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Corrosion-erosion resistance of Zn-Al co-cementation coatings on carbon steels in aqueous media ①

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[Abstract] A novel Zn-Al co-cementation coating was obtained by a pack cementation method. This coating possesses a two-layered structure. The outer layer is mainly composed of Fe_2Al_5 and FeAl intermetallics with a small amount of Zn, and the inner layer consists of Zn, Fe and a small amount of Al. The corrosion-erosion resistance of Zn-Al co-cementation coatings on carbon steel was studied by a rotary corrosion method in various NaCl and H_2S containing solutions and relevant SiO_2 containing media. The experimental results are compared with those of carbon steels and the sherardizing and aluminizing coatings, showing that the Zn-Al co-cementation coatings have excellent corrosion-erosion resistance in various aqueous media.

[Key words] Zn-Al co-cementation; corrosion-erosion resistance; aqueous media
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1 INTRODUCTION

Sherardizing coating, a Zn coating produced by pack cementation, has good anti-corrosion property and has been widely used in petroleum industry and sea environments[1], but its oxidation resistance isn't very good. Several worldwide publications have shown that Al- and Zn-based alloys provide greater durability in aggressive atmospheres than that used individually[2]. This is because that Al can act as a corrosion-resistant barrier that is in conjunction with the protective galvanic effect furnished by Zn. Zn-Al coatings produced by hot-dip, such as zinc-5% aluminum coating and zinc-55% aluminum coating, have been proved with good properties for both of anti-corrosion and anti-oxidation[3]. This technique has also been greatly used in petroleum industry, the environments open in atmosphere and the environments near or on sea. But hot-dip consumes too many metals and often has a high expense, and is not appropriate when dealing with small, irregularly shaped pieces such as screws, bolts and nuts, because their dimensional tolerances need to be maintained[4].

Recently, Rincón et al[4] reported about diffusive Zn-Al coating on carbon steel prepared by a two-step method. In this method, an Al coating was obtained by pack cementation firstly, then the aluminized samples were sherardized at the temperature between 335 ℃ and 350 ℃ about 2 to 4 h. It is shown that this Zn-Al coating has good corrosion-resistance property, better than those of sherardized coating and aluminized coating.

In this research, Zn-Al co-cementation coatings were prepared by pack cementation at a relative low temperature and by a one-step method. It has been proved that Zn-Al co-cementation coatings possess both good corrosion-erosion resistance in aqueous media and excellent high-temperature corrosion resistance that is reported elsewhere[5]. In this paper, corrosion-erosion resistance of Zn-Al coatings in various aqueous media is studied.

2 EXPERIMENTAL

The substrate material used in present experiments is a commercial carbon-steel with ~ 0.2% C (similar to AISI 1020). Short tube specimens (d 25 mm × 2.5 mm × 30 mm) were used in erosion-corrosion tests.

Zn-Al co-cementation, sherardizing and aluminizing were all carried out by pack cementation. In Zn-Al co-cementation, firstly the specimens were pretreated, including removing the grease and rust on the surface, and co-cementation reagent was prepared with certain powders of Zn, Zn-Al alloy, Al_2O_3 and NH_4Cl and whetted equably; then the specimens were put into a cementation pot with co-cementation reagent around; lastly the co-cementation pot was put into a muffle stove, and the temperature of it was raised to 550 ℃ for 10 h and after treatment the pot was taken out, so we got the Zn-Al co-cementation specimens[5]. The surface and cross-

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section morphologies of Zn-Al co-cementation coatings were gained through SEM, and the contents of elements on the surface and along the cross-section were gained through EDS.

In order to evaluate the corrosion-erosion resistance of the Zn-Al co-cementation coatings and simulate the corrosion conditions of heat exchangers[6, 7], a rotary corrosion device was used, as shown in Fig. 1. The short tube specimens were fastened on a rotating disc plate. The rotating rate of the specimens was 1 m/s. The tested solutions were water, 3.5% NaCl solution, 10 mg/L H_2S solution and 3.5% NaCl+ 10 mg/L H_2S solution at 40 ℃. In order to examine the role of solid particles on corrosion, 20 g/L SiO_2 particles with a − 40 grit size were added into the above four kinds of solutions respectively. The corrosion-erosion resistance was evaluated by the mass changes of the specimens in certain time intervals.

