ELECTRODEPOSITION OF Cu-Zn ALLOYS FROM A LEWIS ACIDIC ZINC CHLORIDE-1-ETHYL-3-METHYLIMIDAZOLIUM CHLORIDE MOLTEN SALT

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ABSTRACT

The electrodeposition of Cu-Zn alloys on nickel substrate was investigated in the 50.0-50.0 mol% zinc chloride-1-ethyl-3-methylimidazolium chloride molten salt containing copper chloride. The Zn content in the deposited Cu-Zn alloys can be varied by the deposition potential. Analysis of the chronoamperometric current-time transients suggests that the electrodeposition of pure copper in this melt involves instantaneous three-dimensional nucleation with diffusion-controlled growth. However, as the deposition potential crosses from pure copper metal region into the alloy forming region, the nucleation process changes to progressive nucleation. The X-ray diffraction analysis indicated that the deposited Cu-Zn alloy had α and β phases. The energy dispersive spectroscopy (EDS) and the scanning electron microscope (SEM) were also used to study the composition and surface morphology of the deposits.

INTRODUCTION

The electrodeposition of zinc and its alloys has received considerable attention. However, the electrodeposition of zinc from typical aqueous electrolyte is often complicated by problems involving hydrogen embrittlement and low current efficiency. As a result, aprotic solvents such as molten salts wherein hydrogen evolution is precluded may be ideal alternatives to aqueous plating baths for the electrodeposition of pure zinc and zinc alloys. However, the high melting temperatures associated with most conventional inorganic molten salts often make these salts difficult to use.

The combination of quaternary ammonium chloride salt, such as 1-ethyl-3-methylimidazolium chloride (EMIC), with certain metal chlorides generally produces molten salts that exhibit a melting point much lower than conventional inorganic molten salt systems. For example, the aluminum chloride-1-ethyl-3-methylimidazolium chloride molten salt system (AlCl₃-EMIC) is liquid at room temperature. Because the...
low melting temperature of such molten salt systems makes them easier to handle, these molten salts can be very useful for the electrodeposition of pure metals and alloys.6-13

Like the AlCl3-EMIC melt system, mixtures of ZnCl2-EMIC also exhibit a lower melting temperature than the conventional inorganic molten salt such as ZnCl2-NaCl. In this article, the electrodeposition of Cu-Zn alloy (brass) was investigated in a Lewis acidic 50.0-50.0 mol% ZnCl2-EMIC melt containing CuCl. Cu-Zn alloy deposits are widely used for decorative purposes14 and are also used to promote rubber adhesion to steel.15 Cu-Zn alloy has been plated commercially mainly from cyanide baths, however, the toxicity of the cyanide generates a serious environmental problem. To resolve this, many efforts were concentrated on the use of various non-cyanide baths.16,17 Although many researches devoting in this purpose have been published, there is no report about this topic have been conducted in molten salts.

EXPERIMENTAL

Apparatus

All electrochemical experiments were conducted inside a Vacuum Atmosphere glove box filled with dry nitrogen. The moisture and oxygen level in the box was kept lower than 1 ppm. The electrochemical experiments and the data collection were accomplished by an EG&G Model 273A potentialstat/galvanostat controlled with the EG&G Model 270 software. The electrochemical experiments were performed in a three-electrode electrochemical cell. The electrochemistry and electrodeposition of copper and copper-zinc alloy were studied on a nickel disk electrode (Bioanalytical system, geometric area = 0.071 cm2). Bulk Cu-Zn alloy deposits were prepared on nickel foils (0.5x0.5 cm2, Aldrich, 99.99%). For voltammetric experiments, the counter electrode was a zinc spiral (Aldrich, 99.99%) immersed in pure 50.0-50.0 mol% ZnCl2-EMIC melt. For electrodeposition experiments, the counter electrode was a narrow spiral copper foil directly immersed in the bulk melt. The melt composition of the reference electrode was the same as the counter electrode but a linear zinc wire was used. A Hitachi S-4200 field effect scanning electron microscope (SEM) with an energy dispersive spectroscopy (EDS) working at 15 kV was used to examine the surface topography and the element analysis of the electrodeposits. A Shimadzu XD-D1 X-ray diffraction-meter was used to study the crystalline phases of the Cu-Zn alloy deposits.

