

Corrosion Behaviour of DH36 Steel Used for Oil Platform in Splash Zones

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The splash zone is the most corrosive area of the marine environment, and the corrosion of steel structures exposed in this area is a serious concern. DH36 steel is one of most commonly used steels for offshore oil platforms in China, and its corrosion behaviour in splash zones was studied in this paper. Polarization curves were obtained from the corroded steel exposed in this area while the morphologies and rusts of the rust steel were characterized using scanning electron microscopy and X-ray diffraction. Double rust layers were formed in the splash zone. The inner layer contained magnetite and fine flaky lepidocrocite, and the outer layer was composed of accumulated flaky lepidocrocite and a small amount of goethite. In the wet period, the iron dissolved and reacted with lepidocrocite, and magnetite appeared, while the magnetite was oxidized to lepidocrocite again during the dry period. Electrochemical reduction and chemical oxidation cycled in intermittent wetting and drying periods, and magnetite and lepidocrocite were involved in the reduction reaction, leading to serious corrosion.

Keywords : *steel, corrosion, rust, splash zone*

1. Introduction

The marine is one of the most corrosive natural environments. Corrosion of steels in this environment is a problem that has to be considered during both design and maintenance¹⁻³. The splash zone is the most corrosive area of the marine environment due to high alternation frequency of wetting and drying, large salt deposition, abundant oxygen supply, etc. Intermittent wetting and drying causes serious corrosion. The influence of tide and splash seawater will ensure an ample oxygen and also removal of rusts⁴. The rust layer formed is usually porous and with poor adherence⁵. Therefore, the general corrosion rate in this zone will be higher than on the submerged part of the structure^{6,7}. The steels exposed in this area would seriously corrode^{3,8}.

The DH36 steel is commonly used for offshore platform in China. However, the data available for DH36 steel exposed in marine splash zone is limited. To alleviate the risk of failure from corrosion, it is important to study the corrosion behavior of DH36 steel in splash zone. The corrosion behavior of DH36 steel in splash zone was studied

using polarization curves while the corrosion rusts were characterized using scanning electron microscopy (SEM) and X-ray diffraction (XRD).

2. Experimental Procedure

2.1 Specimens

DH36 steel was used with following chemical compositions (in wt-%): 0.15C, 0.33Si, 1.40Mn, 0.015P, 0.005S, 0.06Cr, 0.07Ni, 0.15Cu, 0.035Al and balance Fe. The material was machined into specimens of 10 mm in diameter and 10 mm in height for electrochemical tests and 20 mm×20 mm×12 mm for rusts characterization. The specimens were wet ground down and then cleaned with distilled water, ethanol and acetone⁹. Specimens were fixed on a plastic shelf and distributed in the splash zone of the self-made device of simulated marine corrosion environment¹⁰ filled with Qingdao seawater. Specimens were removed after 10, 30, 90 and 180 days respectively. Then the samples were used for the electrochemical tests and rust characterization.

2.2 Characterization of corrosion samples

The morphologies of outer, inner and cross-section of the rust layers were characterized using scanning electron

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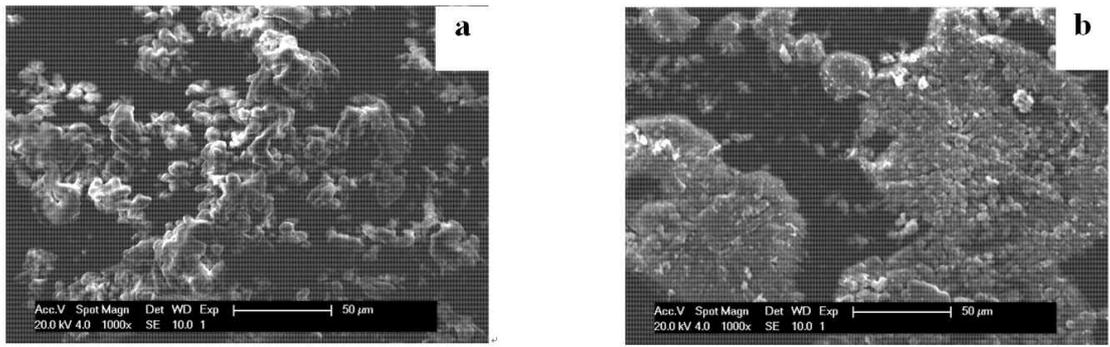


Fig. 1. Cross section morphologies of rusted steels in splash zone in (a) 30 days and (b) 180 days.

