Vol. 6 № 4 **Trans. Nonferrous Met. Soc. China** Dec. 1996

ELECTROPLATING OF AMORPHOUS Al-Mn ALLOYS

(Ⅰ) KINETIC FEATURES OF ELECTRODEPOSITION OF PURE Al ①

Zhao Guangwen, Zhu Teng, Liu Lianyu
Department of Physicochemistry,
University of Science and Technology Beijing, Beijing 100083

ABSTRACT It is shown by cyclic voltammmetry and potentiostatic determination that, charge transfer in the electrodeposition of Al on Mo from $AlCl_3$-NaCl-KCl melt is reversible; the diffusion coefficient of $Al_2Cl_7^-$ ions is quite small, and so are the nucleation rates and the saturated nucleus number densities, suggesting that by ordinary DC electroplating it is impossible to get high quality electroplates of pure Al with fine grains from this melt.

Key words electroplating $AlCl_3$-NaCl-KCl melt electrodeposition pure Al

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] were studied, commercial applications were developed widely[3-6], and continuous experiments of bench scale were finished[7].

To know more about the mechanism, the chemical[8] and the electrochemical[9] studies of $AlCl_3$-NaCl, $AlCl_3$-KCl and $AlCl_3$-NaCl-KCl systems were conducted, but very few on the electrode reactions of the deposition of amorphous Al-Mn alloys. In this paper, the kinetics of the deposition of both pure Al and Al-Mn alloys was studied.

2 EXPERIMENTAL

The molten salt system used in the experiment was $AlCl_3$-NaCl-KCl, in which mole fraction of $AlCl_3$ was more than 50%. All the reagents were analytically pure. NaCl and KCl were dried at 500 K for 4 h before use. In order to avoid hydrolysis of $AlCl_3$, the mixed salts were melted in flowing dried HCl, and HCl was bubbled through the melt for 4 h after melting, then it was flushed away by Ar during the following 48 h pre-electrolysis. After such a treatment, residual current was hardly observed before the deposition of Al (see Fig. 1) and silver white Al deposit could be obtained.

The working electrode was a microelectrode of Mo, its preparation has been reported elsewhere[9]. The reference and counter electrodes were Al wires of 99.99% purity immersed in the same electrolyte. The reactor was made of stainless steel lined with pure Al. Temperature was measured by chromel-alumel thermocouple and controlled by a programmable controller model DTL-812. A potentiostat model HPD-1A and a X-Y recorder of Gould series 60000 were used.

In order to get good data, special attention has been paid to the following: (1) In all experiments, the solution resistance was compensated very carefully by the built-in unit of the potentiostat used. (2) Trace oxgen and vapour were removed by a nitrogen purifier model DC-1B made for semiconductor manufacture. (3) The working electrode was scanned once in the potential range of 0~ 0.8 V before every cyclic voltammogram was taken, and kept at 0.6 V for 3 min before every potentiostatic transient was taken. In this way, the same state of the elec-

---

① Received Dec. 25, 1995; accepted Jun. 3, 1996

trode surface can be kept as good as possible so that reproducible results can be obtained.

3 RESULTS AND DISCUSSION

3.1 Cyclic voltammetric study

The electrodeposition of pure Al on Mo was studied first by cyclic voltammetry, and the results are shown in Fig. 1.

The charge transfer of the deposition of pure Al on Mo is found to be reversible. The criteria are as follows: (1) Almost no change of cathodic peak potentials with scanning rates is found as shown in Fig. 1; (2) The separations between cathodic and anodic peaks do not change with scanning rates, and their mean value is found to be 0.114 V, which is in agreement with the theoretical value of 0.116 V for reversible charge transfer at given conditions; (3) A horizontal straight line of $I_p^c/v^{1/2}$ vs v was obtained as shown in Fig. 2, i.e. $I_p^c/v^{1/2} = 0.44$, which corresponds to simple reversible or irreversible charge transfer[11]. Because there are anodic peaks in Fig. 1, the irreversible charge transfer can be excluded, i.e., the electrodeposition of Al is a simple reversible charge transfer as follows:

