Loughborough
University

This item was submitted to Loughborough's Institutional Repository (https://dspace.lboro.ac.uk/) by the author and is made available under the following Creative Commons Licence conditions.

For the full text of this licence, please go to:
http://creativecommons.org/licenses/by-nc-nd/2.5/

The Electrodeposition of Zinc Alloys from Ionic Liquid Electrolytes

P.A.Cantwell, P.P.Chung, Han Jiang, G.D.Wilcox and G.W.Critchlow

Department of Materials, Loughborough University, Loughborough, Leicestershire, LE11 3TU. UK

Abstract

Electrodeposited zinc alloys have long been recognised as effective barrier and sacrificial coatings for ferrous substrates. The effect of alloying zinc with, in the main, more noble metals, has produced finishes of higher corrosion resistance than simply electrodeposited zinc. In this manner zinc alloys such as zinc-nickel, zinc-cobalt and zinc-iron are routinely electrodeposited on an industrial scale. A further zinc alloy, zinc-manganese, has shown a high level of promise in terms of corrosion resistance but is difficult to electrodeposit from conventional aqueous solutions.

The present investigations are centred around examining the formation of zinc alloys, by electrodeposition, from non-aqueous ionic liquids. These electrolytes are essentially molten salts which maintain their liquid state at, or near, to room temperature. Being non-aqueous they are unlikely to promote significant hydrogen evolution from active metal surfaces - a severe problem for the electrodeposition of zinc-manganese alloys from aqueous electrolytes. Electrodeposition conditions for the latter will be discussed in terms of electrolyte types, current density and solution characteristics such as agitation type and temperature. Zinc-manganese alloy electrodeposits will be characterised in terms of their composition and morphology. Finally corrosion resistance data will be presented and this will be compared with other more conventionally deposited zinc alloys.

Keywords: Electrodeposited zinc-manganese; zinc alloys; ionic liquid electrolytes.

Introduction

Zinc alloys have been widely electrodeposited onto ferrous substrates for a number of years [1]. They have proved to be a more effective method of producing protection than zinc, combining effective sacrificial properties with improved barrier protection. In this manner Zn-Co, Zn-Ni and Zn-Fe are widely utilised as protective finishes, the latter two alloys often being applied to steel sheet in continuous high speed electrodeposition processes. Zn-Sn also finds niche applications as a sacrificial coating for steels. Zn-Mn has been examined by a number of researchers, but although encouraging data from corrosion trials can be found in the literature, little evidence of concerted industrial adoption can be found [2-4].

One application where electrodeposited zinc alloys have been suggested is in the replacement of electrodeposited cadmium finishes. The toxicity of the latter has precluded its use in many mainstream areas and electrodeposited zinc alloys are one class of coatings which can replace cadmium in some of its roles. However, cadmium replacement in more safety-critical areas such as aerospace is less rapid, with a number of properties needing to be achieved such as corrosion resistance, compact corrosion products, inherent lubricity and galvanic compatibility with aerospace aluminium alloys. To date a 'drop-in' replacement fulfilling all these criteria has not been found.

The need to extend the range of electrodeposited zinc alloys could, therefore, be highly useful in perhaps not only extending the effectiveness of current systems but also promoting new candidates for cadmium replacement. Increasing the range of zinc alloys electrodeposited from conventional aqueous electrolytes is difficult. Suitable electrolyte compositions, often containing complexing agents, has promoted the electrodeposition of the five currently reported alloys. However, the ever present constraints of hydrogen evolution tend to preclude the alloys containing zinc with a more reactive metal. Zn-Mn lies on the boundary of what

can be achieved from aqueous electrolytes, and significant manganese contents, often associated with higher levels of corrosion resistance, usually reduce the cathode current efficiencies (CCEs) to unacceptably low values.

