



Durability method on corrosion fatigue performance of AH 32 steel

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ABSTRACT. A durability method in view of cathodic protection is proposed to improve the corrosion fatigue resistance of AH 32 steel in seawater. By aid of corrosion fatigue tests, the effects of thermal spraying Zn (zinc) and Cr (chromium) coating corrosion fatigue lives are quantitatively determined, respectively, and electrochemical measurement and fracture analysis are used to analyze the life-prolonging mechanism of these two coatings on corrosion fatigue. The results show that both Zn and Cr coating improve the corrosion fatigue resistance of AH 32 steel, and the effect enhances with the decrease of stress. The effect of Cr coating on corrosion fatigue of AH 32 steel mainly reflects in extending the crack initiation life for its better corrosion resistance. While the effect of Zn coating on corrosion fatigue lies in not only inhibiting the initiation of corrosion fatigue but also restraining crack propagation as cathodic protection materials. To sum up, Cr coating has a better durability effect than Zn coating at higher stress level, while Zn exceeds Cr at low stress level.

KEYWORDS. Durability method; Corrosion fatigue; Thermal spraying; Crack nucleation; Crack propagation.



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INTRODUCTION

Failure accidents of marine structures result in huge casualties, economic losses, and regional environmental pollution. Therefore, safety and reliability is always a top priority for the design of these marine structures. According to the Swedish damage situation report in 1972, about 70.4% of the damages of marine ships were induced by fatigue [1]. With the increasing capacity and the large-scale construction of the ships and offshore platform, the risk of fatigue damage is becoming more and more prominent. In marine corrosive environment, corrosion, fatigue and their concomitant injuries to the ships and ocean engineering structures cannot be underestimated, although the ships and ocean engineering structures are already equipped with a strict corrosion protection system to ensure the corrosion controlled within the theoretically acceptable range [2-4]. According to the real-time detection, the corrosion protection system is not effective enough in the service period [5]. What's the worse, when the marine engineering structures are subjected to the combined action of fatigue load and corrosion environment, the service time will be shortened obviously. The interaction and coupling of the corrosion environment and fatigue load results in that the corrosion fatigue damage is much severe than the single action of corrosion or fatigue load [6-8]. According to the statistical data, corrosion fatigue

failure accounted for nearly 30% of the total number of accidents of ocean engineering structures [9]. In recent years, more and more attentions have been attached to the corrosion fatigue of ship and marine structure, and corrosion fatigue mechanism and durability design has been a hot research on the account.

AH 32 steel is a hot rolled steel mainly used in the manufacture of hull and deck of the ships and offshore platforms, etc. Due to the large demand of marine shipbuilding industry for AH 32 steel, the mechanical properties and corrosion resistance are the critical factors to ensure the integrity of the ships. Li et. al. [10] studied the hot ductility and strength of AH 32 steel during the continuous casting process, and determined the cracking sensitivity of AH 32 steel under different temperatures and strain rates. Jia et. al. [11] tested the mechanical properties of AH 32 opened plate improved by advanced production equipment and CSP rolling process control. Zhang et.al. [12] performed the fatigue tests of the T-shaped welded specimen for AH 32 steel. Dong et. al. [13] experimentally investigated the low cycle fatigue failure and accumulative plastic damage, as well as their interaction of AH 32 steel in uniaxial cyclic loading. Also, they studied the fatigue crack growth behavior of AH-32 steel with the experimental application of CTOD [14]. Sun et. al. [15] revealed the characteristics of the plastic strain accumulation behavior of AH 32 steel under the combined effect of the cyclic stress and corrosion factors. Minoru [16] clarified the pitting corrosion mechanism through onboard research of AH 32 steel by various corrosion tests, and developed a new corrosion resistant steel (CRS) with trace amounts of alloying elements. However, the failure of AH 32 steel in marine environment is often caused by the interaction of load and corrosion, the researches of interaction mechanism and durability of corrosion fatigue of this material are relatively insufficient. Numerical studies have testified the accelerating effect of corrosion process on fatigue failure [17-20]. Therefore, the methods of inhibiting corrosion have been widely adopted to extend the corrosion fatigue life, such as, surface enhancement by laser [21-22], low plasticity burnishing [23], and cathodic protection [24-25].

