

## Adherence of Carbon Steel Rust on the Corrosion of an Austenitic Stainless Steel Bolt in Marine Atmosphere

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Stainless steel fasteners can fail as a result of stress corrosion cracking (SCC) in coastal atmosphere. In order to have a better understanding of the development of stainless steel fasteners' SCC in marine atmospheric, the corrosion electrochemistry behavior of an austenitic stainless steel contaminated by carbon steel rust component was studied. It was seen that a visible solution film was formed easily on the surface when it was contaminated by carbon steel rust. Pitting and crevice corrosion measurements using smooth and screw specimen show that both the pitting potential and the crevice corrosion sensitive range shift to lower potentials with the increase of chloride ion concentration in the rust. The pitting potential and the crevice corrosion sensitive range under the coverage of carbon steel rust are also lower than that under the coverage of seawater film.

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**Keywords:** carbon steel rust, austenitic stainless steel, marine atmosphere, pitting corrosion, crevice corrosion

### 1. INTRODUCTION

Stainless steel fasteners can fail as a result of stress corrosion cracking (SCC) in coastal atmosphere [1, 2]. The occurrence of SCC was the result of an electrolyte film formation on the surface of stainless steel, which was of very high concentration of chloride and low pH [1-7]. Recent studies on pitting corrosion of stainless steels in marine atmosphere or under droplets [8-11] help the explanation of SCC occurrences, because the pits are possibly the initiation sites of SCC. But the effect of carbon steel rust was rarely mentioned.

The development of SCC is a complex process. Pitting and crevice corrosion may facilitate the initiation of SCC especially during the early stages of electrolyte film formation. Earlier study

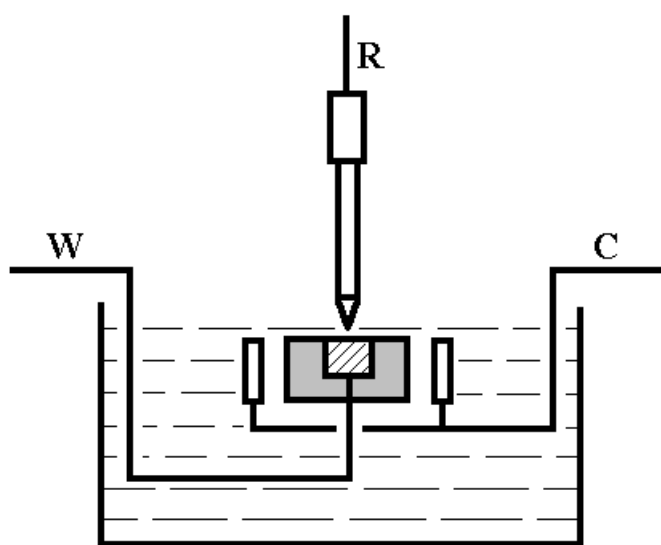
confirmed that alien substances facilitate the formation of corrosive electrolyte film [12]. Carbon steel rust is readily available alien substance near stainless steel fasteners. It can not only facilitate the formation of corrosive electrolyte film but also the corrosiveness of it. Based on these considerations, the pitting and crevice corrosion behavior of an austenitic stainless steel was studied when its surface was contaminated by carbon steel rust. These studies help to explain the SCC of stainless steel fasteners in practical marine atmosphere by confirming the readiness of pitting or crevice corrosion occurring.

## 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. Two types of samples were used. One was a short rod with the end as working surface. Another one was screw sample with inner screw in outer screw. The cross section was the working surface. Both of these samples were grinded to 600# before experiments.

5 kinds of corrosion media were used to simulate the surface film formed on samples. They were natural seawater from Qingdao bay,  $\text{Fe}_2\text{O}_3$  paste wetted by distilled water,  $\text{Fe}_2\text{O}_3$  paste wetted by 1%NaCl, 2%NaCl and 3.5%NaCl solution respectively.