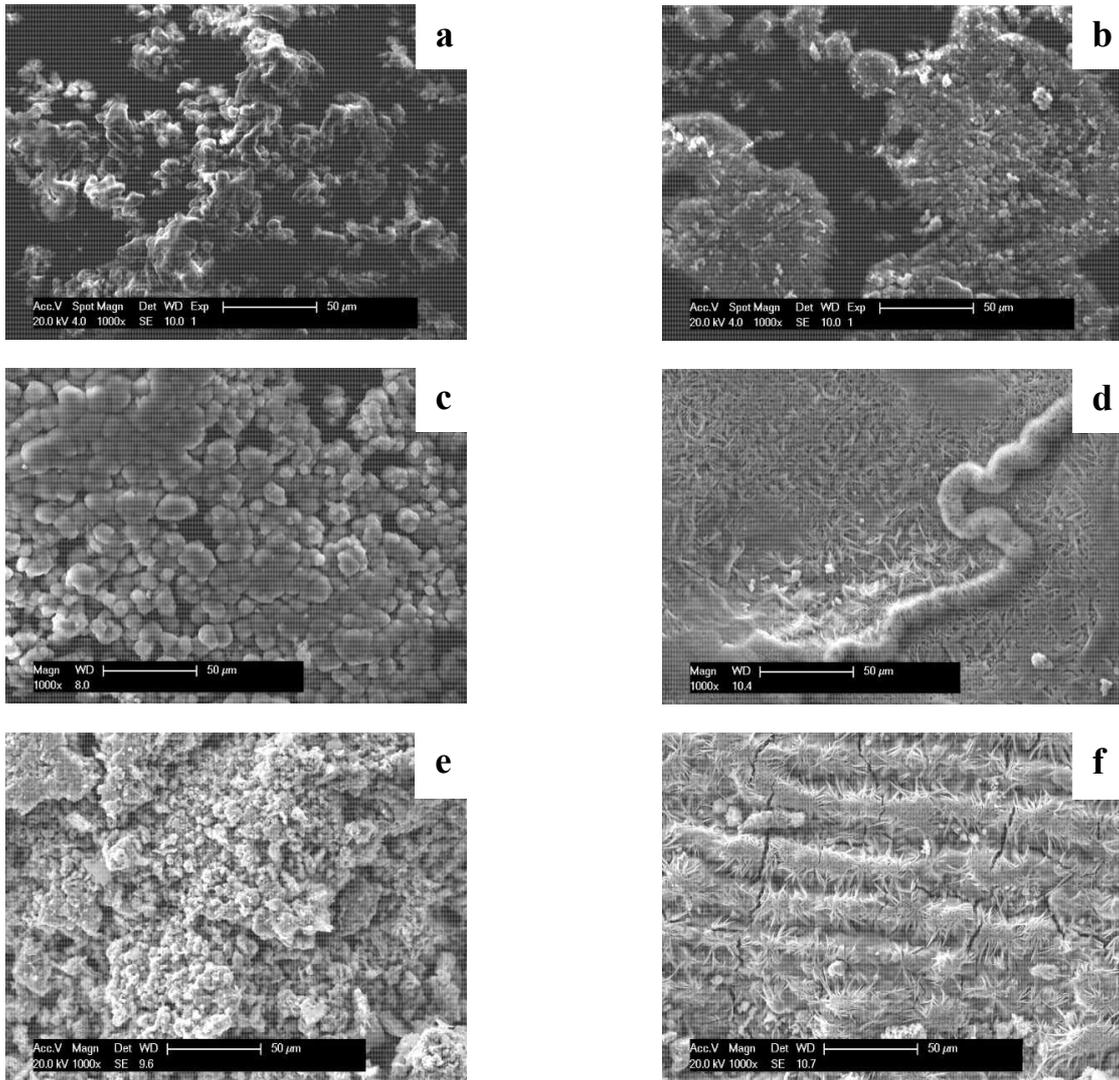


Fig. 2. Morphologies of (a) outer layer and (b) inner layer of rust in 30 days; (c) outer layer and (d) inner layer of rust in 90 days; (e) outer layer and (f) inner layer of rust in 180 days.

microscopy⁶⁾. The corrosion products of the steel samples were characterized using X-ray diffraction. The XRD con-

ditions were 5°/min scanning speed, and 2θ was from 5° to 70° using a Cu target¹¹⁾.