One method of removing the obstacle of appreciable hydrogen evolution is to electrodeposit the zinc alloy from a substantially water-free electrolyte. Until quite recently this was usually achieved through the use of organic electrolytes or molten salt baths. More recently the concept of low melting point molten salts – ionic liquids – has been suggested as a non-aqueous method of electrodepositing a number of single metals and alloys that have been previously difficult or impossible to electroplate from aqueous electrolytes. Recently Zn, Zn-Sn and Zn-Co have been successfully electrodeposited from deep eutectic choline chloride-urea ionic liquid formulations [5]. Zn-Mn has also been electrodeposited from other ionic liquids [6] although the number and scale of the electrodeposition investigations seems relatively small.

The present experimental programme is based upon the investigations into the viability of electrodepositing a range of Zn-Mn alloys from a choline chloride-based ionic liquid electrolyte. Process parameters were investigated such as electrolyte viscosity and conductivity. The electrochemical reactions occurring in the much wider 'electrochemical window' were investigated using simple cathodic polarisation measurements. Finally electrodeposit characteristics were investigated in terms of morphology, composition and corrosion resistance in linear polarisation resistance (LPR) experiments.

Experimental Procedures
Ionic liquid electrolytes were made by combining urea and choline chloride in a 2:1 molar ratio and heating to 80°C with continuous stirring, this was termed the 'bench mark' solution. When a clear solution was achieved zinc and manganese salts, as zinc (II) chloride ($ZnCl_2$) and manganese (II) chloride (as $MnCl_2.4H_2O$ or $MnCl_2.H_2O$) and additives sodium and potassium chloride and/or boric acid, were then added to the solution. Stirring was then continued to reach a homogeneous mixture.

Electrolyte viscosity and conductivity were measured using a Haake VT500 viscometer and a conductivity measuring bridge type MC3 respectively. Measurements were made over a range of temperatures and solution compositions.

Preliminary electrochemical investigations were undertaken utilising an EG&G potentiostat/galvanostat model 263A controlled by PowerSuite software. Cathodic polarisation trials and potentiostatic electrodepositions were carried out in a three electrode cell. During the former measurements the cathode was copper wire or foil (both 99.99%) with the counter electrode (anode) platinum. For the latter experiments only the copper foil was utilised for cathode purposes. Both electrodes were separated by a membrane to reduce the likelihood of contamination by oxidation products. Copper cathodes were immersed in 50% (vol) SG 1.42 nitric acid for 60s to remove oxides from the surface. The samples were then washed in deionised water followed by acetone before thorough drying. The reference electrode used in these experiments was a silver (99.98%)/silver chloride (SSCE) wire against which all potentials were measured.

Deposit morphologies and alloy compositions were examined utilising a Cambridge Stereoscan 360 Scanning Electron Microscope (SEM) together with energy dispersive X-ray spectroscopy (EDX). Analysis was performed at the centre of each sample.

Electrochemical corrosion measurements were undertaken using a linear polarisation resistance (LPR) technique utilising a three electrode cell comprising of an zinc-manganese alloy electrodeposited copper coupon as the working electrode, a platinum foil counter electrode and a saturated calomel reference electrode (SCE). The electrolyte was 5% NaCl solution. Potentials were swept +/- 20 mV around E_{corr} and the current densities measured. LPR values were derived from this initial straight line relationship.

Results and Discussion

Viscosity Measurements

Figure 1 illustrates viscosities of the 2:1 urea/ChCl with $ZnCl_2$ and $MnCl_2.4H_2O$ as a function of temperature and composition. Viscosity values fell with increase in temperature, although still remained in the approximate range of 150-700 mPa s at 298 K. It is acknowledged that water has a dynamic viscosity of 0.891 mPa s at this temperature [7]. The figure also illustrates the effects of possible addition agents. Both sodium chloride and an increased choline chloride content increased the viscosity trends over the temperature range examined.

Figure 2 illustrates electrolyte conductivity data for similar electrolytes. Again both electrolytes containing additives exhibited a reduction in key properties – in this case lower electrolyte conductivities. Conductivities of ionic liquids are normally lower than those of aqueous electrolytes. This is as a result of the property not only being a function of the number of charge carriers, but also their mobility. It is evident that the large constituent ions, a feature of ionic liquid electrolytes, reduce the latter and hence lower the electrolyte conductivity.

