ELECTROPLATING OF NICKEL-ALUMINUM ALLOYS FROM ROOM TEMPERATURE MOLTEN CHLOROALUMINATES

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ABSTRACT

This paper demonstrates the feasibility of the electrochemical deposition of Ni-Al phases from room temperature molten chloroaluminates using either DC or pulsed current electrolysis. Occlusion of the molten salt in the deposits, in many cases followed by rapid degradation in contact with the air, is the main problem to overcome before the process has any real application potential for the preparation of HER-electrodes.

INTRODUCTION

Room temperature molten haloaluminates were introduced by Hurley and Wier (1) in 1951 for practical use as aluminum plating baths. A 2:1 molar ratio mixture of aluminum chloride and N-ethylpyridinium bromide was found to be liquid at room temperature (although the liquidus temperature steeply increases for other compositions) and smooth, adherent aluminum plates were obtained from this composition (2-6).

The subject of room temperature haloaluminates did not receive much more attention until Robinson and Osteryoung (7) combined aluminum chloride and N-(n-butyl)pyridinium chloride (BuPyCl) and obtained an ambient molten salt with low liquidus temperature: these melts are ionic liquids at temperatures only slightly greater than 27°C for all melt compositions in the range 2:1 - 0.75:1 molar ratios AlCl₃ - BuPyCl and acidic, i.e. AlCl₃ - rich, melts remain liquid even at temperatures far below ambient. Later, Wilkes et al. (8) formulated another series of ambient molten salts by combining aluminum chloride and dialkylimidazolium chlorides, typically 1-ethyl-3-methylimidazolium chloride (ImCl). These molten salts exhibit adjustable Lewis acid-base properties and have been used extensively as media for fundamental electrochemical and spectroscopic studies of inorganic and organic solutes (9,10). Furthermore, these molten salts have a technological potential for use as battery electrolytes and as media for electroplating, electrochemical polishing and electrochemical etching. The electrodeposition of aluminum was investigated by several groups (11-15) and the practical electroplating of this metal (including continuous plating) (16, 17) and of aluminum-manganese alloys (18) were successfully demonstrated. Data on the electrochemistry of several other metals in these melts, such as copper (19-21), nickel (22, 23), cobalt (24), bismuth (25), lead (26), silver (27), gold (28) and tin (29) have been reported.

In general most of these studies were conducted with rather low concentrations of the electroactive species (10-20 mM at maximum) while evidently the successfull
application of these molten salts as electrolytes for electroplating baths requires operation at much higher concentrations of metal ions. Furthermore, there are virtually no data available on the anodic behaviour of metals in these melts, although recently anodic passivation has been reported for lead electrodes (26). This paper investigates the possibility of electroplating nickel-aluminum alloys from acidic AlCl₃ - BuPyCl melts and reports some results on the anodic behavior of nickel.

One possible application of this research is to make a contribution to the development of durable and efficient electrode materials for the hydrogen evolution reaction (HER) in alkaline solution. High surface nickel electrode materials have received much attention as they represent a good balance between cost and efficiency. For this reason, Raney-type nickel materials have received much attention (30). Usually, powdered Raney-type nickel-aluminum alloys are used as the starting material for the preparation of HER-electrodes by leaching of aluminum but the direct electrodeposition of thin layers of the alloy may be an interesting alternative worthwhile to explore.

EXPERIMENTAL

The synthesis and purification of BuPyCl, the sublimation of AlCl₃ (Fluka) and the preparation of the melts was described previously (28). Dilute solutions of Ni(II)-ion, up to $\sim 10^{-2}$ are easily prepared by constant current anodisation of nickel in well-stirred acidic melts. However, this method was not convenient for the preparation of more concentrated solutions. Since anhydrous NiCl₂ does not dissolve well in acidic melts, the metal chloride was dissolved in a basic melt which was then rapidly mixed with an excess of 2:1 AlCl₃ - BuPyCl melt, eventually precipitated chloride was filtered off and the acidity was adjusted by addition of solid aluminum chloride (31): this way, solutions containing up to 0.12 M Ni(II)-ion could be prepared (preparation of solid Ni(AlCl₄)₂ (32) eventually may be a nicer way to arrive at the same result).

