ELECTRODEPOSITION OF Al-Mo-X (X: Mn or Ni) TERNARY ALLOYS FROM LEWIS ACIDIC AlCl₃-EtMeImCl MOLTEN SALTS

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ABSTRACT

The electrodeposition of Al-Mo-X (X: Mn or Ni) ternary alloys was examined in the Lewis acidic 66.7-33.3 percent mole fraction aluminum chloride-1-ethyl-3-methylimidazolium chloride (AlCl₃-EtMeImCl) molten salt. The electrodeposition of Al-Mo-Mn was investigated in solutions containing Mo(II) and Mn(II). By adjusting CMn(n)/CMo(ii) in the plating solution and employing different current densities, it was possible to prepare alloys with very different compositions and surface morphologies. All Al-Mo-Mn alloys were dense, compact, and adhered well to the substrate surface. The addition of small amounts of Mn to the Al-Mo alloy resulted in an improvement in its chloride pitting corrosion resistance and metallic brightness. For example, Al₉₀.₁Mo₉.₉ displayed a pitting potential of +725 mV versus Al, whereas Al₈₈.₈Mo₁₀.₀Mn₁₂.₂ exhibited a pitting potential of +868 mV versus Al. Al-Mo-Mn alloys that contained more than about 10 a/o Mo+Mn exhibited a metallic glass structure. Al-Mo-Ni alloys that were electrodeposited from solutions of Ni(II) and Mo(II) in the AlCl₃-EtMeImCl molten salt were fragile and powdery.

INTRODUCTION

The electrodeposition of Al-transition metal alloys from the Lewis acidic composition of the room-temperature chloroaluminate molten salt, aluminum chloride-1-ethyl-3-methylimidazolium chloride (AlCl₃-EtMeImCl), has been investigated as an alternative to conventional nonequilibrium methods for preparing these corrosion-resistant alloys. Among the alloys that have been electrodeposited from this ionic solvent are Al-Ti (1-3), Al-Zr (4, 5), Al-Hf (5), Al-V (6), Al-Cr (7-9), Al-Ni (10-12), Al-Co (13-16), and Al-Cu (17-20). Progress in this area has been reviewed (21). More recently, we reported a method for plating Al-Mo alloys from the 66.7-33.3 percent mole fraction (m/o) composition of this molten salt containing dissolved (Mo₅Cl₈)Cl₄ (22). The resulting electrodeposited Al-Mo alloys showed better resistance to chloride-induced pitting corrosion than any of the alloys listed above, and they exhibited a metallic brightness suitable for surface finishing. Amorphous Al-Mn alloys produced from inorganic chloroaluminate...
molten salts containing dissolved MnCl₂ are also reported to exhibit good metallic brightness and improved resistance to chloride pitting corrosion compared to pure Al (23-26). Although it is possible that the addition of Mn to Al-Mo alloys may result in a ternary alloy with properties superior to those of either Al-Mo or Al-Mn, there is a paucity of reports describing such investigations.

Commercial fuel cell systems that utilize noble metals such as Pt and Ru as electrode materials are under investigation in laboratories around the world. However, the high cost and scarcity of these precious metals may become a serious liability as these systems reach commercial viability. Therefore it is important to investigate other materials that can act as suitable replacements for these noble metals. Among the many candidate materials that have been explored to date, alloys obtained by combining Ni or Cu with Al-Mo exhibit polarization curves in aqueous 0.5 M H₂SO₄ that are very similar to those seen at Pt electrodes, suggesting that Al-Mo-Ni alloys prepared on Cu substrates may be suitable replacements for noble metal electrode materials (27).

In this article, we report the results of a preliminary investigation of the electrodeposition of Al-Mo-Mn and Al-Mo-Ni alloys that was undertaken in the 66.7-33.3 m/o AlCl₃-EtMeImCl molten salt.

EXPERIMENTAL

NOTE: Certain trade names are mentioned for experimental information only; in no case does it imply a recommendation or endorsement by NIST.