2.3 Electrochemical testing

The electrochemical test was measured using 2273 Potentiostat and the test was performed in a typical three-electrode cell which consist of rusted steel as working electrode, platinum counter electrode and a saturated calomel electrode as the reference electrode. The polarization curves were obtained from -200 to +200 mV versus OCP with scan rate of 0.5 mV/s.

3. Results and Discussion

3.1 Characterization

Fig. 1 shows the cross section morphologies of rusted steels in splash zone in 30 and 180 days. In 30 days, the rust was about 35 μm thick, while it grew to over 1100 μm in 180 days. The rust was not uniform, porous and stratified.

Fig. 2 and Fig. 3 show the corrosion morphology and XRD analysis of outer and inner rust layers of DH36 steel.

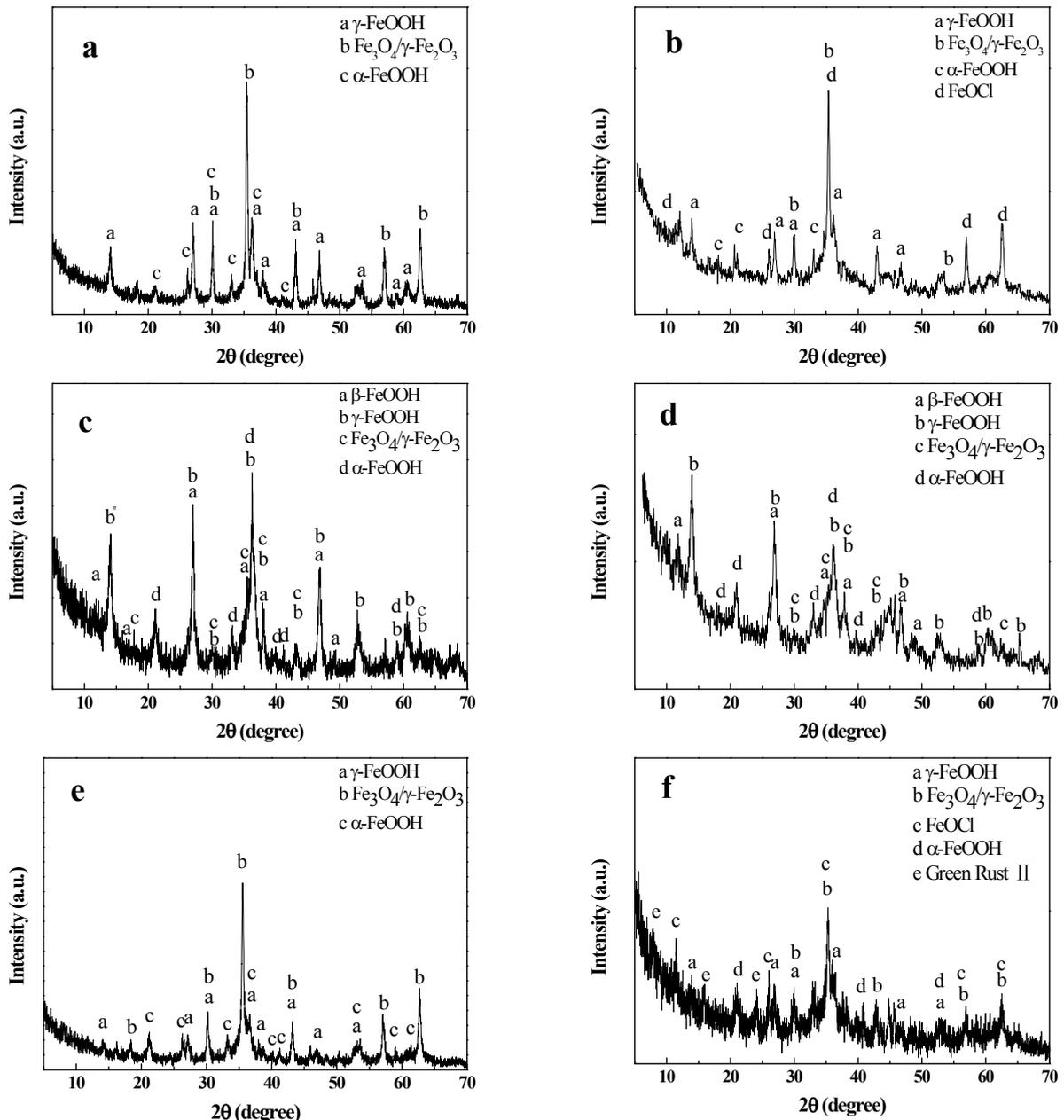


Fig. 3. XRD analysis of (a) outer layer and (b) inner layer of rust in 30 days; (c) outer layer and (d) inner layer of rust in 90 days; (e) outer layer and (f) inner layer of rust in 180 days.

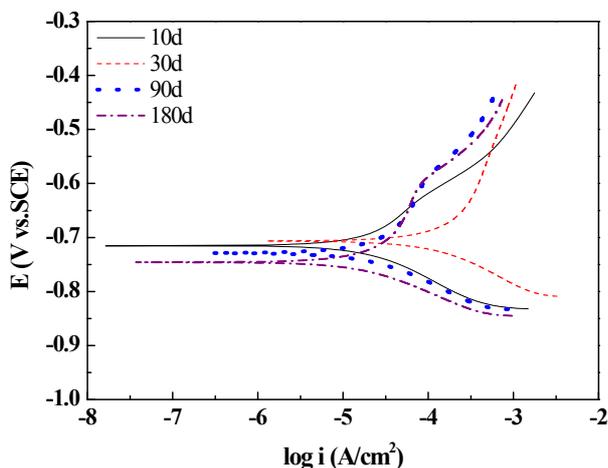
Table 1. Polarization fitting parameters of DH36 rust steel

	E_{corr} (mV)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	β_c (mV)	β_a (mV)
10d	-715.5	29.28	96.06	209.27
30d	-707.5	269.42	114.83	534.97
90d	-732.0	40.83	97.17	396.23
180d	-749.3	33.13	77.88	387.62

The outer layer of rust formed during 30 days was porous and flaky, and the inner layer was fine particles partly covered with flaky crystal. The main components of the outer layer were magnetite and lepidocrocite with a little of goethite while the inner layer was magnetite with lepidocrocite and goethite. The fine flaky crystal was lepidocrocite and it grew to form the outer layer. Ferric oxychloride was detected