ELECTRODEPOSITION AND PITTING CORROSION OF ALUMINUM-MANGANESE ALLOYS FROM ROOM TEMPERATURE CHLOROALUMINATE MOLTEN SALTS

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ABSTRACT

The electrochemical reduction of manganese (II) from acidic AlCl₃:EMIC (aluminum chloride:1-ethyl-3-methylimidazolium chloride) room temperature molten salt results in the co-deposition of aluminum and manganese. Evaluation of the chronoamperometric transient behavior on platinum during electrodeposition at the foot of the wave shows that the co-deposition of manganese and aluminum proceeds via three-dimensional instantaneous nucleation with diffusion controlled growth. The composition and structure of the manganese-aluminum electrodeposits is strongly dependent on both the manganese and aluminum concentrations. Specular τ-phase manganese-aluminum alloys are deposited from melts with high manganese concentrations and low aluminum concentrations. Amorphous manganese-aluminum deposits are produced from melts with low manganese concentrations. These amorphous manganese-aluminum deposits show some improvement in chloride pitting behavior. However, the results are somewhat inconsistent due to the general poor quality of the deposits.
INTRODUCTION

Alloying aluminum with a transition metal such as manganese has been shown to produce enhanced resistance to chloride induced pitting (1,2). However, this improved corrosion resistance often requires aluminum alloys with solute concentrations that are far in excess of the equilibrium solubility limit (ca. 1 a/o). Electrodeposition, with its low cost and high throwing power, is an attractive method for formation of non-equilibrium alloys. Recent work by Stafford and co-workers (3-5) has demonstrated the electrodeposition of nonequilibrium Al–Mn alloys from AlCl₃: NaCl molten salts. Alloys were made in compositions up to 50 a/o, and at molten salt temperatures ranging from 150 – 350 °C. Depending on deposition conditions a wide variety of Al-Mn deposits were observed. For example, at a constant deposition temperature of 150 °C, fcc Al, amorphous Al-Mn, γ-Al₈Mn₅, τ Al-Mn (Al₁₁Mn₄₄) or mixed phases could be obtained by variation of the manganese concentration (3). Moffat et al. (1) investigated the chloride induced pitting of several of the single phase Al-Mn alloys, and they found that several of these Al-Mn alloys exhibited pitting potentials up to 0.4 V more positive than unalloyed aluminum.

The room-temperature acidic 1-ethyl-3-methylimidazolium chloride:aluminum chloride (EMIC:AlCl₃) molten salts provide some unique properties which make them ideal for studying the deposition of aluminum and aluminum alloys. Most importantly, aluminum can be reversibly electrodeposited from acidic molten salt compositions (7-12). Molten salts are excellent solvents for both ionic and molecular species. A great many transition metal salts are soluble in the acidic molten salts. Unlike conventional electroplating baths, the EMIC:AlCl₃ molten salts have very low dielectric constants. This fact, coupled with the low operating temperature, appears to promote preferential orientation of electrochemical deposits, thus making possible epitaxial growth of metals and alloys (21).

We recently demonstrated the deposition of Al–Mn(14) from the acidic EMIC:AlCl₃ room-temperature molten salts. This initial report indicated that similar behavior was observed to the electrodeposition of Al-Mn from the higher temperature NaCl:AlCl₃ molten salts. In this report we have expanded upon these initial experiments in an effort to study in greater detail the electrodeposition of aluminum-manganese from the EMIC:AlCl₃ room-temperature molten salts. We have investigated the deposition process, the deposit morphology, its composition and the corrosion resistance of the alloys produced.

EXPERIMENTAL

The preparation and purification of EMIC and AlCl₃ were performed as described previously described (15). MnCl₂ (Alfa) was dried at ca. 400 °C under a vacuum of 10⁻⁵ Torr for 24 hours. All molten salt preparations and electrochemical experiments were performed in a nitrogen filled Vacuum Atmospheres drybox with O₂ and H₂O levels < 1
ppm. Electrochemical experiments were carried out with an EG&G PARC model 273A potentiostat/galvanostat controlled with the M270 software package. All electroanalytical experiments were conducted at 25 °C in a single compartment glass cell containing a either a Pt or Au working electrode (BAS, 0.02 cm²). An Al wire placed in a separate tube with a vycor tip containing a \( N = 0.60 \) AlCl₃-EMIC melt served as the reference electrode. An Al coil was used as the counter electrode.