Chemicals

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The EMIC was prepared and purified according to the method described in the literature. Anhydrous zinc chloride (99.99%), anhydrous propylene carbonate (98%) and CuCl (99.995+%) were from Aldrich and were used as received. The 50.0-50.0 mol% ZnCl₂-EMIC melt was prepared by mixing equal molar amounts of ZnCl₂ and EMIC in a flask and then heating the mixture to 90 °C for 2 days. The resulting melt was a colorless liquid at temperature near 40 °C.

RESULTS AND DISCUSSION

Staircase cyclic voltammetry for the 50.0-50.0 mol% ZnCl₂-EMIC melt

A typical staircase cyclic voltammogram of the 50.0-50.0 mol% ZnCl₂-EMIC melt on a nickel electrode is shown in Fig. 1. It shows that the reduction of Zn(II) to zinc metal occurs near 0.0 V. As evidenced by a current loop, the electrodeposition of zinc on the Ni electrode requires an overpotential in order to initiate the nucleation and subsequent growth of the zinc deposit. Fig. 1 also shows that the re-oxidation of zinc on the Ni electrode gives a single stripping peak. The nucleation mechanism of zinc on Ni electrode has been studied in detail elsewhere.

Staircase cyclic voltammetry for Cu(I)

Cu(I) was introduced to this melt by addition of CuCl. A typical staircase cyclic voltammogram for Cu(I) in this melt at a Ni electrode is shown in Fig. 2a. A current loop is observed, indicating that the reduction involves nucleation process. This reduction is due to Cu(I) \( \rightarrow \) Cu(0) as confirmed by the X-ray diffraction pattern of the electrodeposits that was obtained by electrodeposition on a Ni foil at a proper potential after this reduction peak. Pure copper deposits could be obtained in this melt containing CuCl; no trace zinc was observed in the EDS analysis. However, if the electrodeposition potential was too negative, the signal of zinc appeared in the EDS analysis of the electrodeposits.

Fig. 2b is the staircase cyclic voltammogram of the same solution as in Fig. 2a at a Ni electrode; however, the potential scan was reversed at a potential where the reduction of zinc occurred. The potential where Zn(II) begins to reduce to zinc metal in Fig. 2b is more positive than that in Fig. 1. This phenomenon implies that the electrodeposition of Cu-Zn alloy at potentials more positive than the potential needed for reducing Zn(II) to zinc metal in Fig. 1 is possible. The peak potential of the first anodic peak, \( a_1 \), in Fig. 2b was close to the reoxidation peak of pure zinc deposits in Fig. 1. However, it occurred at a
more positive potential and the peak current is much lower than that observed in Fig. 1 even though the same potential range was scanned. It is believed that peak a$_2$ corresponds to the oxidation of non-alloyed zinc. Because the percentage of the non-alloyed zinc is low in Cu-Zn alloy deposits, the peak current of peak a$_2$ is much smaller than the stripping peak of the pure zinc deposits shown in Fig. 1. The stripping peak of the alloyed zinc in Cu-Zn alloy deposits is included in the big stripping peak, a$_n$, which overlaps with the stripping peak of pure copper shown in Fig. 2a.

**Nucleation studies of Cu metal and Cu-Zn alloy electrodeposition**

Chronoamperometry experiments were carried out in order to investigate the copper and copper-zinc alloy nucleation/growth process. These experiments were performed by stepping the potential of the working electrode from an initial value, where no reduction took place, to potentials sufficiently negative to initiate nucleation/growth process after a short induction time. The current-time transients for copper and Cu-Zn codeposition resulting from such experiments on a Ni electrode exhibit the classic shape for a nucleation process; a current spike due to the charging of the double layer immediately after the application of potential pulse followed by a brief induction period, $t_0$. At the end of this induction period, the current increases until a broad maximum, $i_m$. After $i_m$ has been reached, the current decay approaches the $t^{-1/2}$ decrease expected for linear diffusion to a plane surface. The time at which $i_m$ occurs, $t_m$, depends on the applied overpotential.

The three-dimensional nucleation with hemispherical diffusion-controlled growth of the nuclei is appropriate to describe the nucleation of copper and Cu-Zn codeposition in the 50.0-50.0 mol% ZnCl$_2$-EMIC melt. The two limiting cases of this model are instantaneous and progressive nucleation. An excellent method for discriminating between these two limiting cases is to compare the dimensionless experimental current-time transients to the theoretical transients.$^{19}$

In Fig. 3 and Fig. 4, the experimental dimensionless current-time transients of copper and copper-zinc codeposition are compared to the theoretical transients. From these figures, they are apparent that the nucleations of copper and Cu-Zn codeposition are of instantaneous and progressive, respectively.

