

Electrochemical Characteristics of an Austenitic Stainless Steel Under Simulated Solution Film Formed in Marine Atmosphere

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Received: 7 September 2011 / Accepted: 14 October 2011 / Published: 1 November 2011

Stainless structures and fasteners can fail as a result of stress corrosion cracking (SCC) in coastal atmosphere. In order to have a better understanding of the marine atmospheric SCC mechanism, the corrosion electrochemistry and hydrogen permeation behavior of stainless steel under surface solution film were studied. The solution film was more easily formed on the surface that was contaminated by alien substances such as rust of carbon steels. The stability of the passive film decreases with the development of the surface solution film and both the pitting potential and the SCC sensitive range shift to lower potentials. The hydrogen entry through stainless steel membrane during cyclic wet-dry corrosion conditions was also detected.

Keywords: Austenitic stainless steel, marine atmosphere, corrosion electrochemistry.

1. INTRODUCTION

The SCC occurrence of coastal stainless steel structures and fasteners were reported [1, 2]. The study showed that an electrolyte film was formed on the surface of stainless steel when SCC occurred, which was of very high concentration of chloride and low pH [1-7].

Generally the SCC experiments were conducted in solutions that simulated the composition of the solution film when the SCC of stainless steel occurred [8-15]. In fact, the solution film changes with the development of corrosion. So, the research in a single simulated bulk solution can't reflect the changing environment. It is necessary to get the electrochemical information and hydrogen permeation behavior during the evolution of stainless steel surface solution film. The conditions of real environment are complex. Dusts can be attached to stainless steel by the blown of wind, which can be an importance factor of corrosive film formation.

In this paper, it is confirmed that alien substances facilitate the formation of corrosive film and the developed solution film that can cause SCC can be easily dispersed on the whole surface of the sample. It is also noticed that the solution film can exist on the sample surface stably in humid atmosphere, and the solution can be fairly thick. The stability of passive film and the SCC sensitive potential ranges were analyzed by the measurement of corrosion-time curves, polarization curves, and fast and slow scan rate polarization curves. The attempt of hydrogen permeation measurement under wet-dry cycles was also included.

2. EXPERIMENTAL

The studied material was AISI 321 stainless steel with the chemical composition of 0.079C, 17.75Cr, 9.31Ni, 1.19Mn, 0.53Si, 0.56Ti, 0.030P, 0.0064S in wt%. The material was heated at 1050°C for 20min and then water quenched. The sample was a short rod with the end as working surface, which was grinded to 600#. The surface solution film formation was observed while little amount of carbon rust and FeCl₃ with sea water was placed on top of the sample surface after drying and compared with bare clean sample. The sample for corrosion potential and polarization curves measurements was embedded in epoxy resin except the working section with an area of 0.785cm². The hydrogen permeation measurement was conducted by using electrochemical technique which was similar to the technique used previously [16]. The sample was 0.1mm thick austenitic stainless steel membrane with working area of 9.62 cm². One side was coated with palladium. The hydrogen detection side, which was coated with palladium was potentiostatically controlled at a potential of 150 mV vs. mercury oxide/mercury electrode for over 24h to reach a stable state before experiment. All experiments were repeated three times and typical data are reported.

3. RESULTS AND DISCUSSION

3.1. Corrosive solution film formation on the surface of stainless steel and solution simulation consideration during the corrosion development

Figure 1 shows the surface solution film formation on stainless steel when it was clean or contaminated by alien pollutants. Seawater, carbon steel rust plus seawater, FeCl₃ plus seawater were placed on top of the samples. After drying, these samples were placed in a chamber with seawater at the bottom. For the bare clean sample, no solution film was visualized after 60 days of exposure, while for those samples with contaminants droplets gradually formed on the surface within 24 hours. For the sample contaminated by FeCl₃, a fairly homogeneous solution film was dispersed on the surface with a pH about 1.8. It can be inferred from here that with the developing of corrosive film formation, the increasing of metal ion concentration and the dropping of pH, the surface of stainless steel will always be well wetted in real marine atmosphere due to the high humidity, which facilitates the development of corrosion process. The alien adhered substances simulate the conditions of stainless steel structures

in practical environments. The corrosion products of carbon steel that blown to the surface of stainless steel can act as corrosion accelerator.

