

Short Communication

Corrosion Behavior of D32 Rust Steel in Seawater

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Rust layers were formed on D32 steel in seawater for 30 days, 90 days and 180 days respectively, and the micrographs and element compositions of the rust were investigated using SEM and XRD. The electrochemical corrosion behavior of the D32 steel with rust layer was investigated with polarization curves and electrochemical impedance spectroscopy. The inner rust layer was bent flaky and composed of Fe₃C mainly. The outer layer was large flaky with cracks and composed of γ -FeOOH mainly. With the metal dissolution, Fe₃C left on the metal forming the inner rust layer. With the presence of Fe₃C, the rust was unable to form a protective layer, resulting in the increased corrosion rate in half a year.

Keywords: marine corrosion; rust; steel

1. INTRODUCTION

With the development and utilization of ocean resources, port, bridge, offshore oil platforms, dolphin and other marine structures are constructed, a large number of metal materials is put to use in marine environment. The offshore environment is one of the most corrosive natural occurring environments. Corrosion of steel structures in marine environment is a problem that has to be considered during both design and maintenance[1-6]. Due to the complexity of the marine environment, iron and steel structures exposed to marine environment will suffer from serious corrosion[7-16], and many kinds of corrosion would happen, including the simple electrochemical corrosion, stress corrosion, microbiologically influenced corrosion, et al.

Although much work has been done by several researchers in the past for many decades, it is still a subject of great interest owing to the complexity of the medium and the behavior of metals under varying conditions of the environment. The D32 steel shows good mechanical properties and corrosion

resistance which is commonly used for offshore oil platform in China. However, literature revealed that investigations have not been made so far about the use of D32 steel for offshore oil platform when exposed in marine environment. To ensure the safety of marine steel structure, it is important to study the corrosion behavior of D32 steel in seawater. The corrosion behavior of D32 steel was studied using polarization curves and electrochemical impedance spectroscopy (EIS) while the rusts of the steel samples were characterized using scanning electron microscopy (SEM) and X-ray diffraction (XRD).

2. EXPERIMENTAL

2.1 Specimens

The material used is D32 steel with chemical compositions (in wt-%) of 0.14C, 0.36Si, 1.38Mn, 0.018P, 0.013S, 0.01Cr, 0.01Mo, 0.02Ni, 0.033Al, 0.03Cu, 0.001V, 0.018Ti and balance Fe. The materials were cut into 0.7854 cm² sizes and 4.0 cm² sizes for rusts characterization. The specimens were wet ground to the 1200 grit and then cleaned with distilled water, ethanol and acetone[17]. These specimens were all immersed into Qingdao seawater. Specimens were removed after 30 days, 90 days and 180 days respectively. Then the samples were used for both the electrochemical tests and characterization.

2.2 Characterization

The morphologies of outer and inner rust layers were characterized using SEM (Philips XL-30)[18]. The rusts of the steel samples were characterized by XRD (Rigaku D/max2500PC). The XRD conditions were 6kW intensity, and 2 θ was from 5° to 70° using a Cu target[19]. The inner rust was obtained with the outer rust layer mechanically scrapped.

2.3 Electrochemical testing

The electrochemical experiments were performed using 2273 Potentiostat and performed in a cell containing three electrodes. The working electrode was the rusted steel. The reference electrode was a saturated calomel electrode, and the auxiliary electrode was a platinum sheet. And also Qingdao seawater was used as electrolyte. Electrochemical impedance spectroscopy measurement was performed in the frequency range of 100 kHz to 10 mHz, with applied 10 mV sinusoidal potential around the open circuit potential[20]. The polarization curves were obtained from OCP -200 to +200mV, the scan rate was 0.5 mV/s[10].

3. RESULTS AND DISCUSSION

3.1 Electrochemical behaviour

Figure 1 shows the polarization curves of D32 rust steels in seawater. The fitting results are shown in Table 1.

