EFFECT OF CURRENT DENSITY ON AMORPHOUS Al-Mn ELECTRODEPOSITON①

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ABSTRACT Amorphous Al-Mn electrodeposition on steel plate was obtained with a molten salt. It was shown that during the electrodeposition, current efficiency, electrodeposition composition, electrodeposition structure and electrodeposition thickness are influenced by current density during the electrodeposition; as the current density increases, Mn content in the electrodeposition decreases; the thickness of the plating layer increases as the current density increases in a certain range; the current efficiency is up to its maximum (90%) when the current density is 45 mA/cm^2.

Key words current density amorphous Al-Mn electrodeposition composition of electrodeposition

1 INTRODUCTION

Attention to amorphous alloys has been widely paid due to their excellent corrosion resistance[1], however, the application of that alloys as corrosion resistance materials is little because of the difficulty to produce bulk amorphous alloys[2]. One of the methods to utilize excellent corrosion resistance of amorphous alloys is to electrodeposit the amorphous alloys on the surface of steels[3-8]. Recently, the possibility to obtain a continuous and homogeneous electrodeposition of Al-Mn amorphous alloys by adding some amount of $MnCl_2$ in $AlCl_3$-NaCl molten salt system[9, 10] was studied. The obtained electrodeposition has a better corrosion resistance than that of Al electrodeposition[10]. For industrial application, the size of current density is an important technique parameter, which influences the quality of electrodeposition. We will consider the effect of current density on current efficiency, electrodeposition composition, electrodeposition structure and electrodeposition thickness.

2 EXPERIMENTAL

A molten salt for electrodeposition consisted of $AlCl_3$, NaCl and $MnCl_2$. The ratio of $AlCl_3$ and NaCl was 4∶1 by adding another 2.5% $MnCl_2$. The substrate was 1020 steel plate in a diameter of 30 mm. The substrate was cleared, dried and weighted on an analytical balance. For electrodepositing, the anode was Al whose purity is 99.99% and the cathode was the substrate. The electrodeposit temperature and the time were 210 ℃ and 0.5 h, respectively. The details for the electrodeposit were reported[10]. Composition and structure analysis were carried out by energy spectrometer and X-ray spectrometer. The current amount of the cathode was measured by a galvanometer. The theoretical mass of electrodeposition was calculated by use of 1st and 2nd Faraday law. Through a comparison between the theoretical calculation and the actually measured mass increase on the cathode, the current efficiency could be calculated.

3 RESULTS AND DISCUSSION

3.1 Effect of current density on composition and structure of electrodeposition

X-ray diffraction analysis curves of electrodeposition obtained under different current densities (J) are shown in Fig. 1. The results

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showed that when $J = 10\,mA/cm^2$, an electrodeposition structure of Al FCC solid solution presents. As J increases to $15\,mA/cm^2$, an electrodeposition structure becomes Al FCC solid solution plus amorphous phase. When $J = 45\,mA/cm^2$, full electrodeposition is amorphous. If $J = 50\,mA/cm^2$, a discontinuous electrodeposition of Al_8Mn_5 phase and amorphous phase form, which is meaningless for the industrial application.

Fig. 2 shows the effect of current densities on Mn content in the electrodeposition. As the current density increasing, Mn content gradually decreases because the deposition velocity is decreased wich increasing current density, referring to Eqns. (1)[9] and (2):

$$w_{f,\,Mn} = \frac{N_{Mn}J_{Mn}/n_{Mn}}{N_{Mn}J_{Mn}/n_{Mn} + N_{Al}/n_{Al}} \quad (1)$$

where $w_{f,Mn}$ is the percentage of Mn in the electrodeposition; N_{Mn} and N_{Al} are mole fraction of Mn and Al, respectively; J_{Mn} and J_{Al} are current fraction of Mn and Al in ampere, respectively; and n_{Mn}, n_{Al} are gram equivalent of Mn, Al, respectively. Because J_{Mn} and J_{Al} are unknown, they could only be estimated by composition of the alloy. If the electrolyte is diluted in some way, the cathode current is far larger than the limit current of diffusion. We assume that the current fraction for diluted Mn^{2+} electrolyte is constant and is equal to the limit current, Eqn. (1) can be rewritten as follows:

$$w_{f,\,Mn} = \frac{N_{Mn}J_{Mn,\,lim}/n_{Mn}}{N_{Mn}J_{Mn,\,lim}/n_{Mn} + N_{Al}(J - J_{Mn,\,lim})/n_{Al}} \quad (2)$$

where $J_{Mn,\,lim}$ is the limit current of Mn in diluted Mn^{2+} electrolyte and J is the total current. From Eqn. (2) it is known that increase of J leads to decrease of $w_{f,\,Mn}$. Hence, through a change of J different compositions of electrodeposition can be obtained.

