Electrodeposition of Al-Mo-X (X: Mn or Ni) Ternary Alloys from Lewis Acidic $AlCl_3$-EtMeImCl Molten Salts

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We have investigated the electrodeposition of Al-transition metal alloys from the Lewis acidic room-temperature chloroaluminate molten salt, 66.7-33.3 mole percent (m/o) $AlCl_3$-1-ethyl-3-methylimidazolium chloride ($AlCl_3$-EtMeImCl) as an alternative to conventional nonequilibrium methods for preparing these unusual alloys. In particular, the Al-Mo-X (X: Mn or Ni) based alloys are promising materials for corrosion protection[1] and for applications in fuel cells.[2] In this paper, we report some observations about the possibility of preparing ternary alloys in the $AlCl_3$-EtMeImCl molten salt by combining Al-Mo with Mn and Ni.

Figure 1a shows cyclic staircase voltammograms (CSVs) for a Pt disk electrode in 66.7 m/o melts containing $(Mo_6Cl_8)Cl_4$ or $MnCl_2$. These voltammograms are identical to those reported peviously.[1,3] However, for melts containing both Mo(II) and Mn(II), the voltammograms vary significantly with the ratio of the Mn(II) and Mo(II) concentrations, $C_{Mn(II)}/C_{Mo(II)}$. At $C_{Mn(II)}/C_{Mo(II)} \leq 1$ (Fig. 1b), the appearance is similar to the voltammogram for the melt containing only Mo(II), but the overpotential for the Al deposition shifts to more negative potentials and the stripping wave becomes more ambiguous as the Mn(II) concentration is increased. The overpotential eventually exceeds 0.13 V when the $C_{Mn(II)}/C_{Mo(II)} = 4$ (Fig. 1c). As described below, these results imply that the electrodeposition behavior of Al-Mo-Mn alloys varies substantially with $C_{Mn(II)}/C_{Mo(II)}$.

Controlled-current techniques were employed to prepare the Al-Mn-Mo alloy samples for detailed compositional and morphological analysis. All bulk deposition experiments were conducted at copper rotating wire electrodes (Cu-RWEs) at 2000 rpm as noted in a previous article.[1] The Mn and Mo content of the Al-Mn-Mo alloys electrodeposited from the melt containing Mo(II) and Mn(II) simply decreased with an increase in the applied current density as found during the electrodeposition of Al-Mo,[1] provided that $C_{Mn(II)}/C_{Mo(II)} < 1$. However, this was not the case when $C_{Mn(II)}/C_{Mo(II)} > 1$. Here the behavior changed substantially, especially at high current density. In order to understand this behavior, the Mn and Mo content of the alloy samples was plotted separately as a function of the current density and concentration. It was found that the Mo content decreased with an increase in the applied current density and/or the Mn(II) concentration as expected when the transition metal component is electrodeposited at the mass-transport-limited rate. The latter is expected because the partial current density for the Mo(II) species is reduced relative to the partial current density for Mn(II). On the other hand, the Mn content increased with the applied current density, and the tendency was enhanced if the $C_{Mn(II)}/C_{Mo(II)} > 1$. Thus, it seems likely that the electrodeposition behavior depends only on the Mn(II) and Mo(II) partial current densities, *i.e.*, the surface concentrations of these species, because the deposition potentials of these species are very similar. This variation is in accord with the voltammograms shown in Fig. 1.

The structure and properties of the Al-Mo-Mn alloys depended strongly on their Mn and Mo content. In visual comparison, these alloys showed a greater surface luster than Al-Mo. The chloride induced pitting potential of the Al-Mo-Mn alloy was identical to that for the Al-Mo alloy.

In order to prepare Al-Mo-X based alloys for use in PEM fuel cells,[2] we investigated the electrochemistry of melt containing both Ni(II) and Mo(II). The resulting voltammograms were comparable to those reported in the 66.7 m/o melt containing Ni(II)[4] and were independent of the Ni(II) and Mo(II) concentration ratio, $C_{Ni(II)}/C_{Mo(II)}$. However, the Ni content of electrodeposited Al-Mo-Ni was clearly reduced relative to those from melts containing only Ni(II).[4] This variation was especially obvious if galvanostatic electrolysis was employed. It is interesting to note that the Mo and Ni content of these alloys was nearly equal and the surface was easily covered with oxide.

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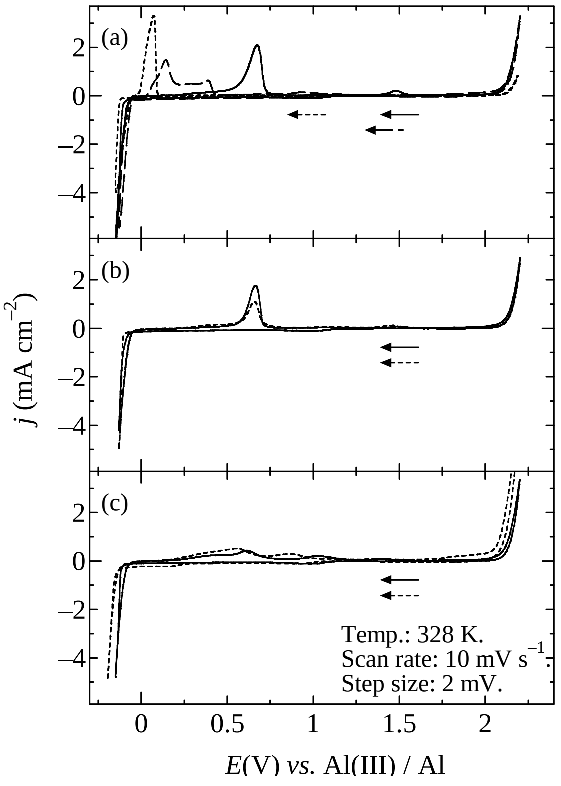

Figure 1. Voltammograms recorded at a stationary Pt disk electrode in the 66.7 m/o melt: (a) (- - -) pure melt, (——) 35.5 mmol L^{-1} Mn(II), and (– – –) 35.5 mmol L^{-1} Mn(II); (b) (——) 35.5 mmol L^{-1} Mo(II) + 17.8 mmol L^{-1} Mn(II) and (- - -) 35.5 mmol L^{-1} Mo(II) + 35.5 mmol L^{-1} Mn(II); (c) (——) 35.5 mmol L^{-1} Mo(II) + 71.0 mmol L^{-1} Mn(II) and (- - -) 35.5 mmol L^{-1} Mo(II) + 142.5 mmol L^{-1} Mn(II).