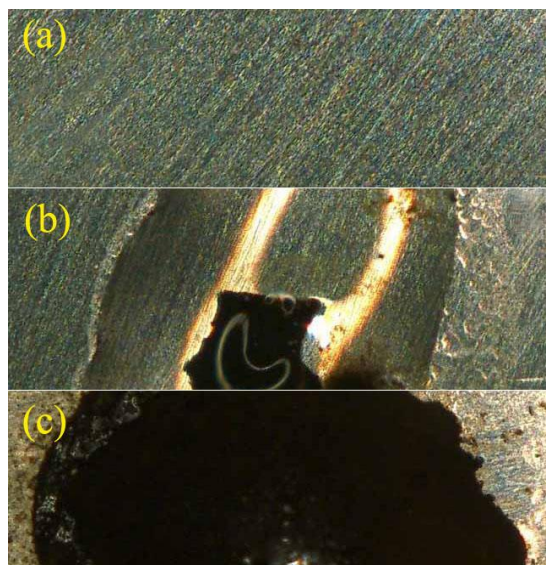


Figure 1. Surface film formation on stainless steel contaminated by alien pollutants (a) clean bare surface after 60 days exposure; (b) carbon steel rust + seawater; (c) FeCl_3 + seawater

Our analysis of the solution after SCC tests of austenitic stainless steel in acidic seawater showed that the concentration of metal ions was proportional to the chemical concentration of stainless steel, showing proportional dissolution of the material.

Rokuro Nishimura et al. [17] also studied the dissolution of austenitic (type 304 and type 316) stainless steels in acidic chloride solutions under applied stress. They noticed that the selective dissolution for type 304 and type 316 specimens was found to be the same as that in the active dissolution region obtained from the anodic polarization curve. From the results of Rokuro Nishimura et al.'s, the ratio of metal ions in the solution is very close to the ratio of the elements in the steel. Practically, they are identical.

The SCC occurs at anodic dissolution potential. So, for the preparation of the simulated solution, a stainless steel sample was dissolved in 0.5mol/L HCl+0.5mol/L NaCl under an anodic potential. The solution at different developing stages was obtained by diluting the high concentration solution.

3.2. Corrosion potential of stainless steel in simulated corrosive surface film solutions

Figure 2 shows the free corrosion potential-time curves in simulated solutions. The potential was stable in distilled water. When the concentration of the solution became $[\text{Fe}^{3+}] = 0.0138 \text{ mol/L}$, $[\text{Cr}^{3+}] = 0.0037 \text{ mol/L}$, $[\text{Ni}^{2+}] = 0.0017 \text{ mol/L}$, $[\text{Cl}^-] = 0.02 \text{ mol/L}$, $\text{pH} = 2$, the potential showed fluctuations. After a period of immersion, the potential shifted to lower potential and fluctuated continuously. With

the increase of solution concentration, the potential fluctuated seriously, showing the unstableness of passive film.