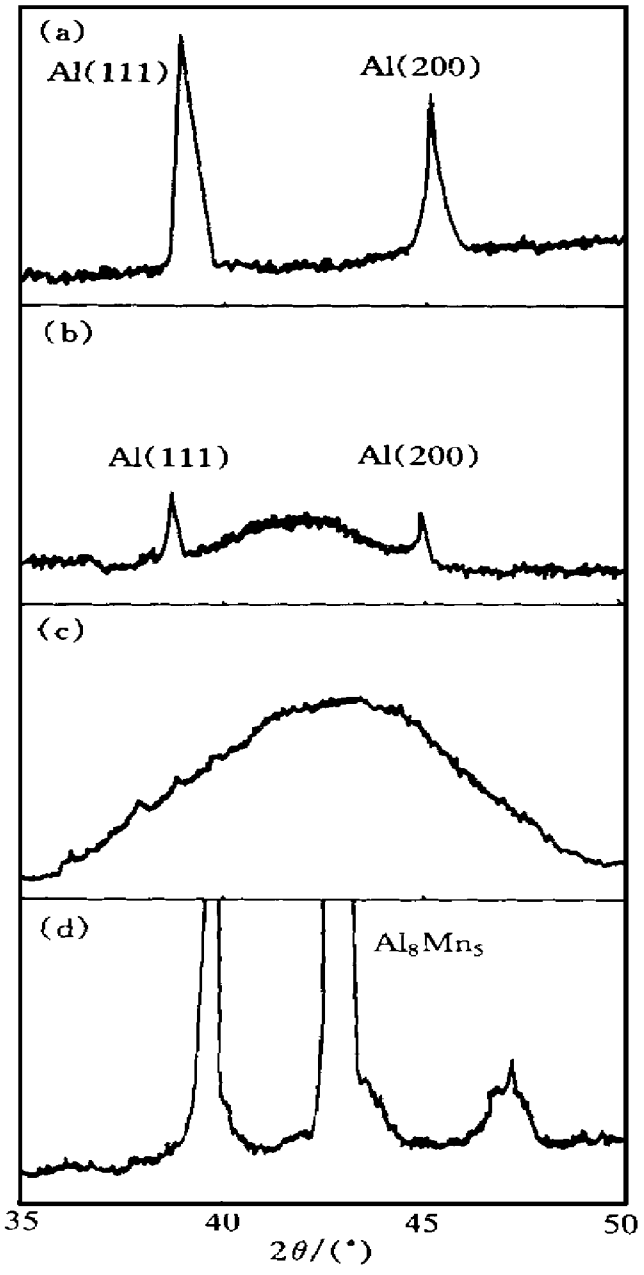

Fig. 1 X-ray diffraction curves of electrodeposition obtained under different current densities (J)

(a) —$J = 10\,mA/cm^2$; (b) —$J = 15\,mA/cm^2$; (c) —$J = 45\,mA/cm^2$; (d) —$J = 50\,mA/cm^2$

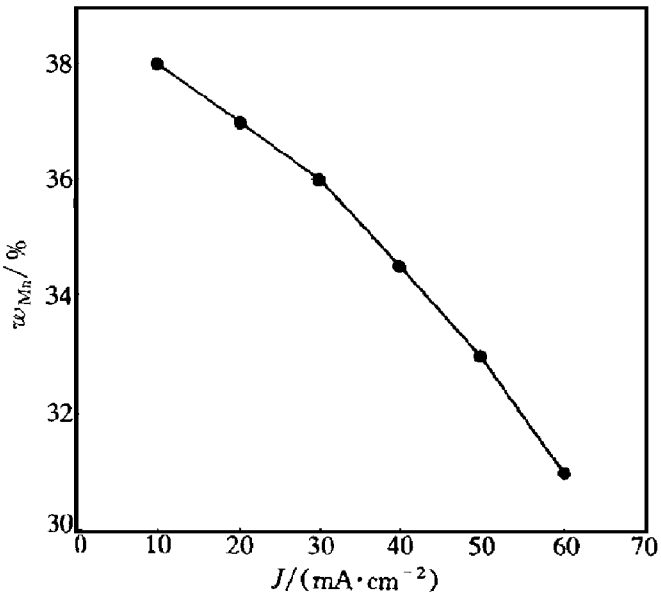

Fig. 2 Effect of current densities (J) on Mn content (w_{Mn}) in electrodeposition

