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Short Communication

Corrosion Behavior of 16Mn Steel under Wet and Dry Cycles

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Compared with immersion samples, the corrosion process of 16Mn steel under wet-dry cyclic condition was studied with polarization curves. The corrosion microstructure and rusts were characterized by Scanning Electron Microscope and X-ray diffraction. The corrosion rate of the wet-dry sample was about 5 times of the immersion sample. The immersion sample was composed of loose, porous γ-FeOOH mainly while the wet-dry sample was composed of fragmented flaky and cracked γ-FeOOH and Fe_3O_4 mainly. The reason, why the wet-dry samples suffered from serious corrosion, was the alternation of wetting and drying. During the drying process, the electrolyte thickness decreased. Oxygen would be much easier to diffuse into the interface of electrolyte and metal, which improved the cathodic reduction process. Except for this, the rust, Fe_3O_4 and γ–FeOOH, took part in the corrosion processes and hence increased the corrosion rate of the wet-dry sample. This is a self-circulation process of chemical oxidation and electrochemical reduction.

Keywords: wet-dry cyclic; immersion; corrosion; 16Mn steel; seawater

1. INTRODUCTION

With the utilization of ocean resources, a large number of metal materials are put to use in marine environment. The offshore environment is one of the most corrosive natural occurring environments, and the splash zone is the most corrosive area [1-13]. The materials exposed in this area would suffer from serious corrosion, and the higher frequency of alternation of wetting was one of the key factors induced serious corrosion in splash zone [14-18]. The corrosion in splash zone of Chengdao sea water is pitting corrosion mainly [19]. Huang and Zhu [20-21] investigated corrosive behaviors of 27 kinds of metals in splash zone of Qingdao sea water in 8 years, the carbon steel and low alloy steel corroded most seriously.

16Mn steel, a high strength low alloy structural steel, is used in marine environment widely. 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. However, literature revealed that investigations have not been made so far about the use of 16Mn steel when exposed in marine environment. To ensure the safety of marine steel structure, it is important to study the corrosion behavior of 16Mn steel in seawater. The corrosion behavior of 16Mn steel under wet-dry cyclic condition was studied using polarization curves 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 16Mn steel, a high strength low alloy structural steel, with chemical compositions (in wt-%) of 0.16C, 0.40Si, 1.45Mn, 0.029P, 0.025S, <0.001Cr, <0.005Cu and balance Fe. The materials were cut into 0.7854 cm^2 sizes. The specimens were wet ground to the 1200 grit and then cleaned with distilled water, ethanol and acetone. Put a drop of solution onto the specimen every 12 hours and dried in room temperature, it last for 10 days to simulate alternating dry and wet process. The immersion samples were used for comparison, they were obtained by immersed the specimen in solution for 10 days. Then the rust samples were used for both electrochemical tests and characterization. Two different solutions, seawater collected from Qingdao and Chengdao area in China, were used respectively. The seawater quality was tested with YSI 6600 Water Quality Sonde made of YSI Incorporated and listed in Table 1.

Table 1. Parameters of seawater quality

Solution	Specific Conductance (mS/cm)	Salinity (%)	DO conc (mg/L)	pH	ORP (mV)
Qingdao seawater	49.99	32.79	7.46	8.33	-32.8
Chengdao seawater	49.11	32.17	7.30	8.35	-30.4

2.2 Characterization

The morphologies of the samples were characterized using SEM (Philips XL-30) and the rusts were characterized by XRD (Rigaku D/max2500PC) [22-24]. The XRD conditions were 6kW intensity, and 2ϴ was from 5° to 70° using a Cu target.

2.3 Electrochemical testing

The electrochemical tests were performed using 2273 Potentiostat and performed in a cell containing three electrodes. The working electrodes were the polished steel, the immersion sample and the wet-dry sample respectively, the counter electrode was Pt electrode, and the reference electrode employed was saturated calomel electrode, Qingdao and Chengdao seawater were used as electrolyte respectively. The scan range were -400~400mV (vs. open potential) and -100~100mV (vs. open potential) separately for the strong and weak polarization, and the scan rates were 1.0 mV/s and 0.5 mV/s respectively.