Figure1 shows the electrochemical cell setup. The working electrode was vertically placed with its surface facing upwards and parallel with the surface of electrolyte. The thickness of the electrolyte above the working electrode was adjusted to be 0.5mm, which is reasonable considering the thickness of the electrolyte formed on the surface in real circumstances [12].



**Figure 1.** The electrochemical cell setup

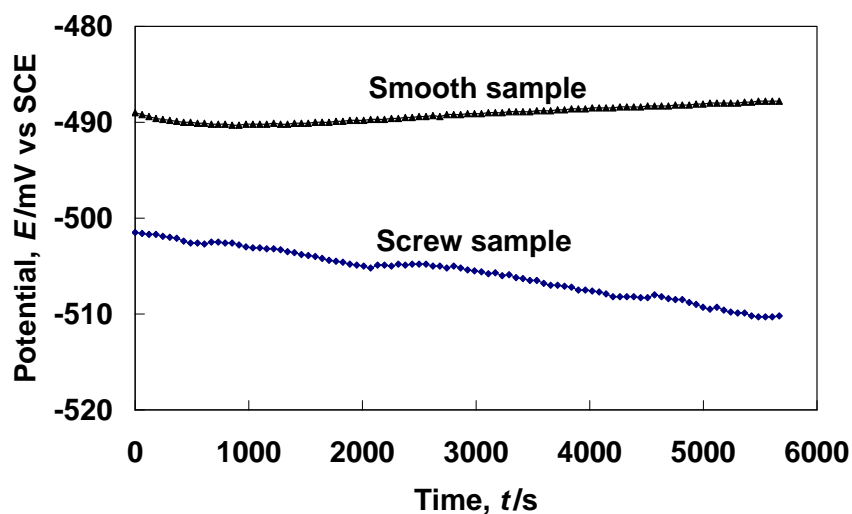
The pitting and crevice corrosion behavior of the samples were analyzed by potentiodynamic polarization measurements. The potential was scanned from free corrosion potential and swept back

while the anodic current reached  $0.5\text{mA}/\text{cm}^2$  at a scan rate of  $10\text{mV}/\text{min}$ . After the experiments, the appearance of the samples was observed. The corrosion potential evolution of the samples covered with seawater film was also observed. Saturated calomel electrode (SCE) was used as reference electrode and the potentials were reported vs. SCE.

### 3. RESULTS AND DISCUSSION

#### 3.1 Time dependence of free corrosion potential for smooth and screw samples covered with thin layer of seawater

Figure 2 shows the free corrosion potential change with time of smooth and screw samples covered with a thin layer of seawater. The free corrosion potential of the smooth sample was comparatively stable, while it decreased with time for the screw sample. These phenomena show that the occurrence of corrosion for screw sample is easier than smooth sample.



**Figure 2.** Time dependence of free corrosion potential of smooth and screw samples covered with thin layer of seawater

#### 3.2 Rust contamination on the electrochemical behavior of smooth and screw samples

Figure 3 shows the polarization curves of smooth samples covered with clean seawater film and thin layer of  $\text{Fe}_2\text{O}_3$  paste prepared with analytical reagent and distilled water. The passivation of the sample in seawater is not stable due to the abundance of  $\text{Cl}^-$ , the anodic current is high and it gradually increases with the increase of potential. If we arbitrarily define the potential on the polarization curve when the anodic current reaches  $0.1\text{mA}/\text{cm}^2$  as the pitting potential [13], then the pitting potential ( $E_p$ ) of the smooth sample under the coverage of  $\text{Fe}_2\text{O}_3$  paste is  $117\text{mV}$ , the  $E_p$  under the coverage of seawater is  $-127\text{mV}$ . Under the coverage of  $\text{Fe}_2\text{O}_3$  paste, the reverse scan still could not intersect with the forward scan curve even at the free corrosion potential. That means the

repassivation potential ( $E_r$ ) is below free corrosion potential (-70mV vs. SCE). Under the coverage of clean seawater, the reverse scan intersects with the forward scan at the potential of -40mV. This potential is higher than its  $E_p$  and hardly be regarded as  $E_r$ , the effect of carbon steel corrosion products on pitting corrosion is clearly shown. With the corrosion product, once the pitting corrosion is initiated, the pitting process is difficult to stop.

