

ELECTROPLATING OF AMORPHOUS Al-Mn ALLOYS

(II) KINETIC FEATURES OF ELECTRODEPOSITION OF Al-Mn ALLOYS^①

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ABSTRACT Effects of MnCl_2 and temperature on the electroplating of Al-Mn alloys are very significant. At lower concentrations of MnCl_2 , solid solution of Mn in Al and amorphous Al-Mn phases can be deposited, while at higher concentrations of MnCl_2 and lower temperatures, only a single amorphous Al-Mn phase can be formed in the stationary melt. The electrodeposition of Al-Mn alloys with amorphous Al-Mn phase is characterized by very small nucleus number density and 2-dimensional growth, leading to high quality electroplates with few defects.

Key words electroplating Al-Mn alloys kinetic features

1 INTRODUCTION

Extensive attention has been paid to amorphous Al-Mn alloys due to their excellent corrosion resistance in humid marine atmosphere, exhaust system and alcohol containing fuel, etc. Electroplating of Al-Mn alloys^[1] and their structures^[2] have been studied. Commercial applications have also been developed and a series of patents granted^[3-6]. Continuous experiments of bench scale have been finished^[7]. Amorphous Al-Mn electroplated steel has been tested by salt spray, in which red rust appeared 4 a later^[7]. The corrosion resistance of Al-Mn alloy plated low grade stainless steel in muffler condensate environment has been shown to be a little better than that of the stainless steel SUS430LX^[7].

So far, very few studies on electrode reactions of the electrodeposition of amorphous Al-Mn have been made; only steady cathodic polarization^[1] and cathodic and anodic polarization^[8] have been reported. Such a situation has had a negative effect on the development of the electroplating of amorphous Al-Mn. It is obvious that

the study on the reaction mechanism of the electrodeposition of amorphous Al-Mn alloys is very important and urgent.

2 EXPERIMENTAL

The molten salt system used in this paper was $\text{AlCl}_3\text{-NaCl-KCl-MnCl}_2$, in which the mole fraction of AlCl_3 was more than 50% and the content of MnCl_2 was 0.4% ~ 1.6%. All the chemical reagents were analytically pure. MnCl_2 was obtained by vacuum dehydration of $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ at 500K for 4h. NaCl and KCl were dried at 500K for 4h before use. The salt mixture was treated carefully by HCl before experiments as stated in the former paper^[9]. Other experimental conditions were the same as before^[9], except that the working electrode was treated in a potential range of 0 ~ 1.6 V before every cyclic voltammetric experiment and treated at 1.6 V for 3 min before every potentiostatic experiment.

3 RESULTS AND DISCUSSION

3.1 The cyclic voltammetric study

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3.1.1 Effects of MnCl_2 on the electrodeposition of Al-Mn

In order to improve the quality of Al electroplates, many studies have been made, including deposition onto various substrates, superposition of alternative current, addition of organic substances and metal chlorides, etc. But remarkable improvement was observed only through the addition of MnCl_2 ^[10]. It was shown later that under some conditions the electroplates of Al-Mn had an amorphous structure^[1,2,7] and very good corrosion resistance^[7].

To find out the conditions of the formation of amorphous Al-Mn and to ensure the quality of the electroplates, study on the electrode reactions of the deposition of Al-Mn was made by the authors.

Voltammograms for the deposition of Al-Mn on Mo at different concentrations of MnCl_2 are shown in Fig. 1.

It can be seen from Fig. 1 that the voltammograms, especially the anodic branches change significantly after the addition of MnCl_2 . Compared with the case without MnCl_2 ^[9], the differences are as follows.

(1) An increase of both cathodic polarization and change of peak potentials with scanning rates can be observed, suggesting that the irreversibility of the reaction increases, therefore the conditions for the electroplating improve.

