

Electrodeposition of Zinc from Low Temperature Molten Salt Electrolyte: Part II - Imidazole – AlCl₃/Zinc Chloride LTMS

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Abstract - Low Temperature Molten salts (LTMS) have a number of applications in metal finishing including electrolytic deposition and anodic processes like polishing and colouring. Imidazolium, pyridinium and choline based cations are normally used in LTMS [1-5]. Zinc deposition was carried out from imidazole - AlCl₃ / ZnCl₂ LTMS electrolyte at temperature < 100° C and the mole ratio was optimized in our research. Surface morphology of electrodeposited coatings was characterized by SEM and XRD. Cathodic and anodic current efficiencies of Imidazole – AlCl₃ / ZnCl₂ LTMS were evaluated. **Keywords:** Low Temperature Molten Salt Electrolyte, Imidazole, Aluminium chloride, Zinc chloride

1. INTRODUCTION

The reactive metals aluminium, magnesium and titanium cannot be deposited from aqueous solutions, since its electrode position occurs at electrode potentials at more negative values of – 1.6 V vs. NHE. Over the last decades, development in ionic liquids resulted in another potential approach for aluminium extraction and refining that offers potential advantages such as low energy consumption, low pollutant emission and low operating cost. The AlCl₃ – imidazolium ionic liquids are liquid at room temperature over a large composition range and possess relatively high electrical conductivity and wide electrochemical potential window. These favourable properties render AlCl₃–imidazolium ionic liquids as potential electrolytes for the plating of aluminium for decorative and functional applications. [6-10]

Zinc can be electrodeposited from molten salt electrolyte of imidazole with supporting salt of Zinc chloride. Zinc chloride forms complex with imidazole as imidazolium ion where nitrogen is delocalized with neighbouring ion in the ring to form Low temperature molten salt electrolyte and zinc was deposited from its Imidazolium Zinc complex as in the previous study [11]. In the present study aluminium chloride act as supporting salt in imidazole molten salt electrolyte which reduces the crystallization temperature of imidazole to 64°C. Addition of zinc chloride to this mixture reduces the crystallization temperature to 57°C. Zinc was deposited from imidazole with aluminium chloride low temperature molten salt electrolyte in the presence of zinc chloride. Minimum temperature for crystallization, cathode and anode current efficiencies and surface characterization of the deposit were analysed.

2.0 METHODS AND MATERIALS

2.1 Electrode preparation

Copper strip was used as cathode. 1cm² copper was exposed for electrodeposition. Electrolytic grade zinc was used as anodes. 0.5 cm×6cm zinc was cut and unexposed area was masked and required anodic area was exposed. Necessary pre-treatment's for both cathode and anode comprise of solvent cleaning, chemical polishing followed by etching and rinsing.

2.2 Electrolyte preparation

All the chemicals used were LR grade only. Known amount of imidazole was weighed out and heated to melt in a hot water bath and allowed to cool. The crystallization temperature (80°C) of imidazole was noted. Known quantity of supporting salt i.e.; aluminium chloride was added and heated until to get clear liquid. Crystallization temperatures of aluminium chloride with imidazole and with zinc chloride in the above mixture were noted. Crystallization temperature of aluminium chloride with imidazole was 64°C and crystallisation temperature of addition of zinc chloride in the above mixture was 57°C

The Addition of salts in single or combination in a particular proportion mostly lowers the eutectic temperature. The minimum temperatures required for the mixture to be in liquid form at different mole ratios of imidazole to AlCl₃ alone and imidazole to AlCl₃ with ZnCl₂ were noted.

2.3 Current efficiency study

Current efficiency is the ratio of the current used for the deposition or dissolution metal to the applied current. Known weight (W1) of pre-treated copper strip was subjected to deposition at specific current (I in ampere) and time (T in seconds) and deposited copper was weighed (W2). Cathode current efficiency (CCE) was calculated from the formula

$$\text{CCE} = \frac{\text{weight of the deposit (gm)}}{\text{theoretical weight (gm)}} \times 100$$

$$\text{Weight of the deposit} = W_2 - W_1$$

$$\text{Theoretical weight} = I \times T \times ECE$$

$$ECE \text{ (electrochemical equivalent of the deposited metal)}$$

Variable Parameters such as Current density, temperature and bath concentration have high impact on CCE.

2.4 Surface characterization

Observing the quality of deposits 3 A.dm⁻² was selected for surface characterization. Surface characterization of the coating was carried out using Scanning Electron Microscopy (SEM, Model S3000H, Hitachi, Japan), Energy dispersive X-ray micro analysis (EDAX) (Model S3000H, Hitachi, Japan) and XRD (Philips X'pert X-ray diffractometer, Netherlands) and the results were analysed.

