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Electrochemical behavior of electroplated Zn-P alloy ①

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[Abstract] The electroplating behavior of Zn-P alloy on copper from light acid chloride solutions (LACS) was investigated using cyclic voltammetry and linear potential sweep method. It is found that, under the experimental conditions, the concentrations of H_3PO_3 and ascorbic acid in LACS change the codeposition mechanism of Zn-P alloy, the addition of H_3PO_3 into LACS promotes the three-dimentional (3-D) instantaneous nucleation/growth, while the addition of ascorbic acid promotes the two-dimentional (2-D) instantaneous nucleation and layer-by-layer growth. H_3PO_3 and zinc ions inhibit the deposition each other. The experimental results also show that H_3PO_3 in the LACS can be reduced on the cathode individually, and low pH value of the LACS promotes the reduction of H_3PO_3.

[Key words] Zn-P alloy; codeposition; electrochemical behavior
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1 INTRODUCTION

Electroplated Zn-P coatings exhibit a range of fascinating properties, such as high corrosion resistance, excellent paintability and phosphoratability, fine weldability and formability[1]. Therefore, in recent years, there have been several investigations on preparing different kinds of Zn-P coatings[2~4]. However, the literatures on the behavior of electroplated Zn-P alloy are few. In this paper the authors intend to study the behavior of Zn-P alloy codeposition by means of cyclic voltammetry and linear potential sweep technique, and try to reveal some basic causes about the promising properties of the electrodeposited Zn-P coatings.

2 EXPERIMENTAL

The basic electrolyte (BE) was prepared with AR grade chemicals and twice distilled water according to the composition listed in Table 1. The intention of adding ascorbic acid into BE(B) was to found the basis for studying Zn-Fe-P alloy electroplating process, where ascorbic acid would be used as a kind of reductor of Fe^{2+}. The LACS were obtained by adding different amounts of Zn^{2+} ions, H_3PO_3 or both of them in the BE. The environment temperature was maintained at 298 K by thermostat. A simple glass electrolysis cell with provision for inlet and outlet for deaerating the LACS with N_2 gas was used. The working electrode (WE) was Cu wire (purity 99.9%) with a plain bottom area of 0.0573 cm^2 exposed. A large area platinum foil was used to polarize the WE. A saturated calomel electrode (SCE) with a Luggin probe near the WE surface was used as reference electrode, which was connected to the electrolysis cell with a double salt bridge system.

Table 1 Composition of BE

Electrolyte	Component	$\rho/(g\cdot L^{-1})$
BE(A)	$Na_3C_6H_5O_7\cdot 2H_2O$	12
	EDTA-2Na	3.6
	H_3BO_3	16
	KCl	160
BE(B)	BE(A)	191.6
	Ascorbic acid	10

HD-1A low-superlow frequency function generator, HDV-7C transistor potentiostat and LZ3-204 X-Y recorder were used for electrochemical measurement. Before each experiment, the exposed surfaces of the WE were polished by Al_2O_3 emery papers from 3 through 1 to 0.5 μm, rinsed with the twice distilled water, washed in acetone, rinsed with the twice distilled water again and then dried in air. Meanwhile, the LACS were deaerated for 15 min.

3 RESULTS AND DISCUSSION

3.1 Reduction of H_3PO_3

Fig. 1 shows the cyclic voltammograms of Cu electrodes in LACS with or without H_3PO_3. According to our previous study[5], the current peak at electrode potential of about −1.20 V corresponded to the reduction of H_3PO_3, which rised with increasing concentration of H_3PO_3 in LACS, while this peak is absent in the BE. The result indicates that, under the experimental conditions, H_3PO_3 in the LACS can be reduced on the cathode individually. Fig. 1 also illustrates that, according to the reduction potential of H^+, the reduction of H_3PO_3 first promotes the reduc-

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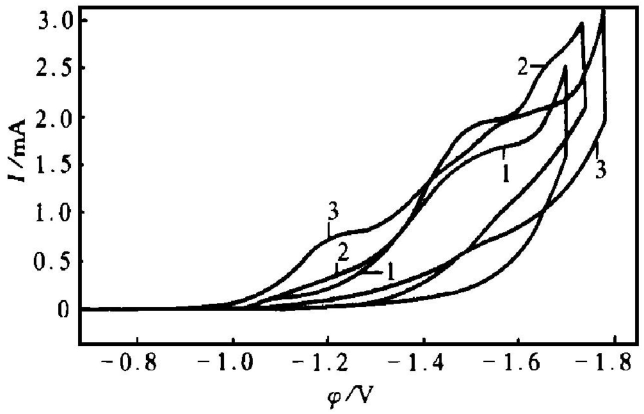

Fig. 1 Cyclic voltammograms of Cu electrodes at potential scan rate 100 mV/s, pH3 and 298 K
1 —BE(A); 2 —BE(A) + H_3PO_3(2 g/L);
3 —BE(A) + H_3PO_3(6 g/L)

tion of H^+, then inhibits the reaction, which allows the electroplating current efficiency of Zn-P alloy to be high.