Figure 3 illustrates the cathodic polarisation data for ionic liquid electrolytes containing zinc and manganese chlorides at different concentration levels. Each curve was an average of four separate trials to allow for experimental variation. The curves were made up of a single potential sweep from -0.2 to -2.0 V vs SSCE at 0.166 mV s^{-1}. As the potential was swept in a cathodic direction a strong peak was evident at approximately 0.7 V. Further increase in cathodic potential resulted in a reduction in current which may be as a result of mass transport limitations. An increase in current occurring at approximately -1.2 V suggested a second process occurring at higher cathodic potentials. Electrolyte concentrations also had a marked effect with the formulation containing 0.4M $ZnCl_2$ + 0.7M $MnCl_2.4H_2O$ having the highest overall currents.
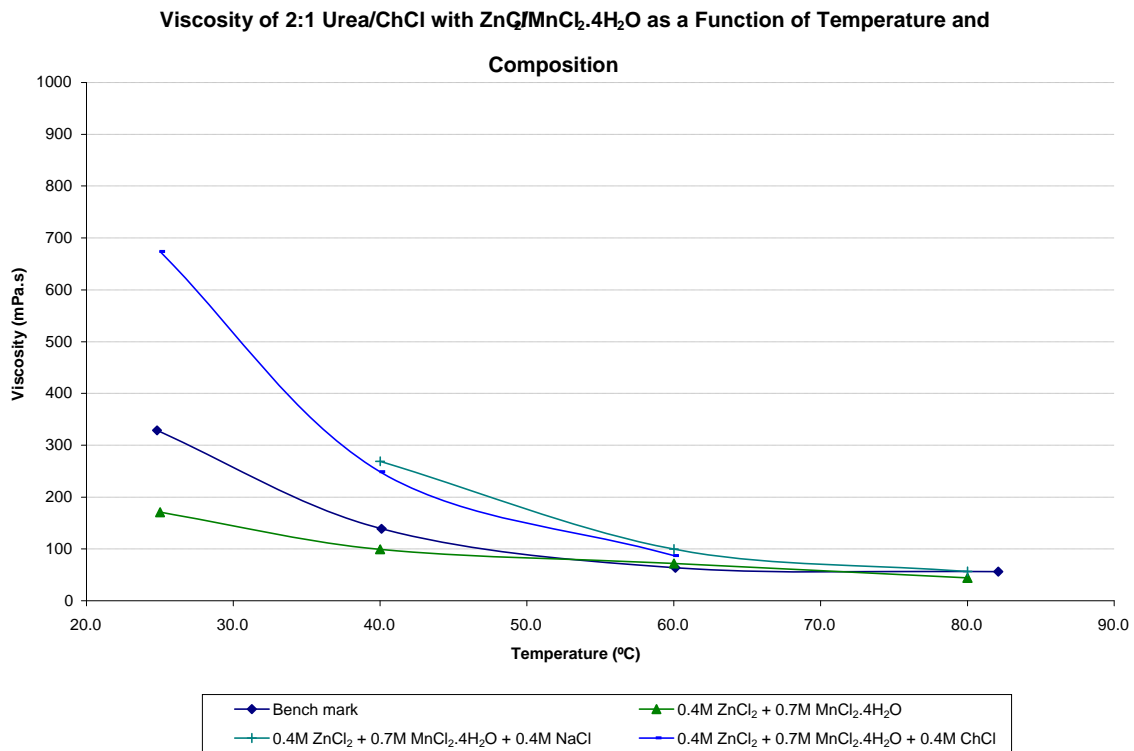
Figure 1 Viscosity of 2:1 urea/ChCl containing 0.4M ZnCl$_2$/0.7M MnCl$_2$.4H$_2$O and addition agents as a function of temperature and composition
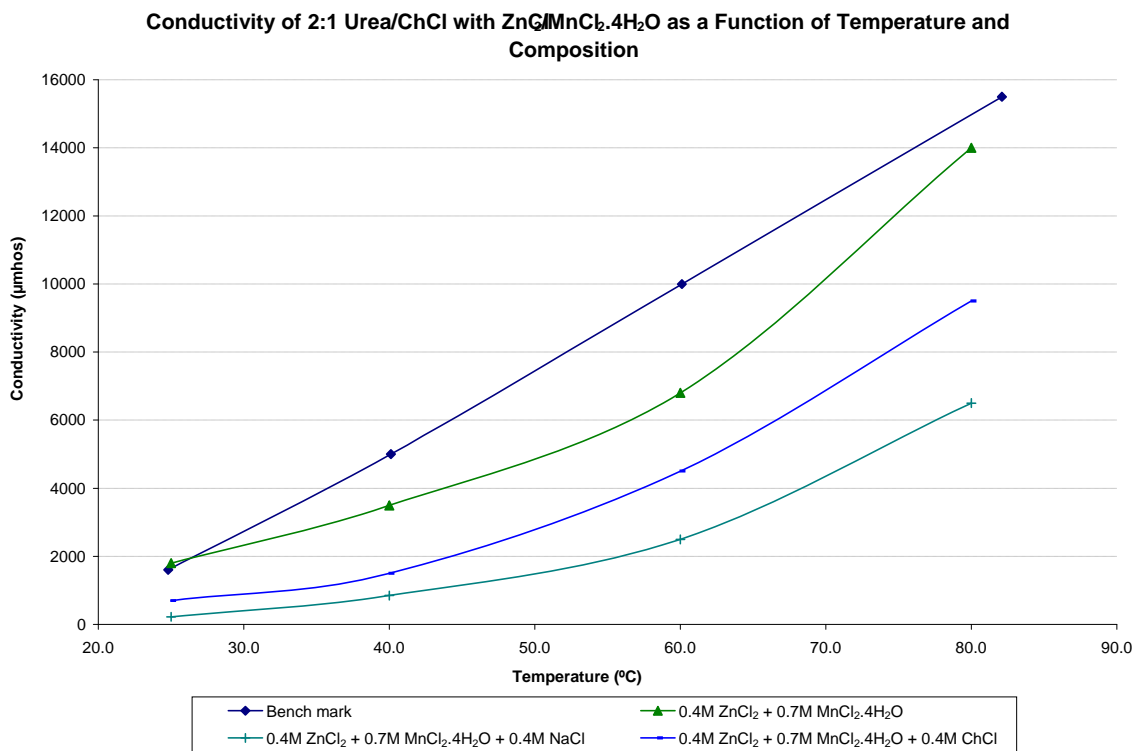