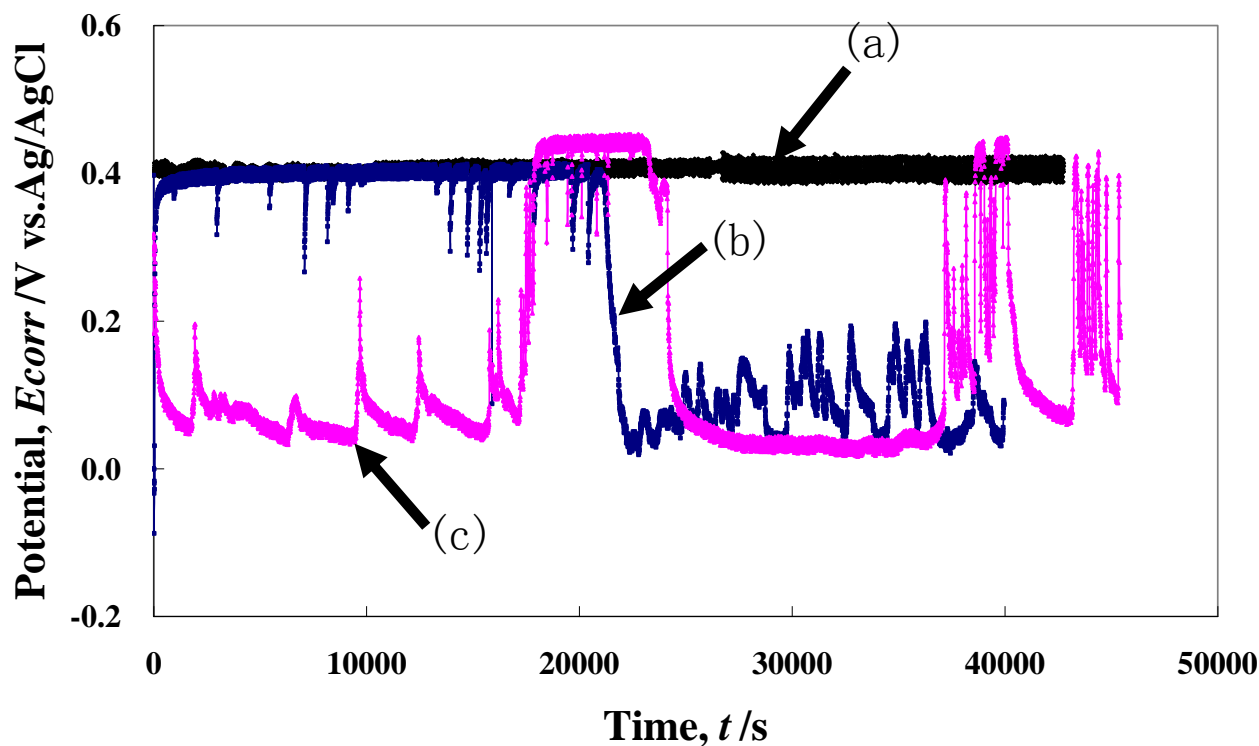


Figure 2. Corrosion potential-time curves of AISI 321 stainless steel in simulated surface film solution (a) distilled water; (b) solution composition : $[\text{Fe}^{3+}] = 0.0138 \text{ mol/L}$, $[\text{Cr}^{3+}] = 0.0037 \text{ mol/L}$, $[\text{Ni}^{2+}] = 0.0017 \text{ mol/L}$, $[\text{Cl}^-] = 0.02 \text{ mol/L}$, $\text{pH} = 2$; (c) solution composition : $[\text{Fe}^{3+}] = 0.138 \text{ mol/L}$, $[\text{Cr}^{3+}] = 0.037 \text{ mol/L}$, $[\text{Ni}^{2+}] = 0.017 \text{ mol/L}$, $[\text{Cl}^-] = 0.2 \text{ mol/L}$, $\text{pH} = 1$

3.3. Polarization curves of stainless steel in simulated corrosive surface film solutions

SCC has correlation with pitting corrosion at initiation stage. It is possible for a SCC crack to initiate at pits. Figure 3 shows the polarization curves of AISI 321 stainless steel in simulated surface film solutions. Plot (a) was obtained in distilled water. The solution concentration increase represented different stages of corrosive surface solution film formation.

No pitting could occur below 1V vs. Ag/AgCl for stainless steel in distilled water and in the solution with concentration lower than that of plot (b). The pitting potentials for plot (b) and (c) are 0.719V, 0.517V (vs. Ag/AgCl) respectively.

While the repassivation potentials are 0.323V, 0.166V (vs. Ag/AgCl) respectively. These data show that the tendency of pitting increases with the development of surface film solution formation. Pits can act as initiation sites for SCC. So, the possibility of SCC also increases with the development of surface film solution formation. The repassivation potential has the same changing tendency with

the development of corrosive solution film, showing that it is hard for a pit to stop growing once it is initialized at high concentration of Cl^- and low pH conditions.