On the other hand, the reduction of H_3PO_3 is mostly affected by the potential of hydrogen of the LACS. Fig. 2 shows that the low pH of the LACS promotes the reduction reaction of H_3PO_3. The phenomenon supports the explanation of some authors using the following equation[6]:

$$H_3PO_3 + 3H^+ + 3e^- \longrightarrow P_{ad} + 3H_2(g)$$

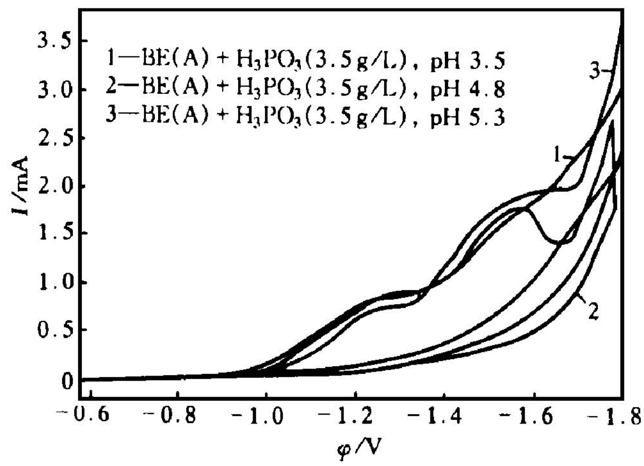

Fig. 2 Reduction of H_3PO_3 at different pH at potential scan rate of 100 mV/s and 298 K
1 —BE(A) + H_3PO_3(3.5 g/L), pH 3.5;
2 —BE(A) + H_3PO_3(3.5 g/L), pH 4.8;
3 —BE(A) + H_3PO_3(3.5 g/L), pH 5.3

where the subscription between "ad" designates adsorbed state.

3.2 Interaction between H_3PO_3 and Zn^{2+}

Fig. 3 shows the influence of H_3PO_3 on the reduction of Zn^{2+}. Deposition of zinc does not occur until the cathodic potential reaches approximately − 0.95 V. This potential, which is about 160 mV more negative than the equilibrium potential of zinc

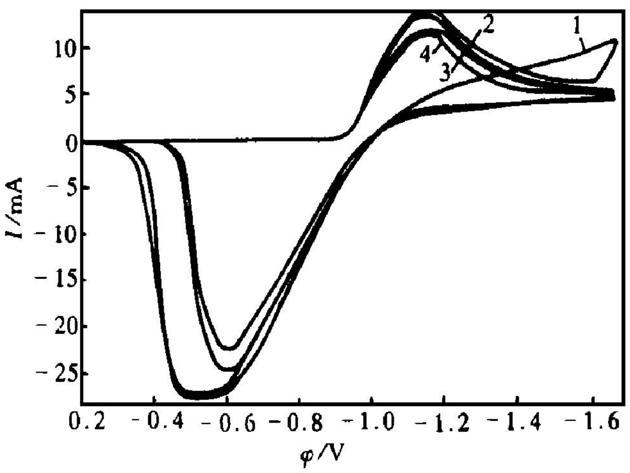

Fig. 3 Influence of H_3PO_3 on reduction of Zn^{2+} at potential scan rate 100 mV/s, pH 3 and 298 K
1 —BE(A) + $ZnCl_2$(86 g/L);
2 —BE(A) + $ZnCl_2$(86 g/L) + H_3PO_3(1 g/L);
3 —BE(A) + $ZnCl_2$(86 g/L) + H_3PO_3(3 g/L);
4 —BE(A) + $ZnCl_2$(86 g/L) + H_3PO_3(7 g/L)

(− 0.778 V vs SCE), indicates that extra energy is needed for zinc to overcome the barrier of heterogeneous deposition on a foreign substance (Cu). In the anodic branches of zinc or zinc-phosphorus deposition, the major dissolution peaks occur at different potentials indicating that different zinc phases were involved. Also, as can be seen from Fig. 3 that the reduction current peak of zinc in the cathodic branch decreases with increasing concentration of H_3PO_3 in the LACS, indicating that H_3PO_3 inhibits the deposition of zinc. The shapes of cyclic voltammogram are different in the solutions containing different amounts of H_3PO_3. In the absence of H_3PO_3, there is a current loop in the cathodic branch of zinc, which indicates a three-dimensional (3-D) nucleation and subsequent grain growth. However, this cross-over is not seen in the LACS with H_3PO_3, which indicates a two-dimensional (2-D) layer-by-layer growth[7~10]. The promising properties of Zn-P alloys over pure zinc coatings may be somewhat attributed to the change of the electrodeposition mechanism of zinc by H_3PO_3.

Meanwhile, good linear relationships were observed between I_p and $1/\varphi_p$ (see Fig. 4), indicating the deposition of Zn or Zn-P following instantaneous nucleation/growth mechanism[7~10], where I_p and φ_p are nondimensional quantities.