Figure 2 Conductivity of 2:1 urea/ChCl containing 0.4M ZnCl$_2$/0.7M MnCl$_2$.4H$_2$O and addition agents as a function of temperature and composition.
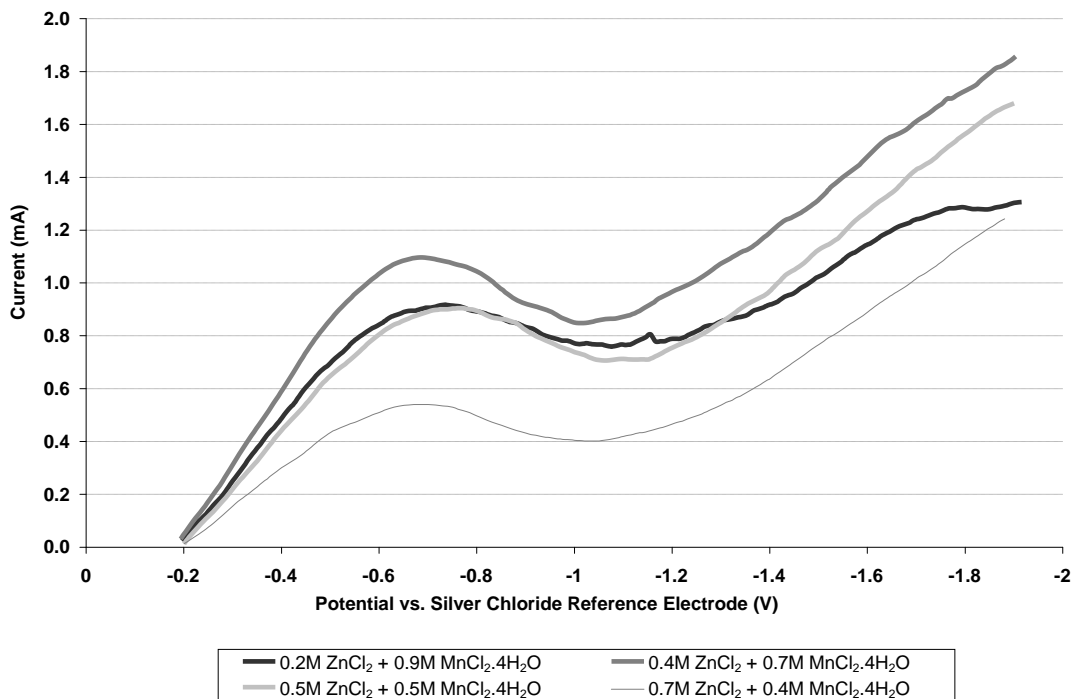
Figure 3 Cathodic polarisation curve of 2:1 urea/ChCl containing ZnCl$_2$ and MnCl$_2$.4H$_2$O as a function of potential and composition. [8]