3. RESULTS AND DISCUSSION

3.1 Characterization

Figure 1 and Figure 2 show the morphology and XRD analysis of the immersion sample and wet-dry sample.

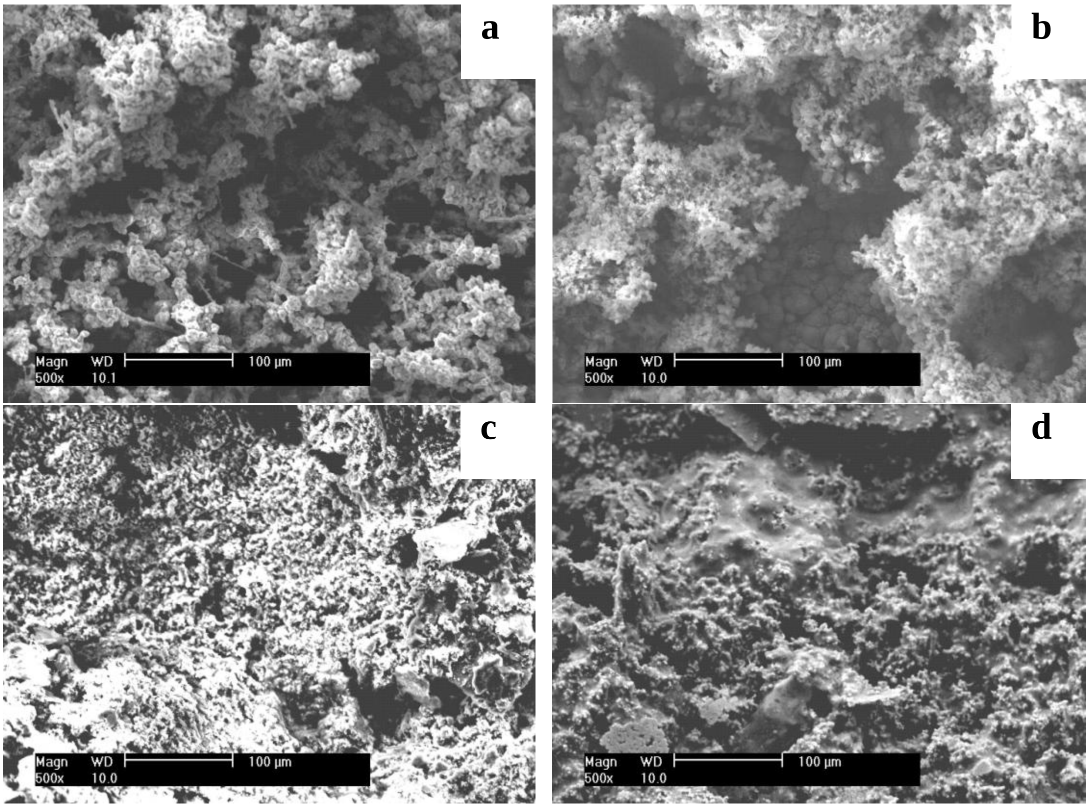

Figure 1. Morphologies of (a) immersion rust steel in Qingdao seawater and (b) Chengdao seawater and (c) wet-dry rust steel in Qingdao seawater and (d) Chengdao seawater

The rust of immersion samples was generally loose, porous, cluster structure showed and partly branched. It was composed of γ-FeOOH mainly and a small amount of Fe_3O_4, α-FeOOH and Green rust I. FeOCl was detected in immersion sample of Qingdao seawater. The rust of wet-dry samples was significantly different from that of the immersion samples, it has a complex morphology. It was fragmented massive, flaky, porous and cracked. The rust was composed of γ-FeOOH and Fe_3O_4 with a small amount of $FeCl_3 \cdot 6H_2O$. β-FeOOH and α-FeOOH were detected in the wet-dry sample of Qingdao seawater, while Green rust I was detected in the wet-dry sample of Chengdao seawater.

