Semiconductivity Conversion of Passive Films on Alloy 800 in Chloride Solutions Containing Various Concentrations of Thiosulfate

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Abstract

Semiconductive properties of the passive films formed on Alloy 800 in 0.1 M chloride solutions containing various concentrations of thiosulfate are investigated using Mott-Schottky analysis. The results indicate that when the concentration of the thiosulfate ions increases, the semiconductivity of a passive film is critical to the corrosion behavior of the alloy.3,4 Chloride and thiosulfate are common ions existing in power-generating systems.5 It has been reported previously that the ratio of chloride to thiosulfate concentration had a remarkable effect on passive film degradation.6,7 There is maximum pitting susceptibility at a certain ratio, the passive layer breakdown potential is significantly lowered,5 while additions of more than 0.5 M thiosulfate inhibited corrosion. They claimed that, at a higher concentration ratio, the passive film was broken down by chloride ions and stabilized by reduction of sulfur within the metastable pits. However, this effect becomes less significant at a lower concentration ratio.6

Experimental

The test specimens were prepared using Alloy 800 SG tubing (Sandvik, heat number 516809, outer diameter of 15.88 mm, wall thickness of 1.13 mm). The outer surface was used for the tests (the inner surface and cross sections were sealed with epoxy resin). Prior to each measurement, the test surface was polished with wet silicon carbide papers (320, 600, 800 and 1200 grits), rinsed with water, then dried in a desiccator for 24 hours. The chemical composition (wt%) of Alloy 800 was: C(0.017), Si(0.46), Mn(0.5), Fe(43.2), Cu(0.02), Al(0.29), N(0.016), Fe(43.2). Potentiodynamic polarization was conducted at 21°C by sweeping the potential in the positive direction at 0.1667 mV/s in deaerated solution. A three-electrode cell was used with the Alloy 800 as the working electrode, a saturated calomel electrode (SCE) as the reference electrode (RE) and a platinum electrode as the counter electrode (CE).

For the Mott-Schottky analysis (M-S), the scan direction was from high to low potential with a stepping interval of 50 mV. An AC signal with a frequency of 1000 Hz and a peak-to-peak magnitude of 10 mV was superimposed on the potential. For the scanning electrochemical microscope (SECM) experiments, an electrochemical cell was mounted on the SECM stage (from CHI, USA). An ultramicroelectrode of Pt (radius of 10 μm) with the side sealed in glass was used as the SECM probe.35 Scanning electron microscope (SEM) and energy-dispersive X-ray analysis (EDX) were used to obtain the surface morphologies and elemental distributions, respectively.

Time-of-flight secondary ion mass spectrometry (ToF SIMS) analysis was carried out using a ToF SIMS IV instrument (ION-ToF Gmbh). The information depth of ToF SIMS analysis was limited to the top 1 to 20 monolayers. Ions from mass 1 (hydrogen) to ∼9000 amu (for cluster ions) were detected with resolutions ranging from 1 ppb to ppm concentrations, depending on the element. In the current work, the analysis source used was Ga⁺, operating at 15 kV; the sputtering source was Cs⁺, operating at 1 kV. The samples were immersed in the solution until the ToF SIMS test to minimize atmospheric oxidation. Before the test, specimens were cleaned with distilled water.

Results and Discussion

Figures 1a and 1b show the polarization curves and the break down potentials, respectively. As shown in Fig. 1b, three regions are divided according to the break down potential values: (1) In the plain chloride solution without thiosulfate or with low thiosulfate concentrations, the addition of 0.01 M thiosulfate lowers the pitting potential to 0.1 V SCE.
As discussed before, Newman et al.\(^7\) found the same phenomenon for 304 SS in 0.25 M NaCl solution containing various concentrations of thiosulfate. This explanation can also be applied to our system. In region (2), the thiosulfate concentration increases to 0.1 M, the pitting potential shows a downward trend (Figure 2b), indicating that the addition of small amount thiosulfate leads to a rapid pitting propagation rate. As the thiosulfate concentration further increases, no pits were found on the surface (Figure 2d and 2e), and the corrosion form is transpassive dissolution.

Figure 3 shows the EDX elemental distributions of one typical pit formed in 0.1 M chloride + 0.01 M thiosulfate. Sulfur is enriched within the pit, i.e., thiosulfate is reduced within the pit to form adsorbed sulfur.\(^9\)

Figure 4a shows the SECM image when the electrode was polarized at 0.3 V\textsubscript{SCE} (metastable pitting occurs) in 0.1 M chloride solutions. Some active spots are possibly related to grain boundary, triple point and/or inclusions.\(^8\) After the SECM image was scanned half way, 0.075 M thiosulfate was added into the chloride-only solution. The surface reactivity increased after the addition of 0.075 M thiosulfate and some “active spots” with high current (blue color) appear in the image, indicating that thiosulfate stabilizes the metastable pits and makes them develop into stable pits. However, if 0.5 M thiosulfate is added into 0.1 M chloride solution, no pits are observed (Figure 4b), suggesting that there is no combined effect when the concentration of thiosulfate is high. The probe approach curves (PACs) shown in Figure 5 also indicate that spot B is active whereas spots A and C are passive.