Electrodeposition experiments were performed in a custom designed cell built from an Ace No. 12 o-ring joint. The working electrode for electrodeposition was a 25 x 25 mm Cu foil compression fit vertically to the o-ring joint by a Chemraz® No. 12 o-ring providing an electrode area of approximately 1.1 cm². The copper flags were either electropolished in 80% phosphoric acid-water solution or hand polished with successive grits of aqueous diamond down to 0.1 um. The copper flags were rinsed, and thoroughly dried prior to deposition. The counter electrode was a 0.5 mm diameter aluminum wire coil. The reference electrode consisted of an Al wire immersed in an \( N = 0.60 \) AlCl₃-EMIC; this melt was contained in a sealed glass compartment in the electrochemical cell. A platinum wire in-glass was used to connect the reference compartment to a built-in luggin capillary. An Al wire coil immersed in the electrolyte was used as the counter electrode.

Al-Mn deposits were made at constant potential. Sufficient charge was passed during each deposition such that deposits were a minimum of 3 µm in thickness. Following each deposition, excess molten salt was removed from the deposit by sequential cleaning with cotton swabs soaked in toluene, hexane, ethanol, and water. The cleaned samples were used for energy dispersive x-ray spectroscopy (EDS), X-ray diffraction (XRD) analysis, and pitting corrosion experiments.

EDS data were collected using a Joel Model JSM 6100 scanning electron microscope equipped with a Kevev model 3600 energy dispersive spectrometer. Aluminum and manganese SEM standards, and a KCl crystal were used as the metal and chloride standards. The EDS data were corrected using the XPP/ASAP correction software supplied with the instrument.

X-ray diffraction spectra were recorded on a Rigaku X-ray diffractometer using Cu Kα radiation in 2θ scan mode with an incident angle of either \( \Theta = 3° \) or 5°. The XRD results were compared against the Joint Committee on Powder Diffraction Standards (JCPDS) reference tables using the platinum or copper substrate as an internal standard.

The pitting potentials of the various Al-Mn alloys were determined using a commercial three-electrode cell (EG & G Flat Cell No. K0235) which exposes a fixed area (0.78 cm²) of the electrodeposit to the electrolyte in conjunction with a Princeton Applied Research (PAR) 273A potentiostat and 352 corrosion software. These experiments were performed in argon deaerated, \( \text{pH} = 9.3 \), boric-borate electrolyte containing 1 g/L NaCl (i.e., 0.017M) at 25 °C. The reference electrode was a BAS saturated calomel electrode. The electrodes were immersed at open circuit for 15 minutes before a linear scan at 0.1 mV/s was initiated.
RESULTS AND DISCUSSION

Voltammetry

The electrochemical behavior the Mn(II) containing acidic molten salts was investigated on Pt and Au disk electrodes (diameters > 1.0 mm). Figure 1 shows a series of staircase cyclic voltammograms at a platinum disk electrode in a $N = 0.545$ AlCl$_3$:EMIC containing 0.0, 25 mM, and saturated MnCl$_2$ (ca. 200 mM). The melt containing no Mn(II) (long dashed line, referred to as the blank) exhibits the typical voltammetry for the deposition and stripping of Al. By comparison, the melts containing 25 mM Mn(II) (solid line) and saturated Mn(II) (short dashed lined) show significant changes in both the anodic and cathodic processes. Most importantly, both voltammograms show a single cathodic wave indicative of simultaneous reduction of both Mn(II) and Al(III). This observation is consistent with the previous work in the NaCl:AlCl$_3$ melts (1,2). In addition, the rising portion of the reduction waves for both Mn(II) containing melts are shifted cathodically, and this shift appears to increase with manganese concentration. The 25 mM Mn(II) shifted ca. 25 mV negative while the saturated Mn(II) shifted ca. 75 mV negative.

