Electrodeposition of Copper and Copper–Aluminum Alloys from a Room-Temperature Chloroaluminate Molten Salt

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ABSTRACT

The electrodeposition of copper and copper–aluminum alloys was investigated in the Lewis acidic aluminum chloride-1-methyl-3-ethylimidazolium chloride (60.0–40.0 mol %) molten salt containing electrogenerated Cu(I) at 40 \pm 1°C. Sampled current and rotating ring-disk electrode voltammetry experiments indicated that it was possible to produce Cu–Al alloy deposits at potentials positive of that corresponding to the electrodeposition of bulk aluminum (~0 V). For a 5.0×10^{-2} mol L⁻¹ solution of Cu(I), the onset of the aluminum codeposition process was found to occur at around 0.30 V vs. the Al(III)/Al couple; however, a limiting current for the reduction of Cu(I) to pure copper metal can be observed in the 0.60–0.30 V potential interval in this solution. The Cu–Al alloy composition was found to be independent of the Cu(I) concentration, reaching a maximum value of 43 percent atomic fraction aluminum at 0 V. The surface morphology of bulk Cu–Al alloy electrodeposits was highly dependent on the aluminum content; pure copper deposits had a dense, nodular appearance, whereas deposits containing appreciable amounts of aluminum consisted of fragile dendrites. X-ray diffraction studies indicated that Cu–Al deposits containing about 7.2 percenter atomic fraction Al retained the face-centered cubic (fcc) copper structure; however, deposits containing 12.8 percent atomic fraction Al were two-phase with the second phase tentatively identified as martensitic β' -Cu₃Al. This phase appears to form before fcc copper becomes saturated with aluminum.

Introduction

During the electrodeposition of binary alloys, the ions of the less noble component are sometimes reduced at potential more positive than is typically observed when the ions of the more noble component are not present in the plating solution. This shift in deposition potential has been attributed to the decrease in free energy accompanying the formation of solid solutions and/or intermetallic compounds and was described by Polukarov and Gorbunova more than 40 years ago.¹ This phenomenon is often called "underpotential alloy deposition" to distinguish it from the classical phenomenon of underpotential deposition of monolayers on metal surfaces.

The electrodeposition of a transition metal-aluminum alloy from a chloroaluminate molten salt at potentials positive of the equilibrium potential of the Al(III)/Al couple was first reported by Hussey et al.² during an investigation of copper (II) electrochemistry in Lewis acidic aluminum chloride-N-methylpyridinium chloride. These workers observed a cathodic voltammetric wave negative of the copper deposition potential and 0.20 V positive of the bulk aluminum deposition in polarograms constructed from current-time transients for the reduction of copper (II) at a tungsten electrode in this room temperature melt. This wave was found to arise from the codeposition of aluminum with copper. Since this initial report, articles describing the electrodeposition of nickel-aluminum alloys from aluminum chloride-1-butylpyridinium chloride (AlCl₃-BupyCl), ^{3,4} aluminum chloride-1-methyl-3-ethylimidazolium chloride (AlCl₃-MeEtimCl), ⁵ and AlCl₃-NaCl⁶ have appeared in the literature

The underpotential codeposition of aluminum also occurs during the reduction of cobalt(II) from the AlCl₃-MeEtimCl melt,^{7,8} and the resulting cobalt–aluminum alloys have been characterized with X-ray diffraction techniques.⁸ However, unlike the nickel–aluminum system, there is a significant difference between the potential at which the mass-transport-limited reduction of cobalt(II) is observed and the potential at which the codeposition of aluminum begins. Thus, it is possible to electrodeposit pure cobalt but not pure nickel from room temperature melts.

