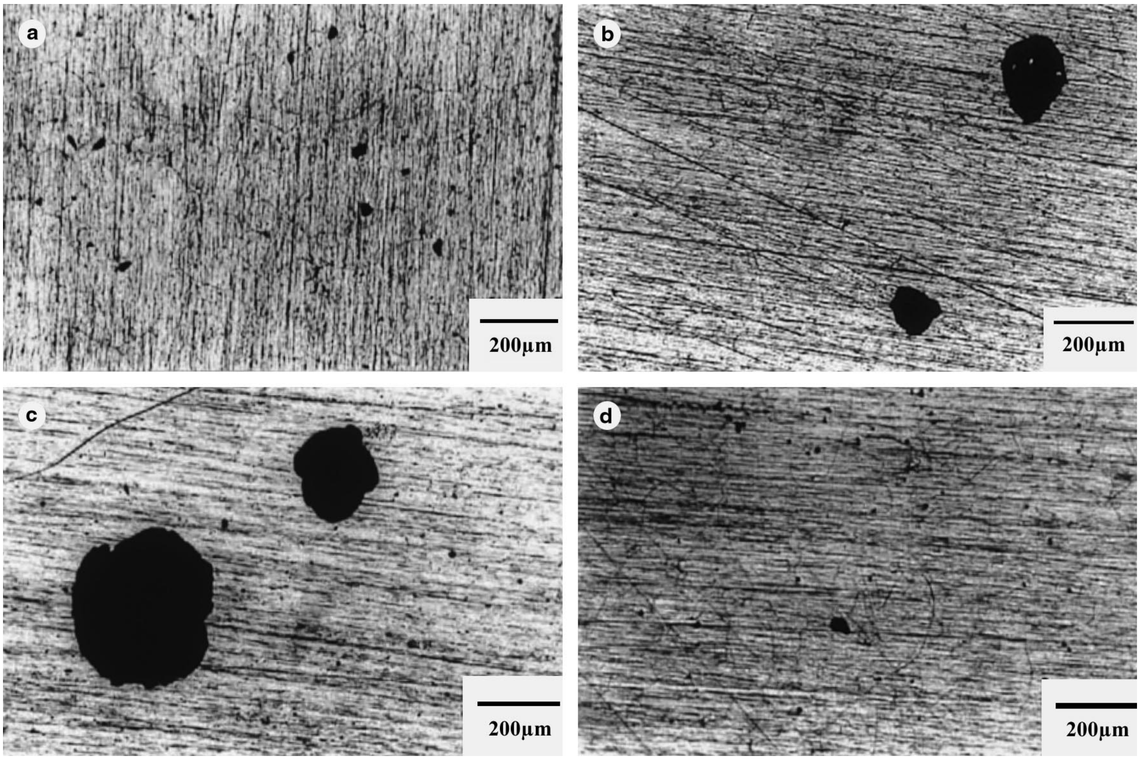


Fig. 3. OM micrographs for Alloy 690 in 1 wt% NaCl solution with $Na_2S_2O_3$ additions after cyclic potentiodynamic polarization tests: (a) blank; (b) 0.001 M; (c) 0.01 M; (d) 0.1 M.

