ELECTRODEPOSITION OF COBALT-ALUMINUM ALLOYS FROM THE ALUMINUM CHLORIDE-1-METHYL-3-ETHYLIMIDAZOLIUM CHLORIDE ROOM-TEMPERATURE MOLTEN SALT

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The electrodeposition of magnetic cobalt-aluminum alloys was investigated in the Lewis acidic aluminum chloride-1-methyl-3-ethylimidazolium chloride (60.0-40.0 mole %) molten salt containing electrogenerated Co(II) at 25 °C. Alloy deposits containing up to 62 atomic % aluminum were produced at potentials positive of that for the bulk deposition of aluminum. The onset of the underpotential driven aluminum co-deposition process occurred at around 0.40 V versus the Al/Al(III) couple. The Co-Al alloy composition displayed an inverse dependence on the Co(II) concentration, but tended to become independent of concentration as the potential was decreased. A RRDE voltammery technique was developed to analyze the composition and structure of the Co-Al alloy deposits. SEM-EDS analysis of bulk electrodeposits revealed that the deposit morphology depends strongly upon the aluminum content/deposition potential; deposits produced at 0.40 V consisted of 10-20 μm diameter multifaceted nodules of pure hcp cobalt whereas those obtained at 0.20 V were dense and fine grained, containing about 4 atomic % Al. Deposits produced at 0 V had the visual appearance of loosely adherent black powder. XRD diffraction measurements revealed a lattice expansion and a decrease in grain size as the hcp cobalt was alloyed with increasing amounts of aluminum.

INTRODUCTION

Transition metal-aluminum alloys are of great interest because of their structural properties, corrosion resistance, and, in some cases, unusual magnetic properties. These materials are often difficult to prepare using conventional metallurgical processes; however, electrodeposition offers a convenient route to some of these materials. Lewis acidic (AlCl3-rich) chloroaluminate molten salts are useful electrolytes for the electrodeposition of transition
metal-aluminum alloys. The attractiveness of these molten salts stems in part from the fact that they constitute a concentrated reservoir of reducible aluminum-containing species such as \( \text{Al}_2\text{Cl}_7 \). Of the extant chloroaluminate melts, the \( \text{AlCl}_3-\text{NaCl} \) system has received the most attention, and the electrodeposition of several nonequilibrium binary alloys, e.g., Cr-Al, Mn-Al, Ni-Al, and Ti-Al, has been achieved in this melt.

Low melting salts are obtained when the alkali chloride component(s) of traditional chloroaluminate melts are replaced with certain unsymmetrical quaternary ammonium chloride salts such as 1-(1-butyl)pyridinium chloride (BupyCl) or 1-methyl-3-ethylimidazolium chloride (MeEtimCl). The physical and electrochemical properties of these organic salt-based molten salt systems have been reviewed. The \( \text{AlCl}_3\)-BupyCl and \( \text{AlCl}_3\)-MeEtimCl molten salts are less conductive and more viscous than the \( \text{AlCl}_3\)-NaCl and related inorganic systems, but in actuality they present fewer experimental challenges. For example, they can be employed at room temperature, and they exhibit no vapor pressure due to the escape of \( \text{AlCl}_3 \) and/or \( \text{Al}_2\text{Cl}_6 \), which is a debilitating characteristic of the Lewis acidic inorganic chloroaluminates.

In a previous article, we described the electrodeposition of magnetic Ni-Al alloys from solutions of nickel(II) in the acidic \( \text{AlCl}_3\)-MeEtimCl melt at 40 °C. Ni-Al alloys containing up to 40 atomic % aluminum were obtained. The mechanism leading to the formation of Ni-Al involves the underpotential deposition (UPD) of aluminum during the mass-transport-limited electrodeposition of nickel. It was recently reported that magnetic Co-Al alloys containing up to 62 atomic % aluminum can be electrodeposited from solutions of cobalt(II) in the \( \text{AlCl}_3\)-MeEtimCl melt and that the co-deposition of aluminum is driven by a UPD mechanism similar to that found for the Ni-Al system. However, few experimental details are given in these reports, and the influence of the cobalt(II) concentration and deposition potential on the composition, surface morphology, and crystal structure of the electrodeposited alloys is unknown. In this article, we describe the results of an investigation of the electrodeposition of Co-Al alloys from the acidic \( \text{AlCl}_3\)-MeEtimCl molten salt. Thin layer Co-Al electrodeposits were studied under the idealized mass transport conditions afforded by rotating electrode voltammetry, and bulk deposits were prepared on copper wire electrodes and characterized by SEM-EDS and XRD techniques.