Chronoamperometry

Chronoamperometry was used to investigate the nucleation and growth process to distinguish between the various 3-dimensional hemispherical diffusion controlled growth mechanisms. Previous studies have shown that the initial stages of electrodeposition of metals from acidic AlCl$_3$:EMIC often involve some form of three-dimensional nucleation process followed by hemispherical diffusion-controlled growth of the developing nuclei (16). The two limiting cases for this type of metal deposition are instantaneous nucleation of a fixed number of active sites and progressive nucleation of an infinite number of active sites (16,17). To differentiate between the two, a comparison of the complete dimensionless experimental current-time transients to the dimensionless theoretical transients was performed. The theoretical transients for the limiting cases of instantaneous and progressive nucleation are given by Equations 1 and 2, respectively (17).

\[
(i/i_{\text{max}})^2 = 1.9542 \left(\frac{t_{\text{max}}}{t_0}\right) \{1-\exp[-1.2564(t/t_{\text{max}})]\}^2 \\
(i/i_{\text{max}})^2 = 1.2254 \left(\frac{t_{\text{max}}}{t_0}\right) \{1-\exp[-2.3367(t/t_{\text{max}})]\}^2
\]

Plots of $(i/i_{\text{max}})^2$ versus $t$ for the data taken from the rising portion of the current-time transients contained a linear segment whose intersection with the $t$-axis allows the estimation of the delay time, $t_o$, the correction corresponding to the maximum current is $t'_{\text{max}} = t_{\text{max}} - t_o$. Figure 2 gives an example of the Plot of $(i/i_{\text{max}})^2$ versus $t/t'_{\text{max}}$ for...
instantaneous and progressive nucleation models superimposed on the dimensionless experimental data. As is clear from Figure 2, the nucleation of Al-Mn on platinum is in good agreement with instantaneous three-dimensional hemispherical diffusion-controlled growth model given by Equation 1.

**Al-Mn Electrodeposition**

Al-Mn alloy films ca. 3-10 μm thick were deposited onto copper and platinum coupons from three different melt compositions \( N = 0.523, 0.545, 0.60 \) and two different Mn(II) concentrations (25 mM and Saturated). In general, Al-Mn deposits made at low over-potentials (i.e. < 0.6 V) tended to be more specular. They were also more adherent and generally had a negligible chloride content. These deposits could be flexed and not break and if torn from the surface came off in a sheet or large flake. Deposits made at higher over-potentials (i.e. > 0.6 V) were generally dull to black in appearance and poorly adherent. These deposits tended to have higher chloride content and thicker deposits often had a surface appearance as a very finely divided black power that was easily rubbed off during the cleaning process.

Energy-dispersive x-ray spectroscopy (EDS) was used to determine the elemental composition of the electrodeposited Al-Mn films, and X-ray diffraction (XRD) was used to evaluate the phase structure. These data are summarized in Table 1. Evaluation of these data indicate several trends in the composition and phase behavior of the Al-Mn deposits produced from the acidic EMIC:A1Cl₃ melts. The concentration of aluminum in the Al-Mn deposits increases with increasing melt acidity (and the corresponding increase in concentration of reducable Al(III)). The concentration of manganese in the Al-Mn is also seen to increase with increasing Mn(II) concentration. The concentration of manganese also appears to be potential dependent with higher concentrations favored at lower overpotentials. This effect is most apparent in the less acidic melts that were saturated with Mn(II).

The observed Al-Mn phases depended strongly on deposition conditions. Examples of the XRD patterns for the four main types of Al-Mn deposits observed from the EMIC:A1Cl₃ melts are shown in Figure 3. Mixed fcc aluminum/amorphous deposits were observed in the more acidic melts and at higher overpotentials. Amorphous Al-Mn deposits were by far the most common deposits observed. They tended to predominate in the less acidic melts. Mixed amorphous/\( \tau \) phase Al-Mn were often observed for deposition at lower overpotentials from the less acidic melts. Pure \( \tau \) phase Al-Mn was the most difficult to obtain. It was observed only for depositions at very low over potentials in the less acidic melts. A comparison of the observed phases in the electrodeposition of Al-Mn from EMIC:A1Cl₃ and NaCl:A1Cl₃ (6-8) is shown in Figure 4. The phase boundaries roughly correspond between the two melts. However, unlike the higher temperature NaCl:A1Cl₃ melts, no \( \gamma \) phase Al-Mn or fcc Al was observed.

**Pitting Corrosion**

Initial studies of the chloride induced pitting behavior of the amorphouse Al-Mn deposits have shown some limited improvement in corrosion resistance. However, the
results, in general, have been inconsistent. The pitting potential polarization curves for the various Al-Mn deposits showed that all samples pitted within 0.1 and 0.3 V of each other and in most cases pitting began at or very near the open circuit potential. For most samples the Al-Mn deposit almost completely delaminated during the course of the experiment. This suggests that the pitting results from a lack of adhesion, possibly due to the deposits' porosity, and does not represent the true corrosion resistance. In addition the observed behavior may result from entrapped melt which is readily hydrolyzed in the pitting solution.

