EQCM Measurements of Cobalt-Aluminum Alloys

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ABSTRACT

Electrochemical quartz crystal microbalance (EQCM) measurements were made in situ on cobalt-aluminum alloy deposition and stripping in room-temperature molten salts. The room-temperature molten salt was AICl3-rich (acidic) AICl3:EMIC (EMIC = 1-ethyl-3-methylimidazolium chloride). In these melt systems, the cobalt-aluminum alloys are electrodeposited between the two metal redox couples of cobalt and aluminum. Cobalt metal is deposited at potentials positive of + 0.4 V, while the CoAlx alloys are produced at potentials negative of +0.4. The value of x in CoAlx gradually increases up to a value of 2 as the electrodeposition potential (Ededeposition) decreases; however, plots of x vs. Ededeposition exhibit sloping plateaus and indicate preferential formation of alloys having integral compositions of CoAl1 and CoAl2. The formation of these alloys can be interpreted as a UPD-based process or as a free energy of alloy formation. Upon oxidation of the alloys, EQCM data indicates that aluminum is stripped out of the alloy matrix separately from the cobalt.

INTRODUCTION

The room-temperature AICl3:EMIC molten salts (EMIC = 1-ethyl-3-methylimidazolium chloride) have proven to be useful solvents for electrochemical and chemical investigations.1-2 Most importantly, aluminum can be reversible electrodeposited from acidic melt compositions (AICl3:EMIC molar ratio > 1).3-9 The molten salts are excellent solvents for both ionic and molecular species; thus, a great many transition metal salts are soluble in the acidic melts. The room-temperature molten salts are also excellent electrochemical solvents: they possess a wide electrochemical window; they are purely ionic, so they have high intrinsic conductivities (ca. 10^{-2} ohm^{-1} cm^{-1}); and they are liquid and thermally stable over a very wide temperature range (-60 to 250 °C). Unlike conventional electroplating baths, the AICl3: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.\textsuperscript{10}

We have demonstrated that EQCM experiments can be effective performed in these AlCl\textsubscript{3}:EMIC molten salts by examining the electrodeposition of aluminum onto a gold EQCM electrode.\textsuperscript{11} The viscosity of the molten salt is comparable to that of ethylene glycol, but does not dampen the frequency change of the rigid layer. By examining the underpotential deposition (UPD) of aluminum on gold/chromium coated quartz crystals, it was possible to get monolayer measurements in this viscous medium which agreed with the expected frequency change for an Al monolayer. Further tests with UPD of PbCl\textsubscript{2} confirmed the applicability of EQCM in these melt electrolytes.

Earlier, we reported the UPD-induced electrodeposition of Co-Al alloys in the AlCl\textsubscript{3}:EMIC room-temperature molten salts.\textsuperscript{11,12} In these studies, we used microelectrodes and energy dispersive spectroscopy (EDS) to analyze the composition of these alloys.\textsuperscript{12} We discussed the electrodeposition behavior (e.g., nucleation mechanism) of Co-Al alloys at platinum macroelectrodes and the role of UPD (both Co-on-Pt and Al-on-Co) in the overall deposition process.\textsuperscript{10} We also presented EDS analyses of the Co-Al electrodeposits and scanning electron microscopy (SEM) images of alloy thin films, showing unusual surface morphologies.

In this paper, we employ an electrochemical quartz crystal microbalance to investigate the mass changes occurring during film formation and growth during electrodeposition and the selective dealloying of these materials during anodization.

**EXPERIMENTAL**

Purification of AlCl\textsubscript{3}:EMIC melt components has been previously described.\textsuperscript{13,14} Protonic impurities were removed by vacuum treatment at \(1 \times 10^{-5}\) Torr for several days.\textsuperscript{15,16} The analyte melt used in this investigation had a AlCl\textsubscript{3}:EMIC molar ratio of \(N = 0.55\) (\(N = \) mole fraction of AlCl\textsubscript{3}) and contained 70 mM Co(II) added as anhydrous CoCl\textsubscript{2}. Polycrystalline gold disk electrodes were made by vapor deposition of approx. 2000 Å of gold onto approximately 50 Å of chromium. The support material was AT-cut 5 MHz Quartz crystals, which were highly polished and 1.0 inch in diameter. The electrochemically active area was 0.34 cm\textsuperscript{2} and the piezoelectric active area was 0.28 cm\textsuperscript{2}. The counter electrode was a platinum coil, and the reference electrode consisted of aluminum wire immersed in \(N = 0.60\) AlCl\textsubscript{3}:EMIC melt contained in separate fritted or Vycor glass compartments.