Preparation of the plating bath. The procedures used for the synthesis of EtMeImCl, the purification of AlCl₃ by sublimation, and the preparation and purification of a Lewis acidic 66.7-33.3 m/o AlCl₃-EtMeImCl molten salt were identical to those described in previous articles (6,28). Anhydrous manganese (II) chloride, MnCl₂ (Aldrich, 99.99 %) and anhydrous molybdenum (II) chloride, (Mo₂Cl₆)Cl₄ (Cerac, 99.5 %) were used as received and were dissolved in the AlCl₃-EtMeImCl molten salt to prepare plating baths. A solution of Ni(II) in the molten salt was prepared by the controlled-potential coulometric anodization of 0.05 cm diameter Ni wire (Aldrich, 99.9 + %) at an applied potential of +1.40 V as described in a previous article (10). After preparing the solutions of Mo(II), Mn(II), and Ni(II) individually, the plating baths for electrodeposition of the Al-Mo-X ternary alloys were adjusted by combining the solutions as needed. All experiments were carried out in a nitrogen gas-filled glove box (VAC Atmospheres NEXUS system) with an O₂ and H₂O content < 3 ppm.

Electrochemical and spectroscopic experiments. Electrochemical experiments were conducted with an EG&G Model 263A potentiostat/galvanostat. This instrument was controlled with a desktop computer utilizing EG&G PARC Model 270 software. The electrodeposition of ternary aluminum alloys described below was performed with an EG&G PARC Model 173 potentiostat/galvanostat equipped with a Model 179 digital coulometer plug-in module. All electrochemical experiments were carried out in three-electrode cells. A Pine Instruments Teflon-sheathed Pt disk electrode with a geometrical area of 0.099 cm² or glassy carbon disk electrode with a geometrical area of 0.247 cm² was employed as the working electrode for voltammetry experiments. Coils of 0.10 cm diameter Al wire (Alfa
Aesar, 99.999 %) were used for the counter and reference electrodes. These electrodes were immersed in melt with the same composition as the bulk melt, but were separated from the bulk melt by a porosity E glass frit (Ace Glass). However, for experiments involving Ni(II), a coil of 0.05 cm diameter Ni wire (Aldrich, 99.9 + %) was used as the counter electrode. The Ni counter electrode was placed directly in the bulk melt.

The Al electrodes were cleaned with a mixture of concentrated H₂SO₄, HNO₃, and H₃PO₄, rinsed with distilled water, and dried under vacuum before use. The Ni electrodes were treated similarly, except that they were cleaned with a dilute aqueous solution of HNO₃. Alloy samples of approximately 10 μm thickness were deposited from solutions of Mo(II) and Mn(II) or Mo(II) and Ni(II) onto working electrodes consisting of a length of 1.25 mm diameter Cu wire. The substrates were rotated at a fixed rate of 2000 rpm with a Pine Instruments AFMSRX electrode rotator as described in previous reports (1, 7, 22). At the conclusion of each deposition experiment, the alloy-plated substrate was removed from the glove box and cleaned with distilled water.

Potentiodynamic pitting measurements were carried out on these alloy samples at room temperature in a 0.1 mol L⁻¹ solution of NaCl in distilled water. This solution was deaerated with nitrogen gas for more than 8 hours before each experiment. The reference electrode for these measurements was a sodium-saturated calomel electrode (SSCE), and the counter electrode was a large surface area Pt wire coil. A known length of the plated Cu wire was exposed to the NaCl solution by using a heat-shrink tubing mask, and the sample was scanned at 0.5 mV s⁻¹ by using linear staircase voltammetry.

UV-visible spectroscopic measurements were obtained by using a Varian CARY 5 spectrometer. Samples were examined in Wilmad No. 107-7 closed-type quartz cells with a 0.10 cm optical path length.

Characterization of ternary aluminum alloy electrodeposits. The crystal structures of the electrodeposits were examined with standard X-ray diffraction (XRD) techniques by using a Siemens D-500 X-ray diffractometer at NIST. This instrument was operated in the θ-2θ scan mode and employed Cu-Kα radiation. The lattice parameters of the fcc Al phase in the alloy deposits were accurately determined by employing the Cu substrate reflections as an internal standard. A minimum of five well-resolved reflections was required for lattice parameter refinement. Surface morphology and elemental analysis of the alloy samples were performed with either a JEOL JSM-6100 (The University of Mississippi) or a JEOL JXA-840 (NIST) scanning electron microscope (SEM). Alloy composition was measured with energy dispersive X-ray spectroscopy (EDS) on the as-deposited surfaces with pure Al, Mo, Mn and Ni as standards.