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Table I. EDS/XRD results for Al-Mn electrodeposits on copper.

**Saturated Mn(II) in N = 0.523 AlCl₃:EMIC**

| Applied Potential | Al at. % | Mn at. % | Al-Mn Phase       |
|-------------------|----------|----------|-------------------|
| -1.2 V            | 84.4     | 14.1     | Amorphous         |
| -0.6 V            | 70.4     | 29.3     | Amorphous         |
| -0.3 V            | 52.9     | 42.0     | Amorphous + τ     |

**25 mM Mn(II) in N = 0.523 AlCl₃:EMIC**

| Applied Potential | Al at. % | Mn at. % | Al-Mn Phase       |
|-------------------|----------|----------|-------------------|
| -1.2 V            | 86.1     | 13.9     | Amorphous         |
| -0.6 V            | 79.5     | 20.5     | Amorphous         |
| -0.3 V            | 76.4     | 23.6     | Amorphous         |

**Saturated Mn(II) in N = 0.545 AlCl₃:EMIC**

| Applied Potential | Al at. % | Mn at. % | Al-Mn Phase       |
|-------------------|----------|----------|-------------------|
| -0.6 V            | 75.5     | 25       | Amorphous         |
| -0.3 V            | 76.6     | 23.4     | Amorphous         |
| -0.25 V           | 71.5     | 28.5     | Amorphous         |

**Saturated Mn(II) in N = 0.545 AlCl₃:EMIC**

| Applied Potential | Al at. % | Mn at. % | Al-Mn Phase       |
|-------------------|----------|----------|-------------------|
| -0.4 V*           | 51.8     | 46.9     | τ Al-Mn           |
| -0.35 V*          | 47.3     | 52.1     | τ Al-Mn           |
| -0.3 V*           | 45.7     | 53.3     | τ Al-Mn           |
| -0.25 V*          | 45.8     | 52.7     | τ Al-Mn           |

*Cell used for these deposits did not employ a luggen capillary. Consequently, because of solution IR drop actual electrode potential values should be 0.05 to 0.1 V more positive than the values in the table.

**25 mM Mn(II) in N = 0.545 AlCl₃:EMIC**

| Applied Potential | Al at. % | Mn at. % | Al-Mn Phase       |
|-------------------|----------|----------|-------------------|
| -1.2 V            | 90.5     | 9.5      | fcc + amorphous   |
| -0.6 V            | 93.1     | 6.9      | fcc + amorphous   |
| -0.3 V            | 90.2     | 9.8      | fcc + amorphous   |
| -0.25 V           | 83.3     | 16.7     | Amorphous         |

**Saturated Mn(II) in N = 0.60 AlCl₃:EMIC**

| Applied Potential | Al at. % | Mn at. % | Al-Mn Phase       |
|-------------------|----------|----------|-------------------|
| -1.2 V            | 79.1     | 20.9     | Amorphous         |
| -0.6 V            | 74.3     | 25.7     | Amorphous         |
| -0.3 V            | 81.9     | 18.0     | Amorphous         |
| -0.25 V           | 81.8     | 18.2     | Amorphous         |

**25 mM Mn(II) in N = 0.60 AlCl₃:EMIC**

| Applied Potential | Al at. % | Mn at. % | Al-Mn Phase       |
|-------------------|----------|----------|-------------------|
| -1.2 V            | 95.7     | 4.1      | fcc + amorphous   |
| -0.6 V            | 95.7     | 4.2      | fcc + amorphous   |
| -0.3 V            | 95.2     | 4.8      | fcc + amorphous   |
| -0.25 V           | 94.6     | 5.4      | fcc + amorphous   |
Figure 1. Cyclic voltammograms of Blank, 25 mM and saturated MnCl₂ solution in $N = 0.545 \text{ AlCl}_3:EMIC$ recorded at a Pt electrode.

Figure 2. Nucleation of 25 mM Mn(II) in $N = 0.545 \text{ AlCl}_3:EMIC$ molten salt at 25 °C.
Figure 3. XRD patterns of Al-Mn electrodeposits; (a) fcc aluminum + amorphous Al-Mn, (b) amorphous Al-Mn, (c) amorphous Al-Mn + τ Al-Mn, (d) τ Al-Mn.
Figure 4. Comparison of the phases observed in electrodeposition of Al-Mn from EMIC:AlCl₃ and NaCl:AlCl₃ as a function of composition.