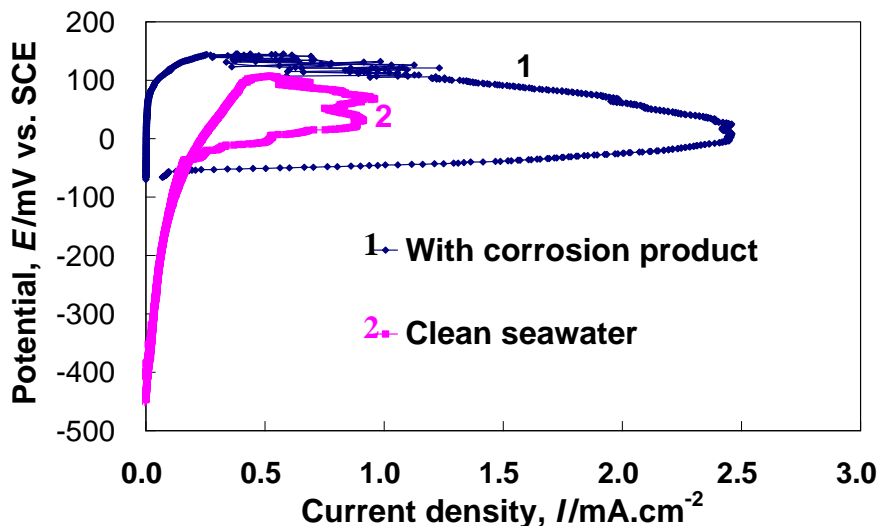


Figure 3. Effect of rust contamination on the electrochemical behavior of smooth sample

Figure 4 shows the polarization curves of screw samples covered with clean seawater film and thin layer of  $Fe_2O_3$  paste. The  $E_p$  under the coverage of seawater is -209mV, while under the coverage of  $Fe_2O_3$  paste is -465mV. The screw sample exhibits screw crevice, which is the weak point of the sample. The  $E_p$  under this circumstance represents the potential that the crevice corrosion initiates at. The promotion of rust on crevice corrosion was also observed.

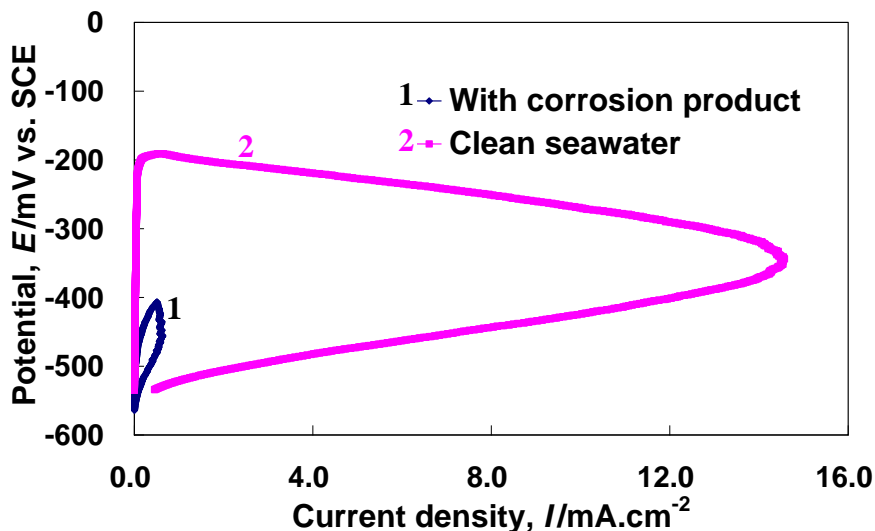


Figure 4. Effect of rust contamination on the electrochemical behavior of screw sample

The results of Dong et. al. [8] show that the pitting potential decreased as the exposure time extended, and were explained as being covered with a rust layer. The difference between current research and Dong et. al.'s is that the rust layer of current research is alien substance, while Dong et. al.'s is formed during corrosion. The acceleration of rust layer on pitting corrosion is confirmed by these researches. It is obvious from here that the adherence of alien rust on stainless steel facilitates the initiation of localized corrosion.