3.0 RESULTS AND DISCUSSION

3.1 Crystallization temperature

The mole ratio of Imidazole to aluminium chloride was varied between 1:0.02 and 1:0.05 and found out the minimum temperature and mole ratio required for the mixture to be as clear liquid. Beyond the ratio of 1:0.04 the liquid become more viscous and turbid. The mole ratio of 1:0.04 shows a lowest temperature of 64°C than other ratios. For further studies 1:0.04 was used and electrolysis was carried out using Platinum anode and copper cathode. Addition of zinc chloride with aluminium chloride shows further reduction of crystallization temperature to 57°C at the mole ratio of imidazole to aluminium chloride and zinc chloride is 1 : 0.05: 0.04. The comparative performance of different mole ratio and crystallization temperature of imidazole with AlCl₃ and imidazole with ZnCl₂ alone as well as imidazole to aluminium chloride and zinc chloride is shown in **Table I**.

Table I: Mole ratio of Imidazole/ AlCl₃/ ZnCl₂ & imidazole/ ZnCl₂ on crystallization temperature

Electrolyte	Mole ratio	Crystallization temperature °C
Imidazole : AlCl ₃	1 : 0.04	64
Imidazole : ZnCl ₂	1 : 0.12	40
Imidazole : AlCl ₃ : ZnCl ₂	1 : 0.05: 0.04	57

3.2 Cathode current efficiency analysis

CCE was separately calculated for imidazole with ZnCl₂ LTMS electrolyte and imidazole with AlCl₃ and ZnCl₂ LTMS electrolyte. Though both systems show low CCE, the later pertaining aluminium chloride electrolyte shows higher CCE than the former without aluminium chloride electrolyte.

3.2.1 Effect of temperature on cathode current efficiency

Cathode Current Efficiencies of imidazole with zinc chloride, imidazole with AlCl₃ and ZnCl₂ at different temperatures are shown in **figure 1**. Figure 1 shows that in both systems there is a reduction in CCE up to 60°C and 70°C and there is an increase in CCE up to 80°C for imidazole - zinc chloride and 90°C for imidazole with AlCl₃ and zinc chloride. Imidazole with AlCl₃ and zinc chloride LTMS has higher cathode current efficiency than imidazole with Zinc Chloride LTMS. This is mainly due to the presence of partial free zinc ions (Zn⁺⁺) in the electrolyte favours the higher rate of deposition which lead to higher CCE than the imidazole/zinc chloride LTMS. When heating the mixtures of imidazole and AlCl₃ to melt, it forms aluminium imidazolium type of ion. The probable delocalization of imidazolium aluminium chloride type of ion is given in **figure 2**.

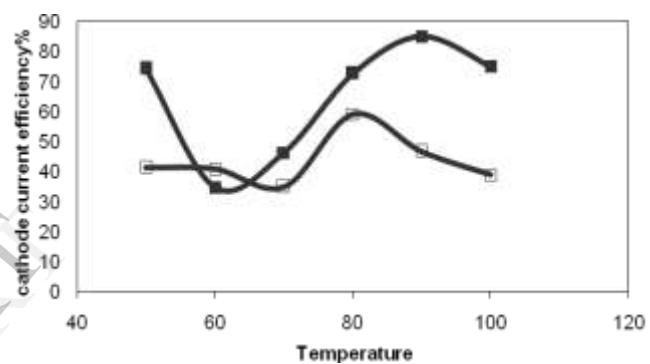


Figure.1 Effect of temperature on CCE

◆ -Imidazole + Aluminium chloride + Zinc chloride □ – Imidazole + Zinc chloride

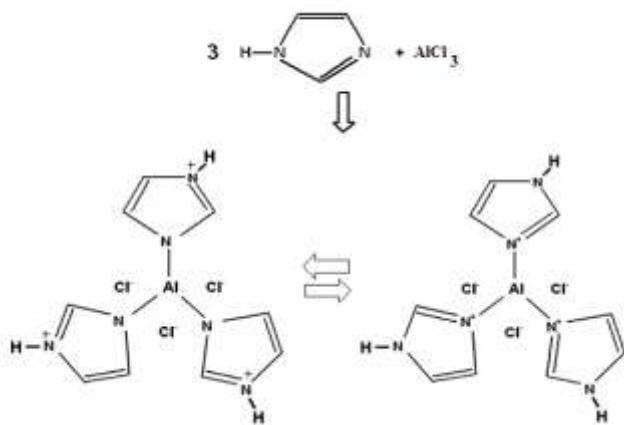


Figure. 2 Delocalisation of imidazolium - aluminium chloride ion

3.2.2 Effect of current density on cathode current efficiency

Cathode Current Efficiencies of imidazole with zinc chloride LTMS, imidazole with AlCl₃ and ZnCl₂ LTMS at different current densities are shown in **figure 3**. Figure 3

shows that CCE increases with CD up to $10 \text{ A} \cdot \text{dm}^{-2}$ in the imidazole – zinc chloride system and after that there is a reduction in trend. Whereas, in the imidazole - AlCl_3 and ZnCl_2 LTMS above $10 \text{ A} \cdot \text{dm}^{-2}$ it shows an almost constant value of CCE. In the present system the zinc content in the electrolyte is insufficient to cope up with the available electrons due to the higher CDs. For the mole ratio of imidazole to AlCl_3 and ZnCl_2 1 : 0.05: 0.04 the maximum operating CD is $10 \text{ A} \cdot \text{dm}^{-2}$

