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Corrosion resistance of electroplated Zn-Co alloy coating①

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[Abstract] By the NSS test and the test in SO_2 gas atmosphere and detecting the $\varphi_{corr}-t$ curves, R_p-t curves and the cyclic voltammogram curves, the corrosion resistance of the electroplated Zn-Co alloy coating was studied. The corrosion resistance of the electroplated Zn-Co alloy coating is three times higher than that of the galvanized coating. Because the corrosion resistance of the Zn-Co alloy coating is especially remarkable in SO_2 gas atmosphere, it is particularly fit to be used as a protective coating in industrial atmosphere. The reason why the Zn-Co alloy coating has such a high corrosion resistance is that its corrosive product has a comparatively great role in depressing the corrosive process.

[Key words] electroplating; Zn-Co alloy; corrosion resistance
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1 INTRODUCTION

As a protective coating, the electroplated Zn-Co alloy coating has been developed and widely used, and is particularly effective for corrosion resistance in industrial atmosphere. Zinc-cobalt electrodeposited steel sheet is adopted for automobile bodies for its high corrosion resistance with small cobalt content. This deposit exhibits fine grains and its refinement mechanism has been discussed[1].

The electroplating of zinc alloys has been developed in order to solve the protective requirements of iron and steel articles used in marine climate and poor environmental conditions[2, 3]. An alkaline zincate process for plating Zn-Co alloys has also been developed, and put into industrial production[4]. Preliminary experiments were carried out in order to electrodeposit a sound and satisfactory Zn-Co alloy from citrate baths[5]. The bath composition is comparatively simple, and easy to maintain and adjust. Furthermore, the bath has an excellent throwing power, and can be obtained by changing the production line from zinc plating[6]. The electroplated coating obtained by this bath shows bright and has a compact crystal lattice. The cobalt content of the coating is 0.6%~ 0.8%.

The composition, properties and morphology of Zn-Co alloy deposited from alkaline sulphate bath have been investigated[7]. The structure and morphology of the electrodeposits depended on many factors including temperature, current density, time of deposition and composition of the bath[8]. The purpose of alloying zinc with more noble metals is to improve its corrosion resistance properties, which depend on microstructure and constitution. The structure, constitution and corrosion resistance of the co-deposited zinc-cobalt alloy have been investigated by means of XRD, EXAFS, SEM and TEM. The results showed that the constitution and corrosion of the deposit changes with cobalt content[9, 10].

Recently, Mary[11] has studied the electrodeposition of ternary zinc-nickel-cobalt alloys from an acidic chloride bath. The influence of cobalt codeposition on surface brightness, and alloy deposit composition as well as cathodic current efficiency of the obtained Zn-Ni-Co alloy, and the effect of plating parameters, such as metals ions concentration, pH, and current density were examined. Tomachuk et al[12] has developed the pulse electroplated Zn-Co alloy.

In this paper, by the NSS test, the 5% NaCl solution immersion test and the SO_2 gas test, and the determining of the $\varphi_{corr}-t$ and R_p-t curves, the corrosion resistance of the electroplated Zn-Co alloy coating are studied systematically.

2 EXPERIMENTAL

2.1 Preparation of specimens

In galvanizing, an alkaline zincate solution was adopted, and in Zn-Co alloy plating the following bath composition was adopted:

ZnO	9~ 11 g/L
NaOH	90~ 110 g/L
$CoSO_4$	1.5~ 3.0 g/L
Stabilizer	30~ 50 g/L
Additive	8~ 12 mL/L
J_k	1~ 4 A/dm^2
Temperature	15~ 35 ℃
Anode	Zn and Fe plates arranged alternatively

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Two kinds of passivating agents were adopted: one was an ordinary tri-acid (sulfuric acid, nitric acid and chromic acid) low-chromium passivating solution, of which the passivated film has an iridescent colour; the other was a newly developed low-chromium passivating solution, of which the passivated film has a colour of olive. The difference of two kinds of the passivated films is the total content of Cr in the passivated film. Its composition and operating conditions are shown as follows:

CrO_3	5 g/L
Accelerating agent	4~ 10 g/L
Temperature	10~ 30 ℃
pH	1.3~ 1.7
Time	20~ 30 s

2.2 NSS test

When the spray method was adopted, intermittent spraying was carried out and every cycle was composed of spraying for 8 h and then holding for 16 h. The specimens used were classified into 3 groups, and each group was made up of 3 specimens. The test results showed that, in Group Ⅰ the specimens were used for alkaline Zn plating with passivated films in a colour of iridescent; in Group Ⅱ and Ⅲ, the specimens were used for Zn-Co alloys plating with passivated films in a iridescent colour and olive colour respectively. The thickness of each electroplated coating was 7 μm.

2.3 SO_2 gas test

The test was performed in a sealed chamber. The method was introduced as follows: First, blend 0.05 mol/L H_2SO_4 with 10 g/L $Na_2S_2O_3$, and then pour the prepared solution into the sealed chamber. The volume of the solution poured in should be as much as 1/50 that of the sealed chamber, and the temperature controlled at (25 ±2) ℃.