**EXPERIMENTAL**

The glove box system and the methods used to prepare and purify the \( \text{AlCl}_3\)-MeEtimCl melt were identical to those employed previously. Rotating-disk electrode (RDE) voltammetry and controlled-potential coulometry experiments were performed with an EG&G Princeton Applied Research Corp. (EG&G PARC) Model 173 potentiostat/galvanostat,

*Certain commercial materials and instruments are identified in this report to adequately specify the experimental procedure. In no instance does such identification imply recommen-
Model 179 digital coulometer plug-in module, and Model 175 universal programmer. Rotating-ring-disk electrode (RRDE) voltammetry experiments were carried out by using a Pine Instrument Co. Model RDE 3 bipotentiostat combined with an EG&G PARC Model 379 digital coulometer. Controlled electrode rotation was provided by a Pine Model AFMSRX electrode rotator. RRDE data were recorded with two Linseis Model 1600 X-Y/Y-t recorders. The electrodes used for RDE and RRDE voltammetry were Pine Instrument Co. Teflon-sheathed platinum disk (geometrical area = 0.196 cm²) and platinum ring-disk (r₁ = 2.29 mm, r₂ = 2.46 mm, and r₃ = 2.69 mm) electrodes, respectively. Before use, these electrodes were polished to a mirror finish with an aqueous slurry of 0.05 μm alumina by using a Buehler Metaserve grinder/polisher, rinsed with distilled water, and dried under vacuum in the glove box antechamber. They were conditioned before each experiment by holding them at the positive limit of the melt (~2.2 V) for about 30 s. The electrode rotation rate employed for all RDE and RRDE experiments was 104.7 rad s⁻¹. The counter electrode was a spiral of 1-mm diameter cobalt wire (Alfa/AESAR, Puratronic) immersed directly in the bulk melt. All potentials were referenced to the Al/Al(III) couple in the 60.0-40.0 mole % (m/o) melt. The reference electrode was identical in design to that described in a previous article, i.e., an aluminum wire (Alfa/AESAR, Puratronic) spiral was placed in a melt-filled tube terminated by an ACE porosity E glass frit. This tube was submerged in the bulk melt in the cell so that the liquid levels inside and outside the tube were equal. Cobalt(II) was introduced into the melt by anodization of a cobalt wire working electrode identical to the counter electrode. However, in this case the counter electrode was similar to the reference electrode described above. The solubility of cobalt(II) in the melt was not determined, but 0.10 mol L⁻¹ solutions of cobalt(II) were routinely prepared by using this procedure. All experiments were conducted in the 60.0-40.0 m/o melt at 25 ± 1 °C.

Protonic impurities were removed from the melt prior to its use in order to avoid the co-deposition of hydrogen. Therefore, the AlCl₃-MeEtimCl molten salt was electrolyzed between aluminum electrodes in the glove box for several days as previously described. After filtering the melt through a medium porosity glass frit to remove aluminum particles that had detached from the aluminum cathode during electrolysis, the melt was evacuated to 1.3 x 10⁻³ Pa for 24 h.

The composition and structure of bulk alloy electrodeposits were probed with scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDS), and x-ray diffraction (XRD) techniques (Cu-Kα radiation) using the facilities at the National Institute of Standards and Technology. SEM and EDS were carried out on polished cross sections of alloy electrodeposited on 1-mm diameter copper wire. Samples were overplated with copper using a copper cyanide strike followed by bright copper from a copper sulfate electrolyte. This does not imply that the material identified is necessarily the best available for this purpose.

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For quantitative analysis, the EDS results were referenced to pure aluminum and cobalt standards. The reported values are the averages of at least six measurements.

RESULTS AND DISCUSSION

Voltammetric Results

Solutions of cobalt(II) in the 60.0-40.0 m/o melt were prepared by the controlled-potential coulometric anodization of a cobalt wire electrode at a potential of 1.30 V. Calculations based on the charge passed and the weight loss of the electrode resulting from anodization confirmed that cobalt(II) was the oxidation product. Figure 1 shows RDE voltammograms recorded point-by-point in 5.00, 10.0, 25.0, and 50.0 mmol L\(^{-1}\) solutions of cobalt(II) at a Pt-RDE. Each data point in these voltammograms is the average of no less than two independent experiments. The procedure used to record these voltammograms involved pulsing the potential of the Pt-RDE from 1.20 V, where no reduction current was observed, to the desired final potential and then holding the electrode at this potential until a steady-state current was obtained. Such a current was usually attained in less than 30 s, and in no case was a continuous rise in the current observed that suggested the growth of a dendritic deposit with dimensions exceeding those of the electrode diffusion layer. After the current for the data point of interest was recorded, the electrode was held at a potential of 2.20 V for 30-45 s to strip the electrodeposit and then the process was repeated at a new potential. The resulting voltammograms were found to be more reproducible than those constructed from potentiostatic current-time transients acquired at a stationary electrode in the traditional way. Also shown in Fig. 1 is a voltammogram recorded in pure melt by using the same technique; no significant reduction current was obtained at the Pt-RDE, indicating that the concentration of reducible protonic impurities was very low in the melt used in this investigation.