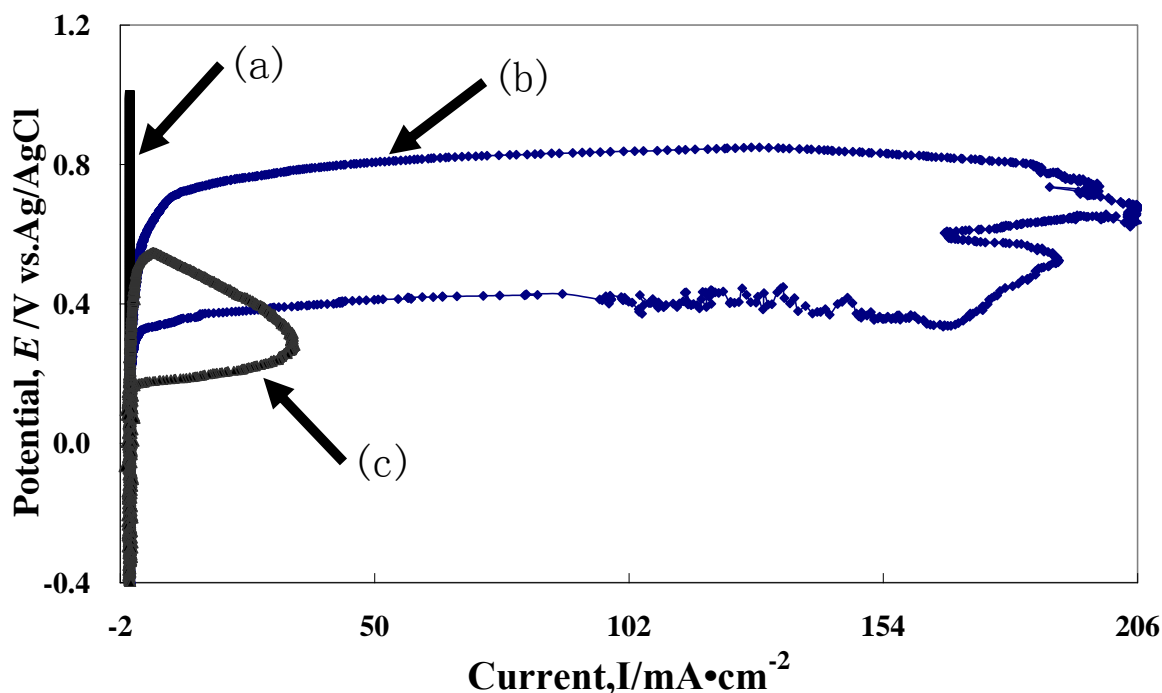


Figure 3. Polarization curves of AISI 321 stainless steel in simulated surface film solution (a) distilled water (b) solution composition: $[\text{Fe}^{3+}] = 0.0138 \text{ mol/L}$, $[\text{Cr}^{3+}] = 0.0037 \text{ mol/L}$, $[\text{Ni}^{2+}] = 0.0017 \text{ mol/L}$, $[\text{Cl}^-] = 0.02 \text{ mol/L}$, $\text{pH} = 2$ (c) solution composition: $[\text{Fe}^{3+}] = 0.138 \text{ mol/L}$, $[\text{Cr}^{3+}] = 0.037 \text{ mol/L}$, $[\text{Ni}^{2+}] = 0.017 \text{ mol/L}$, $[\text{Cl}^-] = 0.2 \text{ mol/L}$, $\text{pH} = 1$

With the progress of surface solution film formation, the concentration of Cl^- increases and the pH decreases. Pitting occurred as a result of adsorption of aggressive anions on passive film followed by penetration of this film under the influence of an electrostatic field [18]. Pits initiated when the field across the film–solution interface reached a critical value. In our work, Cl^- is the aggressive anion. Increasing the Cl^- concentration would enhance the probability of adsorption of Cl^- on the surface, hindering the stability of passive film and eventually reduces the pitting potential. The effect of lower pH on the pitting potential could be attributed to the acceleration of cathodic reaction due to high concentration of H^+ which could cause instability in the passive film [19]. As a combination effect of these two factors, the pitting potential shifted to lower potential.

3.4. Fast and slow scan rate polarization curves of stainless steel in simulated corrosive surface film solutions

The technique was first proposed by Parkins [20]. First, the sample is polarized anodically at a fast scan rate of 1 V/min and then at a lower scanning rate of 10 mV/min . The fast scan represents the behaviour at crack tip, while the slow scan represents the behaviour of side wall. At fast scan rate the

metal has no sufficient time to reach a passive state, while at slow scan rate the metal has. The potential range where the fast and slow scan rate polarization curves exhibit large differences in current is regarded as the SCC sensitive range.

Measurements were done in solutions with different concentrations and pH. Figure 4 shows the results of two conditions only. Under the condition of plot (a), SCC can not occur. At the potential range of -0.067V to -0.250V vs. Ag/AgCl for plot (b), it is possible for the SCC to occur. The SCC sensitive potential tends to shift to lower values as the concentration of the solution increases and the pH decreases.