The electrodeposition of copper-aluminum, nickel-aluminum, and cobalt-aluminum alloys at underpotentials is consistent with the observations of Nicol and Philip,9 who predicted that underpotential alloy deposition is actually related in some way to the classical phenomenon of underpotential deposition of monolayers on metal surfaces and that it is likely to be observed when the work function of the less noble alloy component is smaller than that of the more noble component. Thus, considering the work functions of some of the other first-row transition elements that can be electrodeposited from acidic chloroaluminates, the underpotential codeposition of aluminum ($\phi_{A1} = 4.28 \text{ eV}$)¹⁰ with zinc $(\phi_{Zn} = 4.33 \text{ eV})^{10}$ seems unlikely, whereas this phenomenon is expected during the electrodeposition of copper ($\phi_{Cu} = 4.65 \text{ eV}$)¹⁰ or iron ($\phi_{Fe} = 4.5 \text{ eV}$).¹⁰ An investigation recently completed in this laboratory confirms the first prediction, i.e., the underpotential codeposition of aluminum does not occur during the electrodeposition of zinc.¹¹ Although the underpotential codeposition of alu-minum and copper has been reported,² the electrochemistry and crystal structure of subsequent electrodeposits are not currently understood. In this article, we describe the electrodeposition of copper and the codeposition of aluminum with copper to form copper-aluminum alloys from solutions of copper(I) in the Lewis acidic AlCl₃-MeEtimCl melt.

Experimental

Instrumentation.—The nitrogen-filled glove box system and the method used to evaluate the quality of the glove box atmosphere have been described.¹² The electrochemical instrumentation, electrode rotator, platinum rotating disk electrode (geometrical area 0.196 cm²), platinum-platinum rotating ring-disk electrode (RRDE) ($r_1 = 2.29$, $r_2 = 2.46$, and $r_3 = 2.69$ mm), and the electrochemical cell with reference and counter electrodes were identical to those employed during a previous investigation.⁸ Experiments were conducted in the 60.0–40.0 mol % AlCl₃–MeEtimCl melt at 40 ± 1°C. All potentials are referenced to the Al(III)/ Al couple in this melt.

Preparation and purification of the AlCl₃-MeEtimCl melt.—MeEtimCl was synthesized from ethyl chloride and 1-methylimidazole (Aldrich^a 99%) and recrystallized from

^{*} Electrochemical Society Student Member.

^{**} Electrochemical Society Active Member.

^a Certain commercial materials and instruments are identified in this report to adequately specify the experimental procedure. In no instance does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the material identified is necessarily the best available for this purpose.

acetonitrile–ethyl acetate mixtures as described in the literature.¹³ In order to avoid the codeposition of hydrogen with copper and/or copper–aluminum alloy, it was necessary to remove all traces of protonic impurities from the melt. This was accomplished by pre-electrolyzing the melt between aluminum electrodes (Alfa/ÆSAR, puratronic) for several days while the melt was stirred. The melt was filtered through a medium-porosity glass frit to remove any aluminum debris that may have detached from the cathode during the electrolysis step, and it was then evacuated to 1.3×10^{-3} Pa for 24 h.

Characterization of bulk Cu-Al alloy deposits.—Bulk alloy deposits were characterized with scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDS), and X-ray diffraction (XRD) techniques using the facilities at the National Institute of Standards and Technology. The XRD patterns were collected on a Scintag diffractometer by using Cu K α radiation and a Ge solidstate detector. Reflections from the electrodeposit and nickel substrate were well resolved and were modeled using a regular Pearson VII function. The integrated intensities and d-spacings were obtained from the profile fit. Lattice parameters were determined by least-squares refinement using the reflections from the nickel substrate as an internal standard.

Results and Discussion

Copper(I) was introduced into the melt by the electrodissolution of a copper wire anode at an applied potential, E_{app} , of 0.85 V. The weight loss of the copper anode was determined after the passage of a given charge, and calculations based on these measurements confirmed that copper(I) was the anodization product. The data needed to construct a Nernst plot were obtained by periodically interrupting such anodization experiments after the passage of a known charge and then measuring the equilibrium potential, E_{eq} , of the Cu(I)/Cu couple. A Nernst plot constructed from data taken at 40°C was linear with a correlation coefficient of 0.9999; the intercept of this plot yielded a formal potential, $E^{\circ\prime}$, of 0.837 \pm 0.003 V. The slope of this plot was 0.066 ± 0.002 V, which is in reasonable agreement with the 0.062 V slope expected for a oneelectron reaction at this temperature.

