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## Corrosion behavior of sintered zinc-aluminum coating in NaCl solution<sup>①</sup>

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**[Abstract]** Sintered zinc-aluminum coating (SZAC) was prepared using zinc flakes, aluminum flakes and CrO<sub>3</sub> as main raw materials. The corrosion behavior of SZAC in 3.5% NaCl solution was studied by means of SEM, EDS, EIS and so on. Results indicate that aluminum corroded in advance of zinc to produce speculate or spherical substances, which attaches to SZAC and adds mass to it. Corrosion production passivates metal powders in SZAC, causes  $E_{\text{corr}}$  of SZAC to increase gradually, and causes the arising of the third time constant in EIS, which corresponds to the insulation of corrosion production.

**[Key words]** sintered zinc-aluminum coating; corrosion behavior; NaCl solution

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### 1 INTRODUCTION

Sintered zinc-aluminum coating (SZAC) was also called dacromet. It was a kind of anticorrosion coating mainly for iron and steel<sup>[1]</sup>. It was widely used in Japan, US and Europe in mobile industry, agricultural machinery and so on<sup>[2~5]</sup>. It replaced zinc-electroplating and cadmium electroplating in many cases<sup>[6~8]</sup>. SZAC has been studied in our country since early in 1990s. It developed rapidly, several homemade product lines were built up already.

Nearly no study reports on corrosion behavior and anticorrosion mechanism of SZAC has been seen. It was indicated that SZAC could provide sacrificial anodes protection for iron and steel<sup>[2]</sup>. It was also indicated that aluminum in SZAC could repress white rust<sup>[5]</sup>. But no relevant study details were reported.

The corrosion behavior of SZAC in NaCl solution is studied in this article.

### 2 EXPERIMENTAL

SZAC was prepared on A3 steel substance using zinc flakes, aluminum flakes and CrO<sub>3</sub> as main raw materials. Detail preparation process can be seen in Ref. [9].

To conduct corrosion, samples with SZAC were dipped at room temperature of about 20 °C into 3.5% NaCl solution that was refreshed every 6 d. The top of samples was 2 cm lower than solution surface. In order to investigate the corrosion behavior of SZAC, evolution

of mass, appearance, composition,  $E_{\text{corr}}$  and electrochemical impedance spectroscopy (EIS) with time were researched by means of SEM, EDS, electrochemical methods and so on. In comparison, zinc plated A3 steel, zinc plated and olive passivated A3 steel were also dipped in NaCl solution, observed and weighed.

Microstructural characterization was performed using a S570 scanning electron microscope (SEM). Composition analysis was performed using TN-5502 X-ray energy dispersive spectroscopy (EDS).

Electrochemical tests were performed in aerated 3.5% (mass fraction) NaCl solutions, using a saturated calomel electrode as reference and platinum sheet as auxiliary electrode.

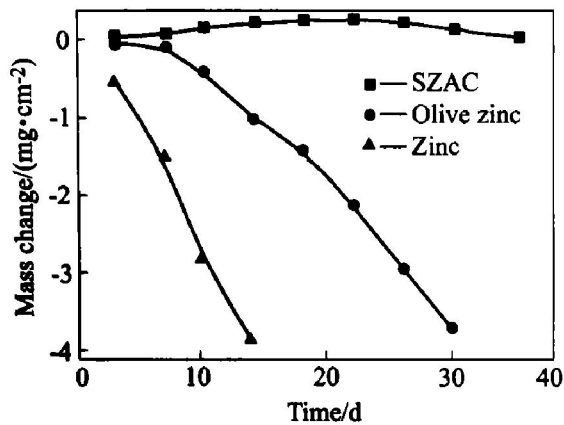
The DC polarization measurements were performed using an EG&G Parc M273 potentiostat controlled via EG&G Parc M352 software, test area was 1 cm<sup>2</sup> and scan rate was 0.5 mV/s.

The small amplitude EIS measurements were carried out using an EG&G Parc M273 potentiostat coupled to an EG&G M5210 lock-in amplifier. The instruments were controlled via EG&G Parc M388 software. The impedance spectra were collected at open circuit potential (OCP) with a 10 mV amplitude.

### 3 RESULTS AND DISCUSSION

#### 3.1 Evolution of mass

Mass changes of the three kinds of coatings—zinc plating, olive passivated zinc plating and SZAC in NaCl solution with time were illustrated in Fig. 1.



**Fig. 1** Mass changes of three coatings in NaCl solution with time

It can be seen that zinc plating and olive zinc plating lost masses during corrosion process. This means that their corrosion products neither attach to them nor pile-up. Such corrosion behavior benefits coatings to continuously serve as sacrificial anodes.

