CATALYTIC EFFECT OF FORMIC ACID UPON

AMORPHOUS CHROMIUM ELECTRODEPOSITION[①]

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ABSTRACT   The characteristics and properties of amorphous chromium deposited from sulphuric acid-catalyzed chromic acidic solution containing formic acid have been investigated. Both bright and satisfactory amorphous chromium deposits have been obtained. The polarization curves on copper and vitreous carbon electrode and current efficiency of the electrolyte have also been examined. The results showed that formic acid was an effective catalyst for electrodeposition of amorphous chromium, which can inhibit reduction of Cr(Ⅵ) to Cr(Ⅲ) and hydrogen evolution, and increase cathodic current efficiency of amorphous chromium deposition.

Key words   amorphous materials   electrodeposition   catalysis   formic acid   chromium

1   INTRODUCTION

Amorphous materials also referred to as glass metals are the single phase alloys without long-range crystalline order, only with short-range order over a few atomic distances ((15 ± 0.1)nm). Recently, because of their extraordinary corrosion resistance, hardness, ductility, and unique electrical and magnetic properties, the studies of amorphous materials are more and more widely emphasized by material scientists[1]. Chromium plating is an important metal finish technique which has been used commercially since the 1920s. The bath most commonly used is still of the type developed by Sargent, i. e. chromic acid with sulphuric acid as catalyst. However, the chromium films depostied in this kind of bath have many defects, such as pin holes and crack defects. Moreover, the hardness of the deposits decreases with increasing temperature over the range of 200 to 400 ℃[2]. The characteristics and properties of amorphous chromium deposits are much superior to the ones of conventional chromium deposits because their component and structure are well-distributed. Bright amorphous chromium films deposited from a chromic acid solution containing formic acid as an additive have been reported[2, 3]. Wang presented the high stability process of amorphous chromium plating from above solutions[4].

In above solutions, formic acid was used as an additive, it not only can make deposits become amorphous, but also can increase cathodic current efficiency of decorative chromium plating[5] and amorphous chromium plating. However, catalysis of formic acid to chromium plating is not well known.

It is the purpose of this investigation to study catalysis of formic acid by comparing polarization curves and measuring current efficiency. A possible detailed mechanism for the catalysis of formic acid to chromium plating is presented.

2   EXPERIMENTAL PROCEDURE

The amorphous chromium was electrodeposited using the bath shown in Table 1[4].

The electrolyte was prepared with double distilled water and reagent grade chemicals. The bath was a beaker of 500 ml containing 400 ml of electrolyte. The anodes were two parallel Pb-5% Sb alloy plates situated vertically at the sides of the bath. The substrate as the cathode was a copper foil.

Table 1　Bath composition for amorphous Cr deposition

species or condition	taken value
C (CrO$_3$)/g·L^{-1}	100
C (H$_2$SO$_4$)/g·L^{-1}	5
C (HCOOH, 88%)/mL·L^{-1}	20
temperature/℃	30
D_k /A·dm^{-2}	40

Cathodes were polished with a fine grit paper, degreased in aceton and lightly etched with dilute hydrochloric acid before plating.

After adding HCOOH to bath for 1 h measurements were carried out.

Constant current was supplied by PARC Model 273 Potentiostat/Galvanostat. All experiments were performed at 30 ℃.

The current efficiency (CE) was calculated by current, time and weight of the deposits. Based on the reduction of Cr^{6+} to metal, the formula of calculation is as follows:

$$CE = \frac{60\,m}{0.324\,It} \times 100\% \qquad (1)$$

where m is the weight of deposits (g), I the constant current through the bath (A), t the plating time (min)

A three electrode-system was used for all electrochemical measurements. The reference electrode was a saturated calomel electrode (SCE). The counters were two high density, unpermeable graphites. The working electrode was copper foil or vitreous carbon. All measurements were carried out using a PARC Model 273 potentiostat/galvanostat connected via Model 273 interface and a microcomputer system (IBM-AT), capable of controlling the experiments, collecting and plotting the data. A ATA-1A rotating disc electrode system was used, disc electrode was vitreous carbon and

area was 0.125 6 cm^2.

3　RESULTS

3.1　Current efficiency (CE)

The variations of the current efficiency of amorphous chromium deposition with increasing content of formic acid are shown in Fig. 1. The current efficiency increased with increasing content of formic acid. When formic acid reached 15 ml/L, the current efficiency was maximum. With further increasing HCOOH the current efficiency decreased apparently. This shows that to a certain extent HCOOH can catalyze deposition of amorphous chromium. In absence of H$_2$SO$_4$, the effects of HCOOH on the current efficiency of amorphous chromium plating are shown in Fig. 2. First of all, the current efficiency decreased with increasing HCOOH. Then when HCOOH reached certain value, the current efficiency started to increase again. Surely, the chromium had been deposited from the bath. Furthermore, the appearance of deposits changed into semibright from coarse and grey. Thus it can be seen that HCOOH can be added to the bath to serve the same purpose as adding sulphuric acid in catalyzing chromium depotition.
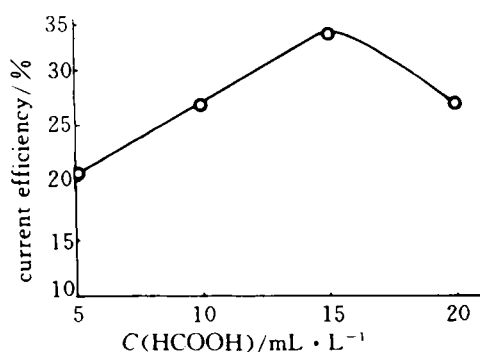