Each of the voltammograms in Fig. 1 displays a well-defined limiting current; this limiting current corresponds to the following mass-transport-limited reaction

\[
\text{Co}^{2+}\text{(solv)} + 2e^- \rightarrow \text{Co(s)} \quad [1]
\]

where Co\(^{2+}\text{(solv)}\) represents cobalt(II) solvated by the molten salt. The average diffusion coefficient for cobalt(II), calculated from the limiting currents of the four voltammograms shown in Fig. 1, is \((3.4 \pm 0.1) \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}\). In pure melt, i.e., melt without dissolved cobalt(II), the bulk deposition of aluminum

\[
4\text{Al}_2\text{Cl}_7^- + 3e^- \rightarrow \text{Al(s)} + 7\text{AlCl}_4^- \quad [2]
\]

was not observed unless the Pt-RDE was held at potentials slightly negative of 0 V. Thus, to avoid interference from this process, all experiments were conducted at or above this potential.
At lower potentials, each of the voltammograms in Fig. 1 exhibits an increase in current due to the co-deposition of aluminum with cobalt. The exact potential at which the onset of this current increase takes place cannot be stated due to the imprecision of the voltammograms shown in Fig. 1, but it does seem to depend on the cobalt(II) concentration, commencing between 0.40 and 0.35 V in the 5.00 mmol L\(^{-1}\) solution and between 0.35 and 0.30 V in the 50.0 mmol L\(^{-1}\) solution. A similar rise in current due to the co-deposition of aluminum with nickel is seen at about 0.40 V during the reduction of nickel(II) on glassy carbon in acidic AlCl\(_3\)-MeEtimCl. However, the onset of aluminum co-deposition and the potential at which the nickel(II) reduction reaction becomes limited by mass-transport coincide (cf. Fig. 2, ref. 8). Thus, in that case, the voltammograms do not exhibit a well-defined limiting current.

For convenience, the co-deposition of aluminum with cobalt can be represented by the following reaction

\[
x\text{Co}^{2+}(\text{solv}) + 4(1-x)\text{AlCl}_3^- + (3-x)e^- \rightarrow \text{Co}_x\text{Al}_{1-x} + 7(1-x)\text{AlCl}_4^- \quad [3]
\]

where \(x\) and \(1-x\) represent the mole fractions of Co and Al in the Co-Al alloy, i.e., \(Co_xAl_{1-x}\). The value of \(1-x\) was estimated from each of the Pt-RDE voltammograms in Fig. 1 with the following expression

\[
1-x = 1/[1 + 1.5i_l/(i_s - i_l)] \quad [4]
\]

where \(i_l\) is the limiting current for the reaction in Eq. 1, and \(i_s\) is the total current at potentials where the reaction in Eq. 3 is observed. Plots of \(1-x\) versus potential that resulted from these calculations are presented in Fig. 2. These graphs show that \(1-x\) is dependent upon both the cobalt(II) concentration and the applied potential. However, the alloy composition becomes nearly independent of both variables as the potential is decreased with \(1-x\) approaching \(0.62\) (62 atomic % Al) at 0 V. This behavior indicates that the aluminum co-deposition process is kinetically limited, i.e., the co-deposition of aluminum can not keep pace with the mass-transport-controlled deposition of cobalt, except at very negative potentials.

Thin-layer Deposition-Stripping Experiments

The composition and structure of Co-Al alloy electrodeposits were examined further by carrying out anodic linear sweep voltammetry (ALSV) deposition-stripping experiments at a Pt-RRDE. These experiments were similar in principle to those described by Andricacos and coworkers\(^{12,14}\) in which a thin-layer alloy film is electrodeposited on a RRDE under controlled-potential conditions in a plating solution and then anodically dissolved from the disk electrode in a suitable stripping solution with slow scan ALSV. During the anodic dissolution step, the ring electrode potential, \(E_r\), is held at a value that results in the oxidation of the metal ions of one of the alloy components produced at the disk. For example, during the anodic dissolution of Ni-Fe alloys, both iron(II) and nickel(II) are produced at the disk.
electrode, and $E_r$ is set to a value where iron(II) is oxidized to iron(III). Because nickel(II) can not be oxidized within the potential window of the solvent, the oxidation waves that correspond to the dissolution of iron from the alloy deposit can be identified by observing the ring current as a function of the disk potential. The alloy composition can be calculated from the ring and disk charges, $Q_r$ and $Q_d$, respectively, and knowledge of the experimental collection efficiency, $N_{exp}$ of the RRDE electrode.

In the present case, neither aluminum(III) or cobalt(II), the Co-Al alloy dissolution products, can be oxidized within the potential window of the melt. However, as discussed above, it is possible to carry out the mass-transport-limited reduction of cobalt(II) without electrodepositing either Co-Al alloy or bulk aluminum. Thus, by setting $E_r$ to 0.500 V, it should be possible to reduce any cobalt(II) produced during anodic dissolution of the Co-Al alloy at the ring, permitting identification of those alloy stripping waves that have a current component arising from the oxidation of cobalt. Before the proposed method can be employed, $N_{exp}$ must be known, and its value must be in reasonable accord with theoretical predictions. Therefore, collection experiments were carried out by electrodepositing cobalt metal on the disk electrode at a deposition potential of 0.500 V in a solution of cobalt(II) with the ring electrode inactive. The cobalt was then anodically dissolved from the disk in pure melt with slow scan (0.002 V s$^{-1}$) ALSV while the ring was held at 0.50 V. These experiments yielded a value of $N_{exp} = 0.221$; this result is in excellent agreement with the theoretical collection efficiency of 0.220 for this electrode, which was calculated from $r_1$, $r_2$, and $r_3$.15

In view of these very favorable results, a series of A S V experiments were carried out at the Pt-RRDE over the range of deposition potentials where the formation of Co-Al alloy is expected, i.e., from 0.400 to 0 V. In these experiments, 425 mC cm$^{-2}$ electrodeposits were produced on the disk electrode in a 5.00 mmol L$^{-1}$ solution of cobalt(II). During a previous study of Ni-Al alloys, the deposit composition was found to depend on the charge density.8 This phenomenon is believed to arise from the thermodynamic instability of aluminum in the alloy in solutions of nickel(II). The Co-Al alloy was found to display similar instability in cobalt(II) solutions, and a minimum charge density of ca. 325 mC cm$^{-2}$ was needed to obtain Co-Al deposits of constant composition. The electrode was then transferred to pure melt, and the Co-Al electrodeposit was slowly oxidized from the disk electrode as described above for the collection experiments.