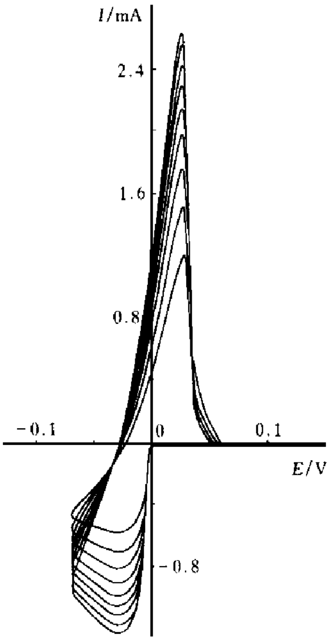

Fig. 1 Voltammograms of the deposition of Al on Mo from $AlCl_3$-KCl-NaCl melt

(v = 20, 30, 40, 50, 60, 70, 80, 90, 100 mV/s, T = 435 K, S_{Mo} = 0.0079 cm^2, reference electrode: $Al_2Cl_7^-$/Al)

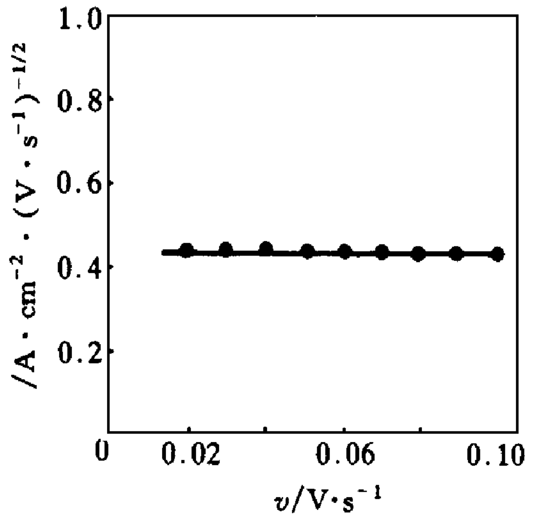

Fig. 2 $I_p^c/v^{1/2}$ vs v for the deposition of Al on Mo from data in Fig. 1

$$Al_2Cl_7^- + 3/4\,e = 1/4\,Al + 7/4\,AlCl_4^-$$

Using Sandles-Sevick equation and peak currents of Fig. 1, diffusion coefficient of $Al_2Cl_7^-$ can be calculated to be (5.26 ± 0.13) × 10^{-7} cm^2/s, which is smaller than Roland's result[9] by an order of magnitude, probably due to the lower temperature and higher concentration of $AlCl_3$ controlled in our work. From half-peak potentials of Fig. 1, the electron number involved in the reaction can be calculated by the following equation:

$$n = 2.2 \times 7RT/\{16[(E_{p/2}^c - E_p^c)F]\}$$

This is an equation derived from reversible charge transfer and the mean value of n was found to be 0.765 ± 0.007, which is agreed with the theoretical one of 0.75.

3.2 Potentiostatic study

The potentiostatic transients are shown in Fig. 3. It can be seen that the nucleation and the growth of Al occur at the potential range of −0.006 ~ −0.011 V vs Al electrode. The overpotentials (η) for the formation of new phase of Al on Mo are so small that the electrodeposition of pure Al should be regarded as reversible.

I^2/I_m^2 vs t/t_m for the deposition of Al on Mo is shown in Fig. 4. It can be seen that the nucleation of Al on Mo should be a progressive one, because the measured points are close to the theoretical curve for progressive nucleation. Using the diffusion coefficient from cyclic voltammetry and the following equations[12]

$$AN_\infty = I_m^4/[(0.4615zFc)^4 D^3 k']$$

$$N_s = (AN_\infty/2k'D)_{1/2}$$

the nucleation rates AN_∞ and saturated nucleus number densities N_s can be calculated as shown in Table 1. Table 1 indicates that the nucleation rates and saturated nucleus number densities are quite small. Thus, it would be difficult to get high quality electroplates of pure Al by ordinary DC electroplating from this kind of melt. By SEM, quite large grains in the Al electrodeposit can be observed (Fig. 5).

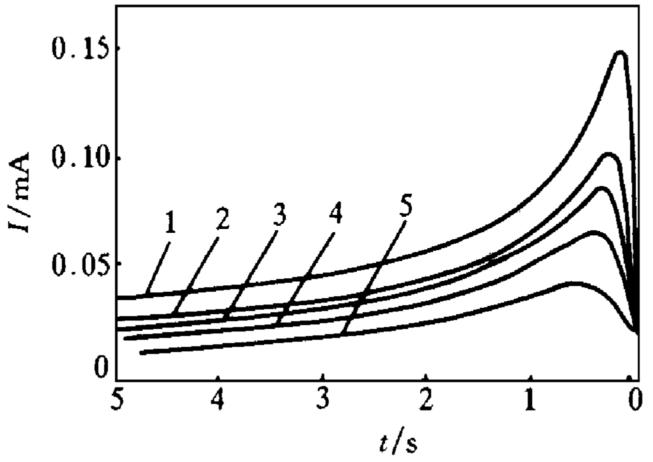

Fig. 3 The potentiostatic transients for the deposition of Al on Mo from $AlCl_3$-NaCl-KCl melt

