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Short Communication

Corrosion Behavior of Sprayed Zinc-Aluminum (ZZA) Coatings in Simulated Marine Environment

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The zinc-aluminum coatings were prepared, parts of them were sealed with organic coatings and then the corrosion behavior and mechanism were studied by salt spray test and electrochemical impedance spectroscope (EIS). Scanning Electron Microscope (SEM) was employed to assess the coatings. It showed that the zinc-aluminum coatings were rough and with some defects, which would discount the protection effect. The organic coating would improve the protection through sealing the defects of the metal coating.

Keywords: Zinc; Organic coatings; Salt spray test; Thermal spray; Aluminum

1. INTRODUCTION

The thermal spraying zinc-aluminum coatings for steel corrosion protection were used from 1920s, and it is still a common method in anti-corrosion. At present, thermal spraying zinc-aluminum coatings for long-term protection of steel structures has been widely used on the bridge, strobe, pipelines and other large anti-corrosion engineering in Europe, the United States, Japan and other developed industrial countries[1-8].

Lots of researches on sprayed zinc-aluminum coatings were carried out through coupon corrosion test. The corrosion behaviors of thermal sprayed coatings were studied, and the common methods were neutral salt spray test, immersion experiment and electrochemical test [9-12]. There are few researches reporting about the corrosion rules and mechanism of metal and organic compound coating. The analysis includes the loss-weight test, potential-time diagram and electrochemical theory [13-15]. But there are no researches on the corrosion rules or mechanism.

2. EXPERIMENTAL

2.1 Corrosion materials

Carbon steel samples were cut to the size of 100 mm × 50 mm × 2mm，then the surface were polished by sand-blasting (Sa3 level). The zinc(GB470, 99.99%) coating and aluminum(GB3190, 99.7%) coating were successively sprayed by the 12E flamy spraying gun(Sulzer-Metco Co. of Ameica) in turn. Organic coatings (chlorinated rubber paints) were prepared on some samples. All of the samples were degreased with alcohol and acetone. The thickness and weight of the samples were measured before tests.

Three types of samples: single organic coating on steel, ZZA coating (zinc coatings 70μm and aluminum coating 30μm), sealed ZZA coating(zinc coatings of thickness 70μm and aluminum coating of thickness 30μm, then coated with organic coating).

2.2 Tests

The FDY-03E salt spray test equipment, made of Qingdao Haiding Electrical Appliance Co., Ltd, was used. It sprayed intermittently, 15 minutes worked and 45 minutes stopped per hour. The test cycles lasted for 156 days. The weight and thickness of samples were measured after tests.

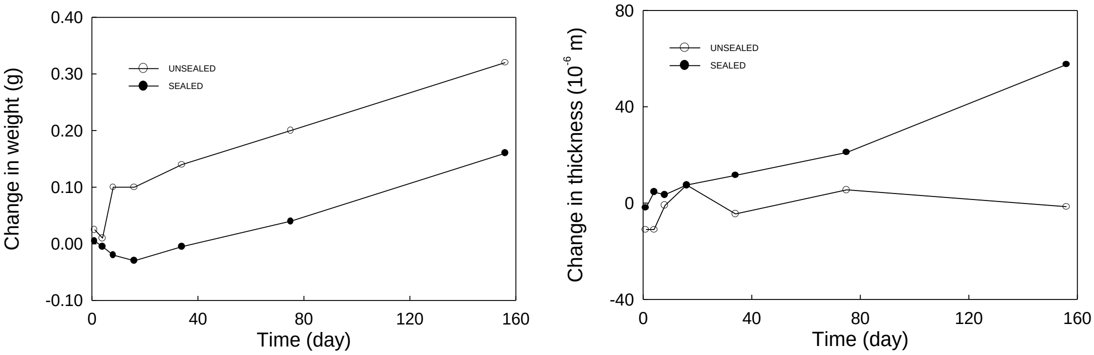
The electrochemical impedance spectroscopy (EIS) experiments were performed in a conventional three-electrode cell arrangement. The counter electrode was Pt and the reference electrode employed was saturated Ag/AgCl electrode in 3% NaCl solution. GPIB potentiostat/current instrument 2000 and S-5720B frequency response analyzing test system were used. EIS measurement was performed on steady state open circuit potential (OCP) disturbed with amplitude of 10 mV a.c. sine wave on unsealed samples while 100 mV a.c. sine wave employed on sealed samples. The scanning frequency ranges from 100 kHz to 10 MHz.