Typical voltammograms illustrating the disk and corrected ring currents that resulted from several of these experiments are shown in Figs. 3 and 4. For deposits produced at 0.400 V, the major feature of the disk voltammogram was a wave with an anodic peak potential, $E_{pA}$, of 0.93 V. The large ring current that was observed as the disk potential was scanned through this stripping wave indicates that a major component of the current arises from the oxidation of cobalt in the deposit. However, the charge corresponding to this wave was slightly larger than the corrected ring charge, $Q_r/N_{exp}$ indicating that some of the current must be due to the oxidation of aluminum. For the deposit prepared at 0.300 V, the disk voltam-
mogram (Fig. 3) revealed oxidation waves with \( E_p^* = 0.83 \) and 0.55 V, respectively. A ring current was associated with the former but not the latter, indicating that the wave at 0.55 V must arise from the selective dealloying of aluminum. The disk voltammograms corresponding to the 0.200, 0.100, and 0 V deposits (Fig. 4) were similar in appearance to that of the 0.300 V deposit, except that the aluminum wave was shifted to \( E_p^* = 0.67 \) V in the case of the 0.200 V deposit and appeared at \( E_p^* = 0.63 \) and 0.56 V in the voltammograms of the 0.100 and 0 V deposits, respectively. A small amount of aluminum was also oxidized from each of these deposits at potentials proximate to the oxidation of cobalt.

These shifts in the position of the aluminum stripping wave indicate that the activity of aluminum in the alloy is changing with the aluminum content of the alloy. However, it is unclear why aluminum dissolution occurs at two different potentials. If one assumes that the deposit is two phase and that the second dissolution is due to aluminum contained in a cobalt-rich phase, then the two phases cannot be in equilibrium because the aluminum activity must be different in each phase. Alternatively, the aluminum associated with the second dissolution process may simply be inaccessible to oxidation until some dissolution of cobalt occurs. The negative shift in the cobalt stripping wave associated with alloyed deposits may then be due to the more favorable dissolution kinetics of a porous cobalt layer over that of a pure, compact deposit.\(^{16}\)

The characteristics of anodic linear sweep voltammograms for the dissolution of an alloy deposit are very sensitive to the composition and structure of the deposit. Theoretical and experimental studies have attempted to correlate peak shape and location with the type of alloy that is electrodeposited.\(^{16,17}\) However, a detailed analysis of the voltammograms in Figs. 3 and 4 beyond that given here would be purely speculative without reliable information about the phase distribution in Co-Al alloys containing up to 62 atomic % aluminum.

The alloy composition \((1-x)\) as a function of deposition potential was calculated from \( N_{\text{exp}} \) and the values of \( Q_a \) and \( Q_d \) that resulted from numerous experiments similar to those described above by using the following expression

\[
1-x = 1/(1 + 1.5[(Q/(N_{\text{exp}}Q_d - Q_a))])
\]

The resulting values of \(1-x\) are plotted as a function of potential in Fig. 2, and they are in very good agreement with the values of \(1-x\) derived from the Pt-RDE voltammetric currents observed in a 5.00 mmol L\(^{-1}\) cobalt(II) solution.

**Preparation and Characterization of Bulk Alloy Electrodeposits**

Bulk electrodeposits were prepared on 1-mm copper wire electrodes at potentials ranging from 0.400 to 0 V in a 50.0 mmol L\(^{-1}\) solution of cobalt(II) at 40 °C. During deposition, the solution in the cell was agitated with a small Teflon-coated stir bar. At the conclusion of each experiment, the copper electrode was rinsed with dry benzene to remove
residual melt. A charge density of 60 C cm$^{-2}$ was used to prepare each deposit. This should result in a deposit thickness of 20 μm, assuming 100 % current efficiency for cobalt. The surface morphology of these electrodeposits is shown in Fig. 5. The as-deposited surface morphology showed significant variations as a function of deposition potential. For example, deposits prepared at 0.400 V (Fig. 5a) were fairly rough, consisting of nodules on the order of 10-20 μm in diameter. At higher magnification, these nodules seemed to be multifaceted, revealing their crystallographic nature. EDS analysis of these deposits indicated that they were pure cobalt and free of chloride. In contrast, smooth, spherical nodules were also occasionally observed. These nodules have an appreciable chloride content and were the likely remnants of electrolyte trapped within the nodular structure. Figure 5b shows that deposits produced at 0.200 V were very dense and fine-grained. Interestingly, nucleation appeared to follow a longitudinal pattern associated with surface defects on the drawn copper wire. For deposits prepared at 0.100 V (Fig. 5c), a nucleation pattern similar to that seen in the 0.200 V deposit was observed; however, the features are much larger and each nodule has a round, smooth appearance. This nodule morphology was quite similar to that observed in amorphous Mn-Al electrodeposits. The darker regions between the rows of nodules have a high chloride content and were extensively cracked. Again this is likely to be due to the inter-nodular entrapment of electrolyte. Electrodeposits prepared at 0 V had the visual appearance of a loosely adherent, fine black powder, which is clearly seen in Fig. 5d.