RESULTS AND DISCUSSION

Absorption spectroscopy. MnCl₂ and (Mo₅Cl₁₀)Cl₄ dissolved readily in the Lewis acidic 66.7-33.3 m/o AlCl₃-EtMeImCl molten salt to produce transparent and yellow solutions, respectively. Electronic absorption spectra of these solutions are shown in Fig. 1. The spectrum for (Mo₅Cl₁₀)Cl₄ is identical to that reported previously (22), whereas no absorption bands were observed in solutions containing only Mn(II). Thus, solutions of Mn(II) must absorb light at wavelengths shorter than 250 nm, which is below the UV cut-off
of the ionic solvent. Except for the decrease in the intensity of the absorption bands due to dilution, the spectrum of the Mo(II) solution is not affected by the addition of either Mn(II) or Ni(II) (Fig. 1), indicating that there are no interactions between the solvated Mn(II) or Ni(II) species and the dissolved Mo(II).

Cyclic staircase voltammetry. Figure 2a shows cyclic staircase voltammograms recorded at a Pt stationary disk electrode in the pure 66.7-33.3 m/o melt and after the dissolution of MnCl₂ and (Mo₆Cl₁₈)Cl₄. To record these voltammograms, the potential scan was initiated from the rest potential to a potential sufficiently cathodic to electrodeposit aluminum. The scan was then reversed until it reached the positive limit of the melt at +2.2 V and was finally returned to the initial potential. The negative and positive potential limits of the Lewis acidic AlCl₃-EtMeImCl molten salt arises from the reduction of the coordinately unsaturated Al₂Cl₇⁻ ion to Al metal and the oxidation of the AlCl₄⁻ ion to chlorine gas, respectively (21).

\[ 4\text{Al}_2\text{Cl}_7^- + 3e^- \rightarrow \text{Al} + 7\text{AlCl}_4^- \]  
\[ 2\text{AlCl}_4^- \rightarrow \text{Al}_2\text{Cl}_7^- + 1/2 \text{Cl}_2 + e^- \]

As is typically observed during the electrodeposition of Al on Pt in the pure melt, a small nucleation overpotential was required to initiate the deposition process.

Voltammograms recorded in solutions containing Mo(II) or Mn(II) are also shown in Fig. 2. These voltammograms are similar to those reported in previous articles (22, 29). Voltammograms that were recorded in solutions containing both Mo(II) and Mn(II) were sensitive to the Mn(II)/Mo(II) concentration ratio, C₆Mo(II)/C₆Mo(II). At C₆Mo(II)/C₆Mo(II) ≤ 1 (Fig. 2b), the appearance of the voltammogram is similar to that recorded in melt containing only Mo(II). However, the overpotential for Al deposition shifts to more negative potentials, and the stripping wave becomes more ambiguous as the Mn(II) concentration is increased. The overpotential for Al deposition eventually exceeds 0.13 V when C₆Mo(II)/C₆Mo(II) = 4 (Fig. 2c). As described below, these results imply that the Al-Mo-Mn electrodeposition process varies substantially with C₆Mo(II)/C₆Mo(II).

Electrodeposition of Al-Mo-Mn alloys. Controlled-current techniques were employed to prepare Al-Mo-Mn alloy samples for detailed compositional and morphological analysis. All bulk deposition experiments were conducted at copper rotating wire electrodes (Cu-RWEs) at a rotation rate of 2000 rpm as described in previous articles (1, 7, 22). As shown in Fig. 3, the combined Mo+Mn content of the Al-Mo-Mn alloys electrodeposited from melt containing both Mo(II) and Mn(II) decreased with an increase in the applied current density as found during the electrodeposition of Al-Mo (22), provided that C₆Mo(II)/C₆Mo(II) ≤ 1. However, the combined Mo+Mn content was independent of the current density when C₆Mo(II)/C₆Mo(II) = 2, but increased with current density when C₆Mo(II)/C₆Mo(II) = 4. In order to understand this phenomenon, the percent atomic fraction (a/o) of Mn and Mo in the Al-Mo-Mn alloy samples was plotted as a function of the current density (Fig. 4). The Mo content is shown as open symbols, and the Mn content is represented by the filled symbols. This plot revealed several important trends. First, the Mo content of the alloy always decreases with an increase in the applied current density. As discussed in an earlier report (22), such behavior indicates that Mo is undergoing electrodeposition at the mass-transport-limited rate. Second, the Mn content is small and...
more or less independent of the current density until \( C_{\text{Mn}^{(II)}}/C_{\text{Mo}^{(II)}} \geq 2 \). When the concentration ratio exceeds this value, the Mn content of the alloy increases with an increase in the current density, becoming very obvious when \( C_{\text{Mn}^{(II)}}/C_{\text{Mo}^{(II)}} = 4 \).