The surface of coatings before and after salt spray test was analyzed by Scanning Electron Microscope (SEM) and Energy Dispersive Spectrdmeter (EDS).

3. RESULTS AND DISCUSSION

3.1 Salt spray test

When organic coatings used only, apparent rusts appeared on the edge of the samples after 75 days, while the edge was completely destroyed and corrosion happened on the middle of the samples after 156 days,. It can be seen that the anti-corrosion performance of organic coatings was limited. After 156 day of salt spray test, there was no corrosion happened on ZZA coatings.



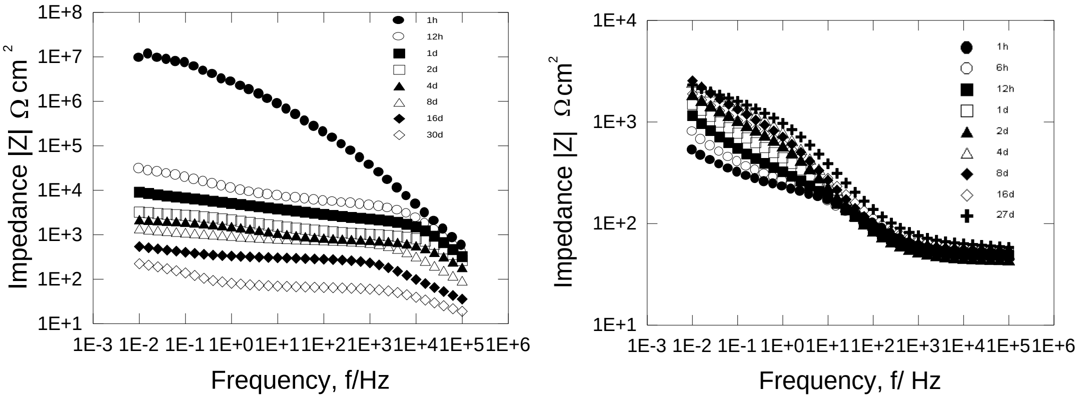
(a) (b)

Figure 1. Change of weight (a) and thickness(b) with time of the sprayed ZZA coatings

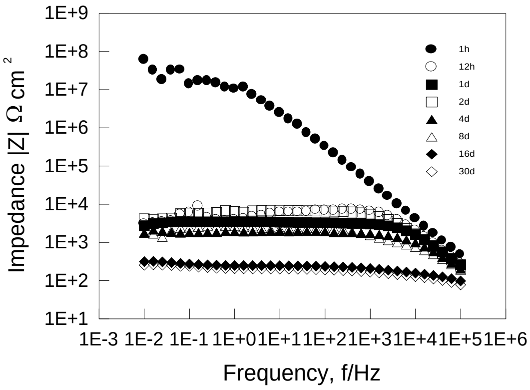
Fig.1 shows the change of weight (a) and thickness(b) with the time of the sprayed ZZA coatings. From Fig.1a it can be seen that the weights of unsealed ZZA coatings increased with time in salt spray test, which may due to electrochemistry reaction happened on the surface and then cracks of the aluminum coating, aluminum hydroxide and other rusts appeared. In the early exposure time, the corrosion reaction happened at the holes and the holes were jamed by corrosion products with the progress of the corrosion, so the weights of sealed sprayed ZZA coatings descended. Along with the exposure time, the weight of sealed ZZA coatings increased because seawater infiltrated via the demolished coatings.