Polished cross-sections of these deposits were prepared and compositions were determined by EDS. All of the deposits, except that prepared at 0 V, yielded cross-sections of sufficient quality that the compositions could be determined quantitatively; i.e., the deposits were free of contaminants such as chloride, and the volume examined was sufficiently large so that the copper substrate and overplate did not interfere with the analysis. The composition results are shown in Fig. 6. Electrodeposits prepared at 0.400 and 0.300 V consisted of pure cobalt. The total x-rays detected from the EDS analysis was 97.5% of that obtained from the pure cobalt standard, indicating that the deposit density was close to that of the metallurgical standard. In contrast to the thin-layer voltammetric results presented above, aluminum was first detected in bulk electrodeposits prepared at 0.200 V. It is presently unclear whether the reduced nodule size of this sample (compare Figs. 5a and 5b) resulted from the addition of aluminum or was a natural consequence of the lower deposition potential. The value of 1-x increased to about 0.16 for deposits produced at 0.100 V. In addition, the deposit density, based on the total x-rays detected, dropped to about 85 % of theoretical relative to the pure cobalt and aluminum standards, indicating either a decrease in the density or an increase in the deposit porosity at the lower deposition potentials. In cross-section, the deposit formed at 0 V appeared as clusters of 0.5-1.0 μm size "islands" of Co-Al in a copper matrix (overplate). Quantitative analysis could not be performed on these samples due to the small volume of Co-Al alloy as compared to the EDS excitation volume. Consequently, a copper-free analysis could not be made; however, a comparison of only the cobalt and aluminum signals suggested that 1-x is on the order of 0.20-0.25 for this deposit. This is likely to be a low estimate of the aluminum content.
The x-ray diffraction patterns for electrodeposits formed at potentials ranging from 0 to 0.400 V are shown in Fig. 7. Several structural changes were observed as the deposition potential was decreased. At 0.400 V, the deposit was clearly hexagonal close-packed (hcp) cobalt. The absence of the (200) reflection, which should appear at 51.5°, suggested that there was no face-centered cubic (fcc) cobalt present in the deposit. At lower deposition potentials, the reflections for hcp cobalt shifted to lower values of 2θ and became somewhat broader. At 0 V, the electrodeposition was entirely amorphous. In addition, reflections due to the copper substrate ((111) at 43.3°, (200) at 50.4°, etc.) began to appear in the deposit prepared at 0.300 V and increased in intensity as the deposition potential was lowered. This implies that the deposits became thinner or that the average atomic weight became reduced as the potential was decreased. Both of these changes would be expected to occur as more aluminum is incorporated into deposits of equal charge density. However, the fact that the copper substrate was seen in the 0.300 V deposit that contained no appreciable aluminum suggests that the appearance of the substrate reflections was not due to chemical changes in the film, but to nonuniform morphology and thickness between samples.

Figure 8 shows the lattice parameters obtained from the diffraction patterns in Fig. 7. The Nelson-Riley technique was used to determine the lattice parameters in order to eliminate systematic errors such as sample displacement. These results indicate that both hcp lattice parameters were near their equilibrium values at a deposition potential of 0.400 V and increased as the deposition potential was reduced, suggesting that the alloying of hcp cobalt was taking place. An overall lattice volume expansion of 0.71% was observed over the range of deposition potentials examined.

The x-ray diffraction patterns in Fig. 7 show that the hcp cobalt reflections became broader as the deposition potential was reduced. The Scherrer equation can be used to estimate the grain size for electrodeposited cobalt from the full-width at half-maximum (FWHM). This grain size must be viewed as a lower limit because the treatment fails to consider microstrain, which can be appreciable in electrodeposits. Figure 9 is a plot of the grain size, calculated from three fundamental reflections, as a function of deposition potential. The data in this figure show that the average grain size drops significantly with decreasing deposition potential. Because the crystallographic grain size is expected to be inversely proportional to nucleation density, the observed decrease in grain size was consistent with electrocrystallization theory that predicts a higher nucleation density with increased overpotential. The grain refinement observed in the x-ray diffraction patterns may also result from the addition of aluminum to the cobalt.

The equilibrium, room-temperature structure of cobalt is hcp. At temperatures between 422 and 1495 °C, the fcc high-temperature variant is stable. The free energy difference of these two structures is quite small; consequently, the fcc structure can be retained at room temperature by rapid solidification. Electrodeposition from aqueous electrolytes has also been used to form both structures at room temperature. The microstructure of electrodeposits produced from low pH (~1.6) electrolytes consists of
highly-faulted fcc regions; at higher pH (~5.7), the hcp phase is formed and the fault density is greatly reduced. It has been proposed that the formation of fcc cobalt, most likely in the form of a metastable hydride, is facilitated by the adsorption and subsequent incorporation of atomic hydrogen into the electrodeposit. The absence of fcc cobalt in electrodeposits produced from AlCl₃-MeEtimCl melts supports this notion of the hydride assisted deposition of the fcc phase. Though it is suspected that the proton content of these melts can significantly alter the deposit morphology, its effect on crystallographic structure has not been investigated. In any case, the level of reducible protonic impurities was very low in the melt used for this investigation.