Figures 6a and 6b show the M-S results and the slopes of the linear region can be related to defect density by:\(^16\)

\[
k = \pm \frac{2}{q\varepsilon\varepsilon_0 N A^2}
\]  

where \(q\) is the elementary charge of electrons, \(\varepsilon\) is the dielectric constant of the oxide, \(\varepsilon_0\) is the vacuum permittivity, \(A\) is the geometrical surface area, \(N\) is the defect density. Positive and negative slopes are for n-type and p-type semiconductors, respectively. The value of \(\varepsilon\) for the system under investigation is unknown and can be considered as constant because the quantity of the incorporated sulfur atoms is very low. The results show that when the thiosulfate concentration increases from 0 to 0.1 M, the slope does not change significantly and the semiconductivity of the passive film is n-type, suggesting that oxygen vacancies and/or interstitial cations are the major defects.\(^16\) When the thiosulfate concentration is higher than 0.1 M, the slopes change from positive values to negative ones, indicating that the semiconductivity of the passive film is p-type and cation vacancies are the major defects. Further increase in the thiosulfate concentration from 0.3 M to 0.5 M results in more cation vacancies.

Figure 7 shows the sulfur intensities as a function of depth on samples passivated at corrosion potential in the chloride solution without thiosulfate or with various concentrations of thiosulfate passivated at the corrosion potential. S intensity was determined by SIMS analysis using Cs\(^+\) sputtering the surface. The results show that as the
Figure 2. SEM images after the polarization test in (a) 0.1 M chloride (b) 0.1 M chloride + 0.01 M thiosulfate (c) 0.1 M chloride + 0.1 M thiosulfate (d) 0.1 M chloride + 0.3 M thiosulfate (e) 0.1 M chloride + 0.5 M thiosulfate.

Figure 3. EDX elemental distributions of one pit formed in 0.1 M chloride + 0.01 M thiosulfate.

Figure 4. SECM images when polarized at 0.3 V SCE: (a) in 0.1 M chloride with/without 0.01 M thiosulfate (b) in 0.1 M chloride with 0.5 M thiosulfate.
thiosulfate concentration increases, the slopes change from positive values to negative ones (Figures 6a and 6b) while sulfur intensity in the passive films monotonically increases (Figure 7) because of the adsorption and reduction of thiosulfate sputtering at the surface into the outer layer of passive film. The change in the slope is directly related to the incorporation of sulfur in the passive film. The adsorbed sulfur atom may accept electrons to become \( S^{2-} \) and occupy the oxygen vacancies, \( V_{O}^{*} \), and enter into the outer layer of the passive film through the reaction \( V_{O}^{*} + S^{0} \rightarrow S_{O}, S^{2-} \); \( S^{0} \) means sulfur ions accept electrons and occupy the oxygen vacancies. When the thiosulfate concentration increases from 0 to 0.1 M, the increase in the incorporated sulfur is very small, the consumption of the electrons is limited. Therefore, the change in the donor density is negligible. The results of Figures 1b, 6b and 7 show that pitting potential is related to both donor density (slope value in the M-S) and the concentration ratio of chloride to thiosulfate ions.

When the thiosulfate concentration is higher than 0.1 M, the adsorption of thiosulfate is enhanced. Thiosulfate can be reduced on the film surface\(^7\) and incorporated into the passive film. When the oxygen vacancies are filled with sulfur ions, the electrons in the n-type semiconductor are consumed. When the thiosulfate concentration further increases to 0.3 M, the electrons are completely consumed; further increase in the incorporated sulfur atoms will generate holes. Therefore, the semiconductivity of passive film is changed from n-type to p-type; the passive film cannot be broken down and transpassive dissolution is observed at high potentials. Further increase in the thiosulfate concentration from 0.3 M to 0.5 M results in more incorporated sulfur as shown in Figure 7, therefore more holes are generated, resulting in the further decrease of the slope. Figure 8 shows XPS spectra of Alloy 800 in 0.1 M chloride + 0.5 M thiosulfate solution. The two peaks in the figure are characteristic peaks of \( S^{2-} \), indicating the incorporation of sulfur in the passive film.
Conclusions

Semiconductivities change from n-type to p-type is due to sulfur incorporation into oxygen vacancies. N-type semiconductors suffer pitting corrosion and p-type semiconductors suffer transpassive dissolution when the film breaks down in this system.

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