3.2 Effect of current density on thickness & current efficiency of electrodeposition

Fig. 3 shows that the current density also changes the thickness of electrodeposition (T). As the current density increasing, the mass of the electrodeposition (the thickness of electrodeposition) increases too. However, when the current density is up to 45 mA/cm^2, this tendency decreases. According to the Faraday law

$$T = JC\eta/\gamma \quad (3)$$

where C is electrochemical equivalent, g/(Ah); τ is an electrodeposit time, h; η is a current efficiency and γ is the specific gravity, g/cm^3. For a certain electrolyte, C is a constant, γ is approximately a constant. Thus, at a certain electrodeposit time, the mass of the electrodeposition is proportional to the current density and the current efficiency in terms of Eqn. (3). Only when J reaches a critical value of 45 mA/cm^2, η begins to decrease (see Fig. 4). Therefore, the tendency of mass increase of electrodeposition becomes smaller.

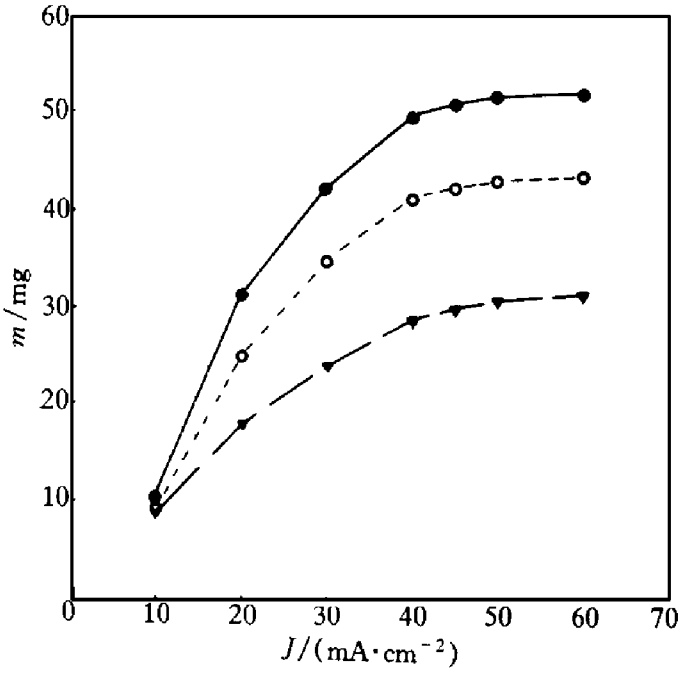

Fig. 3 Relationship between current density (J) and electrodeposition mass (m)
● —2.5% $MnCl_2$; ○—1.5% $MnCl_2$; ◄ —1.0% $MnCl_2$

The effect of current density on the current efficiency is shown in Fig. 4. Before J reaches a critical value of 45 mA/cm^2, η increases. After the critical value, η decreases. The reason can

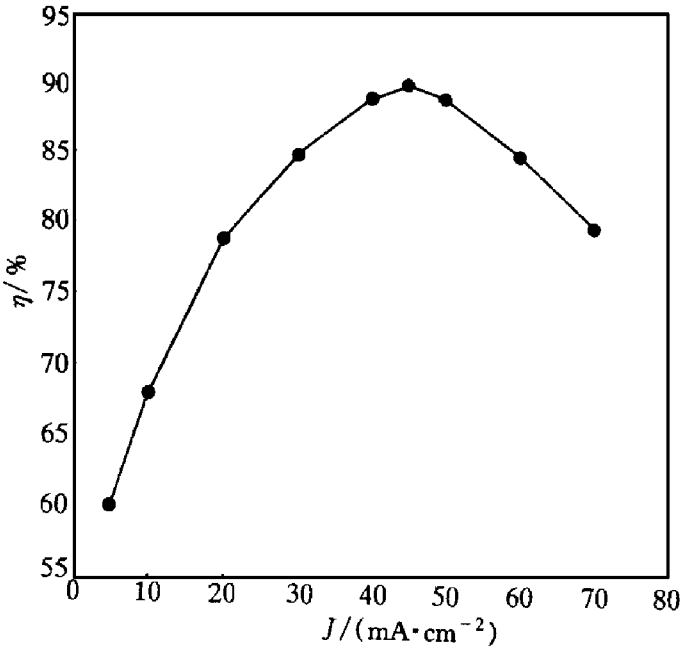

Fig. 4 Relationship between current density (J) and current efficiency (η)

be explained as a common effect of reaction velocity and the diffusion velocity. When J is small, reaction velocity is dominant. As J increasing, the electrodepositing velocity is controlled by diffusion.

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