Fig.1b shows thickness changes of ZZA coatings with time. The thickness of sealed coatings increased more than that of the unsealed coatings.It may be due to the salt solution, infiltrated into the interface of the organic and the metal coatings through the cracks of the coating, reacted with the metal coating and lots of rusts appeared.The rusts filled the pores of the metal coating at first and then attached to the interface of the organic and metal coatings. As the metal coating exposured in wet and warm condition, the rusts entered into the cracks of the organic coating and made the thickness increased.

3.2 EIS test



(a) (b)



(c)

Figure 2. EIS of organic coating (a), unsealed(b) and sealed ZZA coatings(c)

Fig.2 shows the EIS of organic coating (2a), unsealed(2b) and sealed sprayed ZZA coatings(2c). From Fig.2a in can be seen that the value of impedance of organic coating was large at the beginning, while fell dramatically after 12 hours and then fell gradually with time. The reason was that the solution infiltrated into the underside of the coating and the base corroded.The rusts would delay further corrosion. The corrosion process which generated gas bubbles made the organic coating invalidated gradullywith time. It was shown that the anti-corrosion effect of the chlorinated rubber coating only was limited.

It was shown that the impedance value of unsealed ZZA coatings was low in Fig.2b. Along with the immersion time, the solution infiltrated into the zinc coating and zinc coating began to corrode.The corrosion products were insoluble. They were assembled and made the coatings breach. The corrosion products including aluminum hydroxide and the alumina blocked the holes. The “Self-Blocking Effects” of aluminum increased the impedance of the coatings.

It was obvious that the impedance value of sealed ZZA coatings decreased with the immersion time in Fig.3c. At the beginning the impedance was high because the zinc coating possessed fine grain,low porosity ratio and low surface roughness The impedance decreased gradually because the solution of the corrosion products.

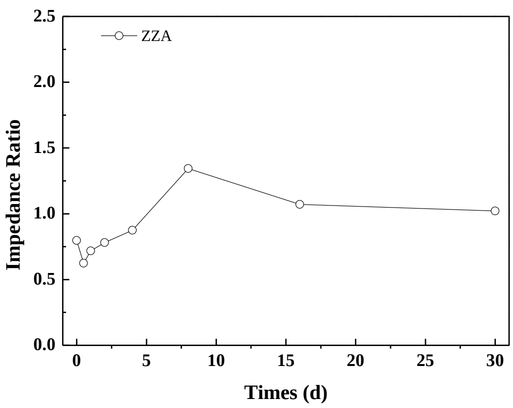


Figure 3. Impedance ratio of sealed metal coating to the the metal coating added the organic coating with time

Fig.3 shows the ratio of sealed ZAA coating impedance to the summation impedances of organic coating and unsealed metal coating with time at high frequency (100k Hz).The impedance ratio increased with the immersion time. It was 1-2. Because the corrosion rate was conversed to the impedance, the service life of coating was longer with the bigger impedance. If the organic coating was compatible with the metal coating, the survice life of the coating would follow the Ing. J. F. H empirical formula,

$T=1.5\sim2.3\ (t_A+t_B)$ (1)

T represents the service life of the sealed coating

t_A represents the service life of the metal coating

t_B represents the service life of the organic coating

According to our results the fomula would amend to: $T = 1 \sim 1.5\ (t_A + t_B)$ (2)