In this paper, we propose a method of thermal coating technology to improve the corrosion fatigue durability of AH 32 steel. Arc spraying Zn and Cr coating are performed respectively, to improve corrosion fatigue life of AH 32 steel in marine environment. The effects of coatings on corrosion fatigue of AH 32 are quantitatively analyzed in virtue of rotating bending corrosion fatigue tests, and the mechanisms of these two coatings' improving corrosion life are discussed in details.

EXPERIMENTAL PROGRAM

Samples and experimental preparation

The selected AH 32 steel for rotary bending fatigue test were manufactured by Anshan Iron and Steel. It contains (w.t. %) 0.09 C, 1.2 Mn, 0.28 Cu, 0.36 Si, 0.37 Ni, 0.006 P, 0.002 S, 0.09 Cr, and Fe rem. The tensile curve of AH 32 is shown in Fig. 1. The yield strength and tensile strength of AH 32 are 358 MPa and 441MPa, respectively. The rod specimens are machined from AH 32 steel bar (Φ 24mm) by wire-cutting and fine grinding to achieve the accuracy requirements.

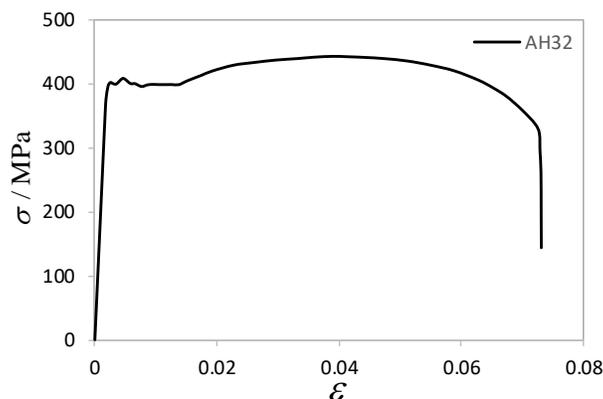


Figure 1: Stress-strain relation of AH 32 steel.

The fatigue and corrosion fatigue failure tests of AH 32 steel are carried out on Cardan low-frequency rotating bending fatigue testing machine. According to the strength characteristics of the steel, eight different stress levels 179 MPa ($0.5\sigma_s$), 191MPa, 203MPa, 215MPa ($0.6\sigma_s$), 233MPa, 251MPa, 269MPa and 286 MPa ($0.8\sigma_s$), are selected for fatigue test. The



loading frequencies are set as 0.5, 1 and 2Hz, respectively. To ensure the interaction of sample and corrosion solution during the fatigue test. A special designed circulating device of seawater is used to maintain the circulation and renewal of the seawater, as shown in Fig. 2. The pump drives corrosive liquid circulate in the tube, and spray it on the test section of the samples through the shower. The surface of testing section of the sample is strapped with a layer of absorbent fiber to ensure the full immersion of the samples in the absorbed solution during the experiment.

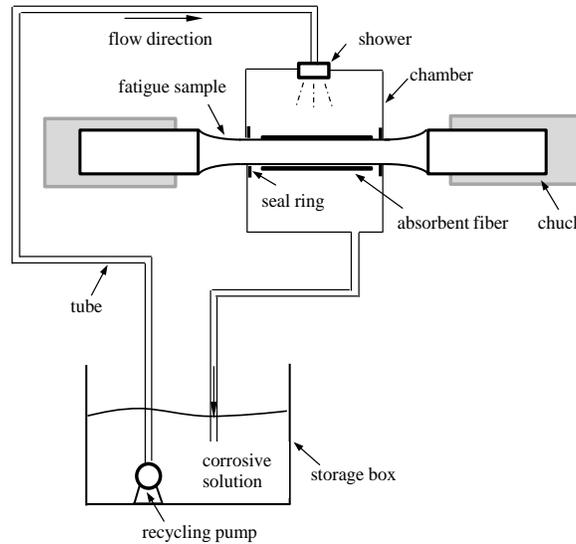


Figure 2: Setup of circulation device of corrosion solution.