2.4 Determining of electrochemical corrosion parameters

In the determination of electrochemical corrosion parameters, the linear polarization method was adopted. The potential scanning rate was 0.2 mV/s. The electrolyte was a 5% NaCl solution. The auxiliary electrode was a Pt electrode. The reference electrode was a saturated calomel electrode.

When the cyclic volt-amper curves were determined, the potential scanning rate was 2 mV/s.

3 RESULTS AND DISCUSSION

The cobalt content of Zn-Co alloy coating by chemical analysis is 0.74% (mass fraction).

3.1 NSS test

Table 1 shows the NSS test results. When the white rust emerges, whose main composition is zinc oxide, the corrosion of coating is beginning to occur; when the red rust emerges, whose main composition is iron oxide, the corrosion of substrate is beginning to take place, therefore the coating can not protect the substrate from corrosion at this time.

As shown in Table 1, the corrosion resistance of the Zn-Co alloy coating treated by passivation is better than that of the galvanized coating, and especially, a Zn-Co alloy coating with passivated film in olive colour is the best. In the NSS test, no red rust was found on such a Zn-Co alloy coating after 1 200 h.

3.2 SO_2 gas test

The SO_2 gas test results are shown in Table 2.

From Table 2, it can be seen that in the atmosphere of SO_2 gas the corrosion resistance of the Zn-Co alloy coating is better than that of the galvanized coating obviously. Therefore, it will be particularly fit to be used as a protective coating in the industrial atmosphere.

3.3 Relationship between corrosion potential and immersion time

Fig. 1 shows the ϕ_{corr} vs t curves determined in a solution containing 5% NaCl.

As can be seen in Fig. 1, at the initial stage of immersion the difference between the ϕ_{corr} of the Zn-Co alloy coating and that of a galvanized coating is very small. After about 15 days, the ϕ_{corr} of the Zn-Co alloy coating begins to move toward the positive,

Table 1 Results of NSS test

Specimen	Time for white rust first appearing/h	Surface condition after 648 h	Time for red rust first appearing/h
Zn (passivated film in iridescent colour)	240	Colour of film faded, white rust appeared everywhere	480
Zn-Co (passivated film in iridescent colour)	480	Colour of film becomes dull, many white rust spots appeared	1200 (nothing appeared)
Zn-Co (passivated film in olive colour)	500	Few white rust spots appear in marginal area	1200 (nothing appeared)

Table 2 Results of SO_2 test

Specimen	Time for white rust first appearing/ h	Surface condition of passivated film (after 20 h)
Zn (passivated film in iridescent colour)	4	All film no blister occurring
Zn-Co (passivated film in iridescent colour)	20	White rust spots appearing everywhere
Zn-Co (passivated film in olive colour)	20	No obvious change

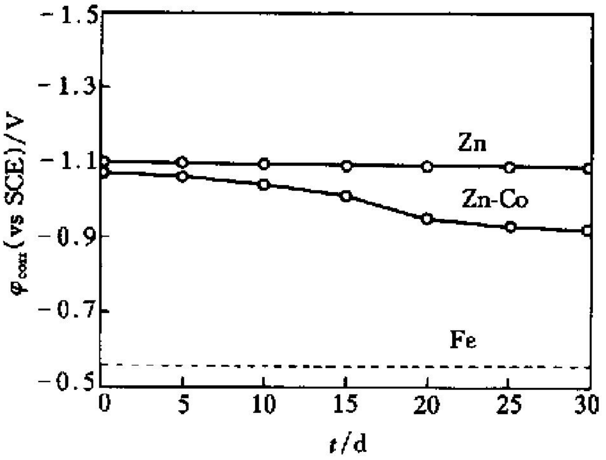

Fig. 1 ϕ_{corr} vs t curves showing contrast between galvanized coating and Zn-Co alloy coating in 5% NaCl solution

but never exceeds the negative potential of Fe (the potential of Fe in this medium is about − 560 mV). Therefore, as far as the Fe substrate is concerned, the Zn-Co alloy is still an anodic coating, but its potential difference becomes smaller and the corrosion rate becomes lower correspondingly. This is the main reason why the corrosion resistance of the Zn-Co alloy coating is better than that of the galvanized coating.

3.4 Relationship between polarization resistance and immersion time

The R_p vs t curves were determined by the linear polarization method (See Fig. 2).