(2) The compositions and phases of the electroplates change with the concentrations of MnCl_2 . At lower concentrations of MnCl_2 , solid solution of Mn in Al and amorphous Al-Mn

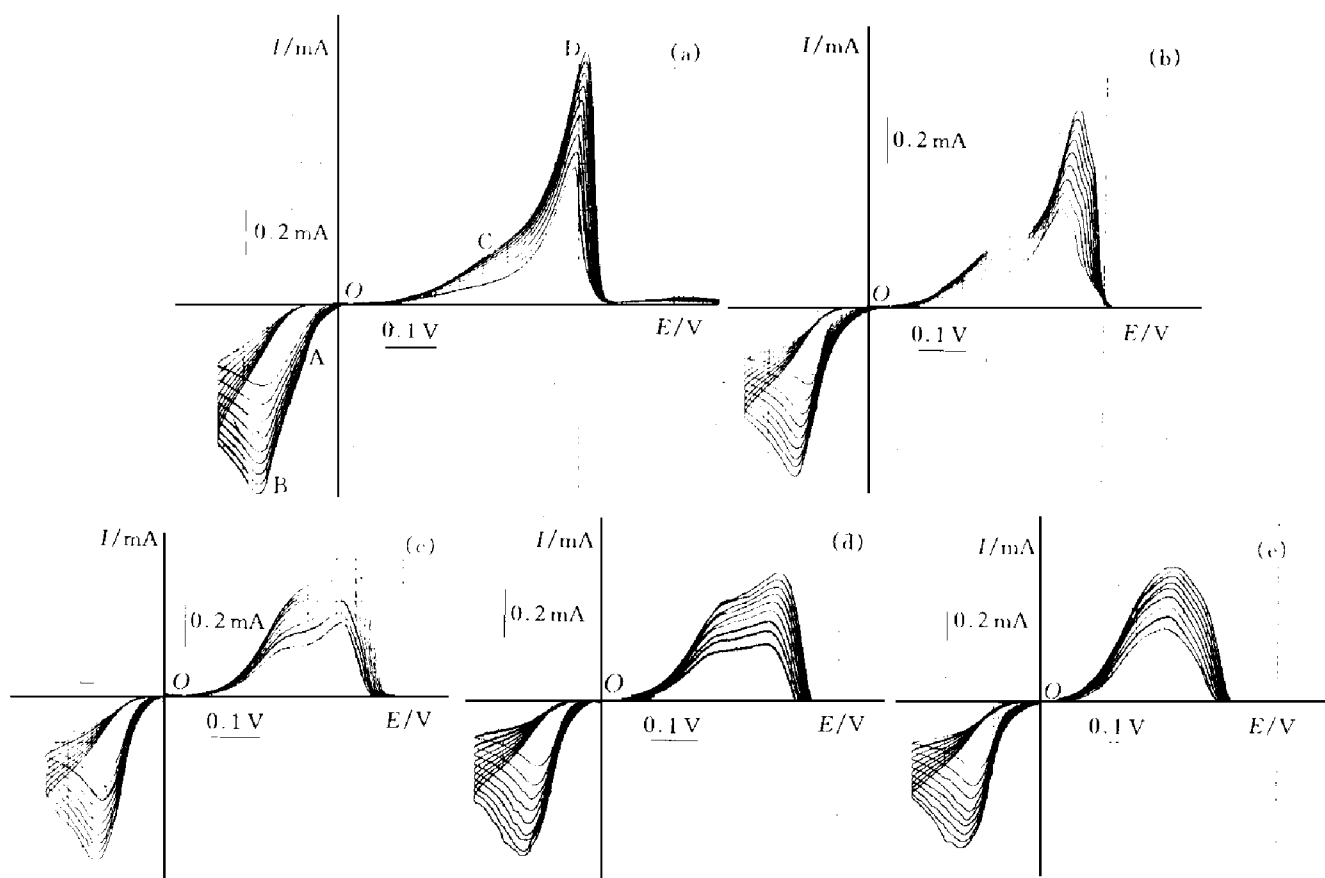


Fig. 1 Voltammograms for the deposition of Al-Mn on Mo at different concentrations of MnCl_2

($T = 449 \text{ K}$, $S_{\text{Mo}} = 0.0079 \text{ cm}^2$,

$v = 20, 30, 40, 50, 60, 70, 80, 90, 100 \text{ mV/s}$, reference electrode: Al)

(a) $-\text{MnCl}_2$ 0.4%; (b) $-\text{MnCl}_2$ 0.7%; (c) $-\text{MnCl}_2$ 1.0%;

