CONDUCTIVITY AND ELECTROCHEMISTRY OF COBALT (II) AND DYSPROSIUM CHLORIDE IN ZINC CHLORIDE-1-ETHYL-3-METHYL-IMIDAZOLIUM CHLORIDE ROOM TEMPERATURE MOLTEN SALT

Hsin-Yi Hsu and Chao-Chen Yang

Graduate School of Engineering Science & Technology (Doctoral Program), National Yunlin University of Science and Technology, 123 University Road, Sec. 3, Touliu, Yunlin, Taiwan 640, R. O. C.

ABSTRACT

In this present study, zinc chloride-1-ethyl-3-methylimidazolium chloride (EMIC) was used to form a room temperature melt. Although these melts are being examined for electrochemical applications, little conductivity data appears in the literature. The sequence of conductivities for the different component melts is \( \text{ZnCl}_2\text{-EMIC} > \text{ZnCl}_2\text{-EMIC-CoCl}_2 > \text{ZnCl}_2\text{-EMIC-DyCl}_3 > \text{ZnCl}_2\text{-EMIC-CoCl}_2\text{-DyCl}_3 \). The results may be explained in terms of the viscosity increase and complex formation when the cobalt chloride or dysprosium chloride is added into the acidic \( \text{ZnCl}_2\text{-EMIC} \) melt. The electrochemistry of cobalt(II) and/or dysprosium chloride in acidic \( \text{ZnCl}_2\text{-EMIC} \) melts at different temperature has been investigated by cyclic voltammetry. The results reveal the reduction of \( \text{Dy(III)} \) to \( \text{Dy(II)} \) or \( \text{Dy(III)} \) to \( \text{Dy} \) may have occurred, and the electrodeposition of \( \text{Co-Dy} \) or \( \text{Zn-Co-Dy} \) alloys was not formed from the melt at 80°C. Nevertheless, the cathodic reduction of \( \text{Co}^{2+}/\text{Dy}^{3+} \) species will occur more readily at 110°C and 120°C than at 100°C.

INTRODUCTION

In recent years, the transition metal (TM) and rare-earth (RE) elements and compounds used as the raw materials in electric (1-10), magnetic (11-24), optical (25-27), corrosion (28-33), superconductor (34-36) and catalytic reactions (37,38) have drawn considerable attention.

Electrodeposited zinc and its alloys are good candidates for highly corrosion-resistant coatings and are normally deposited from aqueous electrolyte solutions. However, there are some problems involving hydrogen embrittlement and low current efficiency for electrodeposition carried out in aqueous electrolyte solutions. Molten salts are aprotic solvents which possess some unique properties, e.g., high conductivity, a wide electrochemical window and low vapor pressure, and may be good alternatives to aqueous plating baths for the electrodeposition of zinc and zinc alloys. Nevertheless, there is some difficulty in using conventional molten salts because these melts can be used only at high temperatures and with special containment. The melting point of room-temperature molten salt (RTMS) compared with conventional molten salts is low and the handling is simplified. Sun et al (30-32) has examined the electrodeposition of Zn, Co, Zn-Co and Zn-Cu alloys...
from the acidic ZnCl₂-EMIC RTMS. However, the conductivities of mixed melts were not reported. Moreover, the electrochemistry and electrodeposition of Zn-RE alloys from the acidic ZnCl₂-EMIC melt have not been investigated.

For the needs of optical data storage, both reading and writing, the preparation of magneto-optical thin film materials has been a major activity. In the present project, the fabrication of magneto-optical thin film materials is the primary focus. Although sputtering and molecular beam epitaxy have traditionally been used to prepare magneto-optical thin films, sputtering and MBE equipment is expensive (39-41), and it is difficult to work with large substrates. Hence, it is necessary to seek a better and more economical method of preparation.