3.3 The effect of Cl<sup>-</sup> in the rust on the electrochemical behavior of smooth and screw samples

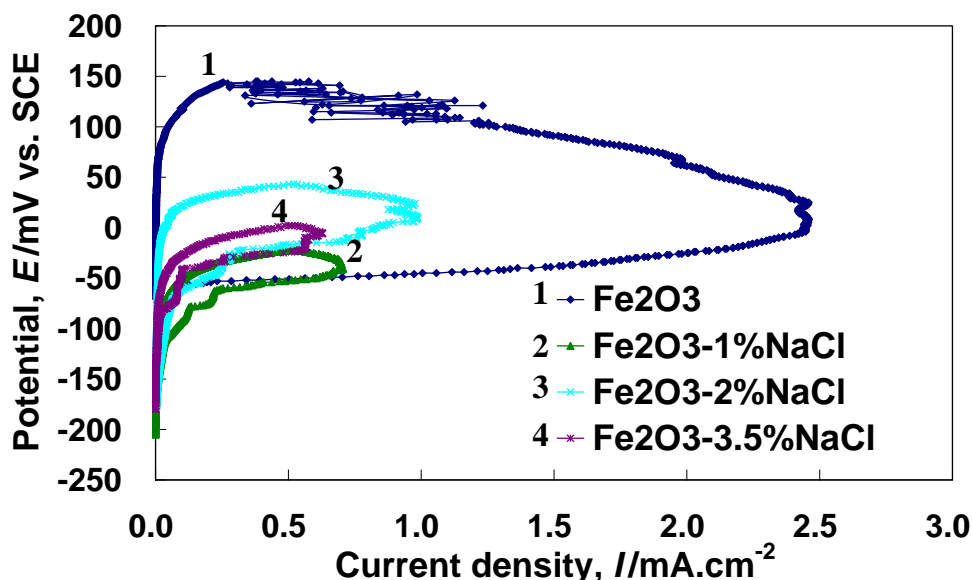


Figure 5. Effect of Cl<sup>-</sup> in the rust on the electrochemical behavior of smooth sample

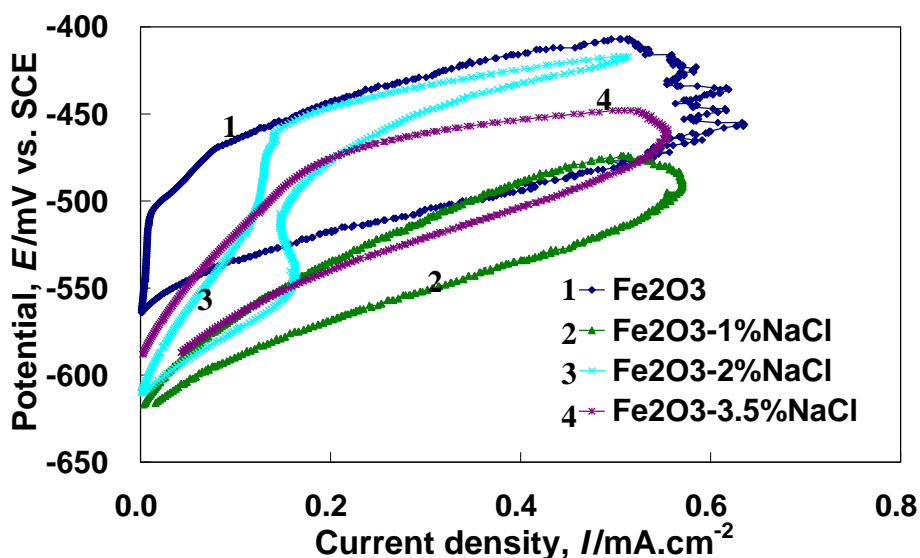


Figure 6. Effect of Cl<sup>-</sup> in the rust on the electrochemical behavior of screw sample