Voltammetric results.—Cyclic voltammograms of a solution of copper(I) at a stationary platinum disk electrode that were recorded with different switching potentials, E_{λ} , are shown in Fig. 1. The main features of the voltammograms with $E_{\lambda} > 0.30$ V are a single reduction wave with a peak potential of 0.69 V and a prominent oxidation wave in the range 0.90–1.00 V, whose exact position varies with E_{λ} . The overall appearance of these voltammograms is typical of that expected for an electrode reaction involving the electrodeposition and stripping of a bulk metal deposit. However, if E_{λ} is set to 0 V, then an additional reduction wave is apparent at about 0.20 V. A rapidly increasing current arising from the electrodeposition of bulk aluminum is observed when the electrode potential is scanned below 0 V, and several additional stripping waves are present in the voltammogram on the reverse scan prior to the stripping of bulk copper.

Figure 2 shows a series of sampled-current or pulse voltammograms constructed from chronoamperometric current-time transients that were recorded at a platinum disk electrode in unstirred 0.010, 0.025, and 0.050 mol L⁻¹ solutions of copper(I) in the 60.0–40.0 mol % melt. The data used to construct these voltammograms were obtained by stepping the electrode potential from an initial value of 1.50 V, where no faradaic reaction takes place, to the potential of interest. The current was sampled at 10 s following the application of the potential pulse. The resulting electrode potential at 1.50 V for 30 s while the solution was stirred, and then the entire process was repeated at another potential. All three voltammograms exhibit well-defined limiting currents due to the mass-transport-controlled reaction



Fig. 1. Cyclic voltammograms recorded at a stationary Pt electrode in a 0.025 mol L⁻¹ solution of Cu(1) in the 60.0–40.0 mol % melt at 40°C. Initial potential was 1.50 V, and the scan rate was 0.050 V s⁻¹.

$$Cu^+(solv) + e^- \rightleftharpoons Cu(s)$$
 [1]

where Cu⁺(solv) represents copper(I) solvated by the acidic melt. In addition, these voltammograms show a rise in current beginning at about 0.25 V, which is due to the codeposition of aluminum with copper to produce a copper–aluminum alloy, Cu_xAl_{1-x}, where 1 > x > 0

$$x \operatorname{Cu}^{+}(\operatorname{solv}) + 4(1 - x)\operatorname{Al}_{2}\operatorname{Cl}_{7}^{-} + (3 - 2x)e^{-} \rightleftharpoons \operatorname{Cu}_{x}\operatorname{Al}_{1-x}$$

 $+ 7(1 - x) \text{AlCl}_{4}^{-}$ [2]

In general, the voltammograms in Fig. 2 are very similar in appearance to those recorded during the electrodeposition of cobalt and cobalt–aluminum alloys from solutions of cobalt(II) in the acidic $AlCl_3$ –MeEtimCl melt (cf. Ref. 8,



Fig. 2. Current-sampled voltammograms recorded at a stationary Pt electrode in solutions of Cu(I) in the 60.0-40.0 mol % melt at 40°C. The Cu(I) concentrations were: (\bullet) 0.010, (\blacksquare) 0.025, and (\blacktriangle) 0.050 mol L⁻¹, and the current was sampled at 10 s following the application of each potential pulse.

Fig. 1). The limiting currents of the voltammograms in Fig. 2 were found to vary linearly with the copper(I) concentration; the diffusion coefficient of copper(I), $D_{\rm Cu(D)}$, was calculated from these limiting currents by using the Cottrell equation. The average value of $D_{\rm Cu(I)}$ is (3.6 \pm 0.5) $\times 10^{-7}$ cm² s⁻¹, and the Stokes–Einstein product, $D_{\rm Cu(I)}\eta/T$, where η and T are the absolute viscosity and temperature, respectively, is 1.9×10^{-10} g cm s⁻² K⁻¹.