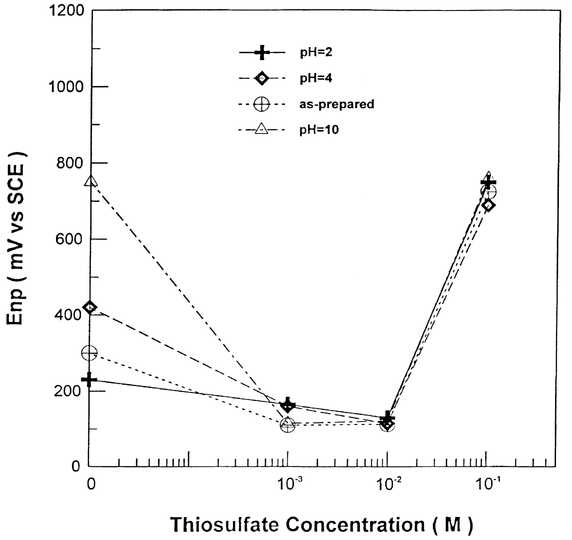
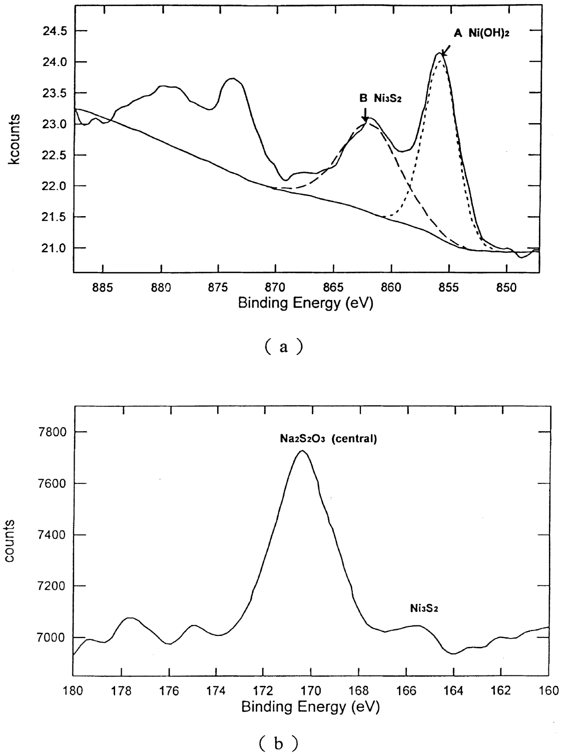


Fig. 4. Effects of thiosulfate concentration and pH on the variation of E_{np} of Alloy 690 in 1 wt% NaCl solution.

evidenced from XPS analysis. Fig. 5 gives the XPS results showing the binding energies of Ni $2p_{3/2}$ and S $2p_{1/2}$, respectively, for Alloy 690 after potentiodynamic polarization measurement in 0.1 M $Na_2S_2O_3$ solution. Ni_3S_2 besides $Ni(OH)_2$ was found on the specimen surface. In plain 1 wt% NaCl solution, XPS results only revealed the presence of chromium oxide and nickel hydroxide. In thiosulfate-containing 1 wt% NaCl solution, nickel sulfides (Ni_3S_2 and NiS) were again found incorporated in the oxide and hydroxide surface film. The enhanced pitting corrosion of Alloy 690 due to the presence of thiosulfate ion was considered to be associated with the nature of the passive film. The effect of preformed film on the pitting corrosion behavior was thus investigated. As can be seen in Figs. 1 and 2, the surface of Alloy 690 would be in passive state in either plain sodium thiosufate solution or in 1 wt% NaCl solution at +250 mV (SCE). The current densities would be expected to decrease to negligible magnitudes due to the formation of passive film if the as-polished specimens were held at +250 mV. The results shown in Fig. 6 depict these changes of current densities with time for Alloy 690 in 0.01M sodium thiosufate solution (Fig. 6(a)) and in 1 wt% NaCl solution under a controlled potential of +250 mV. After this potential held for several thousand seconds, either NaCl or sodium thiosufate was added to make the solutions with a composition of 0.01 M $Na_2S_2O_3$ + 1 wt% NaCl solution in the above two cases. As shown in Fig. 6(a), a significant increase in current density was observed shortly after the addition of NaCl into the 0.01 M $Na_2S_2O_3$ solution. After the tests, pits were seen on the specimen surface, it indicates that the rise of current density was associated with the formation of pits. Nevertheless, the addition of sodium thiosulfate into the 1 wt% NaCl solution did not cause any change in the current density measured (Fig. 6(b)). No pits were found on the specimen surface in this case.