Results of corrosion fatigue tests

Fig. 3 shows the number of cycles to fatigue and corrosion fatigue failure for bare AH 32 steel in seawater under different stress amplitudes. It can be seen corrosion environment impose an obvious influence on fatigue life, and this effect becomes more significant at low stress level. Stress amplitude is the dominant factor determining fatigue and corrosion fatigue life, and fatigue lives increase with the decrease of stress amplitude. The stress frequency also has a significant effect on the corrosion fatigue life, and the corrosion fatigue lives decrease at lower frequencies under the same stress amplitude. It can be explained that the interaction between sample and corrosion environment is more effective in each cycle at low frequencies, which accelerates the evolution of corrosion fatigue damage per cycle [26-27]. In contrast, the effect of frequency on fatigue life is not as significant as corrosion fatigue.

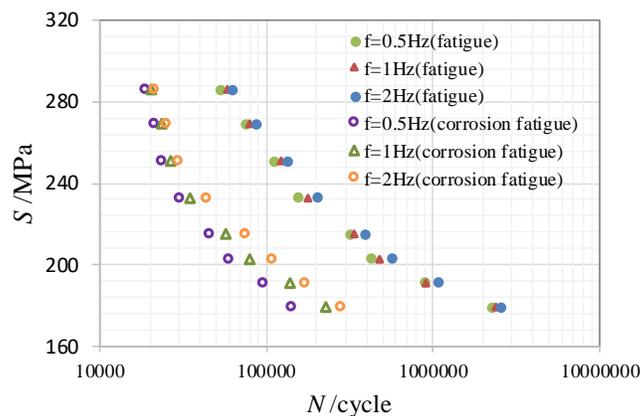


Figure 3: Results of fatigue and corrosion fatigue tests.

Fig. 4 shows the typical fracture surface of the sample under low stress amplitude. From the overall morphology of the fracture shown in Fig. 4(a), there shows symmetry of the morphological development on both sides, and the crack initiation zone, extension zone and fracture zone are in turn from the two sides to the central axis. Fig. 4 (b) shows the morphology of crack nucleation zone, and it can be seen clearly that the corrosion pit promotes the formation fatigue

crack. Fig. 4 (c) is about the crack propagation zone and there exist a series of irregular fatigue crack striations. But the fracture surface is almost covered a layer of corrosion product for the corrosion process.