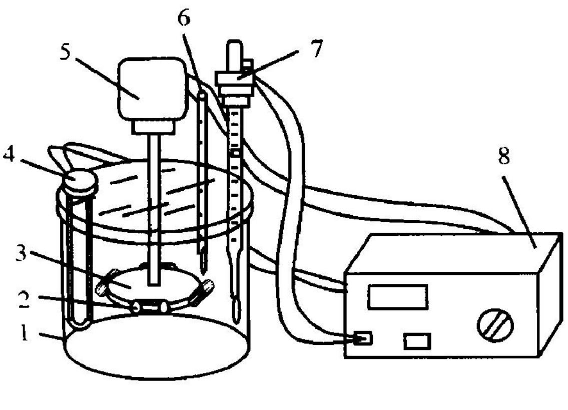

Fig. 1 Rotary corrosion device
1 —Cistern; 2 —Specimen; 3 —Disc;
4 —Heater; 5 —Electrometor; 6 —Thermometer;
7 —Touch thermometer; 8 —Multi-functional beater

3 RESULTS AND DISCUSSION

3.1 Structure and composition of Zn-Al co-cementation coatings

Fig. 2 shows the cross-section morphology and composition of Zn-Al co-cementation coatings. It is shown that the Zn-Al co-cementation coating has a two-layered structure. The outer layer is aluminum-rich, loose, and porous, and the inner layer is zinc-rich and compactive. Fig. 3 shows the XRD analysis result of Zn-Al coating. Obviously, the surface of Zn-Al co-cementation coatings is mainly composed of Fe_2Al_5 and FeAl. This duplex structure in Zn-Al co-cementation coating could be considered a result by piling up an aluminized coating over a sherardized coating.

3.2 Corrosion-erosion resistance in aqueous media

Figs. 4(a) and (b) show the experimental results after erosion in water and water+ 20 g/L SiO_2 at 40 ℃ for 100 h respectively. It can be seen from Fig. 4(a) that all specimens have mass gains after erosion in water, which can be attributed to the corrosive products formed on the surface of specimens. The mass gains of specimens increase in the order: sherardized coating< aluminized coating< Zn-Al co-cementation coating< carbon steel. In Fig. 4(b), all specimens in water+ 20 g/L SiO_2 have a similar order for mass gains, but the values of mass gains are all lower than that in water. The reason for this is the wearing-away action of SiO_2 particles.

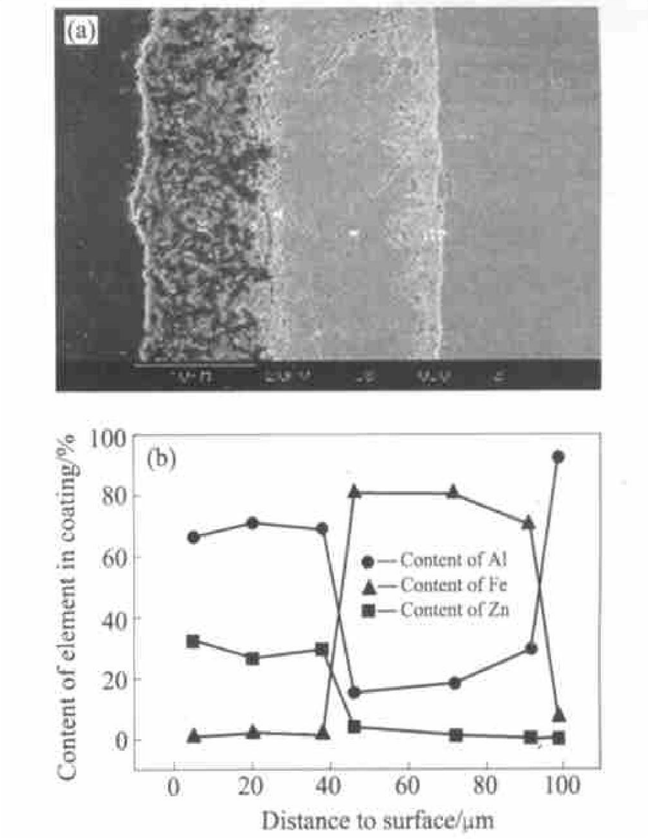

Fig. 2 Cross-section(a) and elemental distribution of Zn-Al co-cementation coating(b)