Figure 5 shows the effect of Cl<sup>-</sup> addition in Fe<sub>2</sub>O<sub>3</sub> paste on the polarization curves of smooth samples. Although the E<sub>p</sub> scatters with the change of Cl<sup>-</sup> concentration, its decrease with the addition of Cl<sup>-</sup> is clear. Figure 6 shows the effect of Cl<sup>-</sup> addition in Fe<sub>2</sub>O<sub>3</sub> paste on the polarization curves of screw samples. The addition of Cl<sup>-</sup> also decreases the E<sub>p</sub>.

3.4 The Comparison of Smooth and Screw Samples

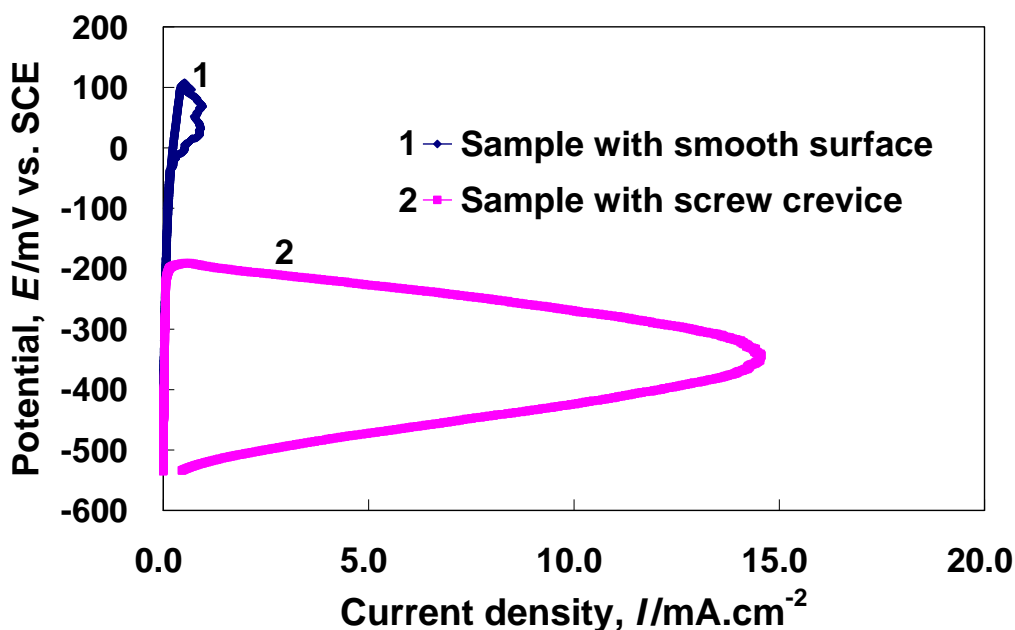


Figure 7. The comparison of the polarization curves of smooth and screw samples under the coverage of clean seawater