The copper–aluminum alloy composition, represented for convenience as the fraction of aluminum in the alloy, 1 - x, was estimated from the voltammograms in Fig. 2 by using the following expression

$$1 - x = 1/\{1 + 3[i_1/(i_1 - i_1)]\}$$
[3]

where i_1 is the limiting current for the reaction depicted in Fig. 2, and i_t is the total current observed at potentials where the codeposition of aluminum is observed. Plots of 1 - x vs. *E* based on these calculations are given in Fig. 3 for several different copper(I) concentrations. Examination of the data in this plot reveals that the copper-aluminum alloy composition is independent of the copper(I) concentrations that were examined in this study.

Taken together, the results presented above suggest that at a fixed potential the rate of alloy formation is determined by the mass-transport-limited reduction of copper(I), and as a result, the rate of alloy formation increases in direct proportion to an increase in the copper(I) concentration. Thus, under the conditions of the present study, the concentration of $Al_2Cl_7^-$ does not play a role in determining the rate of alloy formation because the concentration of this ion is in large excess (1.95 mol L⁻¹) over the copper(I) concentration, i.e., the reaction depicted in Eq. 2 can be considered to be pseudo-first-order in copper(I). This mechanism is very similar to that proposed for the underpotential deposition of CdTe from aqueous solutions of $HeTeO_2^+$ and $CdSO_4$, where the rate of CdTe formation is controlled by the masstransport-limited reduction of the HeTeO2 and is independent of the concentration of the latter.14 The electrodeposition of Ni-Al from AlCl₃-NaCl at 150°C is also independent of the Ni(II) concentration in the melt.⁶ However, somewhat different results were found during previous investigations



Fig. 3. Fraction of Al in Cu–Al alloy, 1 - x, as a function of potential: (\bigcirc) 0.010 mol L⁻¹ Cu(I), from Fig. 2; (\square) 0.025 mol L⁻¹ Cu(I), from Fig. 2; (\triangle) 0.050 mol L⁻¹ Cu(I), from Fig. 2; (\bigcirc) 0.010 mol L⁻¹ Cu(I), from RRDE-ALSV experiments; and (\blacksquare) AAS analysis of bulk electrodeposits.

involving the underpotential deposition of Co–Al⁸ and Ni–Al⁵ in acidic AlCl₃–MeEtimCl. At a fixed potential, the compositions of these alloys varied with the concentrations of the respective transition-metal ions in the deposition solution, even though the transition-metal ions were undergoing reduction at the mass-transport-limited rate during alloy formation. This suggests that in both cases the aluminum codeposition process is kinetically hindered.

Thin-layer deposition-stripping experiments.-Anodic linear sweep voltammetry (ALSV) experiments were carried out at a platinum RRDE in order to further probe the composition and structure of the electrodeposited Cu-Al alloys. This technique is similar to that pioneered by Andricacos and co-workers 15 at the IBM T. J. Watson Research Center and was used successfully in a study of the Co-Al system carried out in this laboratory.⁸ The application of this technique involves two steps. In the first step, the alloy of interest is deposited potentiostatically on the RRDE disk from a solution containing the reducible ions of the transition metal with the ring electrode inactive. Next, the electrode is removed from the plating solution and immersed in pure melt that does not contain transitionmetal ions. The disk electrode is then slowly scanned (0.002 V s^{-1}) anodically from the rest potential while the ring electrode is held at a potential where the limiting current for the reduction of the transition metal ion is observed but positive of that where aluminum codeposition takes place. Thus, transition-metal ions that are produced during oxidation of the disk deposit are reduced at the ring. A ring potential, $E_{\rm ring}$, of 0.55–0.30 V was found to be sufficient to achieve a limiting current for the reduction of copper(I) and avoid the codeposition of aluminum during these experiments.