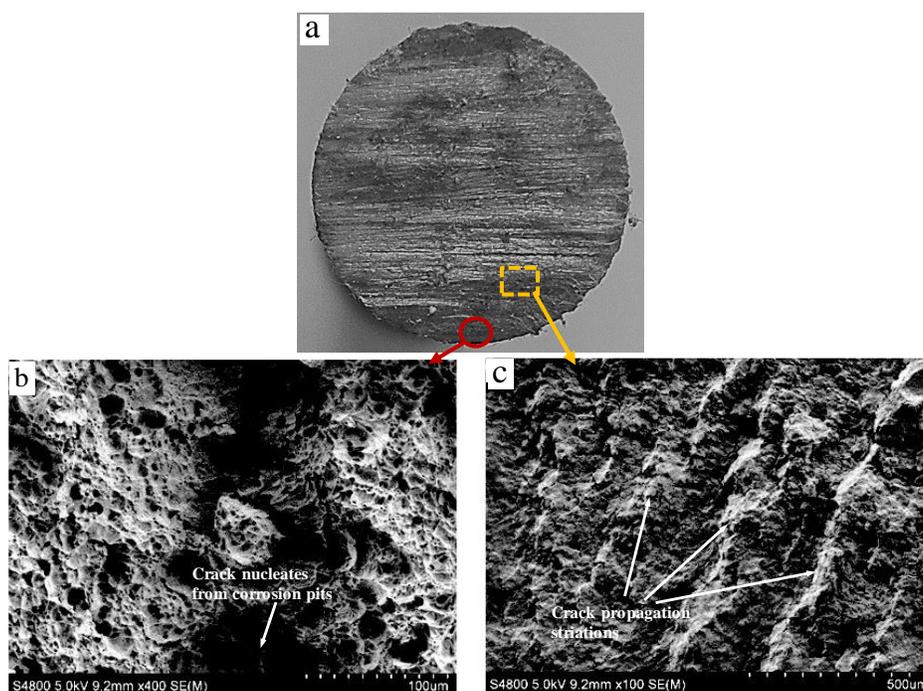


Figure 4: Fracture morphology (a. overall appearance; b. crack nucleation zone; c. crack propagation zone).

DURABILITY TECHNOLOGY

Thermal spraying of Zinc and Cr coating

Through the above analysis, it is found that the corrosion environment has a significant effect on the fatigue life of the structure. Therefore, anti-corrosion treatment always serves as an effective way to prolong the corrosion fatigue life. There are several ways to control corrosion commonly used in engineering, such as reasonable design of engineering structures, selection of anti-corrosion materials, change of corrosion environment, use of corrosion-resistant coatings, electrochemical protection, and substitution of metal structures with non-metallic structures with better corrosion resistance. Compared with the above methods, for AH 32 steel in marine environment, the feasible methods are electrochemical protection by surface coating of cathodic materials. Here, to ensure adhesion between coating and substrate, arc spraying of Zn and Cr coatings are adopted respectively to evaluate their effects on corrosion fatigue.

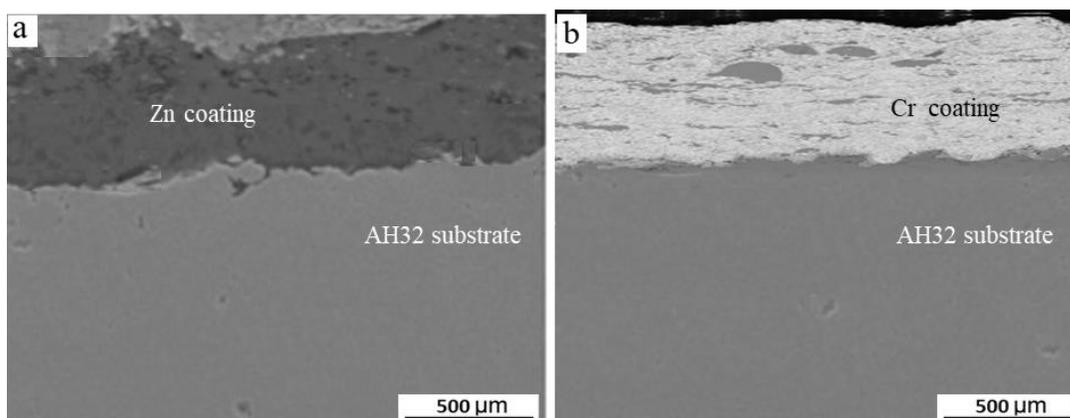


Figure 5: Cross-section microstructures of coated specimens (a. Zn coating; b. Cr coating).