**SEM/EDS and XRD analysis**

Bulk electrodeposits of Cu-Zn alloy were prepared on thin nickel foils (0.5x0.5cm$^2$) for SEM/EDS and XRD analysis. Deposits were prepared by holding a potential for a
certain period of time in an unstirred melt containing CuCl. Following the deposition, the coated nickel foils were washed with dry propylene carbonate, ethanol and deionized water in succession to remove any melt residue and dried in glove box then they were transferred to SEM/EDS or XRD instruments for analysis.

Table 1 shows the results of EDS analysis of the Cu-Zn alloy electrodeposits obtained at different temperatures and at different concentrations of copper(I). These data indicate that the atomic ratios of zinc in the Cu-Zn alloy deposits depended on the applied potentials. More negative potential results in higher zinc content in the Cu-Zn alloy deposits. At the same electrodeposition potential, higher temperature or higher concentration of Cu(I) lead to higher copper content in the Cu-Zn alloy deposits, however, the influence of concentration of Cu(I) is not so obvious as the influence of temperature.

The electrodeposits that contain rich copper content (80% a/o) are reddish then become yellow (Cu 70% a/o) and gray (Cu 60% a/o) as the zinc content increases. The micrographs of Cu-Zn alloy deposits show that the grain shape of the deposited Cu-Zn alloy is influenced by the applied potentials. The grain shape changed from circular to polygonal as the applied potential varied from negative to positive. It should be noted that at more positive potential, the deposits are rich in copper.

Several XRD samples including a nickel foil, the nickel foils coated with pure copper electrodeposits, pure zinc electrodeposits and copper-zinc electrodeposits were analyzed by XRD and these results are shown in Fig. 5. As shown in the literatures, the electrodeposited copper-rich brass exhibits two phases; α and β phases. In Fig. 5, the signals of α and β phases of Cu-Zn alloy are indeed observed and this indicate that these Cu-Zn alloy deposits are crystalline. Fig. 5 also shows that the peak of α phase brass gradually disappears at more negative electrodeposition potential; in other words, the α phase gradually disappears with the increase of zinc content in the Cu-Zn alloy electrodeposits.

**SUMMARY AND CONCLUSION**

The electrodeposition and nucleation process of copper and copper-zinc alloy were investigated at a nickel electrode in a 50.0-50.0 mol% ZnCl2-EMIC melt. Pure copper deposits could be obtained in this melt and the contents of zinc in the deposited copper-zinc alloy are influenced by the applied potentials of electrodeposition. The nucleation mechanism agrees instantaneous mode initially then changes to progressive when the electrodeposition potential was changed from the potential that the unique reaction was
copper reduction to the potential that Cu-Zn codeposition occurred. Analysis of XRD patterns reveals that the Cu-Zn alloy deposits are crystalline and exhibits two phases; α and β brass.

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REFERENCES

1. D. Pletcher, *Industrial Electrochemistry*, Chapman and Hall, p. 187, London (1984).
2. G. D. Wilcox and D. R. Gabe, *Corr. Soc.*, 35, 754 (1993).
3. J. S. Wilkes, J. A. Levisky, R. A. Wilson and C. L. Hussey, *Inorg. Chem.*, 21, 1263 (1982).
4. S. P. Wicelinski, R. J. Gale and J. S. Wilkes, *J. Electrochem. Soc.*, 134, 262 (1987).
5. M. K. Carpenter, M. W. Verbrugge and J. *Mater. Res.*, 9, 2584 (1994).
6. J. Robinson and R. A. Osteryoung, *J. Electrochem. Soc.*, 127, 122 (1980).
7. T. P. Moffat, *ibid.*, 141, L115 (1994).
8. W. R. Pitner, C. L. Hussey and G. R. Stafford, *ibid.*, 143, 130 (1996).
9. R. T. Carlin, P. C. Trulove and H. C. De Long, *ibid.*, 143, 2747 (1996).
10. J. A. Mitchell, W. R. Pitner and C. L. Hussey, *ibid.*, 143, 3448 (1996).
11. M. R. Ali, A. Nishikata and T. Tsuru, *Electrochim. Acta*, 42, 1819 (1997).
12. E. G.-S. Jeng and I-W. Sun, *J. Electrochem. Soc.*, 145, 1196 (1998).
13. X.-H. Xu and C. L. Hussey, *ibid.*, 140, 618 (1993).
14. Staff Report, *Plating Surf. Finish.*, 69(2), 38 (1984).
15. W. J. van Ooij, *Rubber Chem. Technol.*, 57, 421 (1984).
16. A. Brenner, *Electrodeposition of Alloys*, p. 457, Vol. 1, Academic Press, New York, (1963).
17. Y. Fujiwara and H. Enomoto, *Plating Surf. Finish.*, 80, 52 (1993).
18. Y.-F. Lin and I-W. Sun, *Electrochim. Acta*, 44, 2771 (1999).
19. B. Scharifker and G. Hills, *Electrochim. Acta*, 28, 879 (1983).
Table I. Effects of temperature and concentration on composition of Cu-Zn alloy deposits

