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

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ABSTRACT

The electrochemical reduction of manganese (II) in acidic AlCl₃:EMIC (aluminum chloride:1-ethyl-3-methylimidazolium chloride) room temperature molten salt results in codeposition of aluminum and manganese. Constant potential deposition in the region of the reduction peak results in the deposition of manganese rich amorphous manganese-aluminum alloys. Constant potential deposition in the region of diffusion control results in the formation of aluminum rich amorphous manganese-aluminum alloys. Evaluation of the chronoamperometric transient behavior on platinum during electrodeposition at the foot of the wave shows that the codeposition of manganese and aluminum proceeds via three-dimensional instantaneous nucleation with diffusion controlled growth.

INTRODUCTION

Aluminum alloys with enhanced resistance to chloride-induced pitting corrosion have been produced using solute elements such as Ti, Cr, Mn, Cu, Zr, Nb, Mo, Ta, and W(1,2). These "stainless" aluminum alloys are of interest both for use as bulk deposits and as coatings over existing structural aluminum alloys. Producing the improved corrosion
resistance of these aluminum alloys often requires solute concentrations (up to 50 atom percent, a/o) that are far in excess of the equilibrium solubility limit (ca. 1 a/o). Consequently, nonequilibrium methods such as sputter deposition(3), melt spinning(4), and ion implantation(5) have been employed to prepare metastable single-phase aluminum alloys. While these techniques have produced corrosion resistant aluminum alloys, they are of limited commercial utility because of their high inherent cost and the difficulties associated with their application to large structures.

Electrochemical deposition is an alternative method for producing nonequilibrium alloys. It generally does not suffer from the cost and applicability disadvantages of the above methods. The key to application of electrodeposition, however, is finding a system from which the alloys can be deposited.

Over the past few years researchers at the National Institute for Standards and Technology (NIST) have studied the electrodeposition of nonequilibrium Al–Mn alloys from AlCl₃: NaCl molten salts(6-8). Alloys were made in compositions up to 50 a/o, and at molten salt temperatures ranging from 150 – 350 °C. More importantly, several of the single phase Al–Mn alloys exhibited pitting potentials up to 0.40 V more positive than unalloyed aluminum(1). More recently, researchers at NIST have demonstrated the electrodeposition of Al–Cr and Al–Ti alloys from the AlCl₃:NaCl molten salts(2,9). While these results are very promising, electrodeposition from AlCl₃:NaCl molten salts suffer from several disadvantages. The AlCl₃:NaCl molten salts must be operated at elevated temperatures, and they have relatively high aluminum chloride vapor pressures. An alternative to the high temperature AlCl₃:NaCl molten salts are a class of ionic liquids commonly referred to as room-temperature molten salts. These room-temperature molten salts have negligible vapor pressure and by their very nature operate at room temperature.

Successful deposition of Al–Mn(10), Al–Co(11,12), and Al–Ni(13,14) alloys from room–temperature molten salts has recently been reported. Furthermore, these preliminary reports indicate that many of the same Al–Mn alloy phases obtained from the high-temperature molten salts can be electrodeposited from the room-temperature system. These preliminary results demonstrate the feasibility of the room-temperature molten salts for aluminum alloy preparation. We have expanded upon these initial experiments in an effort to study in greater detail the electrodeposition of aluminum alloys from the room–temperature molten salts. This has entailed investigations of both the deposition process and the characterization of the alloys produced.

The room–temperature AlCl₃:EMIC 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(15-20). 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 AlCl_3:EMIC molten salts have very low dielectric constants. This fact, coupled with their low operating temperature, appears to promote preferential orientation of electrochemical deposits, thus making possible epitaxial growth of metals and alloys(10).

EXPERIMENTAL

The preparation and purification of EMIC and AlCl_3 were performed as described previously(22). All chloroaluminate molten salt preparations were performed at room temperature in a nitrogen filled Vacuum Atmospheres drybox with O_2 and H_2O levels < 1 ppm. Protonic impurities were removed by evacuation of the molten salt to 10^{-5} Torr for 48 h. MnCl_2 (Alfa) was soluble in acidic AlCl_3:EMIC molten salts up to concentrations of ca. 200 mM.

