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Semi-conductive properties of melanization of chromate zinc plates ①

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[Abstract] The anodic polarization curves of chromate zinc plates were studied under the condition of with and without illumination. It is found that the chromate film of zinc plate is characterized by an *n*-type semi-conductive property. The illumination on the surface and the addition of Pb in the surface raises the anodic photocurrent and plays a part of the *n*-type property in the film. Contrarily, Ag in the film plays a part of the *p*-type dopant. The effects of quantitative Pb^{2+} and Ag^{+} in bath on the melanization(black patina) of zinc plate after chromate treatment also has been studied by comparing the lightness differences ΔL by means of a whiteness meter. It is found that the lightness decreasing process (the melanization rate) is consistent with the Wagner equation $\Delta L = kt^{1/2} + C$, and that Pb in the film increases k, on the other hand, Ag in the film decreases k of the melanizing rate.

[Key words] zinc sulfate bath; melanization; semi-conductive property
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1 INTRODUCTION

The corrosion of a chromate zinc at the initial stage is the decreasing process of surface lightness, and is usually called melanization (black patina) of zinc plate of which the product is $Zn_{1+\delta}O$ with the property of an *n*-type semi-conductor, and the illumination suppresses the melanization[1]. The most important effecting factor promoting melanization is Pb in the form of micelle existing in sulfate bath, Pb is adsorbed on the coating surface and settles in the chromate film in which its valence state is more than 2[2,3]. Multivalent Pb ions doped in the *n*-type semiconductor ZnO promoting melanization on zinc plate, and so metal impurities with a valence state lower than 2 may exert a contrary action to suppress melanization. It is reported that the chemical reaction and electrochemical reaction of zinc oxide under beaming has been studied[4]. It has also been reported that metal excess ZnO has an *n*-type semi-conductive property at high temperature[5,6]. However, no report on melanization of zinc plate at its initial corrosion stage and the behavior of semi-conductive effects has ever been found in the literatures at home and abroad. Generally, in the sulfate bath at a high flow rate and high current galvanizing the Pb-Ag alloy anode is employed, and in this case Pb^{2+} and Ag^{+} will produce micelle with SO_4^{2-} in the bath before electrodeposition. In this study, the samples were galvanized in sulfate bath containing different amounts of Pb^{2+} and Ag^{+} ions, respectively, and then treated by chromate solution. The anodic photocurrents of chromate zinc plates are studied under the condition of illumination and without illumination, so as to research its *n*-type semi-conductive behavior. And the melanization on their surfaces was cultivated at the same temperature and humidity, and the changes of their lightness differences were used to denote the rate of melanization so as to facilitate investigating the effects of the two ionic compounds with different valence states on melanization.

2 EXPERIMENTAL

2.1 Materials

Cathodes electroplated zinc were of cold-rolled low carbon steel plate with a size of 60 mm × 80 mm × 1 mm.

In the experiment all the chemicals used were of chemical pure and the anode adopted was of high-purity zinc. Composition of the bath without impurities and that of the chromate solution adopted as well as their technological specification are shown in Table 1. The baths with Pb^{2+} or Ag^{+} were prepared by adding Pb^{2+} and Ag^{+} with concentration of 5, 15 mg/L respectively in the forms of $Pb(NO_3)_2$ and $AgNO_3$.

2.2 Measure condition of anodic polarization

M273 electrochemical measure system with a column electrolytic cell and M352 software were used to measure anodic polarization curves at a temperature of (30 ±1) ℃. To decrease the chemical and electrochemical dissolution of chromate films during the test, an electrolyte of 3 % NaCl solution with pH 9 ± 0.1 adjusted with NaOH was prepared and a scanning

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speed of 100 mV/s was adopted[7,8]. The angle of incidence and distance from the light source to cell remained constant. The self-rectifier mercury lamp was used for the illumination source.

2.3 Humidity test

A humidity test was performed on CS501 super-constant temperature bath at a temperature of (50 ± 1) ℃ and a humidity of more than 95%. The lightness of the sample surfaces was measured by three parallel testing every one hour using YQ-Z-48A whiteness meter. The light source was a 12 W fluorescent lamp.

3 RESULTS

3.1 Anodic polarization curves

In this test, the anodic polarization curves were observed three times. We confirmed that the chromate film of testing sample remained a good status. The three curves of a sample have good superposition. Anodic polarization curves of different samples with illumination and without illumination are shown in Fig.1, which shows that the anodic polarization currents obtained from three types baths with illumination are all greater than those without illumination. The photo difference of current density under the potential of 1.8 V (vs SCE) is as follows: pure bath, 1.3 mA/cm^2; bath containing 15 mg/L Pb^{2+}, 5.5 mA/cm^2; bath containing 15 mg/L Ag^{+}, 1.0 mA/cm^2.

It shows that the chromate film of pure zinc plate has an *n*-type semi-conductive property. And Pb plays a part of the *n*-type dopant in the film; Ag plays a part of the *p*-type dopant in the film.

3.2 Rate equations of melanization

In the humidity test without illumination, the relationship between the lightness difference of the surfaces and the duration time is shown in Table 2. The curves of ΔL and $t^{1/2}$ are shown in Fig.2.

The effects of bath containing different ionic contents on the melanizing rate of zinc plate was fitted according to the following Wagner equation:

$$\Delta L = kt^{1/2} + C$$

where k is a rate constant, and C is an intercept of the fitted straight line.