Fig. 1　Effect of HCOOH on CE of amorphous chromium plating in a solution of 100 g/L CrO$_3$+5 g/LH$_2$SO$_4$

3.2　Cathodic polarization curves

Fig. 3 shows linear potential sweep curves on copper for varying concentrations of

HCOOH. The curves show HCOOH can apparently restrain reduction of Cr (Ⅵ) to Cr (Ⅲ) and hydrogen evolution and hence advantages Cr deposition.

Fig. 4 shows potentiodynamic polarization curves on vitreous carbon. It is found that in the presence of 20 ml/L HCOOH the hydrogen evolution is inhibited drastically and Cr deposition is easier.

Fig. 5 demonstrates linear potential sweep curves on a rotating vitreous carbon disc electrode. It is worth notice that the reduction of Cr (Ⅵ) to Cr(Ⅲ) and hydrogen evelution are all strongly affected by rotating rate. It has been known that the reduction of Cr(Ⅵ) to Cr (Ⅲ) is controlled by diffusion[6].
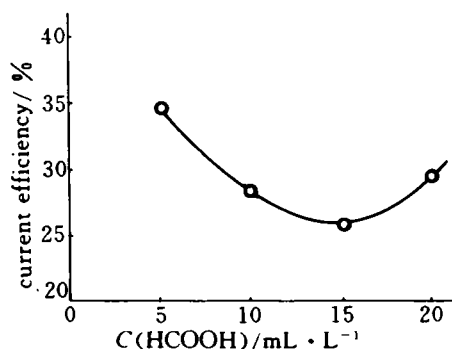
Fig. 6 shows data of Fig. 5 replotted as i against rotating rate $\omega^{1/2}$, a straight line is obtained. According to Levich equation:

$$i_L = 1.554\ D^{2/3}\nu^{-1/6}\omega^{1/2}C_0 \tag{2}$$

where D is the diffusion constant, ν is the kinematic viscosity, i_L is the limiting current, ω is the speed of rotation, and C_0 is the concentration in the bulk solution. The result of Fig. 6 is in accordance with eqn. 2. This indicates hydrogen evolution is also controlled by diffusion.

4 DISCUSSION

In conventional chromium plating bath, when CrO_3/H_2SO_4 has a ratio of $100/1$, the

Fig. 2 Effect of HCOOH on CE of amorphous chromium plating in a solution of $100\,g/L\ CrO_3$

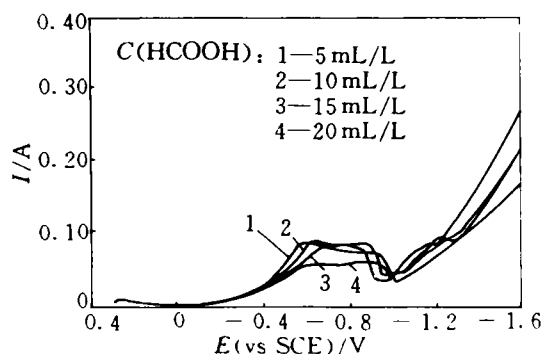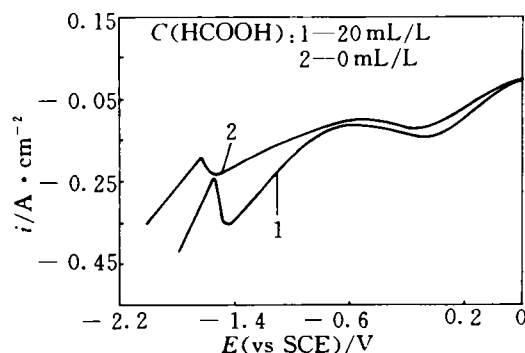**Fig. 4 Potentiodynamic polarization curves for deposition of Cr on vitreous carbon**