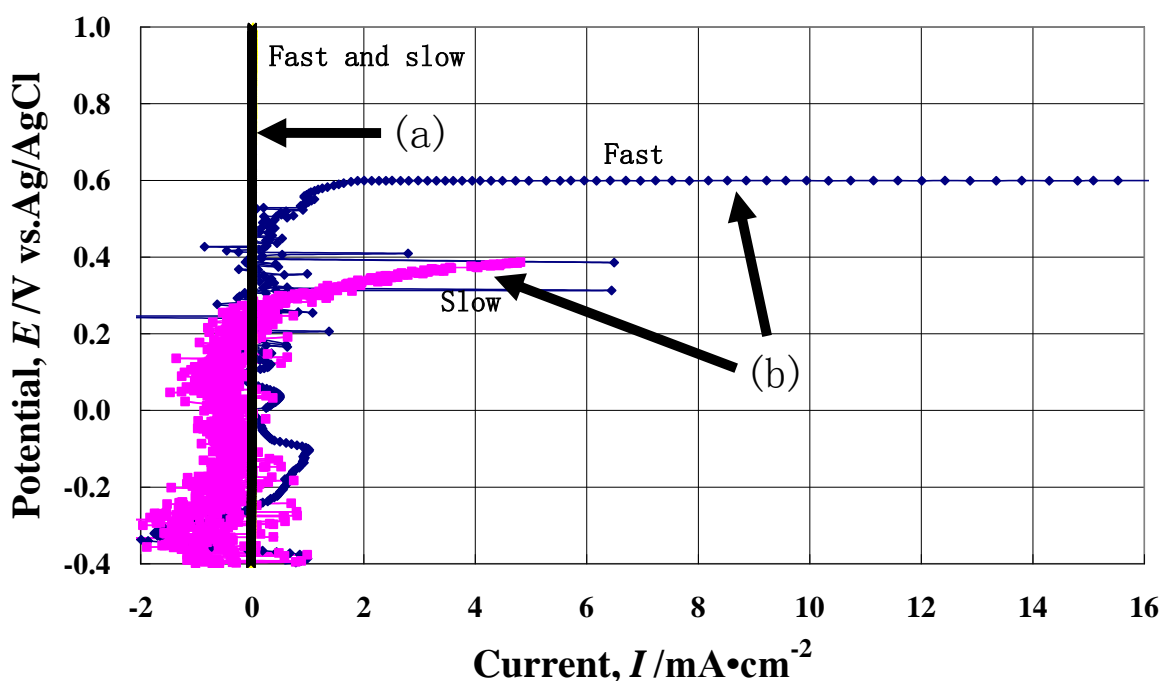


Figure 4. Fast and slow scan rate curves of AISI 321 stainless steel in simulated surface film solution (a) solution components: $[\text{Fe}^{3+}] = 0.000138\text{mol/L}$, $[\text{Cr}^{3+}] = 0.000037\text{mol/L}$, $[\text{Ni}^{2+}] = 0.000017\text{mol/L}$, $[\text{Cl}^-] = 0.0002\text{mol/L}$, $\text{pH} = 4$ (b) solution components: $[\text{Fe}^{3+}] = 0.69\text{mol/L}$, $[\text{Cr}^{3+}] = 0.185\text{mol/L}$, $[\text{Ni}^{2+}] = 0.085\text{mol/L}$, $[\text{Cl}^-] = 1.0\text{mol/L}$, $[\text{H}^+] = 0.5\text{mol/L}$

The shift of SCC sensitive potential to lower potential with the progress of surface solution film formation can be explained similarly as above for the shift of pitting potential. SCC has correlation with pitting corrosion at initiation stage. The initiation of SCC and pitting is the result of the instability of the passive film.

3.5. Hydrogen entry measurement of stainless steel under wet and dry conditions

There exists a contradiction between anodic dissolution and hydrogen embrittlement for SCC mechanisms of stainless steel in acidic chloride solutions. Experiments were done to verify the hydrogen entry in simulated wet and dry conditions.