3.3 Microstructure analysis

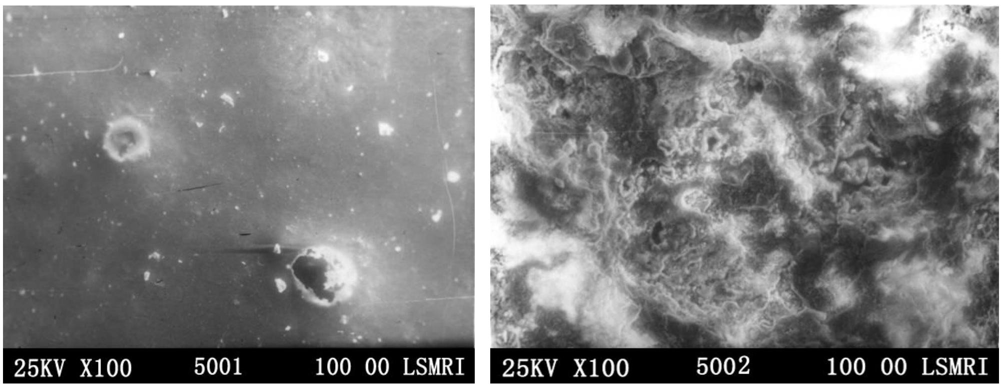


Figure 4. SEM micrographs of organic coatings before(a) and after 5 months salt spray test (b)

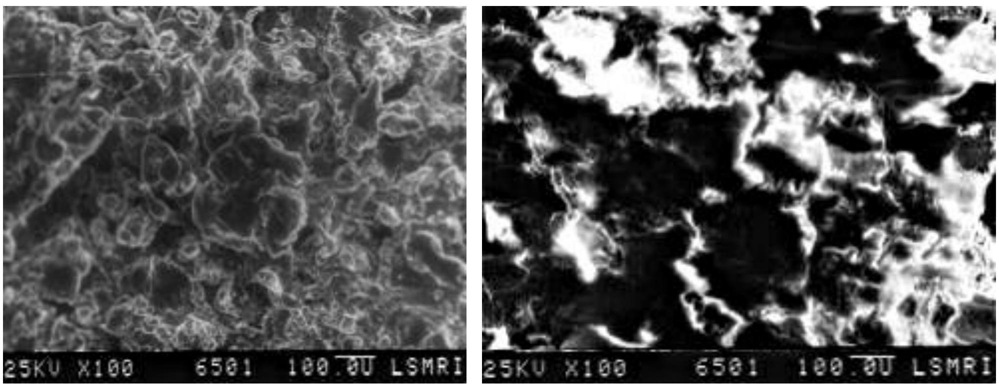


Figure 5. SEM micrographs of ZZA coatings before (a) and after 5 months salt spray test (b)

Fig.4 shows the SEM micrographs of organic coatings before(4a) and after 5 months salt spray experiment (4b). It can be seen the organic coating before test was flat with a few pores in Fig.4a. The two big pores were cauterized by high-voltage electronic beam. It was obvious that lots of corrosion products, pits and and other defects appeared on the organic coatings after salt spray test in Fig.4b

Fig.5 shows the SEM micrograph of ZZA coatings. It can be seen that there were lots of global grains on the surface as shown in Fig.5a. The surface of ZZA coatings was gray and with some white rust points after salt spray test.