SZAC gained fractional masses in corrosion process, it began to lose masses until after 20 d. Masses gain means corrosion products attachment and accumulating that will hinder the succession of sacrificial anode protection.

### 3.2 Evolution of appearance

Loose corrosion products occurred on the surface of zinc and olive zinc platings and resulted in the changes of appearance; both platings exhibited excellent sacrificial performance by not becoming rusty until sizeable substrate area was shown up. While no loose products occurred on the surface of SZAC, thus it had no evident changes in appearance except being darkled. SZAC showed poor sacrificial performance — red rust spot appeared when no substrate can be seen.

Macro changes of SZAC and olive zinc plating appearance are illustrated in Fig. 2.

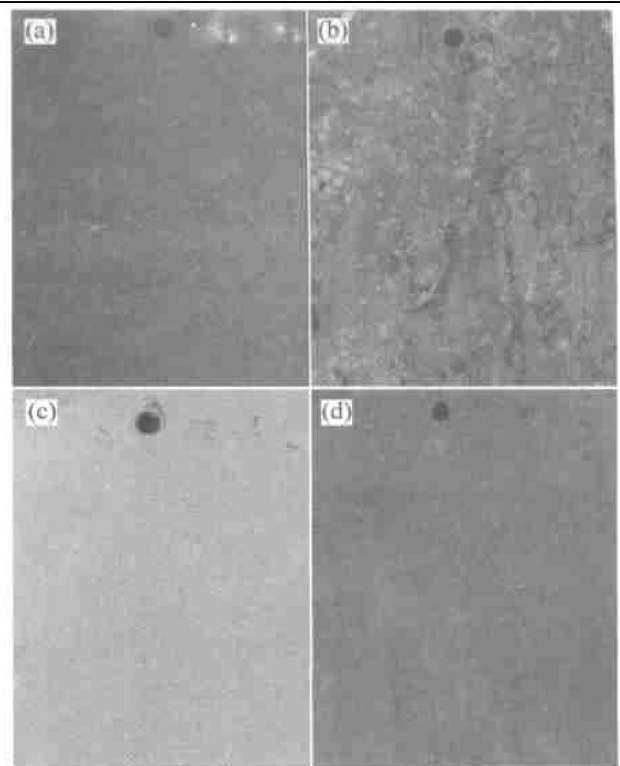
Evolution of SZAC microstructure during corrosion was shown in Fig. 3.

It can be seen that metal flakes piling in the coating before corrosion were gradually covered by spiculate and spherical corrosion products.

### 3.3 Evolution of composition

Composition analysis results of SZAC before and after corrosion and that of corrosion products are shown in Table 1.

It can be found that aluminum and chromium content dropped gradually while the content of zinc and chlorine increased gradually with corrosion time prolonged. It can also be found that more Al and Cl were found in spiculate and spherical corrosion products than in SZAC. So corrosion



**Fig. 2** Macro changes of SZAC and olive zinc plating appearance  
(a) —Olive zinc, 0 d; (b) —Olive zinc, 28 d;  
(c) —SZAC, 0 d; (d) —SZAC, 40 d

**Table 1** Composition of SZAC before and after corrosion and that of corrosion products (w, %)

Sample	Zn	Al	Cr	Cl
0 d	0.81	0.15	0.05	0
6 d	0.83	0.09	0.04	0.04
12 d	0.84	0.07	0.04	0.05
30 d	0.82	0.10	0.03	0.06
spiculate	0.69	0.16	0.01	0.14
spherical	0.63	0.21	0.01	0.16

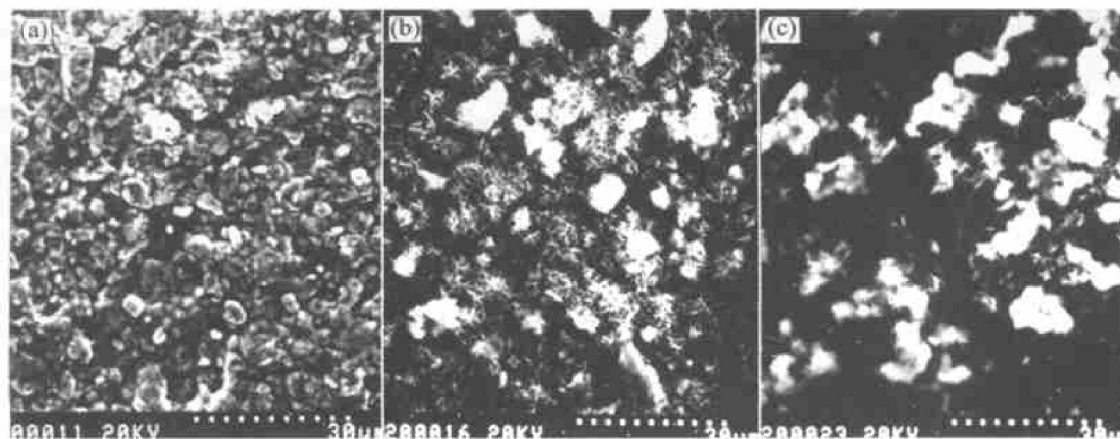
products was speculated to be basic aluminum chloride because aluminum chloride is easy to hydrolyze.