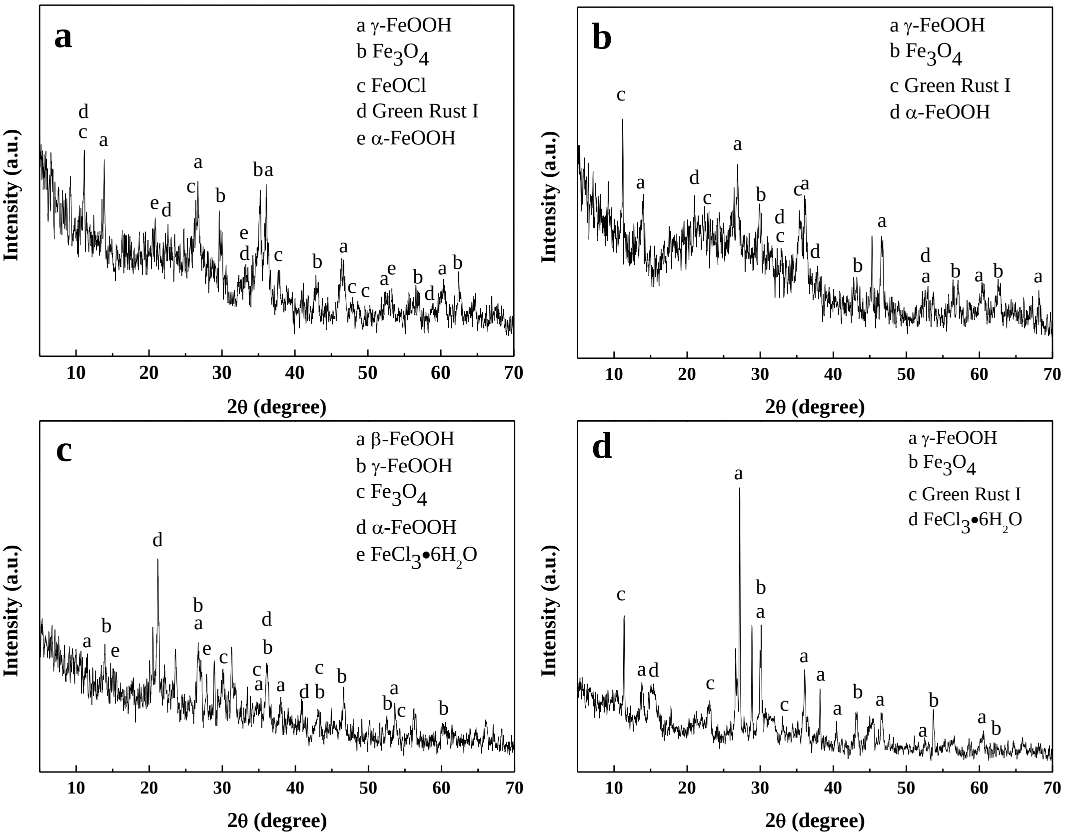

Figure 2. XRD analysis of (a) immersion rust steel in Qingdao seawater and (b) Chengdao seawater and (c) wet-dry rust steel in Qingdao seawater and (d) Chengdao seawater

3.2 Electrochemical behaviour

The open circuit potential were measured before electrochemical tests and shown in Table 2. There is no much difference of the samples between the two kinds of seawater. Compare with the steel, the OCP of immersion samples shifted negatively while the wet-dry samples shifted positively slightly.

Figure 3 and Figure 4 show the strong and weak polarization curves of the polished steel, the immersion samples and the wet-dry samples. The corrosion current density of the samples obtained from the weak polarization curves are shown in Table 2.