According to recent research reports (11-24), the addition of rare earth elements in magneto-optical thin film materials has lead to improvements in the magneto-optical Kerr effect and high coercivity of magneto-optical thin films for short wavelength light. Consequently, the transition metal-rare earth alloy promise as a magneto-optical thin film material. To our knowledge, the electrochemistry and electrodeposition of Co-Dy or Zn-Co-Dy alloys from the acidic ZnCl₂-EMIC melt have not been reported.

In this study, the conductivities of ZnCl₂-EMIC, ZnCl₂-EMIC-CoCl₂, ZnCl₂-EMIC-DyCl₃ and ZnCl₂-EMIC-CoCl₂-DyCl₃ melts are reported for the first time. In addition, the electrochemistry of cobalt(II) and dysprosium chloride in acidic 50-50 mol% ZnCl₂-EMIC melts has been investigated by cyclic voltammetry, to gain information that will lead to the electrodeposition for Co-Dy or Zn-Co-Dy alloys from the acidic 50-50 mol% ZnCl₂-EMIC melts.

**EXPERIMENTAL.**

ZnCl₂ (Merck, anhydrous, 98%), EMIC (1-ethyl-3emethylimidazolium chloride, Aldrich, 98%), CoCl₂ (Merck, anhydrous, 99%) and DyCl₃ (Acros, anhydrous, 99.9%) were used as received. Molten salts of different composition were prepared by continuous stirring for 12 hours followed by standing for 12 hours without stirring under a purified nitrogen atmosphere in a glove box. The electrical conductivities of these melts were measured by the computerized measurement system utilizing the d.c. four-probe method described in (42).

The electrochemical experiments were performed in a sealed three-electrode electrochemical cell. The nickel working electrode (geometric area=0.031 cm²) was made by winding the Teflon tape around a piece of nickel rod (Gredmann, 99.2%) and inserting into a glass tube. The electrode was polished successively with increasingly finer grades of emery paper followed finally by rinsing with distilled water and dried under vacuum. The counter electrode was a zinc spiral (Nilaco, 99.9%) immersed in the bulk electrolyte melt that was contained in a sealed pt wire glass tube. The reference electrode was a zinc wire immersed in a pure 50-50 mol% ZnCl₂-EMIC melt that was contained in a sealed pt wire glass tube. The electrochemical behavior of the melts was determined using an EG&G model 273A potentiostat/galvanostat controlled with EG&G model 270/250 software.
RESULTS AND DISCUSSION

The conductivities of the 50-50 mol% ZnCl₂-EMIC melts with different salt additions are shown as a function of the temperature in Figure 1. The experimental data was least-squares fit to equations of the form \( \sigma = a + bt + ct^2 \), where \( t \) is the temperature in °C. The parameters \( a, b \) and \( c \) are given in Table 1. As the R squared values are larger than 0.998, the above equations fit the experimental data very well. Figure 1 shows that the specific conductivity of all melts increases nearly linearly with temperature and that the sequence of conductivities for the different component melts is ZnCl₂-EMIC > ZnCl₂-EMIC-CoCl₂ > ZnCl₂-EMIC-DyCl₃ > ZnCl₂-EMIC-CoCl₂-DyCl₃. The results may be explained in terms of melt viscosity and complex formation. The observation shows that the sequence of viscosity for these melts is ZnCl₂-EMIC-CoCl₂-DyCl₃ > ZnCl₂-EMIC-DyCl₃ > ZnCl₂-EMIC-CoCl₂ > ZnCl₂-EMIC. The viscosity increase of the melts containing CoCl₂ and/or DyCl₃ apparently results in a decrease in conductivity. Furthermore, it is expected that the formation of complex ions of the transition metal (Co) and rare-earth element (Dy) would reduce the mobility of ions in the melts. Hence, the conductivity of the melts containing CoCl₂ or / and DyCl₃ decreases.