In order to apply this technique to the analysis of Cu–Al alloys, the collection efficiency of the RRDE, $N_{\rm exp}$, must be determined. This was done by electrodepositing pure copper on the RRDE disk at $E_{\rm app} = 0.50$ V with the ring inactive and then anodically stripping the copper from the disk with $E_{\rm r} = 0.50$ V. The average value of $N_{\rm exp}$ resulting from several such experiments is 0.207 ± 0.005 . This result is in good agreement with the theoretical collection efficiency of 0.220 calculated from the dimensions of the RRDE by using the expression given by Albery and Hitchman.¹⁶

The disk and ring voltammograms resulting from typical RRDE-ALSV experiments in which Cu-Al deposits were produced on the disk at $E_{app} = 0.30, 0.20, 0.10, and 0 V$ from a 10.0 mol L⁻¹ solution of copper(I) and then anodi-cally stripped from the disk in pure melt with $E_{ring} = 0.50 V$ are shown in Fig. 4 and 5. A charge density of 510 mC cm⁻² was used to prepare each deposit; this charge density corresponds to a deposit thickness of 0.37 µm, assuming a compact layer of pure copper. These figures show the disk current, $i_{\rm disk}$, and the corrected ring current, $i_{\rm ring}/N_{\rm exp}$, as well as the difference in these two currents, $i_{\text{disk}} - i_{\text{ring}}/N_{\text{exp}}$. The disk voltammogram derived from the deposit prepared at $E_{app} = 0.30$ V (Fig. 4a) exhibits a single oxidation wave located at 0.79 V. As expected, this deposit consists entirely of copper because $i_{\rm disk} - i_{\rm ring}/N_{\rm exp}$ is approximately 0. (In practice, the direct subtraction of $i_{\rm ring}/N_{\rm exp}$ from $i_{\rm disk}$ is imperfect because of small differences in the profiles of the ring and disk waves.) The disk voltammogram associated with the deposit prepared at $E_{\rm app}$ = 0.20 V also consists of a single wave at ca. 0.79 V; however, $i_{\text{disk}} - i_{\text{ring}}/N_{\text{exp}}$ is not zero, indicating that aluminum is also oxidized from the deposit along with the copper. Figures 5a and b show disk and ring voltammograms resulting from RRDE-ALSV experiments with the 0.10 and 0 V deposits, respectively. The disk voltammogram of the former exhibits a large stripping wave at 0.76 V and a smaller oxidation wave at 0.56 V. The wave appearing at more positive potentials arises from the oxidation of both copper and aluminum from the deposit, whereas the wave at 0.56 V results from the oxidation of aluminum. The disk voltammogram derived from the deposit prepared at $E_{app} = 0$ V exhibits three waves located at 0.74, 0.51, and 0.20 V, respectively. Only the first wave has a current component due to the oxidation of copper; the other two obviously arise from the dealloying of aluminum. The presence of multiple stripping waves for alloy deposits has been attributed to the presence of multiple phases in the alloy¹⁷ as well as sequential phase transitions that can occur during the selective dissolution of a single-phase material.¹⁸ Because dissolution of the less noble species is associated with the free-energy of the alloy, one would expect to observe unique stripping waves for each alloy. This is particularly true of intermetallic compounds that generally have very narrow composition ranges. The RRDE-ALSV results in Fig. 4 and 5 suggest that the three deposits formed at 0.2, 0.1, and 0 V each have unique crystal structures in the as-deposited condition. However, little information is available regarding the identity or distribution of these phases in the various electrodeposits.