The room temperature solubility of aluminum into hcp cobalt is quite small, significantly less than 0.5 atomic %. For aluminum compositions above this solubility limit and extending to 42 atomic % aluminum, a two phase field consisting of hcp cobalt and ordered bcc Co-Al (CsCl-type) exists. Aluminum has a much higher solubility in fcc cobalt, and an equilibrium solubility as high as 16 atomic % can be achieved at 1400 °C. Rapidly cooled alloys containing 5 to 16 atomic % aluminum often retain the fcc structure over the two phase hcp-bcc equilibrium structure. However, a martensitic transformation to an hcp structure has been reported in this composition range for alloys quenched from 1300 to -196 °C. The hcp structure is formed by the periodic introduction of stacking faults in the close-packed {111} fcc layers. Four martensitic hcp phases, each having a different stacking fault periodicity have been identified.

The development of the x-ray diffraction patterns of the Al-Co electrodeposits with lower deposition potentials indicates that the addition of aluminum to the alloy causes a decrease in the deposit grain size and an increase in the hcp lattice volume. A further increase in the aluminum content results in amorphization of the deposit. Because the equilibrium phase diagram predicts a two phase terminal hcp-ordered bcc structure, the electrodeposit is clearly metastable over the entire composition range examined.

When considering non-equilibrium processing methods, one can often gain a better understanding of phase development by comparing the free energy of the possible metastable structures over the composition range of interest. The free energy-composition curves for the Co-Al system at 40 °C were calculated using the constitutive equations from Kaufman et al. (Fig. 10). The free energy for the amorphous phase was assumed to be that of the supercooled liquid. In addition, ordering and compound formation were not considered. As a consequence, the free energy of equilibrium Co-Al (ordered bcc) will be somewhat lower than that depicted by the disordered bcc curve. Clearly, the hcp-bcc common tangent minimizes the free energy over most of the composition range giving rise to a two-phase hcp-bcc region from essentially 0 to about 42 atomic % Al. One can see that the free energy of the hcp and fcc structures are quite close, with the fcc becoming more stable for alloy compositions greater than about 4 atomic % aluminum. This stabilization of the fcc structure with the addition of aluminum is seen experimentally in rapidly solidified alloys. Also apparent in the free energy diagram is the thermodynamic stability of the amorphous phase.
with respect to the hcp and fcc structures for alloys containing greater than 25 atomic %
aluminum. If nucleation of the equilibrium bcc phase were kinetically hindered, one might
expect the formation of an amorphous phase over a disordered fcc or hcp structure, based on
these calculations.

We have experimental evidence for the deposition of an hcp Co-Al solid solution and
an amorphous phase, both of which can be rationalized thermodynamically. What is not clear
is the extent of the supersaturation of aluminum in the hcp cobalt and the composition at
which the amorphous phase first nucleates; i.e., does the amorphous phase co-exist with the
supersaturated hcp cobalt or replace it at some critical aluminum concentration? We know
that aluminum substitutes into the hcp lattice causing an increase in the lattice volume (Fig.
8). One would expect such an increase when a larger aluminum atom substitutes for cobalt
in the lattice. The lattice volume for fcc cobalt is reported to increase by 0.17% per atomic
% Al in the 0-16 atomic % Al composition range.22 Exactly how much aluminum is going
into the hcp lattice in these electrodeposited alloys is unclear because lattice paramete-
rer-composition data for hcp Co-Al is not available in the literature. Further, the measured
alloy compositions cannot be associated with the hcp phase alone unless it has been
established that these deposits are single phase.

The electrodeposits containing appreciable aluminum may be a two phase mixture of
supersaturated hcp cobalt and an amorphous phase of higher aluminum composition. Such
phase development has been reported in Mn-Al alloys electrodeposited from chloroaluminate
electrolytes at 150 °C.33 At low manganese concentrations (less than 5 atomic %) the deposit
is single phase, supersaturated fcc and one observes a linear decrease in lattice parameter with
increasing manganese content. Above 5 atomic % manganese, a Mn-Al amorphous phase
(nominally Mn_{0.18}Al_{0.82}) co-deposits with fcc Al, causing a dramatic relaxation in the fcc
supersaturation and an increase in the fcc lattice parameter to that of a 1 atomic % manganese
solid solution. One can clearly determine the potential (or alloy composition) where the
deposit becomes two phase by the discontinuity in the fcc lattice parameter. In the 5 to 15
atomic % manganese composition range, a metastable two-phase equilibrium between the fcc
phase and the amorphous phase is established. In this region, the fcc lattice parameter is
invariant, indicating that only the phase distribution, not the composition of each phase, is
changing with overall alloy composition. One would expect this type of behavior from
common tangent construction in the two phase region. The 15 atomic % manganese
electrodeposit is entirely amorphous. If a metastable two-phase equilibrium does exist in the
electrodeposited Co-Al alloys, then one should be able to estimate the phase distribution from
a common tangent construction of the hcp and amorphous free energy curves in Fig. 10. Such
a construction would predict an hcp phase containing about 4 atomic % aluminum in
metastable equilibrium with an amorphous phase containing about 46 atomic % aluminum.
Applying this to the electrodeposits, the 4 atomic % aluminum deposit would be single phase
hcp, whereas in the 16 atomic % deposit the amorphous phase would co-exist with the hcp
phase. The composition of the hcp phase in each alloy would be identical. Unfortunately, our
x-ray data does not support this scenario. Under the conditions of a two-phase equilibrium,
one would not expect to see an increase in the hcp lattice parameter between the 4 and 16 atomic % aluminum alloy, Fig. 8.