Fig. 5 shows some linear polarization curves in different LACS, which illustrates that the reduction of ascorbic acid increases the reduction overpotentials of H^+ and H_3PO_3. The difference between curve (4) and curve (5) indicates that the zinc ions in the LACS inhibit the reduction of H_3PO_3. The curve-shapes in Fig. 6 also support the above-mentioned views, and further convince that the H_3PO_3 in LACS can be reduced on the WE surface individually.

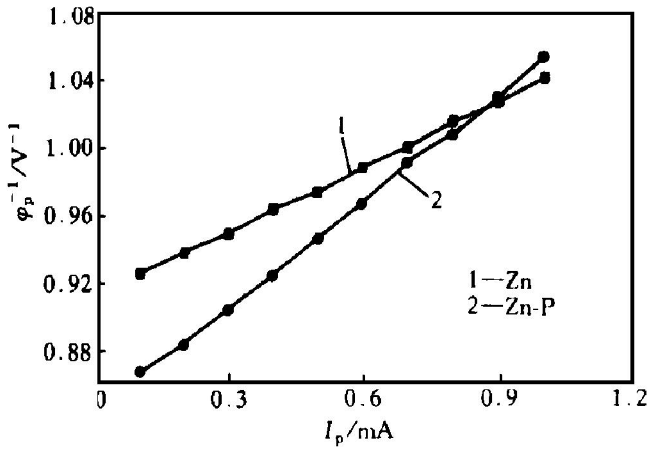

Fig. 4 Plot of I_p vs φ_p of Zn or Zn-P on copper

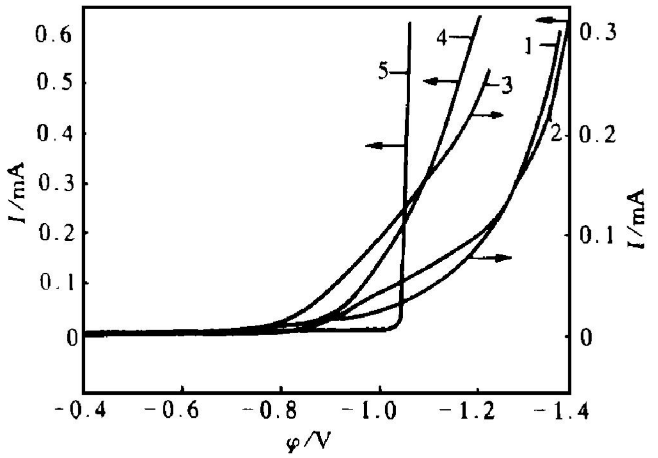

Fig. 5 Linear potential sweep curves of Cu in LACS with Zn^{2+} and H_3PO_3 at potential scan rate 1 mV/s, pH 3 and 298 K

1 —BE(A); 3 —BE(B);

3- BE(A) + H_3PO_3(4 g/L);

4 —BE(B) + H_3PO_3(3.5 g/L);

5 —BE(B) + $ZnCl_2$(86 g/L) + H_3PO_3(3.5 g/L)

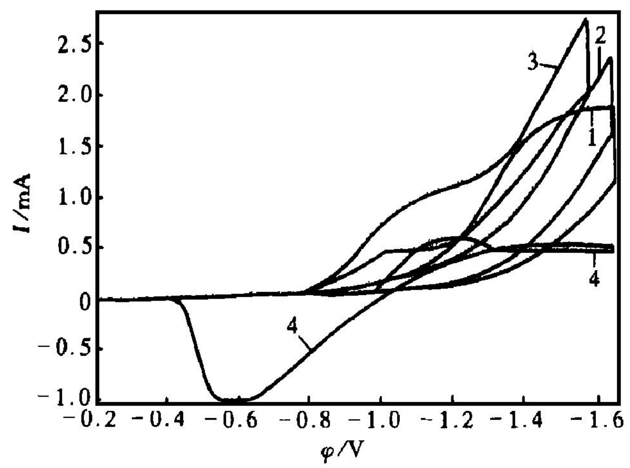

Fig. 6 Influence of Zn^{2+} on reduction of H_3PO_3 at potential scan rate 100 mV/s, pH 3 and 298 K

1 —BE(A); 2 —BE(B); 3 —BE(B) + H_3PO_3(3.5 g/L);

4 —BE(B) + $ZnCl_2$(86 g/L) + H_3PO_3(3.5 g/L)

Meanwhile, the difference between curve (3) in Fig. 3 and curve (4) in Fig. 6 shows the change of the mechanism of Zn-P alloy electroplating caused by adding ascorbic acid into LACS.

4 CONCLUSIONS

1) Under the experimental conditions, H_3PO_3 could be reduced individually, which was promoted by low pH value of the LACS. The codeposition of Zn-P alloy follows the mechanism of three-dimentional instantaneous nucleation/growth or two-dimentional instantaneous nucleation and layer-by-layer growth according to the concentration of H_3PO_3 or the addition of ascorbic acid in LACS.

2) The addition of H_3PO_3 into LACS promotes the 3-D nucleation, while the addition of ascorbic acid leads to the 2-D nucleation. Meanwhile, zinc ions and H_3PO_3 inhibited the deposition of each other.

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