All experiments were carried out under a purified nitrogen atmosphere (VAC dry box ; HE-493 Dri Train) at ambient temperature. Nickel and tungsten wires (eventually rotating) were used as the working electrodes for voltammetric experiments. Plating experiments were performed with a cylindrical rotating copper electrode with an exchangeable sample holder (height = 10 mm ; diameter = 3 mm) or with 1x1 cm² plane stainless steel electrodes (simply using a magnetic stirring bar). A large concentric nickel wire spiral was used as the counter electrode. The reference electrode, an aluminum wire immersed in a 2:1 AlCl₃ - BuPyCl melt, was provided with a Luggin capillary to minimize ohmic drop.

Electrochemical experiments were performed with a EG&G-Princeton Applied Research Corporation (PARC) Model 174 potentiostat, a PARC Model 175 universal programmer, a PARC Model 379 digital coulometer and a Houston Instrument Omnicographic 2000 XY-recorder. Part of the experiments was performed with a Tacussel PJT 24-1 potentiostat/galvanostat coupled with a computer controlled Tacussel IMT-1 interface for electrolysis experiments with pulsed current.
RESULTS AND DISCUSSION

The absorption spectrum of Ni(II) in acidic AlCl₃-BuPyCl melts (fig. 1) indicates that the metal ion has an octahedral coordination in this medium and can be represented either as Ni(Al₂Cl₇)₂ or Ni(AlCl₄)₂. The spectrum does not change with the melt composition whereas the potential of the Ni-Ni(II)-couple decreases by several hundred millivolt in going from a 2:1 melt to less acidic compositions (23, fig. 4). Such a change of potential, which has been observed for many other metal/metal-ion couples in these melts (20,21,27) evidently must be accounted for by the variation in anion speciation with melt acidity. The observation that the absorption spectrum does not change with the melt acidity suggests that the first coordination sphere is not affected and that the metal ion remains coordinated by the same species for all acidic melt compositions (this is tantamount to saying that Al₂Cl₇⁻ and AlCl₄⁻ have very different coordinating strengths!).

![Absorption spectrum of Ni(II) in acidic AlCl₃-BuPyCl melts](image)

**Figure 1** Absorption spectrum of Ni(II) in acidic AlCl₃-BuPyCl melts

Cyclic voltammograms of a Ni(II) solution in 2:1 melts on a tungsten electrode (fig. 2a) show that the deposition of nickel starts at about 0.4 V but the current does not really decay after the peak maximum and develops into a broad region where nickel and aluminum are codeposited, as has been reported previously (22). The anodic portion of the voltammograms show the peak expected for the dissolution of bulk aluminum, a broad current region which is attributed to the dissolution of aluminum from the Ni-Al phase and finally a peak for the dissolution of the electrodeposited nickel. Cyclic voltammograms recorded on nickel wire electrode (fig. 2b) exhibit an additional anodic peak at more positive potentials which corresponds to the dissolution of the base metal. Codeposition of nickel and aluminum is also evident from experiments with rotating tungsten wire electrodes (fig. 3): the voltammograms do not exhibit a well defined limiting current and instead the current increases steadily until the potential is reached where deposition of bulk aluminum starts.
Figure 2  Cyclic voltammetry of Ni(II) in 2:1 AlCl$_3$-BuPyCl melts (a) tungsten electrode (b) nickel wire electrode

Figure 3  Voltammograms of nickel(II)-ion reduction on rotating wire tungsten electrodes at different rotation rates (500, 1000, 1250, 1500 and 2000 rpm)

A series of electrolysis experiments using DC or pulsed current was carried out to confirm directly the results of the voltammetric experiments and to investigate the composition of the electrodeposited layers (in DC experiments the applied current was maximum 30% of the estimated limiting current for nickel deposition; in pulsed current
experiments the rotation rate was kept rather low, maximum 100 rpm, so that relatively long pulse times (0.5 - 2 s) could be applied). The results of some 60 electrodeposition experiments can be summarized as follows:

1. using flat cathodes, it is evident that the current distribution was far from ideal as evidenced by irregular coverage, specially near the edges of the electrode: this may be a more general problem if one tries to use this kind of room temperature molten salts as a medium for electrodeposition since the conductivity is rather low, i.e. as compared with aqueous plating solutions but this difficulty probably can be overcome with a better cell design and eventually by raising the temperature.