Alternatively, the phase development from the hcp to the amorphous structure may proceed by a partitionless or near-partitionless phase transition. Metastable processing methods with very high effective quenching rates are generally required so that the partitionless transformation is kinetically favored over a metastable two-phase equilibrium. Concentration profiles are essentially frozen in place forcing the phases to evolve locally without the aid of long range diffusion. Partitionless transformations have been observed in Zr-Al alloys produced by mechanical alloying. This system is a particularly interesting example because zirconium, like cobalt, is hcp at room temperature and, at equilibrium, it accommodates little aluminum in solid solution. Alloys containing up to 17 atomic % aluminum were reported to be single phase hcp with the zirconium lattice parameters decreasing linearly with composition. Above 17 atomic % aluminum, the alloys were completely amorphous. It was concluded that the continuous decrease of the lattice parameters with composition up to the point at which full amorphization took place was an indication of the absence of a two-phase metastable equilibrium region. Free energy calculations not only indicated that the amorphous structure would be thermodynamically more stable than the alternative polymorphs, but the intersection of the hcp and amorphous free energy curves indicated that the partitionless transition would occur at 20 atomic % aluminum, quite close to the experimental value.

Qualitatively, very similar phase development is seen in the electrodeposited Co-Al alloys. The increase in the hcp lattice parameter up to 16 atomic % aluminum suggests that the supersaturation of aluminum into hcp cobalt extends up to amorphization and that a partitionless transformation takes place between 16 and 25 atomic % aluminum. This is reasonably consistent with the crossover of the calculated hcp and amorphous free energy curves, which occurs at about 25 atomic % aluminum (Fig. 10). Quantitatively, there may be problems applying a partitionless mechanism to the electrodeposited Co-Al data. The lattice volume for an ideal, Co-Al hcp solid solution would increase by about 8 % when the aluminum composition is increased from 0 to 16 atomic %. Over this composition range, the lattice volume of the electrodeposited alloys increases by only 0.71 %. Though ideal behavior is certainly not expected, a lattice expansion that is an order of magnitude less than the ideal case does suggest that not all of the aluminum is going into the hcp solid solution. It appears that a more thorough structural study will be required to resolve this issue.