All electroanalytical experiments were carried out with an EG&G PARC model 273A potentiostat/galvanostat controlled with the EG&G PARC 270 software package. Voltammetric experiments were conducted in a drybox at 25 °C using a single compartment glass cell containing a Pt working electrode (BAS, 0.02 cm²). An Al wire placed in a separate tube with a vycor tip containing a 1.5:1.0 AlCl_3:EMIC molten salt served as the reference electrode. An Al coil was used as the counter electrode. Before each experiment, the working electrodes were polished successively with 1 μ, 0.3 μ and 0.05 μ alumina (Buehler).

The electrodeposition experiments were performed at constant potential in a single compartment glass cell. The working electrode was either a 25 x 25 mm Cu or Pt foil compression fit to the cell by a masked off No. 12 o-ring or a 2.5 cm long 1 mm diameter copper wire; this gave electrode areas of approximately 2.5 cm² and 0.785 cm², respectively. The copper flags and wire were first electropolished in 80% phosphoric acid-water solution, rinsed, and dried thoroughly prior to deposition. The reference electrode consisted of an Al coil submerged into a 1.5:1.0 molten salt contained inside a Luggin capillary. An Al wire coil immersed in the electrolyte was used as the counter electrode. The deposition process was potentiostatically controlled until a charge of 20 C was achieved to ensure a deposit thickness of at least 3 μm. The copper flag deposits made at the foot of the deposition peak (ca. -0.3 V) gave a current density range of 0.3 to 1.0 mA/cm², whereas the deposits formed at the current limiting region (ca. -0.6 V) gave a current density ca. 3.5 mA/cm². Integration of the constant potential curves recorded during the deposition process gave deposits of > 3 μm thick. The copper wire deposits made at the foot of the deposition peak (ca. -0.3 V) have a current density of 15 mA/cm², whereas the deposits formed at the current limiting region (ca. -0.6 V) have a current
density of 3.5 mA/cm². Following each deposition, excess molten salt was removed from the coated Cu or Pt by successive cleaning with cotton swabs soaked in toluene, hexane, ethanol, and water. These cleaned samples were used for the scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD) analysis, and corrosion experiments.

Micrographs of the as-deposited surface were collected using a Joel scanning electron microscope equipped with a Kevex energy dispersive spectrometer. Aluminum or manganese wire, and KCl powder 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 (Model: DMAX/B) in 20 scan mode. The XRD results were compared against the Joint Committee on Powder Diffraction Standards (JCPDS) reference tables using the platinum substrate or copper as an internal standard. Aluminum or manganese metal powder spread on double-sided tape, and copper or platinum foil was used to record standard spectra.

All of the experiments described were carried out in acidic molten salts: either 1.2:1.0 or 2.0:1.0 AlCl₃:EMIC and performed at room temperature.

RESULTS AND DISCUSSION

The first step in our investigation of the Al–Mn alloys involved the electrochemical evaluation of the deposition process from acidic AlCl₃:EMIC molten salts. Experiments were performed on two different molten salt compositions (1.2:1.0 and 2.0:1.0) and at two MnCl₂ concentrations (25 mM and saturated or ca. 200 mM). The choice of a saturated Mn molten salt was made for two reasons. First, to determine if an order of magnitude change in concentration would increase the Mn content of the deposits, and second, to insure that during the electrodeposition the concentration of manganese remained relatively constant.