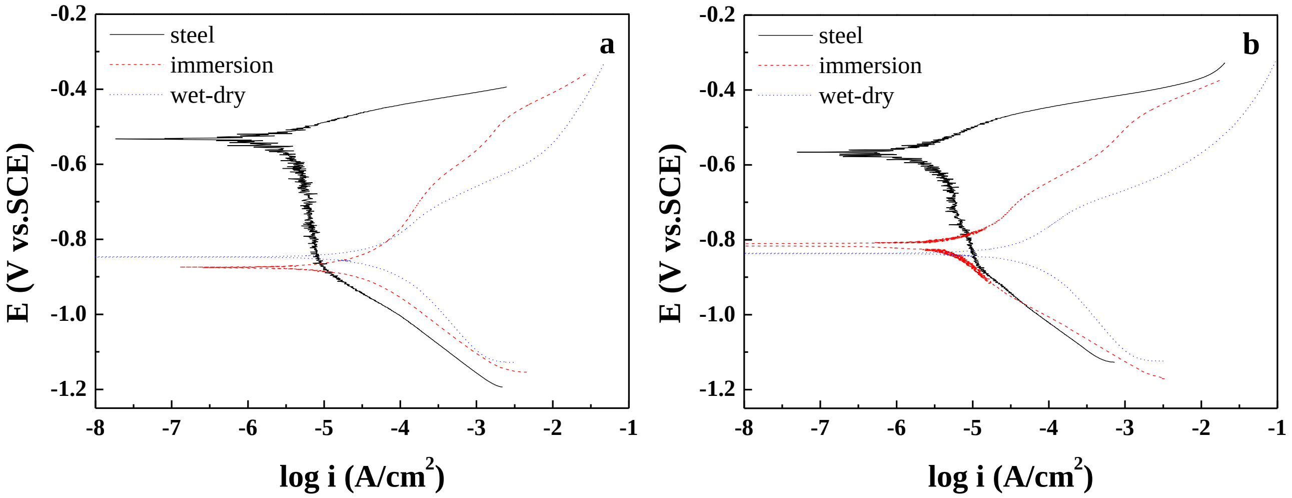

Figure 3. Strong polarization curves of the samples in (a) Qingdao and (b) Chengdao seawater

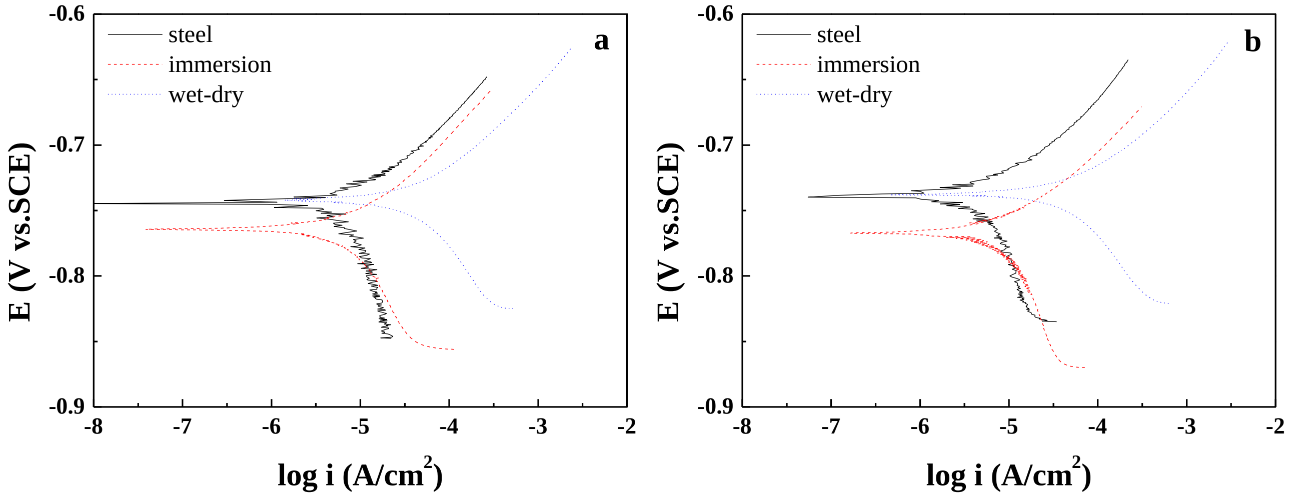

Figure 4. Weak polarization curves of the samples in (a) Qingdao and (b) Chengdao seawater

Table 2. OCP (V vs. SCE) and corrosion current density (μA/cm^2) of different samples

Samples		Steel	Immersion sample	Wet-dry sample
Qingdao seawater	OCP	-0.748	-0.755	-0.724
	corrosion current density	5.315	12.31	57.68
Chengdao seawater	OCP	-0.734	-0.770	-0.720
	corrosion current density	4.647	13.36	69.52

As shown in Figure 3, the cathodic processes of the 16Mn steel in Qingdao and Chengdao seawater were limiting diffusion controlled of dissolved oxygen. The metal was electrochemical dissolved and controlled by charge transfer step when anodic polarized. The anode current grew rapidly as the high conductivity in Qingdao and Chengdao seawater. The cathodic process of the wet-dry sample was likely to be controlled not by the oxygen reduction, but rather by the reduction of corrosion products.