(T = 438 K, S_{Mo} = 0.0079 cm^2, reference electrode: $Al_2Cl_7^-$ / Al)
1 —overpotential η = 0.011 V;
2 — η = 0.010 V; 3 — η = 0.009 V;
4 — η = 0.008 V; 5 — η = 0.007 V

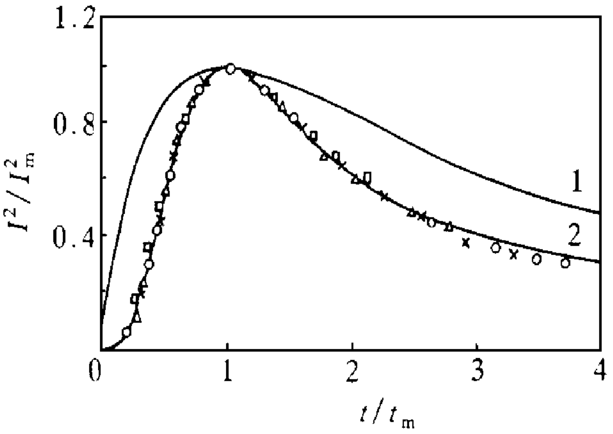

Fig. 4 I^2/I_m^2 vs t/t_m for the deposition of Al on Mo

solid lines —theoretical curves for instantaneous(1) and progressive(2) nucleation;
points —measured data from Fig. 3;
○ — η = 0.011 V; × — η = 0.010 V;
△ — η = 0.009 V; □ — η = 0.008 V

Table 1 Nucleation rates and saturated nucleus number densities for the deposition of Al on Mo

η/V	AN_∞/cm^{-2} · s^{-1}	N_s/cm^{-2}
− 0.011	2.26×10^3	4.40×10^4
− 0.010	0.56×10^3	2.19×10^4
− 0.009	0.24×10^3	1.45×10^4
− 0.008	0.09×10^3	0.90×10^4

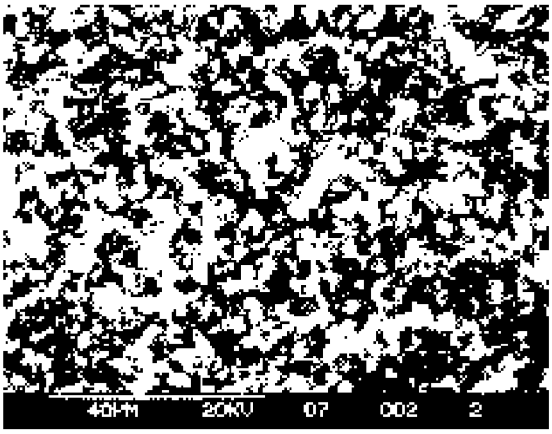

Fig. 5 SEM image of the surface of the Al electroplate obtained at T = 442 K, D_c = 0.19 A/cm^2 and t = 10 min

REFERENCES

1 Stafford G R. J Electrochem Soc, 1989, 136: 635-639.
2 Grushko B, Stafford G R. Metall Trans A, 1990, 21A: 2869- 2879.
3 Yasumoto Y *et al*. JP 02 267 294. 1990.
4 Yasumoto Y *et al*. JP 0 375 351. 1991.
5 Sakota A *et al*. JP 6 393 898. 1988.
6 Yashuhiro yamamoto *et al*. EP 0 498 427 A1. 1991.
7 Jun-ichi Uchida *et al*. The Sumitomo Search, 1990, (44): 126.
8 Boxall L G, Jones H L, Osteryoung R A. J Electrochem Soc, 1973, 120: 223- 231.
9 Roland P, Mamantov G. J Electrochem Soc, 1976, 123: 1299- 1303.
10 Zhao G, Wang C, Yao Y. J Beijing Univ Iron and Steel Technol, (in Chinese), 1987, (1): 80- 86.
11 Nicholson R S, Shain I. Anal Chem, 1964, 36: 706- 723.
12 Sharifker B, Hills G. Electrochimica Acta, 1983, 28: 879- 890.

(Edited by Li Jun)