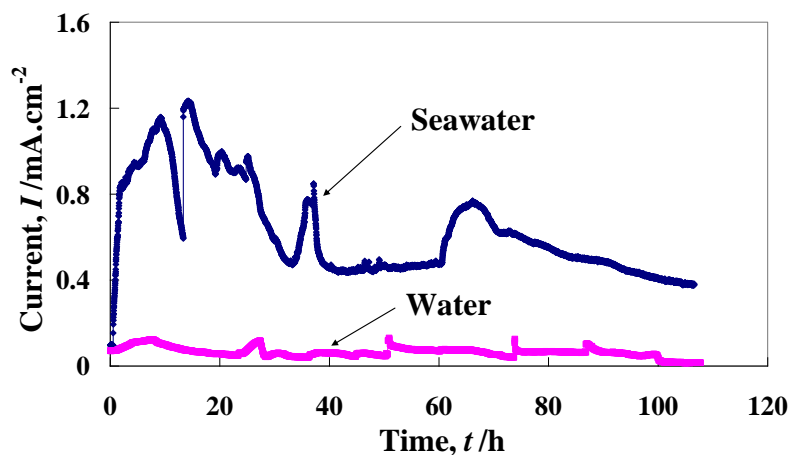


Figure 5. Hydrogen permeation current-time curve of AISI 321 stainless steel under wet-dry conditions. First drop of solution : $[\text{Fe}^{3+}] = 0.0615 \text{ mol/L}$, $[\text{Cl}^-] = 0.885 \text{ mol/L}$, $[\text{H}^+] = 0.2 \text{ mol/L}$; Continuing drops after drying are distilled water

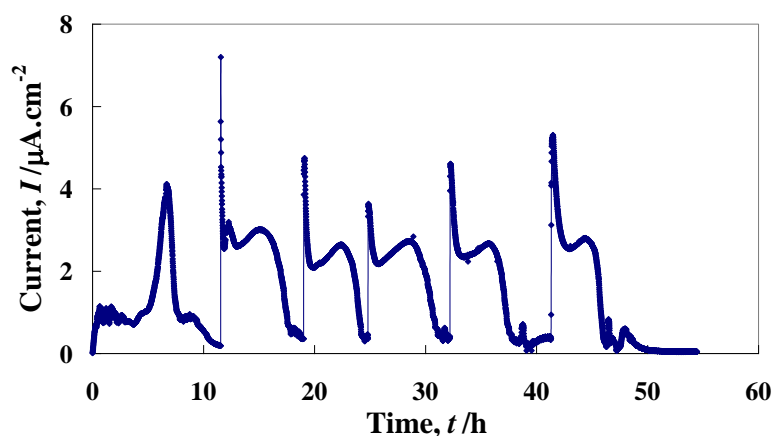


Figure 6. Hydrogen permeation current-time curve of AISI 321 stainless steel under wet-dry conditions. First drop of solution : $[\text{Fe}^{3+}] = 0.0615 \text{ mol/L}$, $[\text{Cl}^-] = 0.885 \text{ mol/L}$, $[\text{H}^+] = 0.2 \text{ mol/L}$; Continuing drops after drying are distilled water.

Figure 5 and Figure 6 show the hydrogen permeation current-time curve under wet-dry corrosion conditions, verifying the hydrogen entry during the development of stainless steel corrosion. For these experiments, first drops of solution are distilled water, seawater and solution containing $[\text{Fe}^{3+}] = 0.0615 \text{ mol/L}$, $[\text{Cl}^-] = 0.885 \text{ mol/L}$, $[\text{H}^+] = 0.2 \text{ mol/L}$, the continuing drops for wetting the surface after drying are distilled water. It can be noticed that even for the wetting of the sample surface by only distilled water, the hydrogen entry into stainless steel is still possible. Adding of seawater on the surface increases the hydrogen entry.

With the corrosion product accumulation on the surface and the dropping of pH the hydrogen entry is more obvious.

This means that hydrogen accumulation in the steel starts at the very beginning the corrosion process, implying the importance to pay attention to the effect of hydrogen especially for the stress corrosion cracking and hydrogen embrittlement study.

4. CONCLUSIONS

Alien corrosion products attached to stainless steel have a strong effect on the corrosive solution film formation on the surface. It is hard for a visible solution film to form on a bare clean surface of stainless steel, while it is quite easy for the solution film to form on the surface attached with corrosion products. The stability of stainless steel passive film decreases with the development of corrosion processes. The pitting potential and the SCC sensitive potential range shift to lower potential as the concentration of the solution film increases and the pH decreases. Hydrogen entry occurs during stainless steel corrosion, making it important to consider the hydrogen effect when studying the environment sensitive fracture of stainless steels.

ACKNOWLEDGEMENTS

This work was financially supported by the National Science Foundation of China No.40876048, China-Australia Special Fund for S&T Cooperation No.41011120050 and Australia-China Special Fund for S&T Cooperation grant CH090106

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