According to the ISO 2063 standard, Zn and Cr coating are deposited by CMD-AS1620 arc spray system. Before spraying, the rust of samples has been removed, and the surface have been blasted by 0.5mm corundum to achieve the roughness of 50-80 μm . The blasting pressure is 0.6 MPa and the blasting distance is 150 mm. After several trials on spray conditions, the filamentary Zn and Cr are heated to the melting state, and blown into a mist by compressed nitrogen gas to form a uniform particle flow and sprayed on the substrate surface. The stand-off distance (distance between the nozzle and the substrate) is kept constant at 150 mm. The stagnation pressure is 0.7MPa and the powder feed rate is 27.78 g/min. During the spraying process, the process parameters are finely adjusted to obtain a constant thickness of $500 \pm 30 \mu\text{m}$. The cross-sections of AH 32 substrate and Zn and Cr coating interface are obtained by optical electron microscope, as shown in Fig.5. It can be clearly observed that a lamellar structure with lamellas parallel to the substrate surface, with a good bonding with close to no porosity. The coating-substrate interface is quite irregular, possibly due to the impact of the high velocity particles that constitute the coating, on the AH 32 substrate. Before deposition, it is evident that the substrate had undergone a severe plastic deformation during the coating process. However, such deformation enhances the mechanical bonding and adhesion of the coating to the substrate. Both Zn and Cr coating show a good build-up and had a final roughly uniform thickness in the range of 470 to 530 μm .

Effect of coating on corrosion fatigue

The corrosion fatigue tests of bare steel, and Zn and Cr coated specimens are carried out under the same test condition, and the S-N curves at 1Hz frequency are shown in Fig. 6. For comparison purposes, and to provide a better understanding of the effect of the corrosive environment on fatigue life of the AH 32, the S-N curve of fatigue testing is also shown in the same figure. It can be seen that both Zn and Cr coating can greatly improve the corrosion fatigue of AH 32 steel, and this effect enhances with the decrease of stress. This is attributed to the interaction of physical isolation, compressive residual stresses induced by arc spray and electrochemistry function of the coating materials [28-30]. An interesting phenomenon is that the effects of Zn and Cr coating on fatigue life extension are dramatically dependent on the stress level. The comparison of corrosion fatigue lives of Zn and Cr coated samples show that Cr coating has better performance than Zn coating at higher stress level, but the opposite is true at low stress amplitude. This can be explained from the contribution of these two coatings to crack nucleation and crack propagation at different stress levels. However, their contributions of each part to corrosion fatigue life is difficult to be quantitatively determined, and we will discuss in detail from the mechanism analysis.

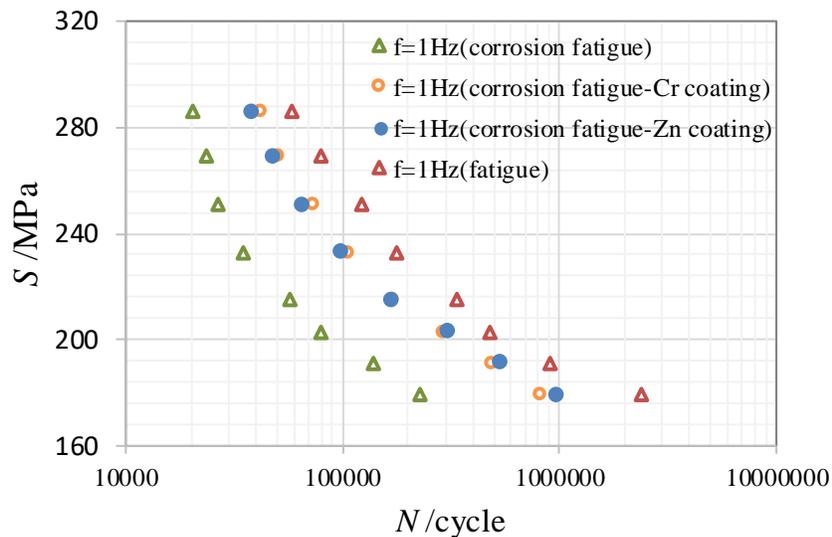


Figure 6: S-N curves of corrosion fatigue tests

The pre-corrosion fatigue tests of Zn and Cr coated specimens are also carried out to investigate their corrosion resistance. The bare samples, Zn and Cr coated specimens are respectively emerged in the seawater for period of 15 d and 30 d, and the typical corroded samples with a period of 15 d are shown in Fig. 7. It can be seen the surface corrosion of test section of bare AH 32 samples is the most serious, followed by Zn coated and Cr coated samples. The fatigue behaviors of the pre corroded samples are tested under the same load as the corrosion fatigue, with results shown in Fig. 8. The fatigue lives of pre corroded Cr coating samples are apparently larger than that of Zn coated samples, and the difference between