Composition results come to such an conclusion that aluminum in the coating corroded earlier than zinc, the former protected the latter.

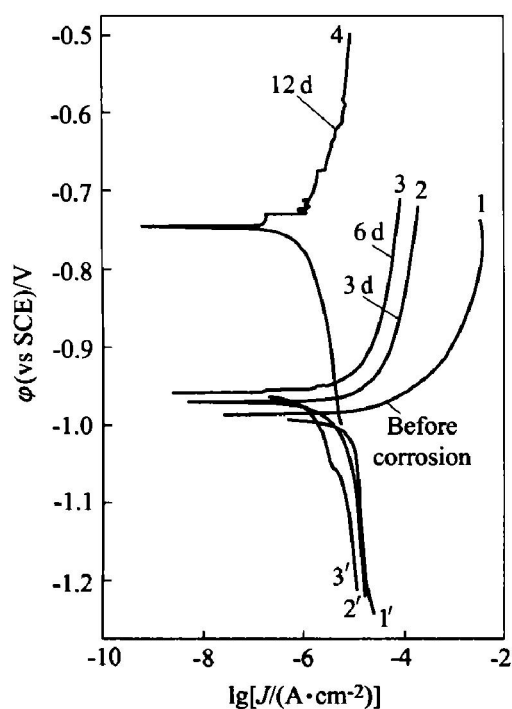
### 3.4 Evolution of polarized curves

Evolution of polarized curves for SZAC with time is shown in Fig. 4.

It can be seen that cathodic process remains nearly unchanged, but anodic reaction is restrained gradually with time. According to this result, it can be explained why SZAC can't continuously act as anode for iron substrate: with corrosion products accumulation on surface, metal powers was passivated, thus  $E_{\text{corr}}$  of the coating