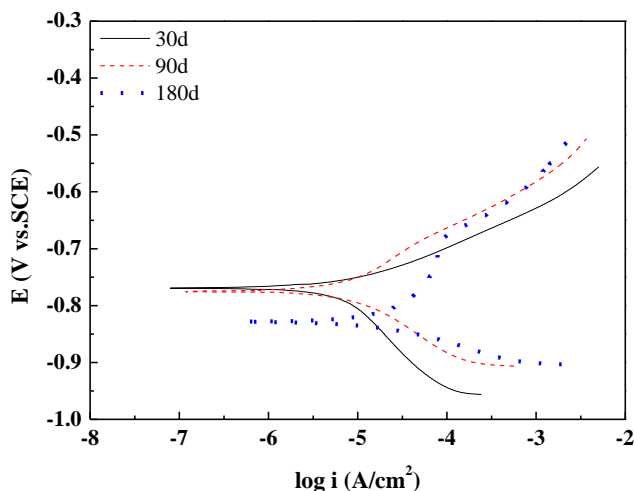


Figure 1. Polarization curves of rust steels

Table 1. Fitting parameters of polarization curves

	E_{corr} (mV)	I_{corr} ($\mu A/cm^2$)	β_c (mV)	β_a (mV)
30 day	-772.1	7.66	182.31	65.05
90 day	-786.9	17.80	130.82	266.78
180 day	-828.5	29.93	57.71	399.49

From the polarization curves, the corrosion current density of D32 rust steels in seawater increased with time. As the immersion time was not enough, there was no perfect protect rust layer formed on the metal, the corrosion rate kept increasing in 180 days. The cathodic Tafel parameters (β_c) decreased with time in 180 days while the anodic Tafel parameters (β_a) increased. It means that corrosion of the rust steel was controlled by anodic reaction gradually with time.

With immersion time longer, more rusts were formed, and the iron ions could not left the metal so easily, so the corrosion was controlled by anodic reaction gradually with time.

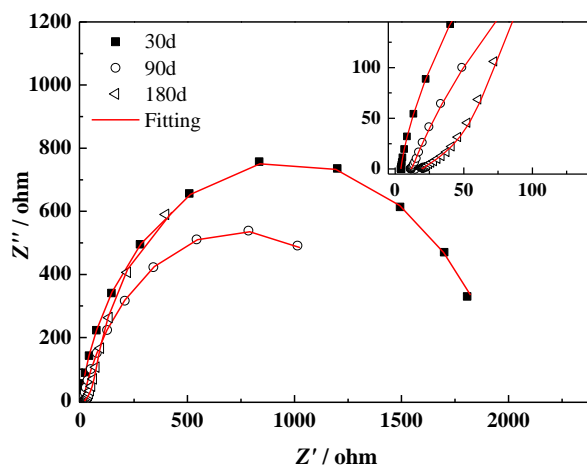


Figure 2. EIS of D32 rust steels in seawater

Table 2. EIS fitting parameters of rust steels

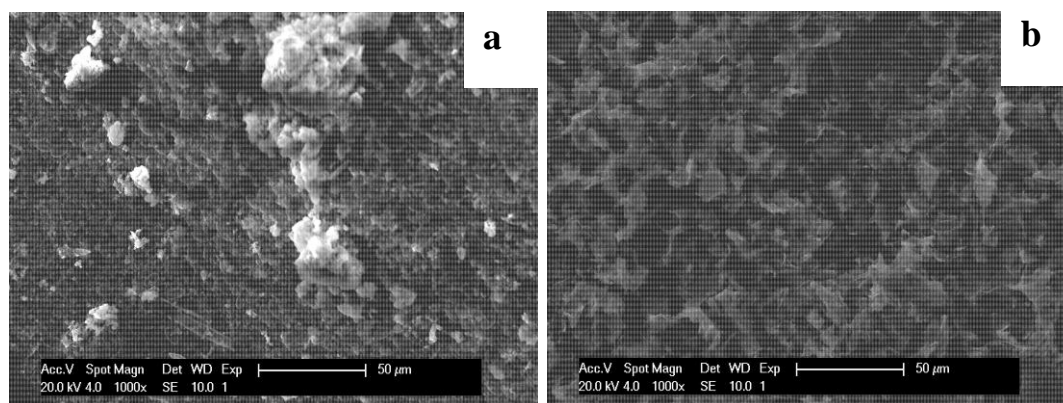
	C_{in} ($F \cdot cm^{-2}$)	R_{in} ($ohm \cdot cm^2$)	Q		R_{ct} ($ohm \cdot cm^2$)	W ($S \cdot cm^{-2} \cdot s^{-5}$)	C_{out} ($F \cdot cm^{-2}$)	R_{out} ($ohm \cdot cm^2$)
			Y_0 ($S \cdot cm^{-2} \cdot s^{-n}$)	n				
30 day	4.73×10^{-4}	4.33	5.31×10^{-4}	0.6979	2008	1.82×10^{10}	3.10×10^{-14}	4.20
90 day	6.69×10^{-4}	2.65	3.07×10^{-3}	0.775	1432	0.07026	6.10×10^{-15}	11.66
180 day	9.36×10^{-4}	16.36	1.15	0.8001	1257	2.05×10^{-3}	1.55×10^{-15}	20.02