The anomalous behavior of the Mn content of the alloy with changes in the Mn(II) concentration in the plating solution or current density can be explained by considering the equilibrium potential of the Mn(II)/Mn couple. In the Lewis acidic AlCl3-NaCl molten salt, the equilibrium potential for this couple lies negative of that for Al(III)/Al (24, 26). Thus, the partial current density for Mn reduction increases as the reduction current density is increased and/or the concentration of Mn(II) in the plating solution is raised, leading to an increased concentration of Mn in the Al-Mo-Mn alloy deposit. Because changes in these deposition parameters lead to a similar increase in the Mn content of alloys electrodeposited from the AlCl3-EtMeImCl melt, the equilibrium potential of the Mn(II)/Mn couple must also be positioned negative of the Al(III)/Al couple in this melt.

Characterization of electrodeposited Al-Mo-Mn alloys. Figure 5 shows SEM images of typical as deposited bulk Al-Mo-Mn alloy samples that were prepared under different deposition conditions. In every case, these alloy samples appeared to nucleate along the striations of the drawn copper wire substrate. The deposition charge used to prepare these samples was sufficient in theory to produce an atomically smooth layer of pure Al that was 10 \( \mu \)m in thickness. All of the alloy deposits prepared during this investigation were found to be chloride-free. Figures 5a and 5b illustrate the surface morphology of ternary alloys produced under the condition that \( C_{\text{Mn}^{(II)}}/C_{\text{Mo}^{(II)}} = 1 \). However, if this ratio is made less than 1, the alloy surface morphology is observed to vary with the applied current density. As the data in Figs. 3 and 4 illustrate, the current density controls not only the Al/(Mo+Mn) ratio in the alloy, but also the Mn/Mo ratio. The deposit shown in Fig. 5a was prepared at a relatively low current density (-10 mA cm\(^{-2}\)) and contains 8.0 a/o Mo and 2.3 a/o Mn. The surface of this deposit consists of spherical or cone-shaped nodules that are 5-15 \( \mu \)m. However, the deposit prepared at a higher current density (-40 mA cm\(^{-2}\)) in the same plating solution (Fig. 5b) contains only 2.2 a/o Mo and 5.4 a/o Mn. This deposit is covered with very small, dense crystals. If \( C_{\text{Mn}^{(II)}}/C_{\text{Mo}^{(II)}} > 1 \), then the deposit prepared at -10 mA cm\(^{-2}\) contains 4.9 a/o Mo and 6.3 a/o Mn and consists of spherical nodules that are 5-10 \( \mu \)m in diameter (Fig. 5c). At -40 mA cm\(^{-2}\), the deposit prepared in this same solution contains 1.6 a/o Mo and 13.2 a/o Mn (Fig. 5d). This deposit exhibits a near specular surface.

X-ray diffraction analysis of the as-deposited samples revealed that those electrodeposits containing less than approximately 10 a/o Mo+Mn were two phase. The diffraction pattern for these deposits consisted of the typical reflections for fcc Al and a single broad reflection due to an amorphous phase. When the combined amounts of Mo and Mn exceeded 10 a/o, only a single reflection centered at \( 2\theta = 41^\circ \) was observed in the diffraction pattern, suggesting that the deposit was completely amorphous. This result was very similar to that seen during the electrodeposition of amorphous Al-Mo (22). That is, the crystal structures of the Al-Mo-Mn deposits are very dependent on the transition metal in the Al alloy deposit, and when this concentration exceeds a certain threshold, the structure of the deposit converts to a metallic glass. In this case, the formation of a glass phase depends only on the amount of Mo+Mn in the alloy.
Pitting potential measurements. The pitting potentials of the electrodeposited Al-Mo-Mn alloys were determined by carrying out potentiodynamic anodic polarization experiments in deaerated aqueous NaCl with the samples described above. Some examples of the resulting potentiodynamic current-potential curves are shown in Fig. 6. As noted for some other electrodeposited stainless aluminum alloys, e.g., Al-Mo (22) and Al-Mn (23), the Al-Mo-Mn alloys are spontaneously passive at the rest potential of the solution. During anodic polarization, they display a stable passive region characterized by a very small potential-independent current followed by a sudden rise in current at the pitting potential. The variation of the pitting potential with alloy composition is depicted in Fig. 7. The addition of small amounts of Mo and Mn to Al results in a significant increase in the pitting potential compared to pure Al. The pitting potentials of Al-Mo-Mn alloys with approximately 10 a/o Mo+Mn are more positive than those containing 10 a/o Mo. Thus, the pitting corrosion resistance of Al is substantially enhanced by the addition of both Mo and Mn compared to Mo alone.