(d) $-\text{MnCl}_2$ 1.3%; (e) $-\text{MnCl}_2$ 1.6%

phases are deposited, while at higher concentrations of MnCl_2 , only amorphous Al-Mn is deposited, which can be clearly recognized from Fig. 1(a). In Fig. 1(a) wave 'A' stands for the deposition of solid solution phase of Mn in Al, 'B' for that of amorphous Al-Mn phase, 'C' for the dissolution of amorphous Al-Mn phase, and 'D' for that of solid solution phase of Mn in Al. With the increasing concentration of MnCl_2 , wave 'A' becomes smaller and smaller and can not be recognized when the concentration of MnCl_2 is more than 1.0%, in such case the whole cathodic waves turn respectively into a single wave 'B'; in accordance with this, wave 'D' becomes smaller and smaller and wave 'C' becomes larger and larger; finally only a single wave 'C' can be seen when 1.6% MnCl_2 was added at 438 K. Therefore, an increase in the concentration of MnCl_2 is favourable for the formation of a single amorphous Al-Mn phase in a stationary solution.

3.1.2 Effects of temperature on the electrode-

position of Al-Mn

Voltammograms for the deposition of Al-Mn on Mo at different temperatures are shown in Fig. 2.

With increasing temperature, potentials at the beginning of cathodic reactions and the peak potentials shift positively, and the single wave for the dissolution of amorphous Al-Mn phase at lower temperature splits into several waves, showing that increasing temperature would lead to a decrease in electrode polarization and that the phases of the electroplates may undergo some changes. When the concentration of MnCl_2 is high, e.g. 1.6%, the deposition wave for solid solution of Mn in Al can not be recognized as shown in Fig. 2, meaning that the Al/Mn ratio would probably be in a range of 6~3 corresponding to Al_6Mn ~ Al_3Mn . At lower temperatures, any electroplates with compositions around intermetallics such as Al_6Mn , Al_3Mn etc, would be amorphous. But at higher temperatures, for any electroplates with above compositions, the probability of transition from amor-