in the inner layer. The outer layer of rust formed during 90 days was stalactite-like and flaky, and the inner layer was complex, it was fine flaky and branched. lepidocrocite and goethite with a small amount of magnetite, and akaganeite were detected in the outer layer while the main component of the inner layer were lepidocrocite and goethite, magnetite, and akaganeite was detected. The fine flaky rust was lepidocrocite, and the branched rust was akaganeite. The outer layer of rust formed during 180 days was loose and present in clear crevice, magnetite, lepidocrocite and a small amount of goethite were detected. The inner rust was complex, the branched rust grew on the flaky rust and present in clear crevice, and the main rust were magnetite and lepidocrocite with minor goethite. Ferric oxychloride and Green rust II were detected.

3.2 Polarization behaviour

Fig. 4 shows the polarization curves of DH36 rust

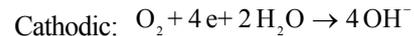
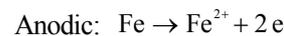
**Fig. 4.** Polarization curves of rusted DH36 steels.

steels. The fitting parameters are shown in Table 1.

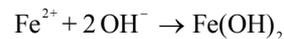
The cathodic process was controlled of charge transfer rather than the oxygen reduction reaction. The main cathodic reaction was rust reduction and the rust acted as depolarizer, which causes the heavy corrosion in splash zone. The corrosion rate of DH36 rust steels in splash zone increased in 30 days and then decreased. At the beginning, the redox current was small as there was a little amount of rust formed. The redox current increased as more rust formed with time and the corrosion rate reached maximum in 30 days. As the rust grew thicker, the rust protected the metal in some extent.

