Electrodeposition of Al-Mg Alloys from Lewis Acidic AlCl$_3$-EMIC-MgCl$_2$ Room Temperature Molten Salts

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Room temperature molten salts, which are obtained by mixing of anhydrous aluminum chloride with either 1-ethyl-3-methyl imidazolium chloride (EMIC) or n-butyl pyridinium chloride (BPC), have received considerable attention as solvents for the electrodeposition of aluminum alloys such as Al-Ni,[1] Al-Co,[2,3] and Al-Cr.[4,5] The electrodeposition of the above mentioned aluminum alloys in the chloroaluminate melts is reasonable from thermodynamic perspectives, since a metal nobler than aluminum is codeposited with aluminum for each of those alloys. On the other hand, the standard potential of the Mg(II)/Mg couple is much lower than that of the Al(III)/Al couple. Therefore, the electrodeposition of Al-Mg alloys in the melts seems implausible and in fact, with the exception of a technical document,[6] there have been no relevant papers published on the topic. In this study, we carried out voltammetric studies on the cathodic reactions in Lewis acidic AlCl$_3$-EMIC melts containing MgCl$_2$. The structure and composition of the deposits obtained from the melt were then analyzed.

The procedures for preparing and purifying AlCl$_3$-EMIC melts are described in a previous paper.[4] Anhydrous MgCl$_2$ was used as received. MgCl$_2$-added melts were prepared by dissolving MgCl$_2$ in a 66.7:33.3 mol% AlCl$_3$-EMIC melt. Voltammetric measurements in the MgCl$_2$-added melt were performed using a three-electrode glass cell. The working electrode was a Pyrex glass-shrouded tungsten wire (1 mm diam.), and the counter electrode was a coiled tungsten wire. An aluminum wire immersed in a 66.7:33.3 mol% AlCl$_3$-EMIC melt was used as the reference electrode and was separated from the bulk solution by a fine glass frit. Inductively coupled plasma spectrometry (ICPS) was used to assess the elemental composition of electrodeposits. Samples for ICPS analysis were prepared by galvanostatic electrolyses using a Pyrex glass cell equipped with platinum or copper cathodes. Structural analyses of the electrodeposits were undertaken with XRD. The temperature was controlled at 303 ± 1 K.

Figure 1 shows the cyclic voltammograms of 66.7:33.3 mol% AlCl$_3$-EMIC melts with and without 0.2 mol kg^{-1} MgCl$_2$. The cyclic voltammogram of the pure AlCl$_3$-EMIC melt showed a reduction wave on the forward scan and a single symmetrical oxidation wave on the reverse scan, which respectively correspond to the deposition and stripping of pure aluminum. The onset potential of the pure aluminum deposition was *ca.* 0.23 V less than the reversible potential of the Al(III)/Al couple. When MgCl$_2$ was added to the melt, the deposition process was promoted such that the same deposition current was obtained at more positive potentials. Moreover, the voltammetric features after scan reversal in this melt were highly dependent on the switching potential; *i.e.*, the potential at which the voltammetric scan was reversed. The voltammogram with the switching potential of –0.13 V exhibited a reduction current starting at *ca.* –0.12 V with a crossover loop after the scan reversal. A single oxidation wave (wave A) appeared in the same potential region as the oxidation wave for the pure aluminum dissolution. When the potential scan was

reversed at –0.18 V, the voltammogram presented a cathodic wave without a crossover loop and an asymmetric anodic wave that presumably consisted of the superimposition of two anodic waves. These anodic waves were successfully divided in the voltammogram when the switching potential was –0.30 V; a well-defined anodic wave (wave B) with a peak potential (*ca.* 0.25 V) more positive than that of the pure aluminum dissolution was seen along with the preceding anodic wave (wave A).

Because of the similarity of the first oxidation wave (wave A) obtained in the MgCl$_2$-added melt to the anodic wave of the pure melt, this oxidation wave can presumably be attributed to aluminum dissolution Therefore, the cathodic reaction in the MgCl$_2$-added melt starts with aluminum deposition, of which the overpotential is reduced by the addition of MgCl$_2$: The presence of Mg^{2+} can be considered to reduce the overpotential of the aluminum deposition attributed to the nucleation process. Another cathodic reaction following the aluminum deposition is suggested by the appearance of wave B, for which the reaction process obviously differs from the dissolution of pure aluminum. This was successfully confirmed by ICPS analyses of the deposits obtained by constant current electrolyses. The result clearly indicated that Al-Mg alloys were electrodeposited in the MgCl$_2$-added melt and that the Mg atomic ratio increased with increasing current density; *i.e.*, with increasing cathodic overpotential. Therefore, wave B corresponds to the dissolution process of Al-Mg alloys. The structure and composition of Al-Mg alloys obtained from AlCl$_3$-EMIC melts containing different concentration of MgCl$_2$ by constant and pulsed current electrolyses were further investigated. The results will be also shown in this paper.

References
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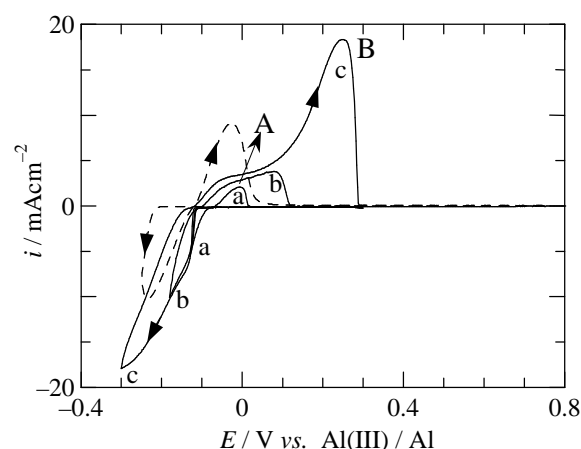6   S. Takahashi, M. Nishihata, and K. Oku, Jpn. Patent 3033596 (2000).

Fig. 1 Cyclic voltammograms of 2:1 AlCl$_3$-EMIC melts with (solid curves) and without (dashed curves) 0.2 mol kg^{-1} MgCl$_2$ at 303 K. Scan rate, 2 mV s^{-1}. Switching potential, -0.13 V (a), -0.18 V (b), -0.30 V (c).