2. some typical results of SEM analysis of the electrodeposits are given in table 1: The aluminum content increases with increasing current density but the increase is far from linear: in this study deposits containing up to 14 atom% aluminum were obtained using pulsed current if the pulse duration was adjusted so that the potential of the electrode was in a region just before the onset of bulk aluminum deposition. Furthermore it was found that the deposits contained a few atom% of aluminum even at relatively low current densities, i.e. almost at the foot of the nickel wave: this suggests that the codeposition of aluminum actually starts much earlier than is evident from the voltammetric results.

| DC  | 3 mA | 180 min | atom% Ni | atom% Al | atom% Cl |
|-----|------|---------|----------|----------|----------|
| PC  | 3 mA | 180 min | 88       | 8.5      | 3.5      |
| PC  | 6 mA | 90 min  | 84       | 11       | 5        |
| PC  | 9 mA | 60 min  | 80       | 14       | 6        |

3. the most striking fact in this table is the fact that all the deposits contain a considerable amount of chloride which evidently points to occlusion of the molten salt, probably caused by the rather high viscosity of the electrolyte (i.e., the molten salt sticks almost like a syrup to the electrode). If this explanation is true, one could consider the use of a cosolvent like toluene to lower the viscosity and to increase the conductivity which would have a beneficiary effect also on current distribution, although the use of aromatic solvents could cause other, e.g. ecological, problems. Another possibility is that occlusion of the molten salt could be prevented by the use of much more stringent procedures for the pretreatment of the electrodes than have been used in the present study (polishing, degreasing with acetone, drying with alcohol).

4. most of the deposits were bright and well-adhering to the cathode substrate when they were removed from the electrolysis cell and washed with toluene to remove the adhering molten salt. For example, in DC experiments, surface roughening and internal stresses seems to be no problem as long as the current is lower than 30 % of the limiting current
and the thickness of the deposits does not exceed 3-4 microns. The deposits did not visibly change as long as they were kept in the dry box used for the electrolysis experiments. However, once out of the dry box about 50% of the deposits degraded rapidly: black spots developed on the surface of the specimens (the deposits became almost "pock-pitted") and the electrodeposited layer was pulverized (in most cases this process did not take more than a few hours): it is believed that reaction of the occluded molten salt with moisture in the air is responsible for this rapid degradation of the deposits.

5. The electrodeposition of Ni-Al phases from a room temperature molten salt is thus demonstrated in principle but occlusion of the molten salt, followed by rapid degradation in contact with the air, is the main problem to overcome before this process can have any real application potential.

![Figure 4 Cyclic voltammogram of nickel in a pure AlCl3-BuPyCl melt: the scan was started from 0.7 V in the anodic direction (20 mV/s). Inset: influence of scan rate: 5, 20, 50, 100 mV/s (different potential scale)](image)

A cyclic voltammogram of nickel in a pure AlCl3-BuPyCl melt, started in the anodic direction (fig.4), exhibits a large peak which corresponds to the anodic dissolution and passivation of the metal (such a peak is also present in fig.2b), as was reported also for lead electrodes (26). The cathodic portion of the voltammogram exhibits a large peak for the deposition of nickel from the saturated solution, at least in the vicinity of the electrode (the solubility of Ni(II)-ion in a 2:1 AlCl3-BuPyCl melt is estimated as 0.15 M); thus the layer formed on the electrode during the anodic scan is either very porous or does not well adhere to the electrode. Application of a constant current results in well defined
transition times for the passivation of the metal. A plot of $i\tau^{1/2}$ vs. $i$ obtained from such experiments (fig. 5) yields an almost horizontal line, suggesting that the process can be described by a simple dissolution-passivation mechanism. However, the scatter of the points is rather large: this may indicate that nucleation of the solid precipitate plays an important role and that the solution at the electrode surface is actually supersaturated before the onset of precipitation. This is confirmed by the fact that $C(x=0,\tau)$, the concentration of Ni(II)-ion at the electrode surface at time $\tau$, calculated from the Sand equation with $D = 8.5 \times 10^{-7} \text{ cm}^2/\text{s}$, is slightly more than 0.5 M, i.e. more than three times the estimated value of the solubility. From a practical viewpoint these experiments merely indicate that electroplating experiments from these molten salts require anodes with a much larger area than the area of the cathode to permit the use of rather concentrated solutions (close to saturation).