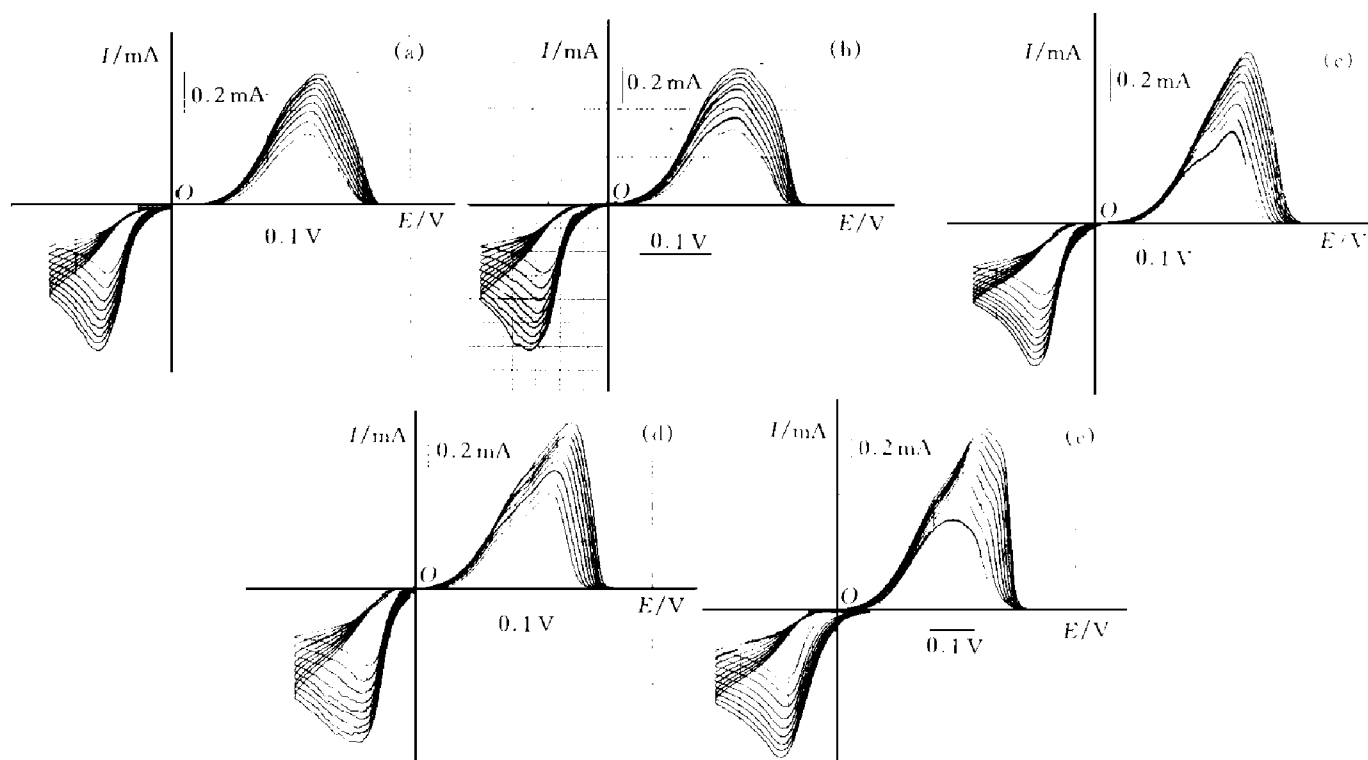


Fig. 2 Voltammograms for the deposition of Al-Mn on Mo at different temperatures

($C(\text{MnCl}_2) = 1.6\%$, $S_{\text{Mo}} = 0.0079 \text{ cm}^2$,

$v = 20, 30, 40, 50, 60, 70, 80, 90, 100 \text{ mV/s}$, reference electrode: Al)

(a) -438 K; (b) -448 K; (c) -458 K; (d) -468 K; (e) -478 K

phous solid to crystal would increase, small amount of crystal Al_6Mn and Al_3Mn would be formed, therefore the corresponding waves for the dissolution of these intermetallics appear in the voltammograms as shown in Fig. 2(e). In fact, above 523 K only crystal AlMn alloys were deposited^[2], indicating that lower temperatures are favourable for the electrodeposition of single amorphous AlMn phase. Besides, lower temperatures would make the vapour pressure of AlCl_3 lower, and thus keep long term stability of the electrolyte.

3.2 Potentiostatic study

The nucleation and growth of amorphous AlMn alloys were studied by potentiostatic determination. A set of potentiostatic transients are shown in Fig. 3.

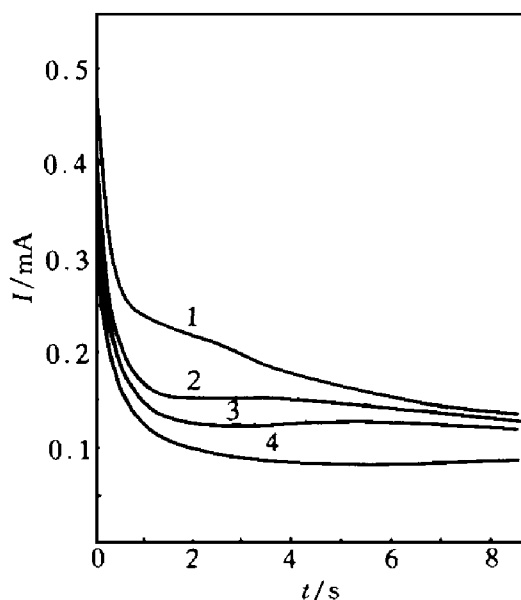


Fig. 3 The potentiostatic transients for the deposition of AlMn on Mo

($C(\text{MnCl}_2) = 0.4\%$, $S_{\text{Mo}} = 0.0079 \text{ cm}^2$,

$T = 449 \text{ K}$, reference electrode: Al)

1—0.100 V; 2—0.090 V; 3—0.085 V; 4—0.080 V

A rising part AB (shown in Fig. 1(a)) in the potentiostatic transients can be observed at the potentials more negative than -0.080 V vs Al, suggesting that electrochemical nucleation and growth were involved^[12] in the deposition of AlMn alloys with amorphous AlMn phase. But the current change in the rising part of the potentiostatic transients is very small, probably due

to the formation of amorphous AlMn . This small change in current indicates that the change in real surface of the electrode caused by nucleation and growth is also very small, which can be explained by small nucleus number density and 2-dimensional growth of the deposits with amorphous AlMn phase. If amorphous AlMn is not formed at the same potentials, this kind of change would become very remarkable as shown in the case of the deposition of pure Al^[9], because crystal is long range ordered, thus newly deposited atoms would be incorporated into the crystal lattices of the nuclei, grow 3-dimensionally into grains and then form crystal with column structure in the cross-section of the plates. In this case, at the beginning of the growth of nuclei, a sharp increase of the real surface area of the electrode would be expected, so a sharp change in the current of growth is reasonable.