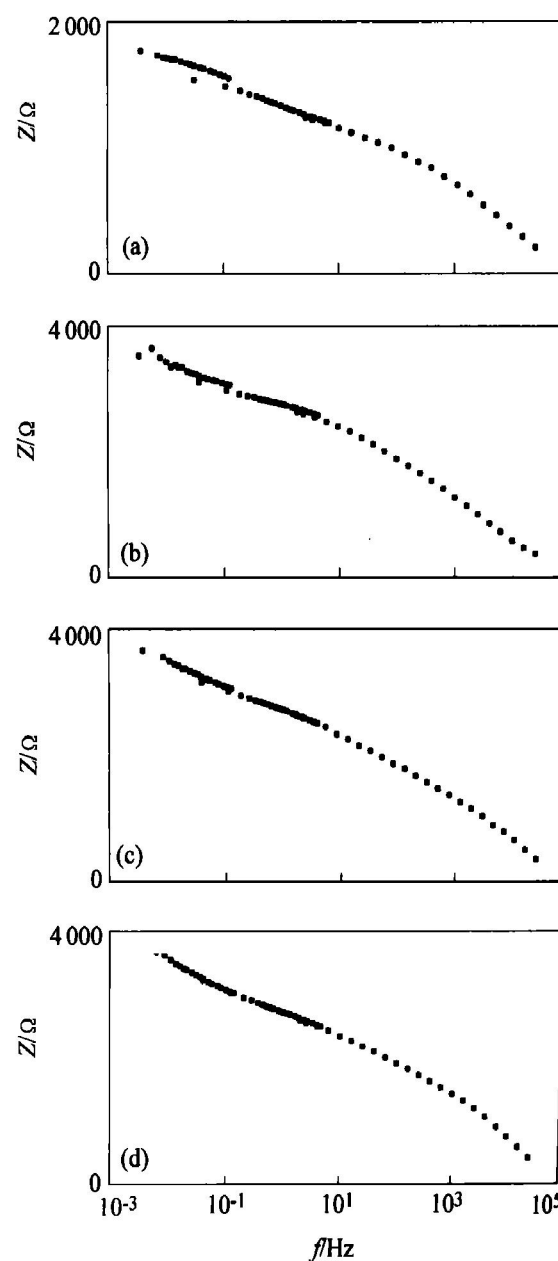


**Fig. 3** Evolution of SZAC microstructure  
(a) -0 d; (b) -18 d; (c) -30 d



**Fig. 4** Evolution of polarized curves of SZAC with time

1 and 1' —Before corrosion; 2 and 2' —3d;  
3 and 3' —6d; 4 and 4' —12d



**Fig. 5** Evolution of Bode diagrams for SZAC( $f$  vs  $z$ )

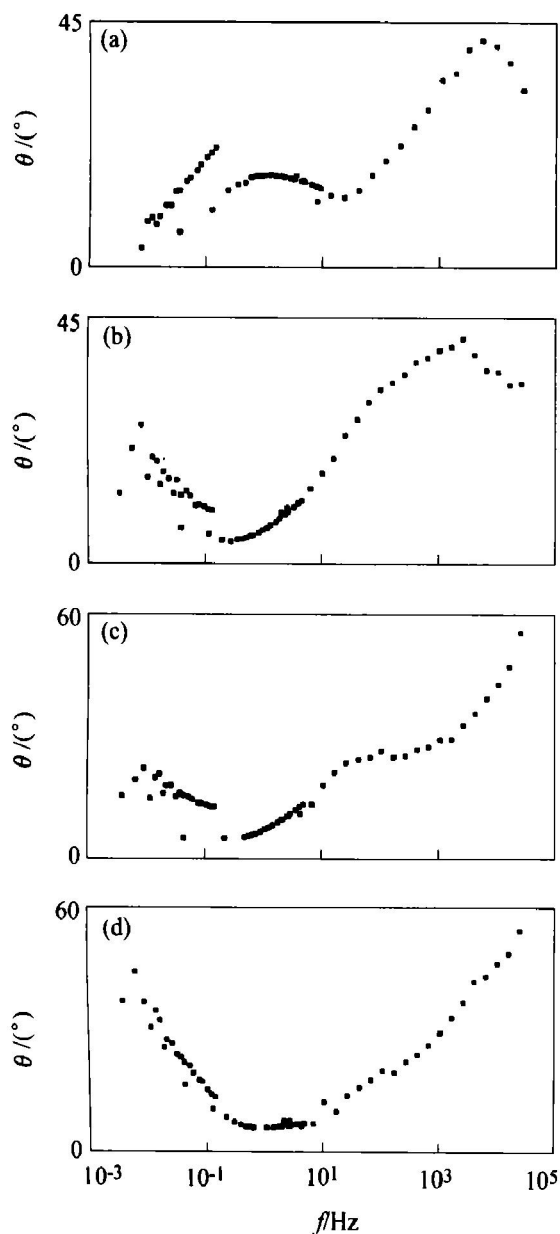
(a) —Before corrosion; (b) —6d;  
(c) —12d; (d) —18d

moved positively, when  $E_{\text{corr}}$  was beyond a limit, SZAC lost the ability to act as sacrificial anode.

### 3.5 Evolution of EIS

Evolution of Bode diagrams of SZAC with time is shown in Figs. 5, 6. There are two time constants in Bode diagram before corrosion, characteristic frequencies changed firstly with corrosion, then the third time constant appeared. The evolution of SZAC Bode diagram was similar to that of zinc-rich paint<sup>[10]</sup>.

Taking above analysis results into account, we suppose that SZAC acted as pure metal in initial stage of corrosion because of good contact between metal powders



**Fig. 6** Evolution of Bode diagrams for SZAC( $f$  vs  $\theta$ )

(a) —Before corrosion; (b) —6d;  
(c) —12d; (d) —18d

in the coating, so in this stage high frequency arc corresponded to charge transfer process of metal corrosion and low frequency arc was produced by oxygen diffusion; while in latter stage of corrosion, new time constant corresponding to the insulation of corrosion products occurred because corrosion products cut off contact between metal powders and with substrate.

## 4 CONCLUSION

Aluminum in SZAC corroded in advance of zinc in NaCl solution to produce spiculate and spherical corrosion products that attached to the coating and added mass to the coating. Corrosion products passivated metal powders in the coating, and elevated  $E_{\text{corr}}$  and resulted in the occurring of the third time constant corresponding to the insulation of corrosion products.

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