Figure 2 shows the EIS and the fitting curves of D32 rust steels in seawater and the fitting parameters are listed in Table 2. The rust was composed of outer and inner rust layers and the equivalent circuit used was $R_s(C_{out}R_{out})(C_{in}(R_{in}(Q(R_{ct}Z_W))))$. R_s is the resistance of seawater, R_{out} , C_{out} and R_{in} , C_{in} are the resistance and capacitance of outer and inner rust layer, Q is CPE parameter, R_{ct} is charge transfer resistance, Z_W is Warburg diffusion impedance. If the rust layer grows uniformly, the resistance increases and capacitance decreases, in proportion to the increase in thickness[21].

From Table 2, the capacitance of the outer layer of D32 rust steel decreased and the resistance increased in 180 days, it means the thickness of the outer layer increased with time in 180 days. The change of the inner layer showed different behavior, the capacitance increased while the resistance decreased at first and then increased, this means the inner rust was complex in both composition and morphology.

3.2 Characterization

Figure 3 and Figure 4 show the morphology and XRD analysis of rust steels in seawater.



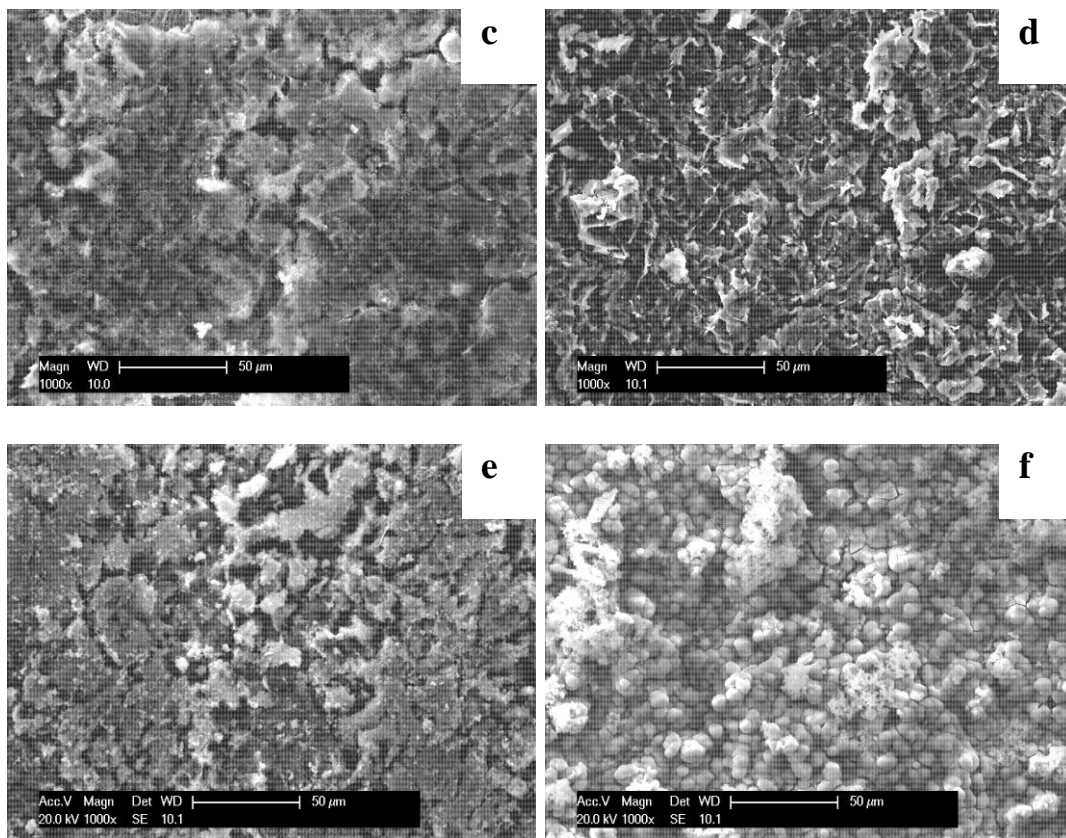
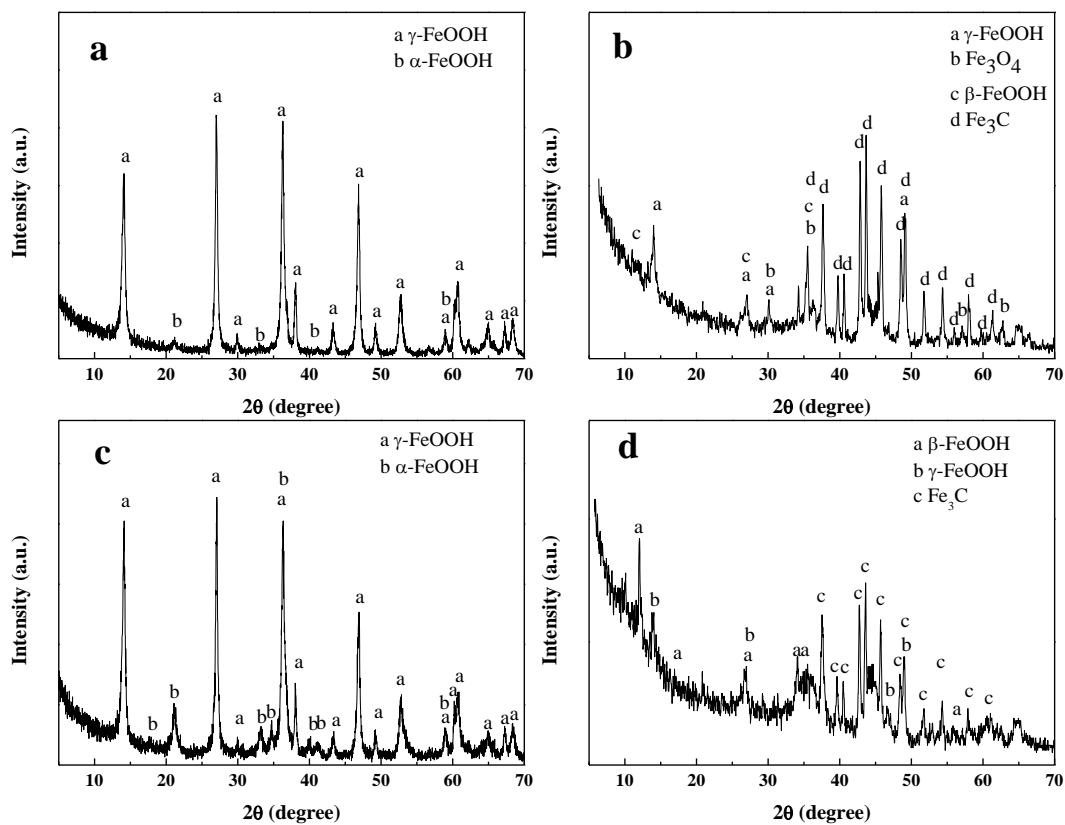


Figure 3. Morphologies of (a) outer layer and (b) inner layer in 30 days, (c) outer layer and (d) inner layer in 90 days, (e) outer layer and (f) inner layer in 180 days of rust steels