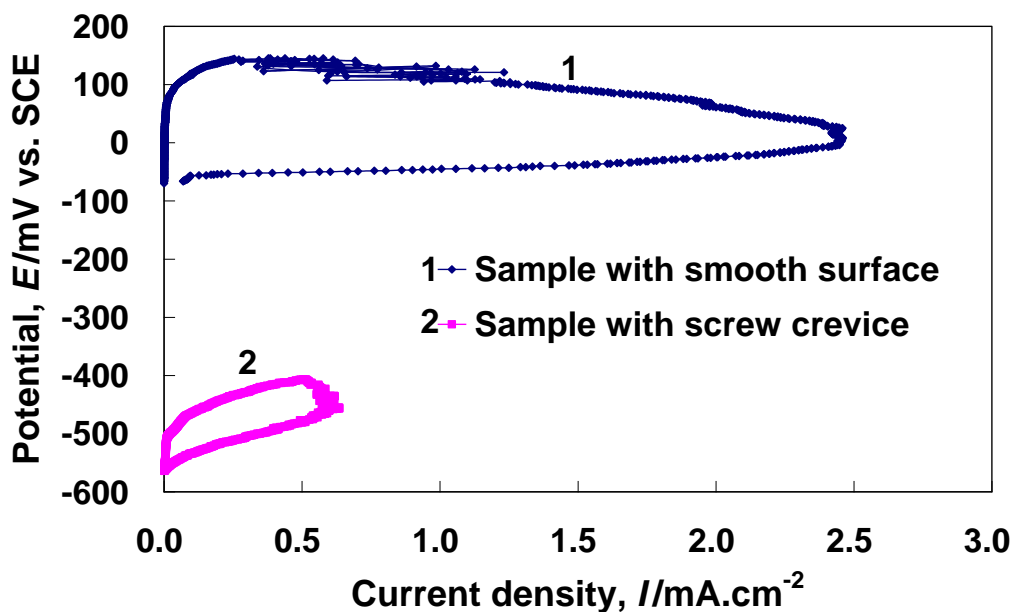
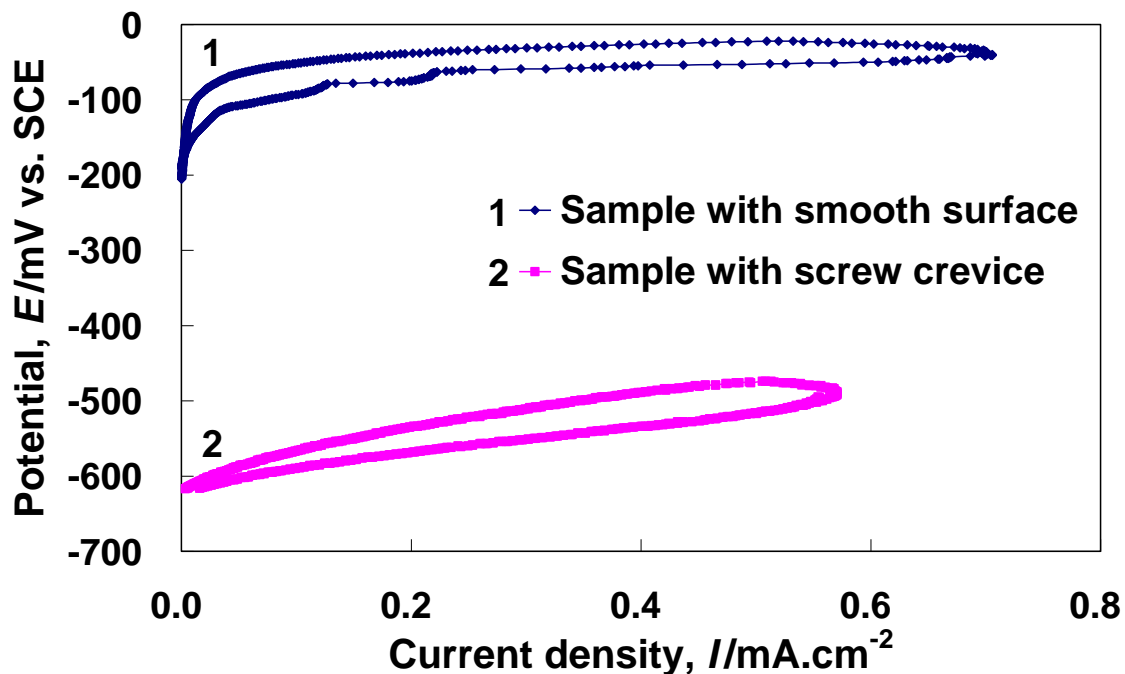


Figure 8. The comparison of the polarization curves of smooth and screw samples under the coverage of a layer of Fe<sub>2</sub>O<sub>3</sub> paste