It is also possible that the partial current due to the oxidation of aluminum that is observed in the same range of potentials as the current for the oxidation of copper may not be associated with a specific phase of the alloy. Instead, it may simply reflect the inaccessibility of some of the aluminum to oxidation as a result of transport limitations, i.e., the inability of some of the aluminum to diffuse through the deposit, and this aluminum cannot be oxidized until at least some of the copper has been anodically dissolved. This result points out the dangers inherent in attempting to analyze electrodeposits solely on the basis of their anodic stripping waves and emphasizes the advantages of employing the RRDE-ALSV for this purpose.



Fig. 4. Disk and ring voltammograms recorded during the oxidation of thin-layer Cu–Al deposits from a Pt-RRDE in pure 60–40 mol % melt. These deposits were produced at a charge density of 510 mC cm⁻² in 0.010 mol L⁻¹ solutions of Cu(I) at the following E_{opp} : (a) 0.30 and (b) 0.20 V, (- - - -) represents i_{dis} – i_{ring}/N_{exp} . The disk electrode was scanned anodically from its rest potential at 0.002 V s⁻¹ while E_{ring} was held at 0.50 V. The angular velocity of the electrode was 104.7 rad s⁻¹.

$$1 - x = 1/\{1 + 3[Q_{\rm ring}/(N_{\rm exp} Q_{\rm disk} - Q_{\rm ring})]\}$$
[4]

The values of 1 - x calculated from Eq. 4 are displayed in Fig. 3, and they are in excellent agreement with those derived from the current-potential curves (vide supra).

Preparation and EDS analysis of bulk electrodeposits.-Several bulk electrodeposits were prepared on 0.10 cm nickel wire at potentials ranging from 0.40 to 0 V from 60.0-40.0 mol $\sqrt[6]{}$ melt containing 0.10 mol L⁻¹ copper(I) at 25°C. Based on the charge passed, the nominal thickness of these deposits ranged from 10 to 15 µm. The compositions of some of these deposits were determined with atomic absorption spectrophotometry (AAS) after the deposits were dissolved from the substrates with 1:1 HNO₃-HCl. Prior to dissolution, the deposits were examined by EDS to ensure that no chloride was present. A chloride signature would indicate the entrainment of electrolyte salts in the electrodeposits; this would render the AAS results meaningless. Within the detection limits of EDS, all the deposits were found to be either pure copper or copperaluminum alloy. The AAS results, which are shown in Fig. 3, are in excellent agreement with the alloy compositions determined with the different voltammetric methods.



Fig. 5. Disk and ring voltammograms recorded during the oxidation of thin-layer Cu–Al deposits from a Pt-RRDE in pure 60–40 mol % melt. Deposits were produced at a charge density of 510 mC cm⁻² in 0.010 mol L⁻¹ solutions of Cu(i) at the following E_{opp} : (a) 0.10 and (b) 0 V, (---) represents $i_{disk} - i_{ring}/N_{exp}$. The disk electrode was scanned anodically from its rest potential at 0.002 V s⁻¹ while E_{ring} was held at 0.50 V. The angular velocity of the electrode was 104.7 rad s⁻¹.



Fig. 6. Scanning electron micrographs of Cu–Al alloy that was electrodeposited from a 0.010 mol L⁻¹ solution of Cu(I) in the 60.0–40.0 mol % AlCl₃–MeEtimCl melt at 25°C. The deposition potentials were (a) 0.40, (b) 0.30, (c) 0.20, and (d) 0.10 V.

Deposit morphology.—The surface morphology of bulk electrodeposits prepared at four different deposition potentials from a 0.010 mol L^{-1} solution of copper(I) is shown in Fig. 6. The deposit morphology changes dramatically as the deposition potential is made more negative and as aluminum is incorporated into the electrodeposit. Pure copper deposits made at 0.40 V are quite dense and have a nodular appearance (Fig. 6a). It is unclear whether the apparent alignment of nodules is coincidental or is the result of nucleation defects at the nickel surface. Often nucleation appears to follow a longitudinal pattern and highlights the surface defects of the drawn wire. However, in this case, the nodules are aligned perpendicular to the longitudinal axis of the wire.