(a)

(b)

Fig. 5. XPS spectra for Ni $2p_{3/2}$ and S $2p_{1/2}$ for Alloy 690 after potentiodynamic polarization measurement in 0.1 M $Na_2S_2O_3$ solution.

The current vs time curves were also determined at +500 mV at the same way as that shown in Fig. 6 (+250 mV). At +500 mV, Alloy 690 was still remained in the passive stage in 0.01 M $Na_2S_2O_3$ solution, and the current density was rather low at this potential (Fig. 7). Similar to that at +250 mV, an increase in current density was seen when NaCl solution was added (Fig. 7(a)), demonstrating the occurrence of pitting corrosion. In 1 wt% NaCl solution, the current density started and continued to rise as soon as the potential was held at +500 mV, as in Fig. 7(b). Since +500 mV was above the pitting nucleation potential of Alloy 690 in 1 wt% NaCl solution, the increase in current density corresponding to the nucleation and growth of pits. The addition of sodium thiosulfate into 1 wt% NaCl solution caused a substantial increase in current density, indicating the acceleration of pit growth rate.

From the above examinations, it is clear that the preformed surface film plays very important role in the pitting corrosion behavior. In plain NaCl solution at a

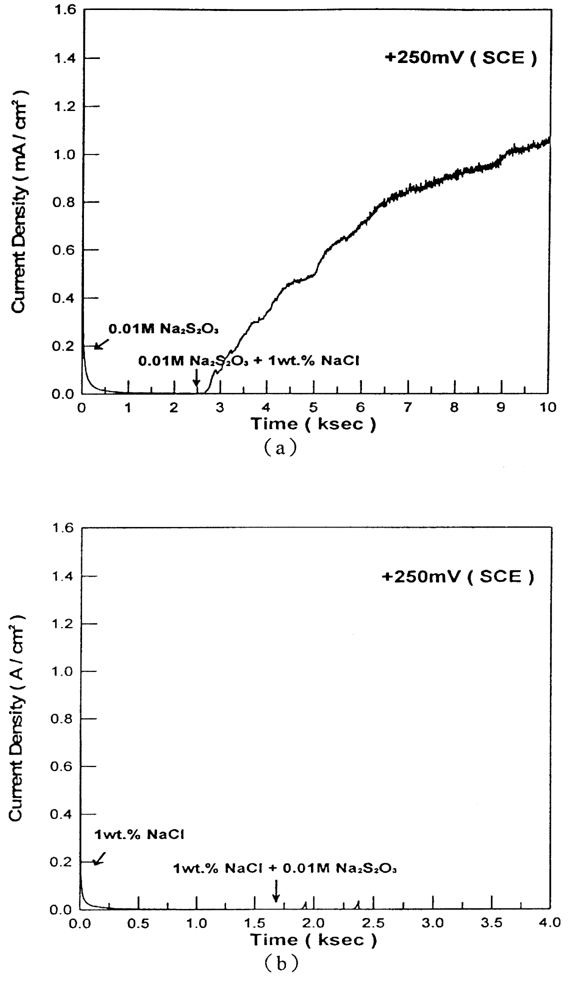


Fig. 6. Current density vs time curves for Alloy 690 in: (a) 0.01 M $Na_2S_2O_3$ solution with latter addition of 1 wt% NaCl; (b) 1 wt% NaCl solution with latter addition of 0.01 M $Na_2S_2O_3$, at +250 mV (SCE).