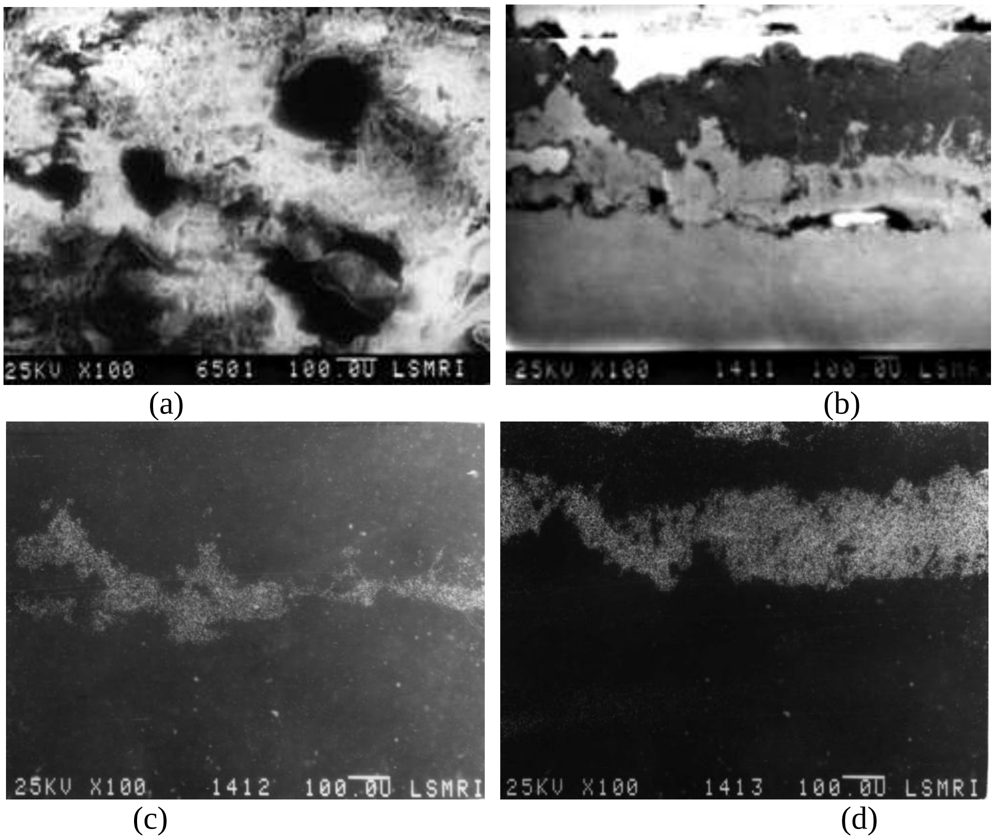
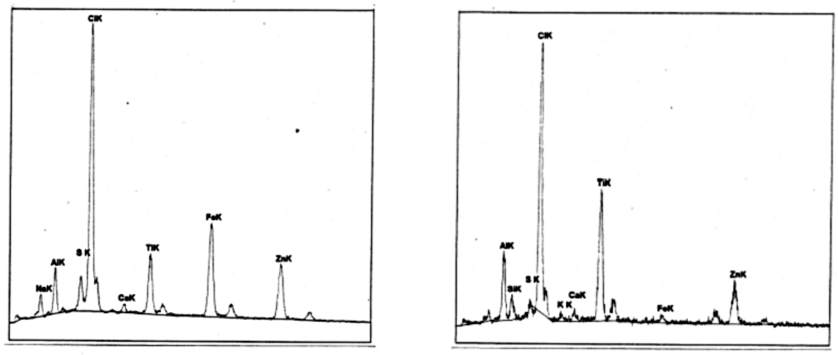


Figure 6. SEM micrographs of sealed coatings: (a) the surface (b) section plane (c) element ZnKα (d) element AlKα

A blue, non-powdery and uniform coating was formed. Fig.6 shows the SEM micrographs of sealed ZZA coatings. The coating provided extremely high coverage observed from Fig.6b. The SEM micrographs of elements ZnK*a*， ClK*a* in section plane indicated that the sealed dope infiltrated to the holes of zinc coatings. The sealed coatings didn’t infiltrate to the basic metal, which confirmed the zinc coatings combined with the aluminum coatings firmly.

3.4 EDS analysis

The results of EDS analyses were shown in Fig.7 and Table 1. The surface of organic coating after salt spray test was mainly composed of chlorine, calcium, titanium and zinc. While the surface of sealed ZZA coatings after salt spray test was mainly composed of chlorine, titanium, zinc and aluminum.



(a) (b)

Figure 7. EDS spectrums of organic coatings after 2 months salt spray experiment (a) and 5 months salt spray experiment of sealed ZZA coatings(b)

Table 1. Results of EDS analysis

coating	experiment cycle	component
Organic coatings	2 months	Chlorine,calcium, Titanium,zinc
Sealed ZZA coatings	5 months	Chlorine,titanium, zinc,aluminum

4. CONCLUSION

(1) The ZZA coatings sealed with organic coatings exhibited good anticorrosion properties. The organic coating blocked the holes and isolated the contact of seawater.

(2) The modulus of Ing. J. F. H empirical formula was amended to 1~1.5.

ACKNOWLEDGMENTS

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