However, as a condition for the formation of an amorphous structure, the need for a very small nucleus number density must be met by quenching^[11], and it seemed to be true in electrodeposition of AlMn with amorphous phase as shown in Fig. 3. The 2-dimensional growth of amorphous phase can be explained thermodynamically. The structure of amorphous solid is short range ordered and long range disordered, once a nucleus is formed, the newly deposited metallic atoms need not incorporate into the lattices of the corresponding crystal metal or alloy, but into some other positions, making the energy of the system the lowest. Obviously, the periphery of a nucleus on the substrate is such a kind of position. In other words, the newly deposited atoms would preferentially incorporate into the periphery, or amorphous electrodeposits tend to grow 2-dimensionally. This growth mode of amorphous electrodeposits can minimize the defects of the deposits and thus improve their properties.

4 TESTS FOR AlMn ELECTROPLATES

The molten salts for electroplating and their pretreatment were the same as mentioned above. The substrates (copper plates of 0.15 mm thick) were degreased and electropolished before use.

The temperature was 445 ± 2 K, the concentrations of MnCl_2 were 0.4% ~ 1.6%, the potentials were $-0.090 \sim -0.300$ V (vs Al), and the current density was 0.05 A/cm^2 . The copper substrates were dissolved by HNO_3 before XRD tests. Under these conditions, all electroplates showed single amorphous structures on their XRD patterns, a typical one of which is shown in Fig. 4. The contents of Mn in the electroplates were determined to be 24.6% ~ 36.3% by EDS.

Morphologies of the surfaces and the cross-sections of the electroplates were detected by SEM, and no defects were observed both on the surfaces and in the cross-sections as shown in Fig. 5.

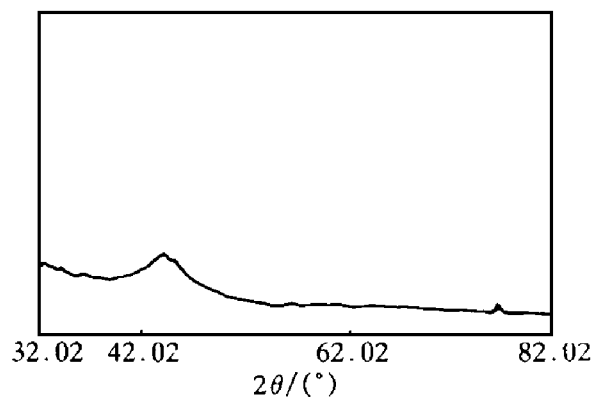


Fig. 4 Typical XRD pattern of Al-Mn electroplate

($C(\text{MnCl}_2) = 1.6\%$, $T = 448 \text{ K}$,
 $E = -0.150 \text{ V (vs Al)}$, $t = 10 \text{ min}$)



Fig. 5 SEM images of the surface (a) and the cross section (b) of Al-Mn deposit
($C(\text{MnCl}_2) = 1.0\%$, $T = 447 \text{ K}$, $E = -0.150 \text{ V (vs Al)}$, $t = 21 \text{ min}$)

5 CONCLUSION

Higher concentration of MnCl_2 and lower temperatures have been shown to be favourable for the formation of amorphous Al-Mn phase, and the growth of amorphous Al-Mn phase seems to be 2-dimensional.

REFERENCES

- Stafford G R. J Electrochem Soc, 1989, 136: 635–639.
- Grushko B, Stafford G R. Metall Trans A, 1990, 21A: 2869–2879.
- Yasumoto Y *et al.* JP 02 267 294. 1990.
- Yasumoto Y *et al.* JP 03– 75351, 1991.
- Sakota A *et al.* JP 63– 93898, 1988.
- Yashuhiro Yamamoto *et al.* EP 0 498 427 A1. 1991.
- Junichi Uchida *et al.* The Sumitomo Search, 1990, (44): 126.
- Junichi Uchida *et al.* ISIJ International, 1993, 33: 1029–1036.
- Zhao G W, Zhu T, Liu L. Trans Nonferrous Met Soc China, 1996, 6(4): 35–37.
- Austin L W, Vucich M G, Smith W J. Electrochem Technol, 1963, 1: 269.
- Dai Daosheng, Han Ruqi. Physics of Amorphous Solids, (in Chinese). Beijing: Publishing House of Electronic Industry, 1989: 529.
- Hills G J *et al.* Electrochem Acta, 1974, 19: 657.

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