In this study sodium chloride (NaCl), potassium chloride (KCl) and boric acid (H$_3$BO$_3$) were examined, respectively, as addition agents in the 2:1 urea/ChCl with 0.4M ZnCl$_2$ + 0.7M MnCl$_2$.4H$_2$O and their impact on the electrodeposition process studied. Potassium chloride (KCl) and boric acid (H$_3$BO$_3$) have been used in obtaining electrodeposition of Zn-Mn alloys from an aqueous acidic chloride bath [9,10]. Both NaCl and KCl were difficult to fully dissolve in the ionic liquid electrolyte. However, electrochemical trials were continued. NaCl had no significant positive effects whilst KCl promoted higher currents at the 0.6 and 0.8M concentrations, although in general gains were not significant at other levels. Additions of H$_3$BO$_3$ changed the format of the polarisation curves. There was no distinguishable current peak or limiting current for zinc electrodeposition. This could be due to close (in terms of potential) codeposition of zinc and manganese having occurred. Hence, further investigation on the ionic liquid with and without H$_3$BO$_3$ as an addition agent were carried out to further identify its effect.

Figure 4 illustrates scanning electron micrographs of Zn-Mn electrodeposits produced potentiostatically at -1.6 and -1.8 V vs SSCE and at 60°C in electrolytes containing H$_3$BO$_3$. The deposits obtained were generally somewhat rough and powdery, and to some extent were less effective than those obtained under the same conditions but at 40°C. This was most likely due to the elevated temperatures inducing the process to reach the limiting current density and thus resulting in burnt deposits. The morphology obtained generally exhibited a larger size of dendrites when compared to those obtained at 40°C. In addition, there was no copper found on the deposits, indicating that elevated temperatures could produce thicker deposits at the same potential. The manganese contents decreased slightly for both electrolytes as the potential was decreased from -1.6 V to -1.8 V. However, the manganese contents were comparable to those