The electrochemical behavior of cobalt(II) and dysprosium chloride in 50-50 mol% ZnCl₂-EMIC melts at various temperatures has been investigated by cyclic voltammetry. The cyclic voltammograms for the 50-50 mol% ZnCl₂-EMIC melt on a Ni working electrode at 80°C for various scan reverse are shown in Figure 2. These voltammograms exhibit a single reduction wave and an associated oxidation wave in the potential range between -0.22 V and 0.02. The reduction wave must be due to the cathodic reduction of Zn(II) species to Zn metal. The oxidation wave must be due to the anodic stripping of the Zn metal that was deposited on the Ni electrode. As can be seen in Figure 2, the oxidation potential shifts to more positive potentials and the peak current increase when the scan reverse potential was changed to more negative potentials (from -0.4V to -0.8V).

Figure 3 shows the cyclic voltammograms for the 50-50 mol% ZnCl₂-EMIC melt following addition of 1.68mol% CoCl₂ on a Ni working electrode at 100°C for various scan reverse potential. The figure exhibits two reduction waves (c₁, c₂) and two major oxidation waves (a₁, a₂). The two reduction waves must be due to the cathodic reduction of Co(II) (wave c₁) and Zn²⁺ species (wave c₂). Figure 3 also indicates that the stripping wave (a₂) of the zinc deposit that is observed in the voltammograms of melt containing Co(II) is different from those from pure 50-50mol% ZnCl₂-EMIC melt. The wave a₂ appears to have a broader shape than the voltammogram of the pure melt. Based on these observations, it is likely that a Co-Zn alloy is electrodeposited and that wave a₂ is associated with the oxidation of this Co-Zn alloy deposit. Moreover, the oxidation wave a₁ must be due to the anodic stripping of the cobalt that was electrodeposited on the Ni electrode at wave c₁. The small oxidation wave a₁ seen in the voltammogram of Figure3 at -0.6V a potential reversal of presumably due to the oxidation of cobalt that has a stronger interaction with the Ni substrate, and is thus it is oxidized less readily than the bulk cobalt deposit.

Figure 4 shows the cyclic voltammograms for the 50-50 mol% ZnCl₂-EMIC melt with the addition of 1.11mol% DyCl₃ on a Ni electrode at 100°C for various scan reverse potentials. There are two reduction waves (c₁, c₂) and a major oxidation wave (a₂) on Figure4. The wave c₂ must be due to the cathodic reduction of Zn²⁺ species and the wave a₂...
must be the associated oxidation wave. Furthermore, the small wave $c_1$ is presumably due to the reduction of Dy(III) to Dy(II) (43) or Dy(III) to Dy with wave $a_1$ must be associated oxidation wave. To our knowledge, no detailed electrochemistry or spectra of DyCl$_3$ in room-temperature molten salts has been reported. Hence, it is important that the electrodeposition of Dy and the electrochemistry of Dy(III) be further explored in order to verify these preliminary results.