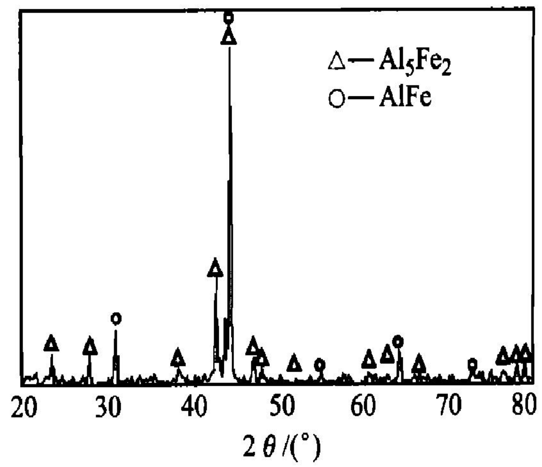

Fig. 3 Result of XRD of Zn-Al coating

From Figs. 4(c) and (d), it is shown that all specimens eroded in 3.5% NaCl solution and 3.5% NaCl + 20 g/L SiO_2 solution have negative mass gains. Comparing them with the results in water and water + 20g/L SiO_2, it can be concluded that erosion is accelerated by Cl^- ions. The mass losses increase in the order: Zn-Al co-cementation coating < sherardized coating < carbon steel < aluminized coating. The mass loss of aluminized coating is even larger than that of carbon steel.

Figs. 4(e), (f), (g) and (h) show the experimental results for four kinds of specimens eroded in the above four kinds of media adding 10 mg/L H_2S respectively. Comparing Figs. 4(e), (f), (g)