When the deposition potential is lowered to 0.30 V (Fig. 6b), the copper deposit loses its nodular appearance. Although the bulk of the deposit remains quite dense, some isolated columnar growth is evident. Many of these particles exhibit fourfold symmetry, suggesting that the growth is crystallographic in nature. Other nodules are rounded and yield little information about the driving force for preferential growth.

The deposit morphology undergoes a considerable transformation as the deposition potential is lowered further to 0.20 V (Fig. 6c). This deposit, which has an aluminum atomic fraction of 21.0%, is still dense and compact; however, the isolated columnar growth gives way to a surface that is clearly becoming dendritic. Deposits formed at 0.10 V (Fig. 6d) are completely dendritic. The poor morphology results in a rather fragile deposit where the dendrites are easily separated from the substrate. It is likely that considerable material is lost during deposition and subsequent cleaning; consequently, insufficient material remained for compositional and structural analysis.

Deposit structure.—The XRD patterns from several electrodeposits are shown in Fig. 7. In all cases, reflections from the nickel substrate (see figure caption) are clearly visible and increase in intensity as the deposition potential becomes more negative. This is a clear indication that the total mass of the deposit is reduced, either by aluminum incorporation or because of reduced thickness. Deposits formed at potentials between 0.30 and 0.40 V exhibit diffraction patterns that are consistent with pure copper. The deposit formed at 0.24 V, which contains 7.2 aluminum, retains the face-centered cubic (fcc) structure. The reflections are shifted to slightly lower values of 20, indicating that the lattice is expanding as aluminum alloys substitutionally with copper.¹⁹ The reflections broaden somewhat, indicating a reduced grain size or the presence of nonuniform strain. The maximum solubility of aluminum into fcc



Fig. 7. XRD patterns (Cu K α) of Cu-Al electrodeposited as described in Fig. 6. The deposition potentials were (a) 0.30, (b) 0.24, (c) 0.22, (d) 0.21, and (e) 0.20 V. The bold vertical lines represent the reflections for copper, JCPDS card no. 4-0836, and the thin vertical lines represent the reflections for orthorhombic Cu₃Al, JCPDS card no. 28-0005. The triangles ($\mathbf{\nabla}$) represent reflections originating from the nickel substrate.

copper under equilibrium conditions is reported to be 19.7 (atomic fraction).^{19,20}

Several changes in the crystal structure are seen in the 0.22 V electrodeposit, which contains 12.7 percent atomic fraction aluminum. The first is the continued expansion of the fcc copper lattice and reflection broadening. The second is the appearance of a second phase, which we have tentatively identified as martensitic Cu_3Al (β'). It is well known that in the Cu–Al system, β' - martensite is formed upon cooling from the high-temperature variant β -Cu₃Al, which has a body-centered cubic (bcc) structure.²¹ There is also precedence for its electrodeposition from a nonaqueous ethylbenzene-toluene solution.²² The crystal structure of the β' phase can be described by a disordered, orthorhombic lattice having lattice constants of a = 4.49Å, b = 5.19 Å, and c = 38.2 Å and consisting of a stacking sequence of 18 close-packed layers.^{21,23-25} Deposits prepared at 0.22 and 0.21 V clearly show the (202) and (1210)reflections for the β' phase. It is not until the deposition potential is reduced to 0.20 V, where the aluminum atomic fraction reaches 21.0%, that the $(0018) \beta'$ reflection can be resolved from the Cu(111). The lattice parameters calculated from the three $\beta'\text{-}\text{Cu}_3\text{Al}$ reflections from this deposit were a = 4.49 Å, b = 5.37 Å, and c = 38.34 Å. Alloys electrodeposited at 0.10 and 0 V showed reflections for the nickel substrate alone. This may be the result of poor deposit morphology (Fig. 6d) and the subsequent loss of material through handling, or it may be an indication that the deposit is simply amorphous.