**Figure 9.** The comparison of the polarization curves of smooth and screw samples under the coverage of a layer of  $\text{Fe}_2\text{O}_3$  paste with 1%NaCl

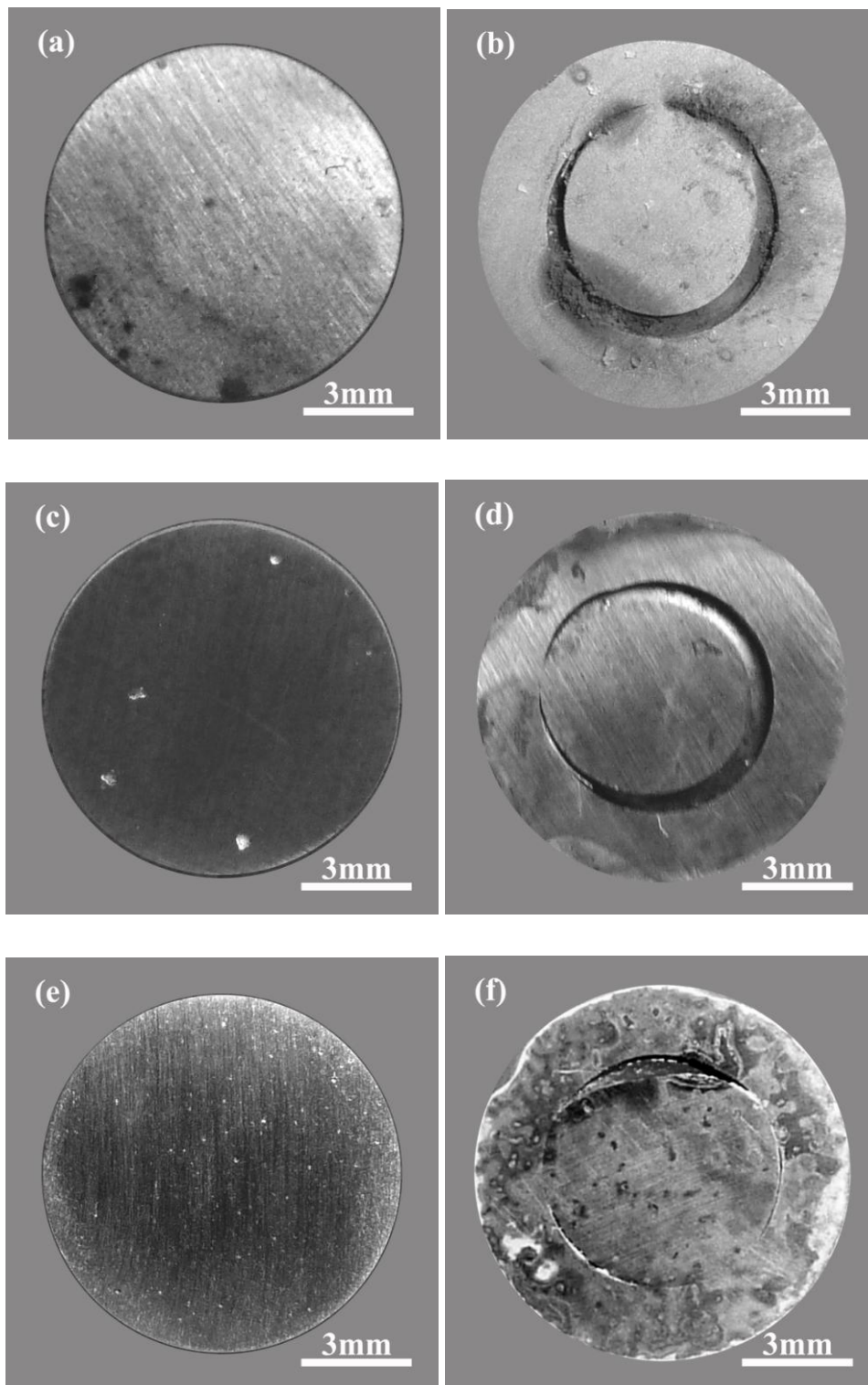
Figure 7 to Figure 9 show the comparison of the polarization curves of smooth and screw samples under various conditions. The  $E_p$  of screw samples was lower than that of smooth samples. These results show that the crevice corrosion occurs easier than pitting corrosion.