As corrosion rate is proportional to corrosion current density, according to the corrosion current density in Table 2, there was no much difference of the corrosion rate of the immersion sample in Qingdao and Chengdao seawater. The corrosion rate of wet-dry sample in Chengdao seawater was bigger than in Qingdao seawater. The corrosion rate of the immersion sample was bigger than the steel in seawater, and that of the wet-dry sample was bigger than the immersion sample.

3.3 Discussion

The corrosion rate of the wet-dry sample was about 5 times of the immersion sample in both Qingdao and Chengdao seawater. The reason, why the wet-dry samples suffered from serious corrosion, was the alternation of wetting and drying. During the drying process, the electrolyte thickness decreased and chloride concentration increased. Oxygen would be much easier to diffuse into the interface of electrolyte and metal, which improved the cathodic reduction process. Except for this, the rust itself took part in the corrosion processes and hence increased the corrosion rate of the steel samples. The immersion sample was composed of loose, porous γ-FeOOH mainly while the wet-dry sample was composed of fragmented flaky and cracked γ-FeOOH and Fe_3O_4 mainly. Compared with the immersion sample, there was more Fe_3O_4 detected in the wet-dry sample.

During the wet period at beginning, the anodic and cathodic reactions occur.

Anodic: $\mathrm{Fe} \rightarrow \mathrm{Fe}^{2+} + 2\,\mathrm{e}$

Cathodic: $\mathrm{O_2} + 4\mathrm{e} + 2\,\mathrm{H_2O} \rightarrow 4\,\mathrm{OH}^-$

And then the following reaction happens,

$$\mathrm{Fe}^{2+} + 2\,\mathrm{OH}^- \rightarrow \mathrm{Fe(OH)_2}$$

Because of the abundant oxygen and chloride, $Fe(OH)_2$ changed to Green rust I， which was detected in 30 days, and then oxide to Fe_3O_4 [25].

$$6\,\mathrm{Fe(OH)_2} + \mathrm{O_2} \rightarrow 2\,\mathrm{Fe_3O_4} + 6\,\mathrm{H_2O}$$

As the water dried, Fe_3O_4 oxide to γ-FeOOH,

$$\mathrm{Fe_3O_4} + \frac{1}{4}\mathrm{O_2} + \frac{3}{2}\mathrm{H_2O} \rightarrow 3\gamma\text{-FeOOH}$$

During the next wet period, Fe^{2+} left the metal and swam to the rust layer interface through the rust crevice and reacted with γ-FeOOH.

$$8\gamma\text{-FeOOH} + \mathrm{Fe}^{2+} + 2\mathrm{e} \rightarrow 3\,\mathrm{Fe_3O_4} + 4\,\mathrm{H_2O}$$

As the water dried, Fe_3O_4 oxide to γ-FeOOH again. The overall reaction was

$$\mathrm{Fe} + 8\gamma\text{-FeOOH} + 3\,\mathrm{Fe_3O_4} + \frac{3}{4}\mathrm{O_2} + \frac{1}{2}\mathrm{H_2O} \rightarrow 9\gamma\text{-FeOOH} + 3\,\mathrm{Fe_3O_4}$$

That is, after each wet-dry cycle, every 8 mol γ-FeOOH involved in the reaction and 9 mol γ-FeOOH obtained, 1 mol γ-FeOOH net increased. This is a self-circulation process of chemical oxidation and electrochemical reduction, Fe_3O_4 and γ-FeOOH acted as catalysts. The rust itself took part in the corrosion processes and hence increased the corrosion rate of the wet-dry sample [26].

4. CONCLUSIONS

(1) The immersion sample was composed of loose, porous γ-FeOOH mainly while the wet-dry sample was composed of fragmented flaky and cracked γ-FeOOH and Fe_3O_4 mainly.

(2) The corrosion rate of the wet-dry sample was about 5 times of the immersion sample in both Qingdao and Chengdao seawater.

(3) The rust, Fe_3O_4 and γ-FeOOH, took part in the corrosion processes and hence increased the corrosion rate of the wet-dry sample. This is a self-circulation process of chemical oxidation and electrochemical reduction.

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