**Figure 5** Plot of $i\tau^{1/2}$ vs. $i$ for constant current anodization of nickel metal in pure 2:1 AlCl$_3$-BuPyCl melts

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REFERENCES
1. F.H. Hurley and T.P. Wier, J. Electrochem. Soc., 98, 203 (1951)
2. F.H. Hurley, U.S. Pat. 2,446,331 (1948)
3. T.P. Wier and F.H. Hurley, U.S. Pat. 2,446,349 (1948)
4. T.P. Wier, U.S. Pat. 2,446,350 (1948)
5. F.H. Hurley and T.P. Wier, J. Electrochem. Soc., 98, 207 (1951)
6. W.H. Safranek, W.C. Schickner and C.L. Faust, J. Electrochem. Soc., 99, 53 (1952)
7. J. Robinson and R.A. Osteryoung, J. Am. Chem. Soc., 101, 323 (1979)
8. J.S. Wilkes, J.A. Levisky, R.A. Wilson and C.L. Hussey, Inorg. Chem., 21, 1263 (1982)
9. C.L. Hussey, Advances in Molten Salt Chemistry. Vol. 5, G. Mamantov, Editor, p. 185, Elsevier, New York (1983)
10. C.L. Hussey, Pure Appl. Chem., 60, 1763 (1988)
11. J. Robinson and R.A. Osteryoung, J. Electrochem. Soc., 127, 122 (1980)
12. P.K. Lai and M. Skyllas-Kazacos, Electrochim. Acta, 32, 1443 (1987)
13. Y. Chryssoulakis, J.C. Poignet and G. Manoli, J. Appl. Electrochem., 17, 857 (1987)
14. P.K. Lai and M. Skyllas-Kazacos, J. Electroanal. Chem., 248, 431 (1988)
15. R.T. Carlin and R.A. Osteryoung, J. Electrochem. Soc., 136, 1409 (1989)
16. S. Takahashi and I. Saeki, Molten Salts, 33, 195 (1990)
17. S. Takahashi, K. Ida and S. Mori, Proceedings of the Seventh International Symposium on Molten Salts, C.L. Hussey, J.S. Wilkes, S.N. Flengas and Y. Ito, Editors, p. 661, The Electrochemical Society Softbound Proceedings Series, Pennington, NJ (1990)
18. A. Shibuya, T. Tsuda, Y. Yamamoto, T. Uchida and H. Seto, Molten Salts, 33, 129 (1990)
19. C.L. Hussey, L.A. King and R.A. Carpio, J. Electrochem. Soc., 126, 1029 (1979)
20. Chenniah Nanjundiah and R.A. Osteryoung, J. Electrochem. Soc., 130, 1312 (1983)
21. T.M. Laher and C.L. Hussey, Inorg. Chem., 22, 3247 (1983)
22. R.J. Gale, B. Gilbert and R.A. Osteryoung, Inorg. Chem., 18, 2723 (1979)
23. T.M. Laher and C.L. Hussey, Inorg. Chem., 21, 4079 (1982)
24. C.L. Hussey and T.M. Laher, Inorg. Chem., 20, 4201 (1981)
25. L. Heerman and W. D'Olieslager, J. Electrochem. Soc., 138, 1372 (1991)
26. C.L. Hussey and Xiao-Hong Xu, J. Electrochem. Soc., 138, 1886 (1991)
27. Xiao-Hong Xu and C.L. Hussey, J. Electrochem. Soc., 139, 1295 (1992)
28. Xiao-Hong Xu and C.L. Hussey, J. Electrochem. Soc., 139, 3103 (1992)
29. Xiao-Hong Xu and C.L. Hussey, J. Electrochem. Soc., 140, 618 (1993)
30. L. Chen and A. Lasia, J. Electrochem. Soc., 140, 2464 (1993) and other references cited in this paper
31. This method was suggested to us by B. Gilbert, University of Liège (Belgium)
32. J. Brynestad, H.L. Yakel and G.P. Smith, Inorg. Chem., 9, 686 (1970)