3.3 Discussion

The whole corrosion process in splash zone as follows. The seawater splashed on the steel surface. In oxygen dissolved seawater, the anodic reaction was metal dissolution, and cathodic reaction was reduction of oxygen.



And then ferrous hydroxide was formed:

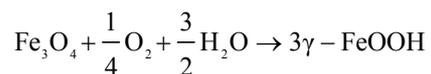


Then ferrous hydroxide was oxidized to magnetite:

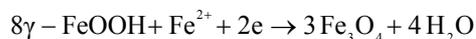


During the drying process, the electrolyte became thicker and chloride concentration increased. Oxygen would be much easier to diffuse into the metal/electrolyte interface, which benefit for the cathodic reaction.

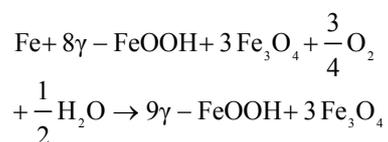
As the water dried, magnetite was oxide to lepidocrocite,



The fine flaky lepidocrocite was formed. During the next wet period, the seawater in rust crevice supplied ion channels and the Electrons flow along the magnetite rust. The Fe^{2+} left the metal and swim to the rust layer interface through the rust crevice and reacted with lepidocrocite.



Magnetite was oxide to lepidocrocite again in the next dry period. The overall reaction was:



That is, after each wet-dry cycle, every eight moles of lepidocrocite involved in the reaction and nine moles of lepidocrocite obtained. This is a self-circulation process of chemical oxidation and electrochemical reduction, magnetite and lepidocrocite acted as catalysts.

With time the flaky rust grew bigger. And double layers were formed, the inner rust was magnetite and fine flaky lepidocrocite crystals grew on magnetite and the outer rust was big flaky lepidocrocite. The flaky lepidocrocite accumulated and played a protective role in some extent. In addition, the lepidocrocite in outer layer would change to goethite partially with time.

4. Conclusions

(1) Double rust layers were formed in splash zone. The inner layer contained magnetite and fine flaky lepidocrocite, the outer layer was composed of accumulated flaky lepidocrocite and a little of goethite.

(2) The cathodic process was controlled of charge transfer rather than the oxygen reduction.

(3) In wet period, the iron dissolved and reacted with lepidocrocite and magnetite appeared while magnetite was oxidized to lepidocrocite again during dry period. It is a self-circulation of electrochemical reduction and chemical oxidization, and magnetite and lepidocrocite were involved in the reduction reaction and lead to serious corrosion in the splash zone.

Acknowledgments

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References

1. W. Chalee, T. Sasakul, P. Suwanmaneechot, and C. Jaturapitakkul, *Cement Concrete Comp.*, **37**, 47 (2013).
2. R. E. Melchers, *Corros. Sci.*, **68**, 186 (2013).
3. R. E. Lye, *Mater. Performance*, **40**, 40 (2001).
4. R. Jeffrey and R. E. Melchers, *Corros. Sci.*, **51**, 2291 (2009).
5. K. V. S. Ramana, S. Kaliappan, N. Ramanathan, and V. Kavitha, *Mater. Corros.*, **58**, 873 (2007).
6. J. G. Castaño, C. A. Botero, A. H. Restrepo, E. A. Agudelo, E. Correa, F. Echeverría, *Corros. Sci.*, **52**, 216 (2010).
7. A. Aghajani, *Mater. Performance*, **47**, 38 (2008).
8. M. Smith, C. Bowley and L. Williams, *Mater. Performance*, **41**, 30 (2002).
9. Q. X. Li, Z. Y. Wang, W. Han, and E. H. Han, *Corros. Sci.*, **50**, 365 (2008).
10. B. Hou, J. Duan, Z. Zhang, H. Y. Sun, and Y. Li, *Mater. Performance*, **41**, 45 (2002).
11. P. Refait, D. D. Nguyen, M. Jeannin, S. Sable, M. Langumier, R. Sabot, *Electrochim. Acta*, **56**, 6481 (2011).