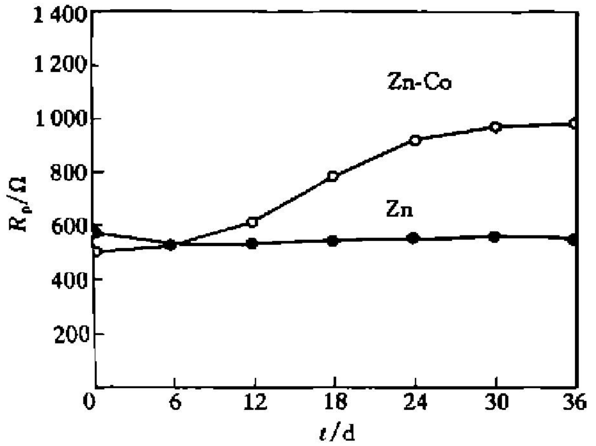

Fig. 2 R_p vs t curves showing contrast between galvanized coating and Zn-Co alloy coating in 5% NaCl solution

From Fig. 2, it can be seen that at the initial time the R_p of the Zn-Co alloy coating is very similar to that of a galvanized coating. However, with the increase of immersion time, the R_p of the Zn-Co alloy coating becomes greater, whereas that of the galvanized coating becomes smaller. In other words, the corrosion resistance of the Zn-Co alloy coating basically keeps unchanged. It can be deduced that the corrosive product of the Zn-Co alloy coating plays a comparatively great role in depressing the corrosion process and that is the reason why the corrosion rate becomes lower after corrosion has extended to a certain degree in the Zn-Co alloy coating.

3.5 Cyclic voltammogram curves

Fig. 3 shows a contrast between the cyclic voltammogram curves of the Zn-Co alloy coating and the galvanized coating in a NaCl solution.

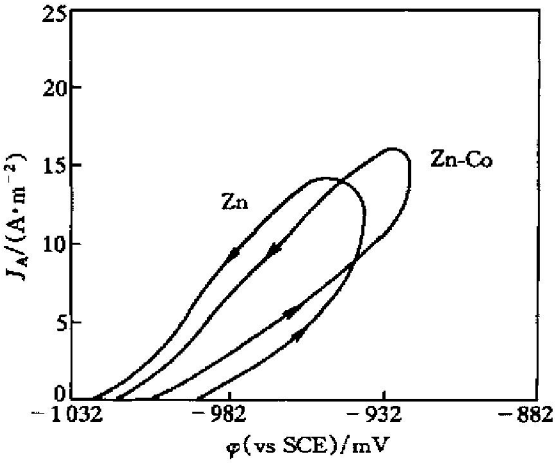

Fig. 3 Cyclic voltammogram curves between Zn and Zn-Co alloy coating in 5% NaCl solution

As can be seen in Fig. 3, the scanning area of the Zn-Co alloy coating is smaller than that of the galvanized coating, and in addition, the retrace line of the Zn-Co alloy coating is below that of the galvanized coating. This fact also illustrates that the corrosive product of the Zn-Co alloy coating plays a greater role in depressing the corrosion process than that of the galvanized coating.

Fig. 4 shows the cyclic voltammogram curves of electroplated coatings of Group Ⅰ, Ⅱ, and Ⅲ As can be seen in Fig. 4, the cyclic voltammogram curves of the Zn-Co alloy coating and Zn coating after passivation treatment basically coincide with each other, and their retrace scanning curves are very approximate to the ortho-scanning curves. It follows that the properties of all the passivated films formed on the electroplated coatings in the three groups are basically similar to one another. That is to say, they have not only, to a certain extent, an excellent role to depress the anodizing process, but also have an excellent degree of self-repair. It is known from Ref. [13] that passive films of the Zn-Co alloy and Zn coating are composed of CrO_3, Cr_2O_3, $Zn(OH)_2$, ZnO and H_2O. However, the former contains more Cr^{6+}, and the abundance of cobalt metal layer is formed between interface of deposit layer and passive film. This is the main provision that Zn-Co alloy possesses high corrosion resistance.

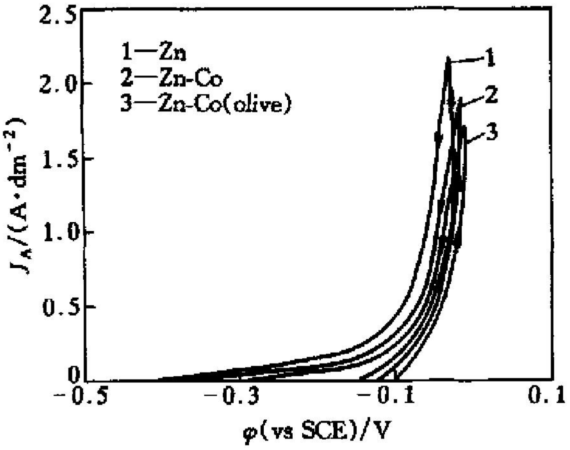

Fig. 4 Cyclic voltammogram curves of Zn and Zn-Co alloy coating after passivation treatment in 5% NaCl solution

4 CONCLUSIONS

1) The corrosion resistance of the electroplated Zn-Co alloy coating is better than that of the galvanized coating. When the thickness of the two kinds of coatings is same, the corrosion resistance of the former is three times higher than that of the latter.

2) The corrosion resistance of the Zn-Co alloy coating is especially remarkable in SO_2 gas atmosphere. Therefore, the alloy coating is particularly fit to be used as a protective coating in industrial atmosphere.

3) The reason why the Zn-Co alloy coating has such a high corrosion resistance is that its corrosive product has a comparatively great role in depressing the further corrosive process.

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