### 3.5 Appearance of samples after experiments

Figure 10 shows the appearance of the samples after polarization scans. For smooth samples, when the sample was covered with a layer of clean seawater, the corrosion on the surface was comparatively homogeneous with few shallow pits; when it was covered with a layer of  $\text{Fe}_2\text{O}_3$  paste, a few large pits appeared on the surface; when it was covered with a layer of  $\text{Fe}_2\text{O}_3$  paste containing 1%NaCl, a high density of small pits appeared on the surface. For screw samples, no or fewer pits were observed compared with the corresponding smooth samples. The polarization information of screw sample mainly reflects the corrosion of screw crevice.

### 3.6 The measurements of pH under various films of corrosive media

Table 1 shows the results of pH measurements beneath various films of corrosive media. It is clear that the interface between corrosive surface film and the sample was acidified.



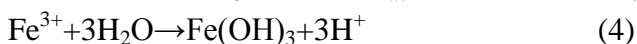
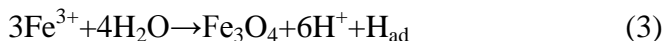
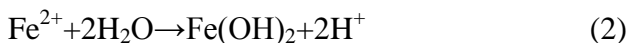
**Figure 10.** Appearance of samples after polarization scans (a) Smooth sample covered with clean seawater film (b) Screw sample covered with clean seawater film (c) Smooth sample covered with a layer of  $\text{Fe}_2\text{O}_3$  paste (d) Screw sample covered with a layer of  $\text{Fe}_2\text{O}_3$  paste (e) Smooth sample covered with a layer of  $\text{Fe}_2\text{O}_3$  paste containing 1%NaCl (f) Screw sample covered with a layer of  $\text{Fe}_2\text{O}_3$  paste containing 1%NaCl



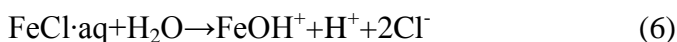
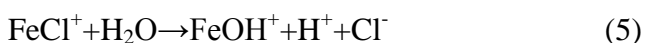
**Table 1.** Measurements of pH under various films of corrosive media

Fe <sub>2</sub> O <sub>3</sub> paste prepared with distilled water	Fe <sub>2</sub> O <sub>3</sub> paste prepared with 1% NaCl solution	Fe <sub>2</sub> O <sub>3</sub> paste prepared with 2% NaCl solution	Fe <sub>2</sub> O <sub>3</sub> paste prepared with 3.5% NaCl solution
2.58	2.65	2.73	2.78

The following reactions can result in the acidification,



When the corrosive surface film contains Cl<sup>-</sup>,



From above studies, it is known that the occurrence of crevice corrosion is easier than pitting corrosion. The corrosion of screw sample follows the mechanism of crevice corrosion. The solution in the screw crevice can be further acidified. The crevice solution contains strong oxidant Fe<sup>3+</sup> and passive film destructive ion Cl<sup>-</sup>. The characteristic of high acidity together with the high chloride content makes the stainless steel screw sensitive to SCC [14,15].

#### 4. CONCLUSIONS

The hydrolysis of carbon steel corrosion products attached to stainless steel decreases the pH of corrosive solution film formed on the surface. The Fe<sup>3+</sup>, Cl<sup>-</sup> in the film and the pH decrease lowers the stability of the passive film, making the initiation of localized corrosion easier. The occurrence of crevice corrosion is easier than pitting corrosion. The acidified crevice solution with high concentration of Fe<sup>3+</sup> and Cl<sup>-</sup> is the cause of SCC of stainless steel in marine atmosphere.

#### ACKNOWLEDGEMENTS

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