Fig. 3 Linear potential sweep curves on copper for different concentrations of HCOOH (Potential sweep rate: 10 mV/s)
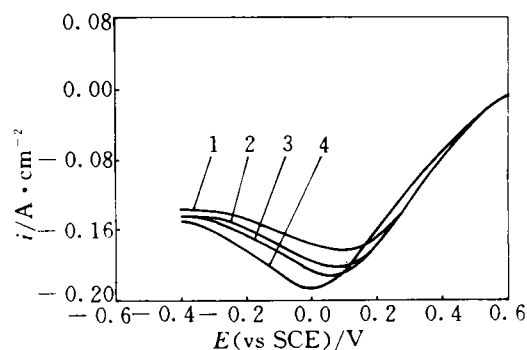
Fig. 5 Linear potential sweep curves on a rotating vitreous carbon disc electrode
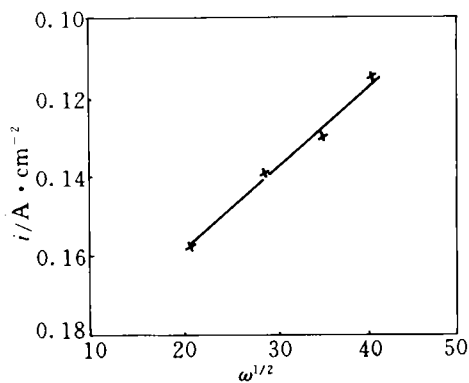1—500 r/min; 2—800 r/min; 3—1 200 r/min; 4—1 600 r/min; Sweep rate was 10 mV/s
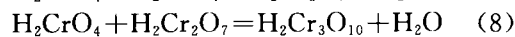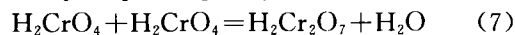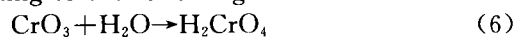
**Fig. 6　Data of Fig. 5 replotted
as i against $\omega^{1/2}$**

optimum result can be obtained; whereas when a ratio is less than 80/1 or more than 120/1, a satisfactory result can seldom be achieved. In this study, although CrO_3/H_2SO_4 is a ratio of 20/1, a bright like mirror amorphous chromium coating can be obtained due to adding of HCOOH. Besides, it can also be found that the current efficiency in amorphous chromium plating bath is apparently higher than in conventional chromium plating bath.

During chromium plating, no matter what amorphous chromium plating or conventional chromim plating, cathodic reactions are probably as follows:

$$Cr^{6+} + 3e \rightarrow Cr^{3+} \tag{3}$$

$$Cr^{6+} + 6e \rightarrow Cr \tag{4}$$

$$2H_3^+O + 2e \rightarrow 2H_2O + H_2 \tag{5}$$
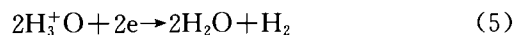
In a solution of CrO_3, the formula for chromic acid may be written as $H_2Cr_3O_{10}$ according to the following reaction[6].

$$CrO_3 + H_2O \rightarrow H_2CrO_4 \tag{6}$$

$$H_2CrO_4 + H_2CrO_4 = H_2Cr_2O_7 + H_2O \tag{7}$$

$$H_2CrO_4 + H_2Cr_2O_7 = H_2Cr_3O_{10} + H_2O \tag{8}$$

When HCOOH is added to the bath, following reaction will also occur

$$2H_2Cr_3O_{10} + 9HCOOH + 18H^+ \rightarrow 6Cr^{3+} + 9CO_2 + 20H_2O \tag{9}$$
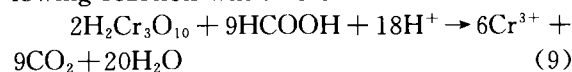
According to reaction (9), theoretically, 20 ml/L HCOOH (88%) should produce Cr (Ⅲ) 16. 18 g/L. In fact, the amount of Cr (Ⅲ) formed is only 11. 99 g/L, then, the small amount of HCOOH remaing in the bath.

Fig. 2 has shown that in absence of H_2SO_4 a semi-bright coating can still be obtained and the CE is higher than conventional chromium plating. So, HCOOH can be used as a purposes as sulphuric·acid and catalyzed amorphous chromium electrodeposition.

Ignatev's study[8] showed that a large amount (20 g/L) of Cr (Ⅲ), an increased amount (5. 4 ml/L) of sulphuric acid and 250 g/L of CrO_3 increased the current efficiency. Furthermore, this study showed that the introduction of formic acid generates Cr (Ⅲ) (reaction (9)). Simultaneously, when Cr(Ⅵ) is reduced in the cathode film, some of the intermediate oxidation states such as Cr(Ⅴ), Cr (Ⅳ) and Cr(Ⅰ) diffuse out and, by interacting with Cr(Ⅵ), produce Cr(Ⅲ) in the diffusion layer. As the Cr(Ⅲ) concentration in the bulk solution increases, the rate of diffusion from the cathode film to the bulk solution decreases, which results in increasing of Cr(Ⅲ) concentration in diffusion layer. Therefore, reacton (3) which is controlled by diffusion[7] is suppressed while reaction (4) is enhanced.

Thus, for amorphous chromium plating the mechanism catalyzed by HCOOH is chiefly because reaction (3) and reaction (5) can be suppressed due to addition of HCOOH and hence reaction (4) can be strengthened.

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