Electrodeposition and characterization of Al-Mo-Ni alloys. Figure 8a shows cyclic staircase voltammograms recorded at a glassy carbon stationary disk electrode in the 66.7-33.3 m/o melt containing only Ni(II). These voltammograms are identical to those reported in a previous study carried out in this laboratory (10). In the Al-Ni alloy system, the electrodeposition of Al with Ni is known to occur at underpotentials whereas the electrodeposition of Al-Mo takes place at potentials proximate to the potential at which the electrodeposition of Al is normally observed. In contrast to the results described above for solutions containing both Mo(II) and Mn(II), the voltammogram in Fig. 8a was unchanged after the addition of Mo(II) (Figs. 8b and 8c). The potential dependence of the Al-Mo-Ni alloy composition was examined by carrying out controlled-potential experiments. The current-potential data in Fig. 8 was used to guide the selection of the potentials chosen for these electrolysis experiments. As expected, alloy deposits prepared at potentials close to the Ni(II) reduction wave showed a high Ni content, but the Ni content dropped sharply if the potential was less than 0 V. However, the Ni content in the electrodeposited Al-Mo-Ni alloy was clearly reduced relative to deposits prepared in melt that contained only Ni(II) (10). This result was especially obvious when galvanostatic electrolysis was employed as described below.

The dependence of the alloy composition on the reduction current density was examined by plating alloy samples under controlled-current conditions. The results of these galvanostatic experiments are shown in Fig. 9. Generally, the Mo+Ni content of the alloy increases as the overall current density decreases, i.e., the partial current densities for these alloy components is a larger fraction of the total current density when the overall current density is small or the applied potential is more positive. At higher current densities and correspondingly more negative deposition potentials, both the Mo and the Ni deposition reactions have reached their limiting partial current densities and any increase in the overall current density is reflected by an increase in the Al partial current density. Under normal conditions, deposition of the binary Al-Ni alloy from the 66.7-33.3 m/o melt containing 25.0 mmol L⁻¹ Ni(II) at -5 mA cm⁻² produces an alloy with a Ni content of about 90 a/o (10). However, when experiments were carried out with this plating solution under the same conditions with added Mo(II), the Ni content of the resulting alloy was less than 10 a/o. Obviously the Ni deposition process is significantly affected by the addition of Mo(II).
During the attempted characterization of the electrodeposited Al-Mo-Ni alloys, it was found that the deposits were very fragile and powdery, and they were easily dislodged from the substrate. Thus, it was not possible to fully characterize these alloys or to measure their chloride-induced pitting potentials. As a result, these alloy deposits were not subjected to further investigation.

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Figure 1. UV-visible spectra of the 66.7-33.3 m/o AlCl₃-EtMelmCl melt: (a) (——) 36.2 mmol L⁻¹ Mo(II); (— -) 36.2 mmol L⁻¹ Mn(II); (- - -) 36.2 mmol L⁻¹ Mo(II) + 36.2 mmol L⁻¹ Mn(II); and (b) (------) 17.9 mmol L⁻¹ Mo(II); (— - -) 10.0 mmol L⁻¹ Ni(II); (— - -) 19.9 mmol L⁻¹ Mo(II) + 10.0 mmol L⁻¹ Ni(II). The temperature was ~ 298 K, and the cell path length was 0.10 cm.

Figure 2. Cyclic voltammograms recorded at stationary Pt disk electrodes in the 66.7-33.3 m/o AlCl₃-EtMelmCl melt: (a) (- - -) pure melt, (——) 35.5 mmol L⁻¹ Mo(II), (— - -) 35.5 mmol L⁻¹ Mn(II); (b) (——) 35.5 mmol L⁻¹ Mo(II) + 17.8 mmol L⁻¹ Mn(II), (— - -) 35.5 mmol L⁻¹ Mo(II) + 35.5 mmol L⁻¹ Mn(II); and (c) (——) 35.5 mmol L⁻¹ Mo(II) + 71.0 mmol L⁻¹ Mn(II), (— - -) 35.5 mmol L⁻¹ Mo(II) + 142.5 mmol L⁻¹ Mn(II). The temperature was 328 K, and the scan rate was 10 mV s⁻¹.
Figure 3. Relationship between the plating current density, the percent atomic fraction of Mo+Mn in the Al-Mo-Mn alloy, and the composition of the plating solution: (•) 35.5 mmol L⁻¹ Mo(II) + 7.8 mmol L⁻¹ Mn(II), (○) 35.5 mmol L⁻¹ Mo(II) + 35.5 mmol L⁻¹ Mn(II), (▲) 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). The temperature was 328 K, and the substrate was rotated at 2000 rpm during deposition.