which become obvious with the prolongation of period of pre corrosion and the decrease of stress amplitude. It follows that corrosion resistance of Cr coating is stronger than that of Zn coating. With the prolongation of pre-corrosion time, the surface corrosion of zinc coating is more serious than Cr coating, and corrosion defects are more likely to induce fatigue crack nucleation under fatigue load, thus accelerating the fatigue failure of zinc coating samples.

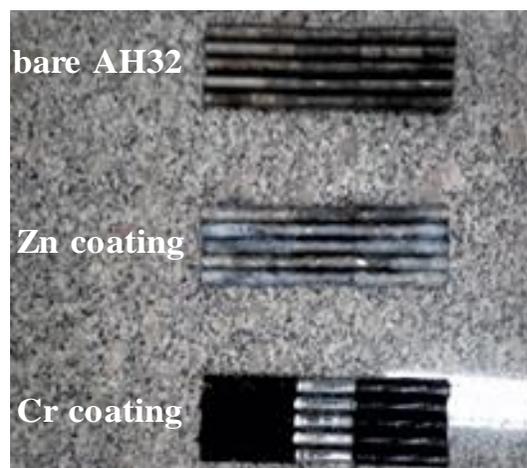


Figure 7: Morphology of the corroded samples.

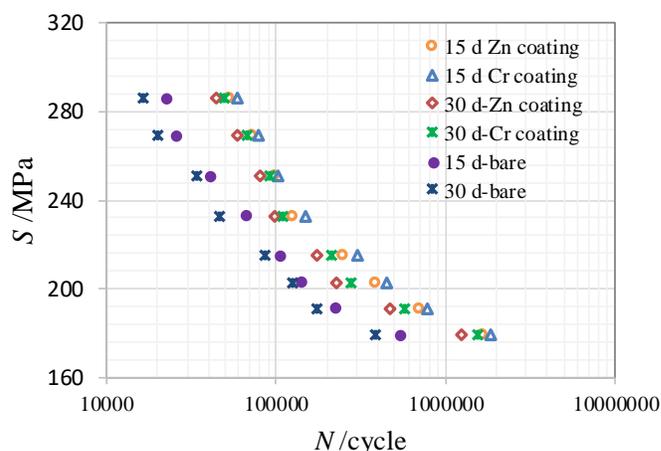


Figure 8: S-N curves of corrosion fatigue.

Mechanism of Zn and Cr coating on corrosion fatigue

To make insight into the mechanism of Zn and Cr coating improving corrosion fatigue resistance of AH 32 steel. The electrochemical measurements of the two coating materials and AH 32 substrate in the seawater are performed by a Perkin-Elmer M283 three-electrode-cell constant potential electrochemical testing system. Cyclic potentiodynamic Tafel polarization are measured starting from -250mV (vs open circuit potential), and scanned toward more positive direction with scanning rate of 0.5mV/s.