Initially, the electrochemical behavior of the system was investigated at inert disk macroelectrodes (diameters > 1.0 mm) such as platinum, and gold. Standard electrochemical techniques including chronoamperometry, and staircase cyclic voltammetry have been used to characterize the deposition process. Figure 1 is a series of three cyclic staircase voltammograms taken with a platinum disk electrode (2 mm dia.). The dashed line is that of pure 1.2:1.0 AlCl₃:EMIC and is typical for the deposition and stripping of aluminum. In this composition of molten salt, there is ca. 450 mM of the reducible aluminum species available. The solid line is that of 25 mM Mn⁺⁺ in 1.2:1.0
AlCl₃:EMIC. The reduction wave of this cyclic staircase voltammogram traces that of pure aluminum and is distinguished only by the oxidation waves typical for an aluminum metal alloy. This masking of the metal deposition by the aluminum wave is unusual in metal deposition and is seen again in the saturated Mn molten salt (dotted line). We also see that the rising portion of the reduction waves are shifted cathodically with increased concentration. Taken together this indicates that at smaller cathodic overpotentials the deposition process, with respect to the alloy composition, is kinetically controlled. At higher cathodic overpotentials it becomes mass transported limited in Mn²⁺ and Al₂Cl₇⁻.

Chronoamperometry was used to investigate the nucleation and growth process. Previous investigations have shown that the initial stages of electrodeposition of metals from acidic AlCl₃:EMIC often involves some form of three-dimensional nucleation process followed by hemispherical diffusion-controlled growth of the developing nuclei(23). The two limiting cases for this type of metal deposition are instantaneous nucleation on a fixed number of active sites and progressive nucleation on an infinite number of active sites(23,24). 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 are given by Equations 1 and 2 respectively(24).

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

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

Figure 2 demonstrates the simultaneous electrodeposition of aluminum and manganese at a polycrystalline platinum electrode in unstirred 25 mM and saturated Mn²⁺ solutions. Plots of \((i/i_{\text{max}})^3\) 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, \(t_0\), the correction corresponding to the maximum current is \(t_{\text{max}}' = t_{\text{max}} - t_0\). Plots of \((i/i_{\text{max}})^2\) versus \(t/t_{\text{max}}'\) calculated from Equations 1 and 2 and using the chronoamperometry data are shown in Figure 2. It is apparent from Figure 2 that the nucleation of manganese on platinum is in good agreement with instantaneous three-dimensional hemispherical diffusion-controlled growth model given by Equation 1.

Following the initial electrochemical experiments, Al-Mn alloy films ca. 3-10 µm thick were deposited onto copper and platinum coupons (deposition area ~ 2.5 cm²). Scanning electron microscopy (SEM) was used to evaluate the morphology of the as-deposited films, and energy-dispersive x-ray spectroscopy (EDS) was employed to determine their elemental composition. Figures 3 and 4 show the as-deposited surface.
morphologies of electrodeposits formed from electrolytes containing 25 mM and saturated Mn++, respectively. At lower overpotentials of -0.25 and -0.3 V the surface is nodular in appearance and free of surface molten salt. The deposits are more adherent and brighter in appearance, than deposits made at the higher overpotentials. At higher overpotentials, -0.6 and -1.2 V, the cleaned surface appears smoother with much smaller nodules. These cleaned deposits are much darker, and are less adherent than the lower overpotential deposits. The EDS analysis for these electrodeposits is seen in Table 1. At lower overpotentials the current density is ca. 1 mA/cm² and at the higher overpotentials it is 3.5 mA/cm². All of the deposits except the -0.6 V deposit had a low chloride content indicating that little or no molten salt was entrained in the deposit. Any molten salt retained by the deposit would not lend itself to corrosion experiments or exposure to an oxygen or water atmosphere due to hydrolysis of the AlCl₃.

X-ray diffraction measurements of the lower overpotential deposits were used to determine if the alloys are crystalline or amorphous, and if crystalline, what phase is present. Figure 5a indicates that an amorphous deposit is present in the -0.3 V deposits from both 25 mM and saturated manganese solutions, the region centered at 43 degrees, and most important, no crystalline aluminum is present. The sharp Bragg peaks are those of the copper substrate. Figure 5b is the XRD of the deposit at higher overpotential and shows no indication of an amorphous deposit. This may be due to the thinness of the deposit or the lack of an amorphous compound. The former seems more likely in light of the SEM/EDS results which indicate a high aluminum content.