| T(°C) | Concentration of Cu(I) (mM) | E_{deposition}(V) | Cu(a/o) | Zn(a/o) |
|-------|----------------------------|------------------|---------|---------|
| 200   | 0.09                       | 73.07            | 26.93   |
|       | 0.07                       | 68.39            | 31.61   |
|       | 0.05                       | 64.10            | 35.90   |
|       | 0.01                       | 51.08            | 48.92   |
| 50    | 0.11                       | 80.56            | 19.44   |
| 250   | 0.09                       | 75.96            | 24.04   |
|       | 0.05                       | 66.16            | 33.84   |
|       | 0.00                       | 60.68            | 39.32   |
| 300   | 0.11                       | 82.62            | 17.38   |
|       | 0.09                       | 75.49            | 24.51   |
|       | 0.05                       | 72.23            | 27.77   |
|       | 0.00                       | 51.89            | 48.11   |
| 80    | 0.11                       | 83.20            | 16.80   |
| 250   | 0.09                       | 79.73            | 20.27   |
|       | 0.03                       | 73.81            | 26.19   |
|       | -0.01                      | 63.02            | 36.98   |
| 300   | 0.11                       | 86.95            | 13.05   |
|       | 0.07                       | 77.26            | 22.74   |
|       | 0.03                       | 73.83            | 26.17   |
|       | -0.01                      | 68.41            | 31.59   |
| 100   | 0.09                       | 83.29            | 16.71   |
| 250   | 0.07                       | 82.67            | 17.33   |
|       | 0.05                       | 75.80            | 24.20   |
|       | -0.01                      | 61.95            | 38.05   |
| 300   | 0.11                       | 89.38            | 10.62   |
|       | 0.07                       | 79.90            | 20.10   |
|       | 0.01                       | 74.88            | 25.12   |
|       | 0.00                       | 66.46            | 33.54   |
|       | 0.11                       | 87.09            | 12.91   |
|       | 0.07                       | 79.60            | 20.40   |
|       | 0.03                       | 74.04            | 25.96   |
|       | -0.01                      | 72.36            | 27.64   |

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Fig. 1. The staircase cyclic voltammogram for the 50.0-50.0 mol% ZnCl$_2$-EMIC melt on a Ni electrode at 50 °C. The scan rate was 50 mV/s.
Fig. 2. The staircase cyclic voltammograms for 200mM CuCl in 50.0-50.0 mol% ZnCl₂-EMIC melt on a Ni electrode at 80 °C. (a) scan reversed at 0.4 V and (b) scan reversed at -0.3 V. The scan rate was 50 mV/s.
Fig. 3. Comparison of the dimensionless experimental current-time transients derived from the chronoamperometric experiments for electrodeposition of copper from 200 mM CuCl in 50.0-50.0 mol% ZnCl₂-EMIC melt on Ni at 80 °C. Values of applied potentials are given above each plot.
Fig. 4. Comparison of the dimensionless experimental current-time transients derived from the chronoamperometric experiments for electrodeposition of Cu-Zn from 200 mM CuCl in 50.0-50.0 mol% ZnCl₂-EMIC melt on Ni at 80 °C. Values of applied potentials are given above each plot.
Fig. 5. XRD patterns (Cu Ka) of Ni substrate and electrodeposits of pure copper, pure zinc and electrodeposits of Cu-Zn from 200 mM CuCl in 50.0-50.0 mol% ZnCl$_2$-EMIC melt at 80 °C. The electrodeposition potentials are shown in the plot.