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REFERENCES

1. T. P. Moffat, J. Electrochem. Soc., 141, L115 (1994).
2. G. R. Stafford, ibid., 136, 635 (1989).
3. G. R. Stafford, B. Grushko, and R. D. McMichael, J. Alloys and Compounds, 200, 107 (1993).
4. T. P. Moffat, J. Electrochem. Soc., 141, 3059 (1994).
5. G. R. Stafford, ibid., 141, 945, (1994).
6. R. A. Osteryoung, in Molten Salt Chemistry: An Introduction and Selected Applications, G. Mamantov and R. Marassi, Editors, pp. 329-364, Reidel, Dordrecht (1987).
7. C. L. Hussey, in Chemistry of Nonaqueous Solutions: Current Progress, G. Mamantov and A. I. Popov, Editors, pp. 227-275, VCH, New York (1994).
8. W. R. Pitner, C. L. Hussey, and G. R. Stafford, J. Electrochem. Soc., 143, 130 (1996).
9. R. T. Carlin, H. C. DeLong, and P. C. Trulove, Abstract 652, p. 981, The Electrochemical Society Extended Abstracts, Vol. 95-1, Reno, NV, Meeting, May 21-26, 1995.
10. H. C. DeLong and R. T. Carlin, Abstract 647, p. 974, The Electrochemical Society Extended Abstracts, Vol. 95-1, Reno, NV, Meeting, May 21-26, 1995.
11. L. J. Durney, Electroplating Engineering Handbook, 4th ed., pp. 185-188, Van Nostrand Reinhold, New York (1984).
12. P. C. Andricacos, J. Tabib, and L. T. Romankiw, J. Electrochem. Soc., 135, 1172 (1988).
13. K. H. Wong and P. C. Andricacos, ibid., 137, 1087 (1990).
14. J. Horkans, I-C. H. Chang, P. C. Andricacos, and E. J. Podlaha, ibid., 138, 411 (1991).
15. A. J. Bard and L. R. Faulkner, Electrochemical Methods, p. 302, John Wiley and Sons, New York (1980).
16. S. Swathirajan, J. Electrochem. Soc., 133, 671 (1986).
17. V. D. Jovic, R. M. Zejnulovic, A. R. Despic, and J. S. Stevanovic, J. Appl. Electrochem., 18, 511 (1988).
18. T. P. Moffat, G. R. Stafford, and D. E. Hall, J. Electrochem. Soc., 140, 2779 (1993).
19. B. D. Cullity, Elements of X-Ray Diffraction, 2nd ed., Addison-Wesley, Redding, MA (1978).
20. L. V. Azaroff, Elements of X-Ray Crystallography, McGraw-Hill, New York (1968).
21. Binary Alloy Phase Diagrams, T. B. Massalski, Ed., ASM (1986).
22. H.-L. Luo and P. Duwez, Can. J. Phys., 41, 758 (1963).
23. Yu. M. Polukarov, Russ. J. Phys. Chem., 34, 68 (1960).
24. J. Goddard and J. G. Wright, Br. J. Appl. Phys., 15, 807 (1964).
25. J. Scoyer and R. Winand, Surf. Tech., 5, 169 (1977).
26. S. Nakahara and S. Mahajan, J. Electrochem. Soc., 127, 283 (1980).
27. I. Croll, IEEE Trans. on Mag., 23, 59 (1987).
28. R. Sard, C. D. Schwartz, and R. Weil, J. Electrochem. Soc., 113, 424 (1966).
29. A. J. Bradley and G. C. Seager, J. Inst. of Metals, London, 64, 81 (1939).
30. B. I. Nikolin and N. N. Shevchenko, Fiz. Metal. Metalloved., 51, 316 (1981).
31. L. Kaufman and H. Nesor, CALPHAD, 2, 325 (1978).
32. L. Kaufman, CALPHAD, 1, 1 (1977).
33. B. Grushko and G. R. Stafford, Met. Trans. A, 20, 1351 (1989).
34. E. Ma, J. Mater. Res., 9, 592 (1994).
35. W. L. Johnson, Y. T. Cheng, M. van Rossum, and M.-A. Nicolet, Nucl. Instrum. Methods in Phys. Res., B 7/8, 657 (1985).
36. E. Ma and M. Atzmon, Mod. Phys. Lett., 6B, 127 (1992).
Figure 1. Voltammograms recorded point-by-point at a Pt-RDE for the reduction of Co(II) in the 60.0-40.0 m/o melt. The Co(II) concentrations were (●) 5.00, (■) 10.0, (▲) 25.0, and (♦) 50.0 mmol L\(^{-1}\). Also shown is a voltammogram recorded in pure melt before the addition of Co(II) (▼). The angular velocity of the electrode was 104.7 rad s\(^{-1}\).

Figure 2. Alloy composition as a function of potential as derived from the RDE voltammetric currents in Fig. 1 by using Eq. 4. The Co(II) concentrations were (●) 5.00, (■) 10.0, (▲) 25.0, and (♦) 50.0 mmol L\(^{-1}\). Also shown are the results of ALSV-RRDE experiments (○).

Figure 3. Disk and ring voltammograms recorded during the oxidation of thin-layer Co-Al electrodeposits from a Pt-RRDE in pure 60.0-40.0 melt. These deposits were produced with a charge density of 425 mC cm\(^{-2}\) in melt containing 5.00 mmol L\(^{-1}\) M Co(II) at the following deposition potentials: (—) 0.400, (— —) 0.300, and (•••) 0.200 V. During stripping, the disk electrode was scanned at 0.002 V s\(^{-1}\), and \(E_r\) was held at 0.500 V. The angular velocity of the RRDE was 104.7 rad s\(^{-1}\).
Figure 4. Disk and ring voltammograms recorded during the oxidation of thin-layer Co-Al electrodeposits from a Pt-RRDE in pure 60.0-40.0 melt. The deposits were prepared as described in Fig. 3 at the following deposition potentials: (—) 0.200, (−→) 0.100, and (→••) 0 V. The stripping conditions were the same as those used to produce Fig. 3.

Figure 5. SEM micrographs of bulk Co and Co-Al alloy electrodeposits on a copper wire substrate. These deposits were produced in a 50.0 mmol L\(^{-1}\) solution of Co(II) in 60.0-40.0 m/o melt at 40 °C. The deposition potentials were (a) 0.400, (b) 0.200, (c) 0.100, and (d) 0 V.

Figure 6. Co-Al alloy composition as a function of deposition potential for the electrodeposits described in Fig. 5.

Figure 7. XRD patterns (Cu-Ka) of the electrodeposits described in Fig. 5. The deposition potentials were (a) 0, (b) 0.100, (c) 0.200, (d) 0.300, and (e) 0.400 V. The dashed vertical lines represent the reflections for pure hcp cobalt, JCPDS card# 5-0727. The reflections due to the copper wire substrate are denoted by the heavy tic marks on the 2θ axis.
Figure 8. Lattice parameters of electrodeposited hcp cobalt as a function of deposition potential taken from the diffraction patterns shown in Fig. 7: (∙) $a_0$ and (■) $c_0$.

Figure 9. Estimated grain size of electrodeposited hcp cobalt as a function of deposition potential calculated from the diffraction patterns shown in Fig. 7. Grain size was estimated from the peak broadening of the (∙) (100), (■) (002), and (▲) (101) reflections using the Scherrer equation.

Figure 10. Calculated free energy of formation diagram for the Co-Al system at 40 °C using liquid cobalt as the reference state. The constitutive equations of Kaufman et al. were used in the calculations.