The mixing enthalpies of various Co-Dy alloys have been reported (44). The experiments were carried out in a high temperature twin solution calorimeter at 1818 K in purified He medium. Consequently, the formation of Co-Dy alloys is feasible at high temperature. Moreover, the rare earth (R) and cobalt elements can form a unique group of intermetallic compounds with the hexagonal CaCu$_3$ structure. RCo$_5$ intermetallic compounds have received considerable attention, primarily due to the large magneto-crystalline anisotropy energy of the SmCo$_5$ compound observed at low temperatures (45). However, the electrochemistry and electrodeposition of Co-Dy or Zn-Co-Dy alloys from the RTMS have not been reported. In order to research the feasibility of the preparation of Co-Dy or Zn-Co-Dy alloys from the RTMS, the cyclic voltammograms for the 50-50 mol% ZnCl$_2$-EMIC melt with the addition of 1.68mol% CoCl$_2$ and 1.11 mol% DyCl$_3$ using a Ni electrode at different temperature and various scan reversals were measured, the results are shown in Figures 5 and 6. There are two reduction waves and two oxidation waves on Figure 5. Wave $c_2$ must be due to the cathodic reduction of Zn$^{2+}$ species, while wave $a_2$ is likely the oxidation of the Co-Zn alloy deposit as described on Figure 3. Moreover, wave $c_1$ may be due to the cathodic reduction of Co$^{2+}$ or Co$^{2+}$/Dy$^{3+}$ species, however further research is required to verify this. Figure 6 shows the temperature dependence of the voltammetry. The single reduction wave shifts to more positive potentials with increasing temperature. The results suggest that Co-Dy alloys may be not formed from the melt at 80°C, and that the cathodic reduction will occur more readily as the temperature is increased. It is clear from Figure 7, that the electrodeposition of Co-Zn and Co-Dy alloys is possible from the 50-50mol% ZnCl$_2$-EMIC melt containing CoCl$_2$ and DyCl$_3$. The oxidation wave $a_2$ is more positive than the stripping wave of Zn, hence, it is suggested that the wave $a_2$ is the oxidation wave of a Co-Zn alloy deposit. For the same reason, the oxidation wave $a_1$ may be due to the anodic oxidation of Co-Dy or Zn-Co-Dy alloys. However, it is necessary that these Co-Dy and Zn-Co-Dy alloys be electrodeposited and properly characterized before this can be confirmed.

CONCLUSIONS

The sequence of conductivities for the different component melts is ZnCl$_2$-EMIC > ZnCl$_2$-EMIC-CoCl$_2$ > ZnCl$_2$-EMIC-DyCl$_3$ > ZnCl$_2$-EMIC-CoCl$_2$-DyCl$_3$. The results may be explained in terms of the viscosity increase and complex formation when the cobalt chloride or dysprosium chloride is added to the acidic ZnCl$_2$-EMIC melt.

The cyclic voltammograms for 50-50mol% ZnCl$_2$-EMIC melt with the addition of 1.11 mol% DyCl$_3$ on a Ni electrode at 100°C was studied. The results reveal the reduction of Dy(III) to Dy(II) or Dy(III) to Dy. Cyclic voltammograms for the 50-50 mole% ZnCl$_2$-EMIC melt with the addition of 1.68mol% CoCl$_2$ and 1.11 mol% DyCl$_3$ on a Ni electrode at different temperature and scan reversals was also examined. The results
suggest that the electrodeposition of Co-Dy or Zn-Co-Dy alloys is not likely from the melt at 80°C. However, the cathodic reduction of Co²⁺/Dy³⁺ species will occur more readily at 110°C and 120°C than at 100°C.