obtained at 40ºC and ranged approximately from 10-36 wt-%. The smoothest Zn-Mn alloy electrodeposits were produced at -1.5 V vs SSCE where manganese contents ranged from 2-22 wt-% depending on the H_3BO_3 content in the 0.4M $ZnCl_2$ + 0.7M $MnCl_2.H_2O$ electrolyte.
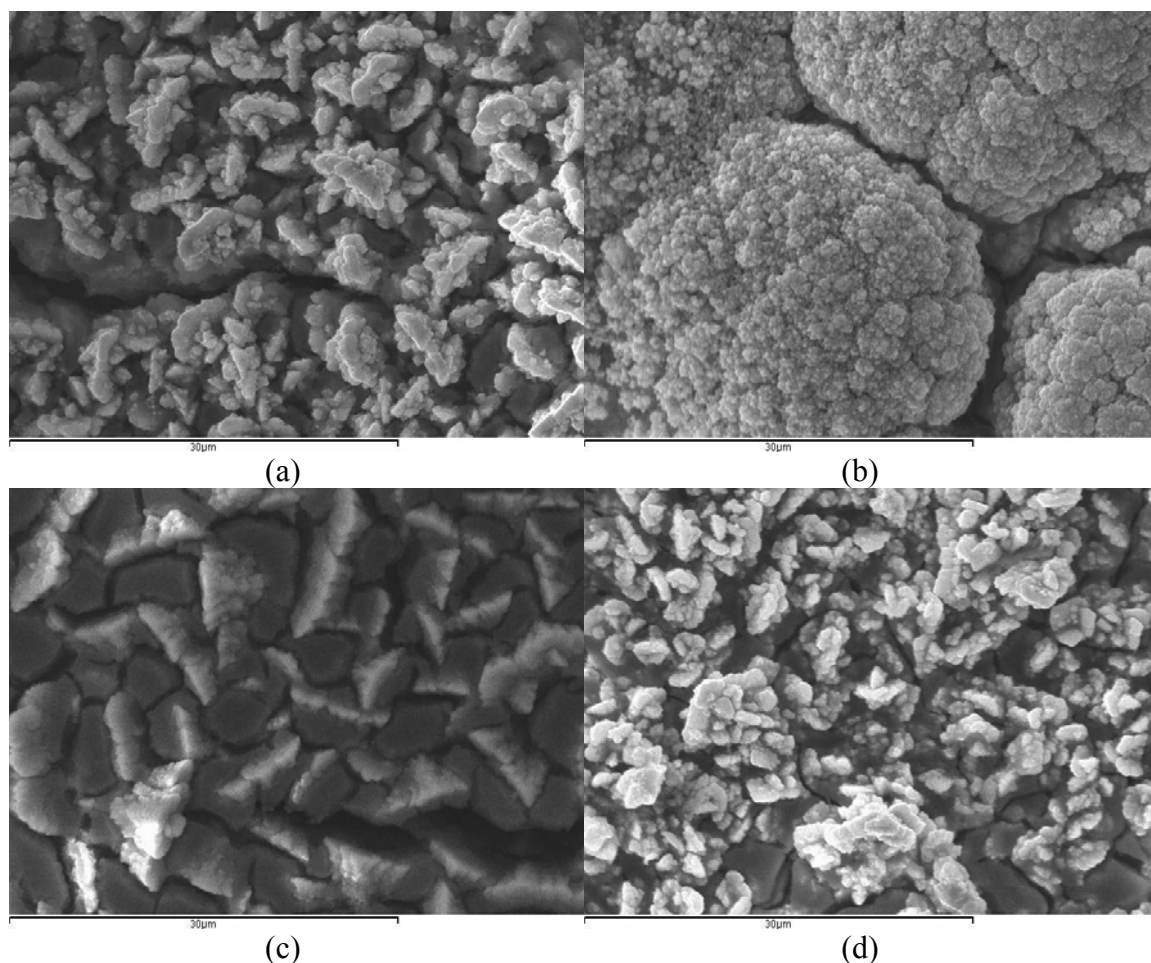

| (a) | (b) |
| (c) | (d) |

Figure 4 Scanning electron micrographs obtained from the electrodeposition of 2:1 urea/ChCl containing 0.4M $ZnCl_2$/0.7M $MnCl_2$ and H_3BO_3 at 60ºC at different potentials for 10min. a) 0.4M H_3BO_3 at -1.6V; b) 0.4M H_3BO_3 at -1.8V; c) 0.8M H_3BO_3 at -1.6V; and d) 0.8M H_3BO_3 at -1.8V.