Thin films (~ 3 μm) of Al-Mn alloys were also electrodeposited onto copper wire (deposition area ~ 0.19 cm²). The morphology and composition of these deposits were different than those on the copper coupons. The deposit made at -0.3 V was the only one that survived the overplating and polishing process. This chloride free film had a manganese content of ca. 11 at. % and an aluminum content of ca. 89 at. %. This represents a 3 fold decrease in manganese in wire deposits versus deposits made on copper coupons. The current density of the wire deposit was 15 mA/cm², which is 15 times higher than the coupon deposit and may explain the lower manganese content of this deposit. The XRD of this deposit indicates two phases; an amorphous deposit and crystalline fcc aluminum. The fcc aluminum may result from the higher current density used for the depositions on copper wire.

**CONCLUSIONS**

The cyclic staircase voltammetry indicated that at lower overpotentials the deposition of aluminum-manganese is kinetically controlled and at higher overpotentials it becomes mass transported limited in Mn²⁺ and Al₂Cl₇⁻. The mechanism for nucleation and growth
of Al-Mn alloys on platinum was shown to be instantaneous in both 25 mM and saturated manganese solutions.

Deposits made on electropolished copper coupons at constant potentials in the lower overpotential region of ca. -0.3 V produced an amorphous aluminum-manganese alloy free of chloride and crystalline aluminum. The higher overpotentials deposits at ca. -0.6 V gave no indication of crystalline aluminum or an amorphous deposit.

Deposits made on copper wire showed a three fold decrease in manganese content and the presence of crystalline fcc aluminum. These deposits had a 15 fold increase in their current density versus those made on copper coupons which may explain the manganese content and fcc aluminum presence.

The results for the electrodeposition of Al-Mn alloys from the high temperature molten salts and our preliminary results from the room-temperature molten salts provide an excellent starting point for continued experimentation.

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Figure 1. Cyclic voltammograms of Blank, 25 mM, and saturated Mn solutions in 1.2:1.0 AlCl₃:EMIC recorded at a Pt electrode.
Figure 2. Comparison of the 25 mM Mn\textsuperscript{+} current-time transients to the theoretical transients for progressive and instantaneous 3-dimensional hemispherical diffusion controlled growth.
Figure 3. 25 mM Mn$^{++}$ deposits from 1.2:1.0 AlCl$_3$:EMIC
Figure 4. Saturated Mn$^{++}$ deposits from 1.2:1.0 AlCl$_3$:EMIC.
Figure 5a. XRD of deposits made at the lower overpotentials from 25 mM and saturated manganese solutions respectively.
Figure 5b. XRD of deposits made at the higher overpotentials from 25 mM and saturated manganese solutions respectively.
Table 1. EDS results of deposits onto copper coupons. The current passed was sufficient to deposit a minimum of 3 microns and at the current density, j, noted.

| Applied Potential | Al at. % | Mn at. % | Cl at. % | 25 mM Mn ++ 1.2:1.0 Molten salt |
|-------------------|---------|----------|----------|-------------------------------|
| -1.2 V            | 78.7    | 19.5     | 0.9      | j = 3.5 mA/cm²                |
| -600 mV           | 69.8    | 23.1     | 7.1      | j = 3.5 mA/cm²                |
| -300 mV           | 63.7    | 35.8     | 0.52     | j = 0.7 mA/cm²                |
| -250 mV           | 66.8    | 32.7     | 1.0      | j = 0.3 mA/cm²                |

| Applied Potential | Al at. % | Mn at. % | Cl at. % | Saturated Mn ++ 1.2:1.0 Molten salt |
|-------------------|---------|----------|----------|------------------------------------|
| -1.2 V            | 33.7    | 56.4     | 10.7     | Thin deposit j = 3.9 mA/cm²        |
| -600 mV           | 33.3    | 60.6     | 6.1      | Thin deposit j = 3.4 mA/cm²        |
| -300 mV           | 31.7    | 65.6     | 2.7      | j = 1.7 mA/cm²                    |
| -250 mV           | 33.2    | 60.9     | 5.8      | j = 1.0 mA/cm²                    |