Figure 4. Relationship between the plating current density, the percent atomic fraction of either Mo or Mn, and the plating solution composition. The open symbols refer to the Mo content and the filled symbols refer to the Mn content of the electrodeposited Al-Mo-Mn alloys: (○, ●) 35.5 mmol L⁻¹ Mo(II) or 35.5 mmol L⁻¹ Mn(II); (□, ■) 35.5 mmol L⁻¹ Mo(II) + 17.8 mmol L⁻¹ Mn(II); (▲, △) 35.5 mmol L⁻¹ Mo(II) + 71.0 mmol L⁻¹ Mn(II); (△, ▲) 35.5 mmol L⁻¹ Mo(II) + 142.5 mmol L⁻¹ Mn(II); and (○, ●) 35.5 mmol L⁻¹ Mo(II) + 142.5 mmol L⁻¹ Mn(II).
Figure 5. SEM images of the electrodeposited Al-Mo-Mn alloy samples described above: (a) Al$_{89.7}$Mo$_{8.0}$Mn$_{2.3}$, -10 mA cm$^{-2}$, 35.5 mmol L$^{-1}$ Mo(II) + 35.5 mmol L$^{-1}$ Mn(II); (b) Al$_{92.4}$Mo$_{2.2}$Mn$_{5.4}$, -40 mA cm$^{-2}$, 35.5 mmol L$^{-1}$ Mo(II) + 35.5 mmol L$^{-1}$ Mn(II); (c) Al$_{88.8}$Mo$_{4.3}$Mn$_{6.3}$, -10 mA cm$^{-2}$, 35.5 mmol L$^{-1}$ Mo(II) + 142.5 mmol L$^{-1}$ Mn(II); and (d) Al$_{85.2}$Mo$_{1.6}$Mn$_{13.2}$, -40 mA cm$^{-2}$, 35.5 mmol L$^{-1}$ Mo(II) + 142.5 mmol L$^{-1}$ Mn(II).
Figure 6. Anodic polarization curves recorded in deaerated 0.1 mol L⁻¹ aqueous NaCl for (a) pure Al, (b) Al₉₅.₈Mn₄.₂, (c) Al₉₀.₈M₀₅.₃Mn₇.₇, and (d) Al₈₇.₉M₇.₆M₄.₅. The temperature was ~ 298 K, and the scan rate was 0.5 mV s⁻¹.

Figure 7. Pitting potentials of electrodeposited Al-Mn-Mo alloys: (●) pure Al, (○) Al-Mn, (▼) Al-Mo, and (▲) Al-Mo-Mn.
Figure 8. Cyclic voltammograms recorded at stationary glassy carbon disk electrodes in the 66.7-33.3 m/o AlCl₃-EtMeImCl melt: (a) 20.0 mmol L⁻¹ Ni(II); (b) 10.0 mmol L⁻¹ Mo(II) + 20.0 mmol L⁻¹ Ni(II); and (c) 40.0 mmol L⁻¹ Mo(II) + 20.0 mmol L⁻¹ Ni(II). The temperature was 328 K, and the scan rate was 50 mV s⁻¹.

Figure 9. Relationship between the plating current density, the percent atomic fraction Mo and/or Ni in the alloy, and the composition of the plating solution. In the lower panel, the open symbols refer to the Mo content and the closed circles refer to the Ni content of the Al-Mo-Ni alloy deposits: (○) 10.0 mmol L⁻¹ Mo(II) + 20.0 mmol L⁻¹ Ni(II); (◇) 20.0 mmol L⁻¹ Mo(II) + 20.0 mmol L⁻¹ Ni(II); (△, ▲) 40.0 mmol L⁻¹ Mo(II) + 20.0 mmol L⁻¹ Ni(II). The temperature was 328 K, and the rotation rate was 2000 rpm.