Table 1 illustrates LPR data for zinc-manganese alloys electrodeposited from 0.4M $ZnCl_2$ + 0.7$MnCl_2.H_2O$ containing 2:1 urea/ChCl ionic liquid electrolytes. Also included in the table are data for similar thickness (8 μm) commercially electrodeposited cadmium coatings. As can be seen the alloys electrodeposited at 0.2 and 0.4 A dm^{-2} exhibited LPR values approaching those for cadmium. Clearly this illustrates an effective level of corrosion resistance in flooded dilute chloride media. It doesn't, however, convey any information concerning galvanic corrosion properties, particularly in the context of aluminium and its alloys used in aerospace applications.

Coating System	Current density (Adm^{-2})	Manganese (wt.%)	Cathode current efficiency (%)	Average polarisation resistance (Ω)
Cadmium to Def. Stan. 03-19/1 *	Commercially applied	N/A	Commercially applied	271
0.4M $ZnCl_2$ 0.7 M $MnCl_2.H_2O$	0.4	40	90	240
0.4M $ZnCl_2$ 0.7 M $MnCl_2.H_2O$	0.2	30	94	200
0.4M $ZnCl_2$ 0.7 M $MnCl_2.H_2O$	0.07	20	97	130

* M. Simmons, '*Zinc based composite coatings as an Alternative to Electrodeposited Cadmium*' Ph.D. Thesis, Loughborough University 2001.

Table 1 Polarisation resistance data, alloy composition and cathode current efficiencies for commercially applied electrodeposited cadmium and Zn-Mn coatings electrodeposited from ionic liquid electrolytes. Coatings nominally 8µm.

Conclusions

The investigations carried out and related in this paper outline preliminary trials to investigate the electrodeposition of zinc-manganese alloys from an ionic liquid non-aqueous electrolyte. It is apparent that the alloy can feasibly be electrodeposited from a urea/choline chloride electrolyte containing zinc chloride and manganese chloride, along with boric acid as an additive for improved deposition. The electrodeposits produced under the optimum conditions produced electrodeposits of up to approximately 40 wt-% and had corrosion resistances in simple LPR tests approaching those for cadmium. More in-depth investigations need to be carried out before zinc-manganese alloys can said to be effectively electrodeposited from this electrolyte system. However, these early trials appear promising.

Acknowledgements

References
1. G.D.Wilcox and D.R.Gabe, Corrosion Science, **35** (1993) 1251.
2. M.Sagiyama, T.Urakawa, T.Adaniya and T.Hara, SAE Technical Paper, **860** (1986) 268.
3. G.Govindarajan, V.Ramakrishnan, S.Ramamurthi, V.Subramanian and N.V.Parthasaradhy, Bulletin of Electrochemistry, **5** (1989) 352.
4. G.D.Wilcox and B.Petersen, Transactions of the Institute of Metal Finishing, **74** (1996) 115.
5. A.P.Abbott, G.Capper, D.L.Davies, R.K.Rasheed and V.Tambyrajah, Transactions of the Institute of Metal Finishing, **79** (2001) 204.
6. P.Y.Chen and C.L.Hussey, Electrochimica Acta, **52** (2007) 1857.

7. R.D.Harrison (edt), 'Book of Data, Nuffield Advanced Science', Longmans Group, London (1972).

8. P.P.Chung, P.A.Cantwell, G.D.Wilcox and G.W.Critchlow, Transactions of the Institute of Metal Finishing, **86** (2008) 211.

9. D.Sylla, C.Rebere, M.Gadouleau, C.Sevall, J.Creus and Ph.Refait, Journal of Applied Electrochemistry, **35** (2005) 1133.

10. C.Savall, C.Rebere, D.Sylla, M.Gadouleau, Ph.Refait and J.Creus, Materials Science and Engineering, **A430** (2006) 165.