For electrolyte containing Pb^{2+} 15 mg/L

$$\Delta L = 1.0827\, t^{1/2} + 0.0417 \quad (r = 0.9993)$$

For electrolyte containing Pb^{2+} 5 mg/L

$$\Delta L = 0.9069\, t^{1/2} + 0.0695 \quad (r = 0.9974)$$

For pure bath of zinc sulphate

$$\Delta L = 0.7580\, t^{1/2} + 0.1099 \quad (r = 0.9905)$$

For electrolyte containing Ag^{+} 5 mg/L

$$\Delta L = 0.6351\, t^{1/2} + 0.0916 \quad (r = 0.9891)$$

For electrolyte containing Ag^{+} 15 mg/L

$$\Delta L = 0.5761\, t^{1/2} + 0.0114 \quad (r = 0.9907)$$

The constants of the melanizing rate are compared as

$$k(15\ mg/L\ Pb^{2+}) > k(5\ mg/L\ Pb^{2+}) > k(\text{pure bath}) > k(5\ mg/L\ Ag^{+}) > k(15\ mg/L\ Ag^{+})$$

It was found that under the humidly hot condition the corrosive behavior of zinc plate at its initial stage is consistent with Wagner equation, and the

Table 1 Composition of bath and chromate solution and operation conditions

	Composition	Operation conditions			
Bath	250 g/L $ZnSO_4 \cdot 7H_2O$ + 120 g/L Na_2SO_4	R.T.	pH 1.7	5 min	6.3 A/dm^2
Chromate solution	90 g/L CrO_3 + 6 g/L $BaCO_3$	R.T.	pH 1.3	20 s	

Fig.1 Anodic polarization curves with and without illumination
(a) —Pure; (b) —Containing Pb^{2+}; (c) —Containing Ag^{+}
— With illumination; ··· Without illumination

Fig.2 Relationship between ΔL and $t^{1/2}$

Table 2 Surface lightness difference (ΔL) at different duration times and in different solutions

t/h	$\Delta L/(cd \cdot m^{-2})$				
	Pure bath	5 mg/L Ag^+	15 mg/L Ag^+	5 mg/L Pb^{2+}	15 mg/L Pb^{2+}
0	0	0	0	0	0
1	0.96	0.78	0.68	1.04	1.17
2	1.27	1.08	0.81	1.43	1.62
3	1.49	1.27	0.9	1.65	1.93
4	1.63	1.38	1.12	1.88	2.16
5	1.78	1.46	1.34	2.06	2.46
6	1.85	1.55	1.47	2.25	2.68

melanizing rate of the zinc plates from the bath containing Pb^{2+} is higher than that of the plates from the bath of pure Zn, while the melanizing rate of the plates from the bath containing Ag^+ is lower than that of the plates from the pure bath. This implies that the existence of Pb^{2+} in bath promotes melanization and Ag^+ plays a contrary action. The changes of rate constants are almost corresponding with their concentrations.

3.3 Effects of illumination on melanization

The results of surface lightness difference of the two faces of a sample are shown in Table 3, of which one face is under illumination and the other face is not under illumination during melanization. The relationship between the lightness difference of the surfaces and the duration time is shown in Table 3, and the relationship between ΔL and $t^{1/2}$ is shown in Fig.3.

Fig.3 shows that Pb promotes the generation of melanization and Ag suppresses it nevertheless with or without illumination. And the rates of melanization with illumination on three samples are all less than the rates of melanization without illumination.

4 DISCUSSION

As for the typical n-type semi-conductor of $Zn_{1+\delta}O$, the width of forbidden band is 3.2 eV, and when multi-valent metal compounds settle in $Zn_{1+\delta}O$, they will play a part of the n-type dopant and reduce greatly the width of its forbidden band width,

Table 3 Surface lightness difference (ΔL) of samples with and without illumination

t/h	ΔL					
	Pure zinc sulfate bath		20 mg/L Pb^{2+}		20 mg/L Ag^+	
	WI	WHI	WI	WHI	WI	WHI
0	0	0	0	0	0	0
1	10.24	0.96	1.07	1.55	0.05	0.25
2	0.40	1.27	1.89	2.07	0.16	0.41
3	0.63	1.49	2.51	2.96	0.21	0.68
4	0.90	1.78	2.86	3.82	0.22	0.74

WI represents melanization with illumination; WHI represents melanization without illumination.

Fig.3 Relationship of surface difference (ΔL) to $t^{1/2}$ with and without illumination

(a) —Pure solution; (b) —Containing Pb; (c) —Containing Ag

● — Without illumination; ○ — With illumination which causes the increasement of the melanizing reaction rate. Contrarily, when one-valent metallic oxides settle in $Zn_{1+\delta}O$, they will play a part of the p-type dopant and increase its forbidden band width, which decreases the melanizing reaction rate. It can be conceived that if one-valent metal ions can be added in electrolyte and combined with SO_4^{2-} to produce an insoluble salts or micelles, this salt will be helpful to suppress melanization on zinc plate. The experimental results show that the melanizing process is in fact an oxidizing process in an n-type semi-conductive Zn oxide.

5 CONCLUSIONS

1) The chromate film of zinc plate has an n-type semi-conductive property. Both illumination on the surface of the film and the addition of Pb, Ag in the film raise the anodic photocurrent and Pb plays a part of the n-type dopant in the film, contrarily, Ag in the film plays a part of the p-type dopant.

2) The rates of melanization of zinc plate electro-deposited from pure zinc bath, and from bath containing Ag^+ or Pb^{2+} after chromate treatment are all consistent with the Wagner equation.

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