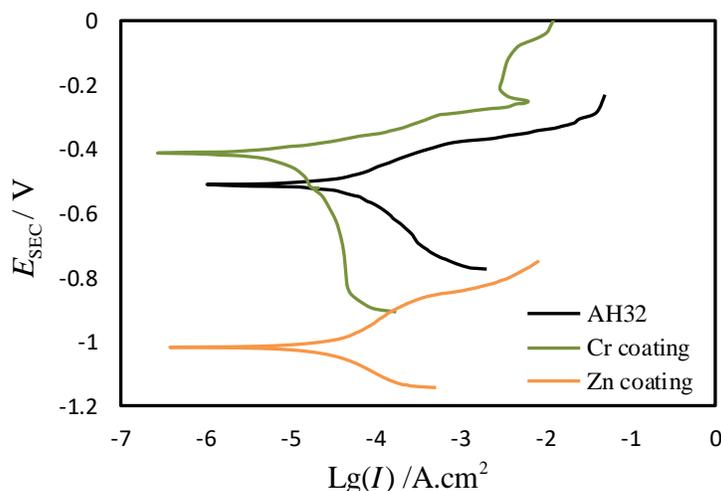


Figure 9: Tafel polarization curves of coatings and substrate

The instantaneous Tafel polarization curves of AH 32, Zn and Cr in seawater are depicted in Fig. 9, and the electrochemical parameters from polarization analysis are listed in Table 1. The corrosion current densities at different immersion periods are also listed in Table 2 for comparison. Compared with AH 32 substrate, Zn has a more negative corrosion potential than Cr, while Cr has a better corrosion resistance. Therefore, Zn is more suitable for cathodic protection, and often mixed with aluminum or magnesium to form an alloy coating for cathodic protection of engineering materials [32-34]. While Cr is often added to the substrate material as alloy element, to improve the corrosion resistance of the substrate [35-36].

Material	E_{corr} (V)	i_{corr} (mAcm ²)	b_a (V.dec ⁻¹)	b_c (V.dec ⁻¹)	R_p (Ω.cm ²)
AH 32	-0.510	0.0489	0.405	0.157	1005.962
Zn	-1.103	0.0110	0.572	0.203	592.203
Cr	-0.411	0.0078	0.128	0.281	4901.968

*Polarization resistance (R_p): $R_p = b_a * b_c / [2.3 * i_{corr} * (b_a + b_c)]$ [31]

Table 1: The instantaneous electrochemical parameters from polarization curve.

Material	Test period	0h		15 d		30 d	
		E_{corr} (V)	i_{corr} (mAcm ²)	E_{corr} (V)	i_{corr} (mAcm ²)	E_{corr} (V)	i_{corr} (mAcm ²)
AH 32		-0.510	0.0489	-0.557	0.0187	-0.564	0.0125
Zn		-1.103	0.0110	-1.176	0.0073	-1.192	0.0065
Cr		-0.411	0.0078	-0.427	0.0062	-0.430	0.0059

Table 2: Comparison of corrosion current density of AH32 and coating materials in different immersion periods.

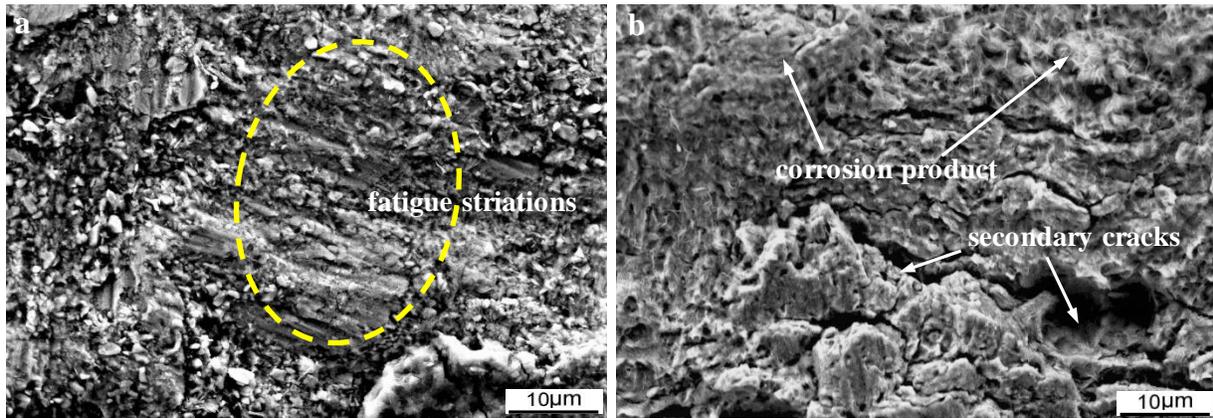


Figure 10: Morphology of crack propagation zone (a. Zn coating, b. Cr coating).