REFERENCES

1. E. Rosercher, S. Delage, Y. Campidelli, F. Arnaud d’Aritaya, Electron. Lett., 20, 762 (1984).
2. J. Tiren, U. Magnusson, M. Rosling, H. Bleicher, S. Berg, Sol. State Electron, 32, 993 (1989).
3. L. Pahun, Y. Campidelli, F.A. d’Aritaya, P.A. Badoz, Appl. Phys. Lett., 60, 1166 (1992).
4. I. Sagnes, Y Campidelli, G. Vincent, P.A. Badoz, Mater. Sci. Eng. B, 21, 312 (1993).
5. L.P. Sadwick, P.P. Lee, M. Patel, M. Nikuls, R.J. Hwu, J.E. Shield, D.C. Streit, D. Brehmer, K. McCormick, S.J. Allen, R.W. Gedridre, J. Crystal Growth, 164, 285 (1996).
6. Y. Park, S. A. Song, Materials Science and Engineering B, 47, 28 (1997).
7. S. Sanchez, C. Lucas, G.S. Picard, M.R. Bermejo, Y Castrillejo, Thin Solid Films, 361-362, 107 (2000).
8. Mei-Chen Lin, Po-Yu Chen, and I-Wen Sun, J. Electrochem. Soc., 148(10), C653 (2001).
9. T. Koide, Y. Isogai, Y. Fujiwara, Y. Takeda, Physica E, 10, 406 (2001).
10. A. Travlos, N. Salamouras, Thin Solid Films, 397, 138 (2001).
11. W. K. Hwang, Te-ho Wu and H.P.D. Shieh, J. of Magn. Soc. Jpn, 20, 157 (1996).
12. W.K. Hwang, Te-ho Wu, and H.P.D. Shieh, J. of Appl. phys., 81(11), 7437 (1997).
13. Te-ho Wu, J. C. Wu, B.-M. Chen and H.P.D. Shieh, J. Magn. Soc. Jpn, 22, 145 (1998).
14. V. Stepankin, physica B, 211, 345 (1995).
15. S. Pokrzywnicki, J. of Alloys and Compounds, 225, 163 (1995).
16. M.C. Luche, A. Baudry, P. Boyer, J.L. Rouviere, C. Fermon, C. Miramond, J. Magn. Magn. Mater., 150, 175 (1995).
17. R. Pottgen, G. Kotzyba, J. of alloys and Compounds, 245, L9 (1996).
18. C. Dufour, K. Dumesnil, Ph. Mangin, G. Marchal, M. Hennion, J. Magn. Magn. Mater., 156, 425 (1996).
19. P. Schoibinger-Papamantellos, C. Ritter, K.H.J. Buschow, J. of Alloys and Compounds, 264, 89 (1998).
20. L. Smardz, A. Jezierski, A. Kowalczyk, J. Magn. Magn. Mater., 205, 209 (1999).
21. E. Talik, M. Kulpa, T. Mydlarz, J. Kusz, H. Bohm, J. of Alloys and Compounds, 308, 30 (2000).
22. E. Culea, I. Bratu, J. of Non-Crystalline. Solids, 262, 287 (2000).
23. R.S. Mottram, B. Davies, V.A. Yartys, I.R. Harris, International J. of Hydrogen Energy, 26, 441 (2001).
24. C. Schubler-Langeheine, E. Weschke, H. Ott, A. Yu. Grigoriev, A. Moller, R. Meier, C. Mazumdar, G. Kaindl, J. of Electron Spectroscopy and Related Phenomena, 114-116, 795 (2001).
25. D. E. Azofeifa, N. Clark, J. of Alloys and Compounds, 305, 32 (2000).
26. Z. Hong, W. L. Li, D. Zhao, C. Liang, X. Liu, J. Peng, D. Zhao, Synthetic Metals, 111-112, 43 (2000).
27. A.I. Voloshin, N.M. Shavaleev, V.P. Kazakov, J. of Photochemistry and Photobiology A: Chemistry, 134, 111(2000).
28. G Xie, K. Ema, Y. Ito, Z. M. Shou, J. of appl. Electrochem., 23, 753(1993).
29. F. Mansfeld, F.J. Perez, Thin Solid Films, 270, 417(1995).
30. N. Koura, T. Endo, Y. Idemoto, J. of Non-Crystalline Solids, 205-207, 650(1996).
31. Yu-Feng Lin, I.-Wen Sun *, Electrochim. Acta, 44, 2771(1999).
32. Po-Yu Chen, Mei-Chen Lin, and I-Wen Sun, J. Electrochem. Soc., 147, 3350(2000).
33. Po-Yu Chen, I-Wen Sun, Electrochim. Acta, 46, 1169(2001).
34. M.K. Gupta, J.C. Vyas, D.P. Gandhi, K.P. Muthe, D.K. Aswal, S.K. Gupta, G.P. Kothiyal, S.C. Sabharwal, J. of Crystal Growth, 156, 74(1995).
35. J. Kurian, S.P. Pai, P.K. Sajith, K.V.O. Nair, K.S. Kumar, J. Koshly, Physica C, 316, 107(1999).
36. M. B. Maple, M. C. de Adrade, J. Herrmann, R. P. Dickey, N. R. Dilley, S. Han, J. of Alloys and Compounds, 250, 585(1983).
37. Ya.B. Losovyj, I.V. Ketsman, P.P. Kostrobij, Yu. Suchorski, Vacuum, 63, 277(2001).
38. R. A. Batey, D. A. Powell, A. Acton and A. J. Lough, Tetrahedron Letters, 42, 7935(2001).
39. J. C. A. Huang, J.Crystal Growth, 1393, 63(1994).
40. W. Kockelmann, W. Schager, J.K. Yakinthos, P. A. Kotsanidis, J. of Magn. Magn. Mater., 177-181, 792(1998).
41. J. C. A. Huang, Y. H. Lee, Y. M. Hu, T. C. Chang, J. Appl. Phys., 79, 6267(1996).
42. H. -Y. Hsu and C. -C. Yang, Z. Naturforsch. 56a, 670(2001).
43. T. Uda, T. H. Okabe, Y. Waseda, K.T. Jacob, J. of Alloy and Compounds, 284, 282(1999).
44. N. I. Usenko, M. I. Ivanov, J. of Alloys and Compounds, 261, L4(1997).
45. S.G. Sankar, V.U.S. Rao, E. Segal, W.E. Wallace, W.G.D. Frederick, H. J. Garret, Phys. Rev., 11,435 (1975).