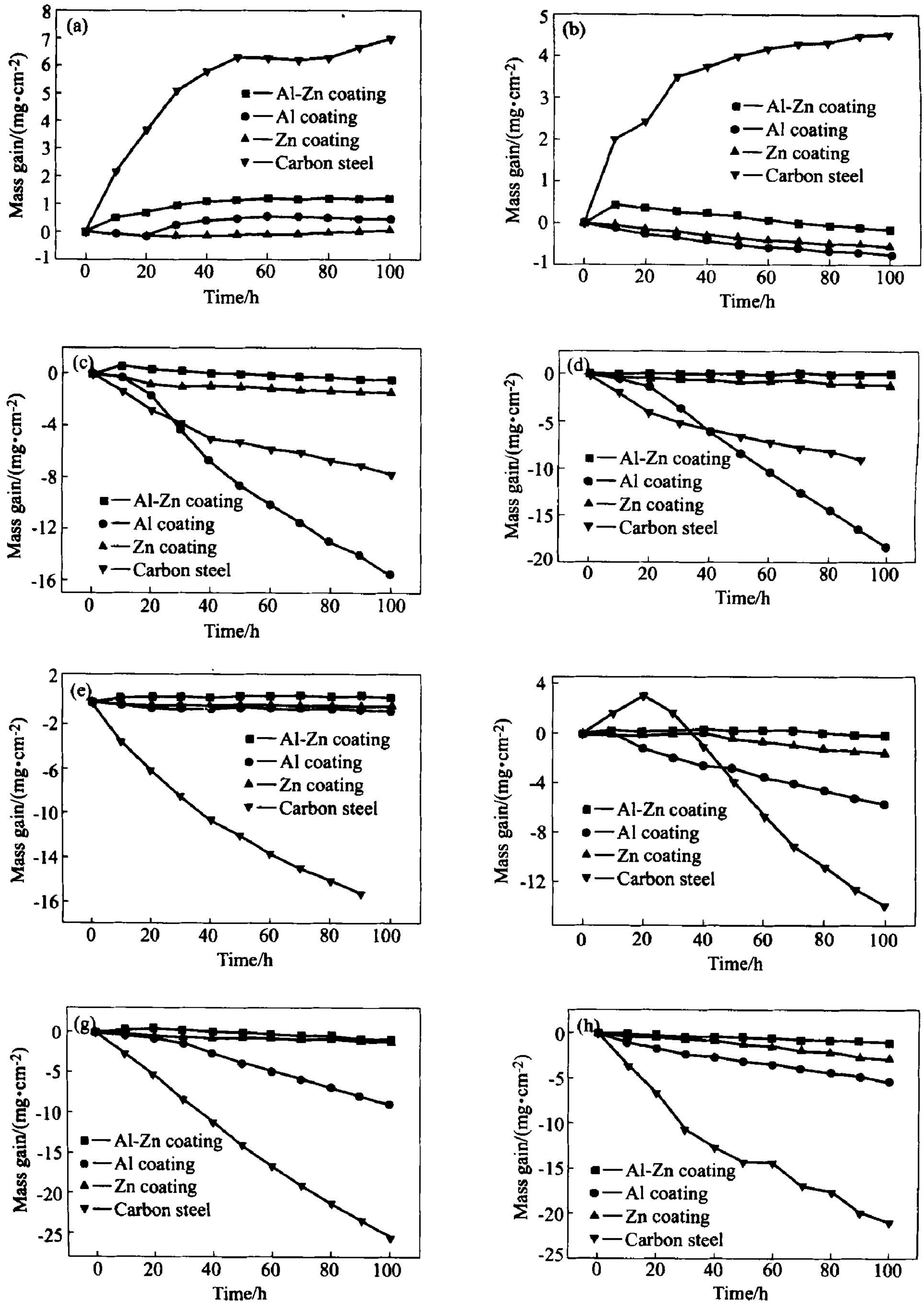

Fig. 4 Mass gains versus time plots of erosion in different media at 40 ℃

and (h) with Figs. 4(a), (b), (c) and (d) respectively, it can be found that, by the addition of 10 mg/L H_2S, the erosion rate of carbon steel is accelerated greatly; the erosion rate of sherardizing coating and Zn-Al co-cementation coating only increases a little; but the erosion rate of aluminizing coating decreases remarkably although it is much higher than that of the sherardizing coating and Zn-Al co-cementation coating.

From all figures in Fig. 4, in a comprehensive view, it can be concluded that the Zn-Al co-cementation coating has the best erosion resistance among all specimens in eight different erosion media. It can also be seen that, for carbon steel, the sherardizing coating and the Zn-Al co-cementation coating, there is a synergistic effect of Cl^- ions, H_2S and SiO_2 particles on the increase of erosion rate. However, for the aluminizing coating, only Cl^- ions, and SiO_2 particles can accelerate the erosion rate synergistically, while H_2S can decrease the erosion rate reversibly. It is interesting to see that a lot of yellow rust formed on the surface of aluminized coatings in all eight different erosion media, but not on the surfaces of the sherardized and Zn-Al co-cementation coatings. This implies that the corrosion mechanism of aluminized coatings is different from that of the sherardized and Zn-Al co-cementation coatings.

The poor corrosion resistance of aluminized coatings is believed to be related to its potential conversion in these environments. Aluminized coatings have the tendency to form a passive film, therefore are more prone to pitting corrosion than the Zn-rich coatings in aqueous solutions. These pits lead to the corrosion of substrate steel, resulting in the yellow rust on the surface of aluminized coatings. For the sherardized coatings, pitting tendency is not strong since the potential conversion does not occur in aqueous solutions at 40 ℃[8]. The Zn-Al co-cementation coating has an Al-rich outer layer; potential reversion phenomenon should also occur. However, the pitting corrosion and yellow rust did not take place on this type of coatings due to the inner Zn-rich layer, which can protect the steel substrate from corrosion-erosion. Therefore, the Zn-Al coatings have the best corrosion-erosion resistance among all the tested samples.

4 CONCLUSIONS

1) Zn-Al coatings were gained by pack co-cementation on the surface of carbon steels. It has a two-layered structure, an aluminum-rich outer layer and a zinc-rich inner layer.

2) It is proved that Zn-Al co-cementation coating has the best corrosion-erosion resistance among all specimens in eight different erosion media. The excellent corrosion-erosion resistance of Zn-Al co-cementation coating can be attributed to its duplex structure, because the Al-rich outer layer tends to be passive, which is beneficially to decrease the uniform corrosion, at the same time, pitting corrosion and yellow rust can not take place on this type of coatings due to the inner Zn-rich layer, which can protect the steel substrate from corrosion.

3) There is a synergistic effect of Cl^- ions, H_2S and SiO_2 particles on the increase of erosion rate for Zn-Al co-cementation coating. It should be pointed out that aluminized coating has very poor corrosion-erosion resistance, which is even poorer than that of carbon steel in 3.5% NaCl solution.

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