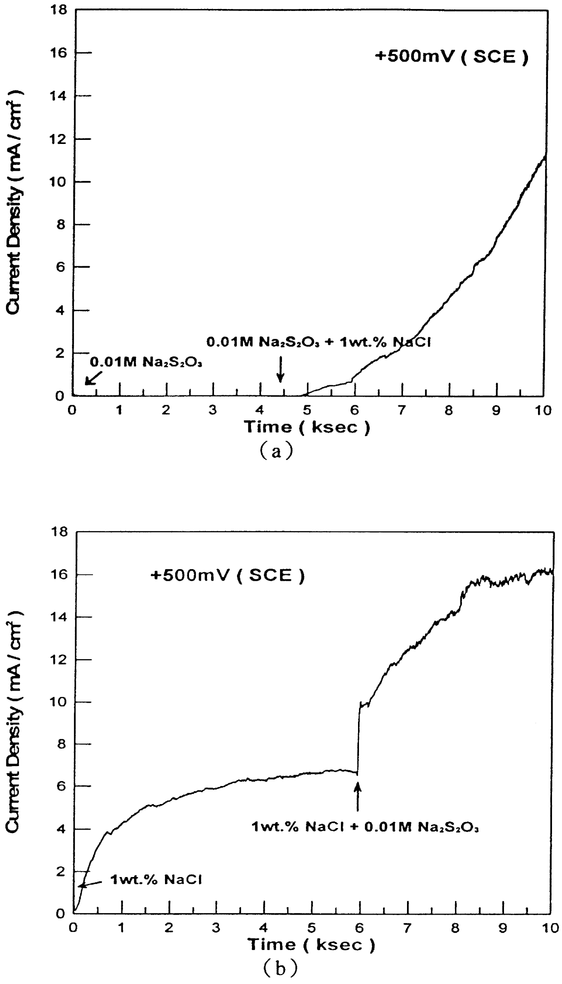


Fig. 7. Current density vs time curves for Alloy 690 in: (a) 0.01 M $Na_2S_2O_3$ solution with latter addition of 1 wt% NaCl; (b) 1 wt% NaCl solution with latter addition of 0.01 M $Na_2S_2O_3$, at +500 mV (SCE).

potential lower than the pitting corrosion potential ($E_{\mathrm{pit}}^{\mathrm{Cl}^-}$) but greater than the pitting corrosion potential in a mixed 1 wt% NaCl + 0.01 M $Na_2S_2O_3$ solution ($E_{\mathrm{pit}}^{\mathrm{mix}}$), a stable oxide film was formed and remained unchanged with the latter addition of sodium thiosulfate. In plain sodium thiosulfate solution and at +250 mV, sulfide incorporated with oxide was formed initially on the surface of Alloy 690. The surface film modified with sulfide was less protective than the oxide film. Once NaCl was added into this solution, however, the preformed surface became unstable and led to local breakdown for pitting corrosion to occur.

As the initial potential was greater than $E_{\mathrm{pit}}^{\mathrm{Cl}^-}$, pitting corrosion would occur in plain NaCl solution. Once pits were formed, the addition of $S_2O_3^{2-}$ activated the dissolution within the pits. A rise in current density as shown in Fig. 7(b) was thus observed. In plain sodium thiosulfate solution, the formation of sulfide film at +500 mV also provided passivity, though less effective than oxide, and a low current density was seen. The later addition of Cl^- into this solution again caused the breakdown of the surface film and resulting in the formation of pits. The results obtained in this study demonstrated that preformed surface film was important to the initiation of pitting corrosion.

4. Conclusions

1. In 1 wt% NaCl solution, pitting corrosion of Alloy 690 was enhanced by the simultaneous presence of 0.001 and 0.1 M $Na_2S_2O_3$. The detrimental effect of $Na_2S_2O_3$ on pitting corrosion was diminished as its concentration increased up to 0.1 M.

2. In plain 1 wt% NaCl solution, E_{np} of Alloy 690 increased with increasing pH. However, E_{np} became independent of pH when $Na_2S_2O_3$ was added into 1 wt% NaCl solution.

3. The preformed nickel sulfide surface film due to the presence of $Na_2S_2O_3$ caused Alloy 690 to become more susceptible to pitting corrosion with later addition of 1 wt% NaCl to the thiosulfate solution. In 1 wt% NaCl solution, on the contrary, the oxide/hydroxide surface film initially formed at potential less than E_{pit}^{Cl-} provided pitting corrosion resistance with later addition of $Na_2S_2O_3$ and at $E > E_{pit}^{mix}$.

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