Through the above research, it is not difficult to find that the mechanisms of Zn and Cr coating to improve AH 32 corrosion fatigue resistance are different. The effect of Zn coating on corrosion fatigue prolongation embodies in not only crack nucleation but also crack propagation. Before crack nucleation, the Zn and Cr coating only acts as physical isolation. Because of the interaction of electrochemical process and fatigue, Zn coated specimens are more likely to form crack on the surface. In comparison, the surface corrosion of Cr coating samples develops more slowly for the better corrosion resistance, as obtained from pre-corroded tests. Therefore, Cr coated samples have longer crack nucleation lives than that of Zn coated ones, under the same corrosive load. Once cracks nucleate and propagate, Zn transform its role from physical isolation to sacrificial anode material, to a certain extent, to restrain the corrosion reaction of crack surface and crack tip and to avoid the acceleration effect of corrosion products on crack propagation. However, the electrochemical activity of chromium is not as good as AH 32, but worse than Zn. Cr coating cannot play the role as sacrificial anode to protect crack propagation of the substrate. Fig. 10 shows the crack propagation zone of Zn and Cr coated samples, respectively. In the fracture surface of Zn coated sample, the crack striations in crack propagation is very clear, and the corrosion status is not serious. While the corrosion at the fracture of Cr coated sample is serious covered with a layer of corrosion fatigue. What's more, there also exists several deep secondary cracks. It has been testified that the corrosion products and secondary cracks have close relation with the crack propagation behavior [37-38]. Therefore, the phenomena in Fig. 6 can be explained as the superposition of the contribution of Zn and Cr coating to crack nucleation and crack propagation. At low stress level, corrosion fatigue crack propagation life is relatively longer, so the effect of Zn coating on



crack propagation is remarkable and the overall improvement effect of Zn exceeds that of Cr coating. Conversely, at high stress level, Cr coating has better effect because of its contribution to crack nucleation.

CONCLUSION

In the present study, durability method to improve corrosion fatigue resistance of AH 32 steel in seawater are conducted by arc spraying Zn and Cr coatings. Pre-corrosion fatigue and corrosion fatigue tests are carried out to quantitatively determine the effect of coatings on corrosion fatigue behavior of AH 32 steel in seawater, and the mechanism of coating improving corrosion fatigue characteristics are investigated. The main results obtained can be concluded as follows:

- (1) Corrosion fatigue failure always initiates from corrosion defects at the surface of the specimen, because the stress concentration occurs at these corrosion defects, under cyclic loading, accelerates the nucleation of fatigue crack. The effect of corrosion in fatigue life of AH32 steel become more obvious at low stress level. The effect of loading frequency which determine the corrosion time at every cycle on corrosion fatigue life also cannot be ignored.
- (2) The results of corrosion fatigue and pre corrosion fatigue tests of Zn and Cr coated AH32 steel show that both Zn and Cr coating can greatly improve the corrosion fatigue of AH 32 steel, and the effect enhances with the decrease of stress. Cr coating on corrosion fatigue of AH 32 steel mainly reflects in extending the crack initiation life because of its better corrosion resistance. While the effect of Zn coating on corrosion fatigue of AH 32 steel mainly lies in not only inhibiting the initiation of corrosion fatigue but also restraining crack propagation as cathodic protection materials. To sun up, Cr coating has better durability effect than Zn coating at higher stress level, while Zn exceeds Cr at low stress level.

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