All experiments were performed in glass-constructed cells sealed under a UHP Helium atmosphere in a Vacuum Atmospheres dry box at room temperature. Cyclic voltammetry was performed with an Intertech Systems HB-111 Analog Function Generator and a PS151 Potentiostat / Galvanostat controlled by the Asyst 4.01 software.
environment using a GTSI 486DX/33MHz computer. Data acquisition was performed with a Data Translation DT-2801A D/A board and a DT-707 screw board. The oscillator circuit was a 5 MHz crystal operating in the normal mode.17

RESULTS AND DISCUSSION

Cyclic voltammetry for cobalt, aluminum, and its alloys in a $N = 0.55 \text{AlCl}_3:\text{EMIC}$ melt is represented in Fig. 1. Data are plotted with reduction proceeding to the left. Starting from the right side of the voltammogram and scanning to less positive potentials, one sees an initial peak at +0.5 V corresponding to the electrodeposition of Co metal, a plateau at +0.3 V due to formation of a 1:1 Co-Al alloy, a plateau at +0.1 V corresponding to a 1:2 Co-Al alloy, and finally the electrodeposition of bulk aluminum at -0.1 V. The presence of the two preferred alloys compositions CoAl$_x$ and CoAl$_2$ has been verified by SEM-EDS and microelectrode work,10,12 although all compositions from CoAl$_x$ with $x = 0$ to 2 are accessible. This earlier work led to the use of EQCM to obtain further data on the electrodeposition and oxidative stripping of these unusual alloys.

The acidic chloroaluminate room-temperature molten salts have a viscosity of approximately 15-20 centipoise which is about the same as ethylene glycol. This tends to slow the EQCM response time and necessitates the use of slower scan rates. From the weight changes and a knowledge of the material electrodeposited the frequency data from the EQCM can be converted to a current response dataset. This calculated dataset should agree with the current response data taken from the cyclic voltammetry experiments. Deviations from a perfect match in the data often indicates the uptake of solvent or a mixed transport phenomenon. To eliminate the possibility of mixed transport, limitation of transportable species is achieved and the number of different redox events are limited. In the case of molten salts, it is possible to get solvent entrapment on roughened surfaces by occlusion.

Upon obtaining simultaneous current and frequency data as a function of potential, standard EQCM analysis provides the total weight change as a function of potential. To differentiate the weight changes assigned independently to Co and to Al during electrodeposition and stripping, it is necessary to combine the changes in total weight ($\Delta W_{\text{total}}$) and the changes in the total charge ($\Delta Q_{\text{total}}$) according to the formulations below.

Assuming total weight and charge are from Co and Al deposition and stripping only, then Eqns. 1 and 2 are valid.

$$\Delta W_{\text{Total}} = \Delta W_{\text{Co}} + \Delta W_{\text{Al}} \hspace{1cm} [1]$$

$$\Delta Q_{\text{Total}} = \Delta Q_{\text{Co}} + \Delta Q_{\text{Al}} \hspace{1cm} [2]$$
Using the constants $K_1 = (3F)(\text{Atomic Mass Al})^{-1}$ and $K_2 = (2F)(\text{Atomic Mass Co})^{-1}$ to convert charge to weight, Eq. 2 is substituted into Eq. 1 to give Eq. 3.

$$
\Delta W_{Co} = \frac{(\Delta Q_{\text{Total}} - K_1 \Delta W_{\text{Total}})}{(K_2 - K_1)}
$$

Then, $\Delta W_{Co}$ is substituted back into Eq. 1 to calculate $\Delta W_{Al}$. Finally both weight changes are converted to micromoles and plotted (see Figure 2) against potential to determine the selective material gain or loss during deposition or stripping, respectively, of the metals and alloys.

In Fig. 2, both Co and Al are seen to deposit in the alloy forming region during the negative potential sweep; however, the deposition peaks are not clearly defined, and so the cathodic currents are not discussed in this study. On the other hand, the oxidation currents display well resolved stripping peaks for both Al and Co, which are used to examine the selective dealloying processes during alloy oxidation. From the pronounced stripping peaks of only Al at +0.2 and +0.5 V, it appears that Al is selectively stripped from the alloys before Co. Cobalt oxidation appears to take place in two steps at +0.6 and +0.95 V — potentials positive of the Co metal reduction potential. Importantly, Al deposits before its reduction potential to form an alloy with Co via a UPD mechanism, and it strips from the alloy first. The formation of Co-Al alloys in this system is supported by EDS results that do not show any discrete islands of individual metal forming on the surface.

Finally, Fig. 2 also shows that only Al is depositing in the Al bulk deposition region. This serves as a test of the model used to derive Eq. 3, because only a large micromolar change in Al should be seen in the bulk Al deposition region.

**SUMMARY**

From this EQCM study the following conclusions can be made:

1. The composition of the Co-Al alloy can be changed dramatically by adjusting the plating potential. This results in a range of CoAlₓ alloys where x is predominantly 1 or 2.

2. Aluminum can be selectively stripped out of the CoAlₓ structure (dealloying), leaving behind a cobalt superlattice. The remaining Co can then be stripped from the surface at potentials positive of the Co reduction potential.

3. At more negative potentials, it is possible to plate bulk Al on top of the predeposited alloy underlayer.
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Figure 1. Cyclic voltammogram at 0.34-cm$^2$ Au EQCM electrode in $N = 0.55$ AlCl$_3$:EMIC containing 70 mM Co(II).

Figure 2. Plot of $\Delta W_{Co}$ (dotted line) and $\Delta W_{Al}$ (solid line) in micromoles versus potential. Arrows indicate the approximate potentials where the electrodeposition of Co metal, CoAl$_1$ (alloy 1), and CoAl$_2$ (alloy 2) begin.