Figure 8 is a plot of the lattice parameter for the fcc copper phase as a function of deposition potential. The lattice parameters for the 0.30 and 0.40 V deposits are identical to that listed in JCPDS no. 4-0836 for pure copper. As aluminum becomes incorporated into the electrodeposit, the lattice parameter is seen to increase quite dramatically. Figure 9 is a comparison of the alloy composition determined by AAS to the composition of the copper solid solution as determined from the lattice parameter.¹⁹ The deposits prepared at 0.26 and 0.24 V are single-phase, fcc solid solutions, since the compositions determined by both AAS and lattice parameter measurements are identical within experimental error. This is also consistent with the XRD patterns for these electrodeposits. When β' -Cu₃Al appears with fcc copper at 0.22 V, the electrodeposit contains more aluminum than can be accounted for by the fcc phase alone. This supports the diffraction pattern of the 0.22 V deposit and is a clear indication that the electrodeposit is two phase.

An interesting feature of this phase development is the fact that the β' phase forms well before fcc copper becomes saturated in aluminum. This is quite evident in Fig. 8 and 9, where the lattice parameter and consequently the Al content of the fcc phase continue to increase for all the deposits examined, down to a deposition potential of 0.18 V. The largest lattice parameter measured for fcc copper was



Fig. 8. Lattice parameters for fcc Cu–Al alloys as a function of deposition potential.



Fig. 9. Composition of Cu–Al alloy electrodeposits as a function of deposition potential: (\bigcirc) determined by AAS, and (\diamondsuit) determined from lattice parameter measurements for fcc Cu–Al solid solutions.¹⁹

3.669 Å, indicating that the atomic fraction of aluminum concentration in this phase was about 21.0 percent atomic fraction or slightly higher than the 19.7% solubility limit shown in the phase diagram. The fact that the aluminum concentration in the copper solid solution continues to increase in the presence of the β' -Cu₃Al certainly suggests that the fcc copper and β' -Cu₃Al in this two phase region are not in metastable equilibrium.

The crystallographic texture of the Cu-Al, fcc solid solution was examined as a function of deposition potential using the method developed by Harris.²⁶ In this treatment, $p_{\rm hkl}$ is defined as the fraction of grains that have {*hkl*} plane normals lying perpendicular to the surface of the electrodeposit. The values of $p_{\rm hkl}$ are in normalized units so that $\Sigma(p_{\rm hkl}/n)$ is equal to 1, where *n* is the total number of reflections being considered. A value of $p_{\rm hkl}$ equal to 1 indicates that the fraction of oriented grains is equal to 1 that of a randomly oriented sample. Values of $p_{\rm hkl}$ greater than 1 show that the corresponding crystallographic direction is preferentially oriented to the surface of the deposit. The $p_{\rm hkl}$ for the (111), (200), (220), and (311) reflections were calculated by using the following expression

$$p_{\rm hkl} = \frac{I_{\rm hkl} / I_{\rm r,hkl}}{1/n \sum I_{\rm hkl} / I_{\rm r,hkl}}$$
[5]

 $I_{\rm hkl}$ is the integrated intensity obtained from the Pearson VII profile fit, and $I_{\rm xhkl}$ is the integrated intensity for a randomly oriented sample. The values listed on JCPDS no. 4-0836 were used for the $I_{\rm xhkl}$ of randomly oriented copper.

The p_{hkl} for the (111), (200), (220), and (311) reflections for fcc copper in the Cu–Al electrodeposits are shown in Fig. 10. The pure copper deposits have no preferred orientation; all the p_{hkl} are within 10% of 1.0. This is indicative of the dense, nodular growth seen in Fig. 6a. As aluminum



Fig. 10. Normalized integrated intensity from XRD fundamental reflections of fcc Cu–Al as a function of deposition potential.

becomes incorporated into the deposit, the fcc phase takes on a fairly strong (111) orientation, whereas the (100) is clearly less pronounced. This change in crystallographic texture is likely related to the morphological instability observed at the more negative deposition potentials.

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