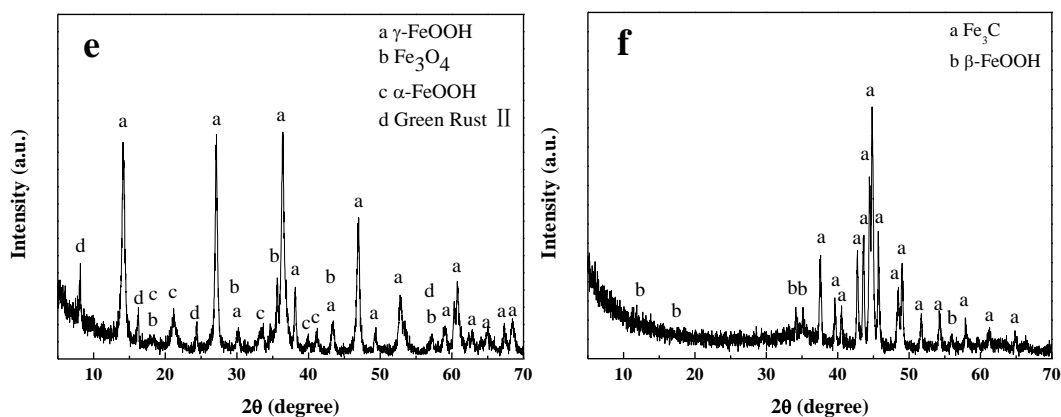


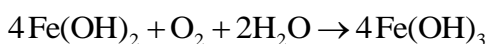
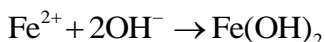
Figure 4. XRD analysis of (a) outer layer and (b) inner layer in 30 days, (c) outer layer and (d) inner layer in 90 days, (e) outer layer and (f) inner layer in 180 days of rust steels

From Figure 3 and Figure 4, the outer rust in 30 days was flaky, and cluster distribution in some local part. The main composition was γ -FeOOH and with a small amount of α -FeOOH. The flaky rust was γ -FeOOH. The inner rust layer was bent flaky and evenly distribute relatively, the main ingredient was Fe_3C with a small amount of Fe_3O_4 , γ -FeOOH and β -FeOOH. The outer rust in 90 days was large flaky with many cracks. The composition was same as that in 30 days. The inner rust layer was still bent flaky, but it was bigger than in 30 days. It was composed of Fe_3C and a small amount of γ -FeOOH and β -FeOOH. The outer rust in 180 days was large flaky with more cracks. The rust composed of Fe_3O_4 and a little of Fe_3O_4 , α -FeOOH and Green rust II were detected. The inner rust was stalactite-like and composed of Fe_3C and a small amount of β -FeOOH.

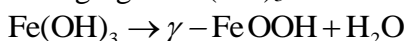
3.3 Discussion

The thickness of the rust layer increased with immersion time in seawater. The inner rust layer was bent flaky, it was composed of Fe_3C and a small amount of β -FeOOH mainly. The outer layer was large flaky with cracks, which was composed of γ -FeOOH and some α -FeOOH, Fe_3O_4 . Large amount of Fe_3C was detected in inner rust, which was less reported in seawater corrosion. Fe_3C is formed at high temperatures, so it was not corrosion rusts in a marine environment, which is originally present in the steel material. As the main carbon form in the steel, Fe_3C was cathode and iron was anode.

The cathodic reaction was oxygen reduction and the anodic reaction was iron dissolution. Fe^{2+} ions and OH^- ions were combined to iron(II) hydroxide, and it was oxidized by air[22-24].



The aging of $\text{Fe}(\text{OH})_3$ leads to dehydration in the presence of water and formed γ -FeOOH[22].



With the metal dissolution, Fe₃C did not corrode and left on the metal forming the inner rust layer. With the presence of Fe₃C, the rust was unable to form a protective layer, resulting in the increased corrosion rate in half a year.

β-FeOOH is a typical rust in Cl⁻ contained environment and no use in protecting the metal. In addition, the γ-FeOOH in outer rust layer was partially transformed to α-FeOOH with time.

4. CONCLUSIONS

(1) The inner rust layer was bent flaky and composed of Fe₃C mainly. The outer layer was large flaky with cracks and composed of γ-FeOOH mainly.

(2) The thickness of the outer layer increased with time while the inner rust was complex in both composition and morphology in 180 days.

(3) Large amount of Fe₃C was detected in inner rust and acted as cathode. With the metal dissolution, Fe₃C left on the metal forming the inner rust layer. With the presence of Fe₃C, the rust was unable to form a protective layer, resulting in the increased corrosion rate in half a year.

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