Table 1. Parameters for the electrical conductivity equation of 50-50 mol% ZnCl2-EMIC added different component.

| Melt component       | a×10^2 | b×10^4 | c×10^6 | R squared | Temp. (°C) |
|----------------------|--------|--------|--------|-----------|------------|
| blank                | -0.996 | 1.4594 | 1.8778 | 0.9994    | 70-150     |
| 1.687mol % CoCl2     | -1.5099| 2.615  | 1.0826 | 0.9982    | 70-150     |
| 1.114mol % DyCl3     | -1.1098| 1.5703 | 1.4956 | 0.9990    | 70-150     |
| 1.687mol % CoCl2 + 1.114mol % DyCl3 | -0.35  | -0.00425 | 2.0567 | 0.9997    | 70-150     |

Electrochemical Society Proceedings Volume 2002-19 695
Figure 1. The conductivities of the 50-50 mol% ZnCl$_2$-EMIC melts added different component as a function of the temperature. Different component: ♦, blank; ●, 1.687mol% CoCl$_2$; ×, 1.114mol% DyCl$_3$; ▲, 1.687mol% CoCl$_2$ and 1.114mol% DyCl$_3$.

Figure 2. Cyclic voltammograms for the 50-50 mol% ZnCl$_2$-EMIC melt on a Ni electrode at 80°C and various scan reverse potentials. Scan rate: 50 mv/s.
Figure 3. Cyclic voltammograms for the 50-50 mol% ZnCl₂-EMIC melt added 1.68 mol% CoCl₂ on a Ni electrode at 100°C and various scan reverse. Scan rate: 50 mv/s.

Figure 4. Cyclic voltammograms for the 50-50 mol% ZnCl₂-EMIC melt added 1.114 mol% DyCl₃ on a Ni electrode at 100°C and various scan reverse. Scan rate: 50 mv/s.
Figure 5. Cyclic voltammograms for the 50-50 mol% ZnCl₂-EMIC melt added 1.687 mol% CoCl₂ and 1.114 mol% DyCl₃ on a Ni electrode at 100°C and various scan reverse. Scan rate: 50 mv/s.

Figure 6. Cyclic voltammograms for the 50-50 mol% ZnCl₂-EMIC melt added 1.687 mol% CoCl₂ and 1.114 mol% DyCl₃ on a Ni electrode at various temperatures. Scan rate: 50 mv/s.
Figure 7. Cyclic voltammograms for the 50-50 mol% ZnCl₂-EMIC melt added different component on a Ni electrode at 100°C. Scan rate: 50 mv/s.