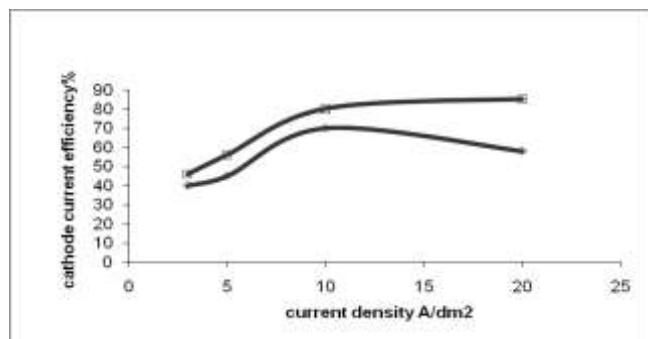


Fig.3 Effect of Current density on Cathde current efficiency

□ – Imidazole +Aluminium chloride + Zinc chloride ◇ – Imidazole+Zinc chloride LTMS

4. SEM

Surface morphological studies of electrodeposited zinc coatings from imidazole with AlCl_3 and zinc chloride LTMS were carried out using SEM. SEM of Zinc deposits from acid bath is shown in **figure 4a**. Imidazole with zinc chloride alone is shown in **figure 4b**, imidazole with AlCl_3 and zinc chloride is shown in **figure 4c** with the magnification of X2000. SEM of acid bath shows interlinked chains like structures whereas imidazole with zinc chloride bath shows uniform microcrystalline structure just like pulse zinc electrodeposition of alkaline non cyanide. Figure 4c implies the presence of aluminium as impurity as different clusters of cauliflower like structure and the rate of deposition is also higher as compared to zinc chloride with imidazole. In the previous study the bath containing zinc chloride alone, zinc forms zinc imidazolium ion complex and hence higher energy is needed to dissociate zinc ion from its complex whereas in the present study supporting salt of aluminium chloride forms imidazolium aluminium complex and the inclusion of aluminium shows

cauliflower like structure which is similar to zinc deposits obtained from zinc sulphates in the presence of antimony [12-18].

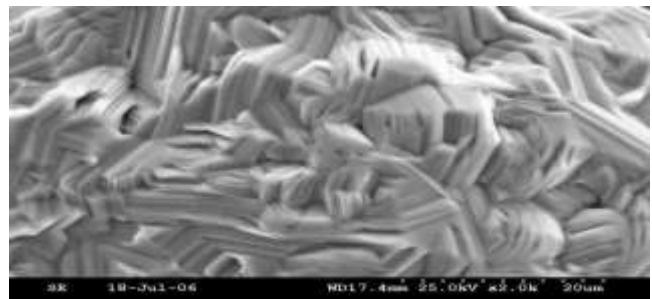


Figure 4a. SEM of acid chloride zinc

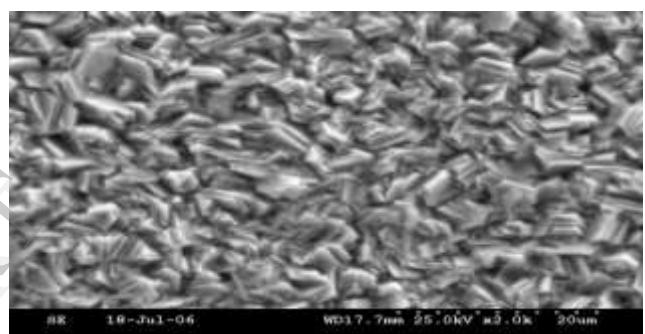


Figure 4b. SEM of zinc from imidazole+zinc chloride

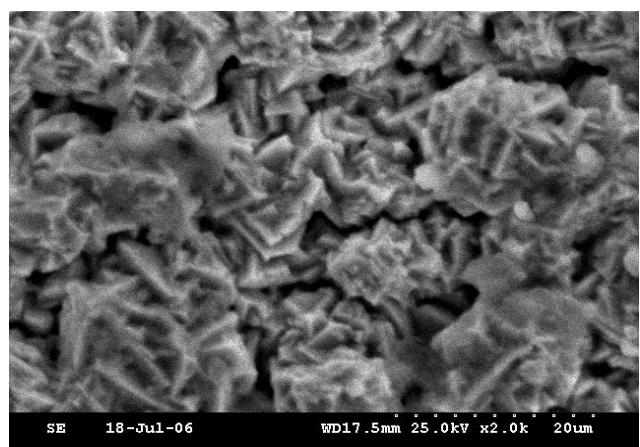
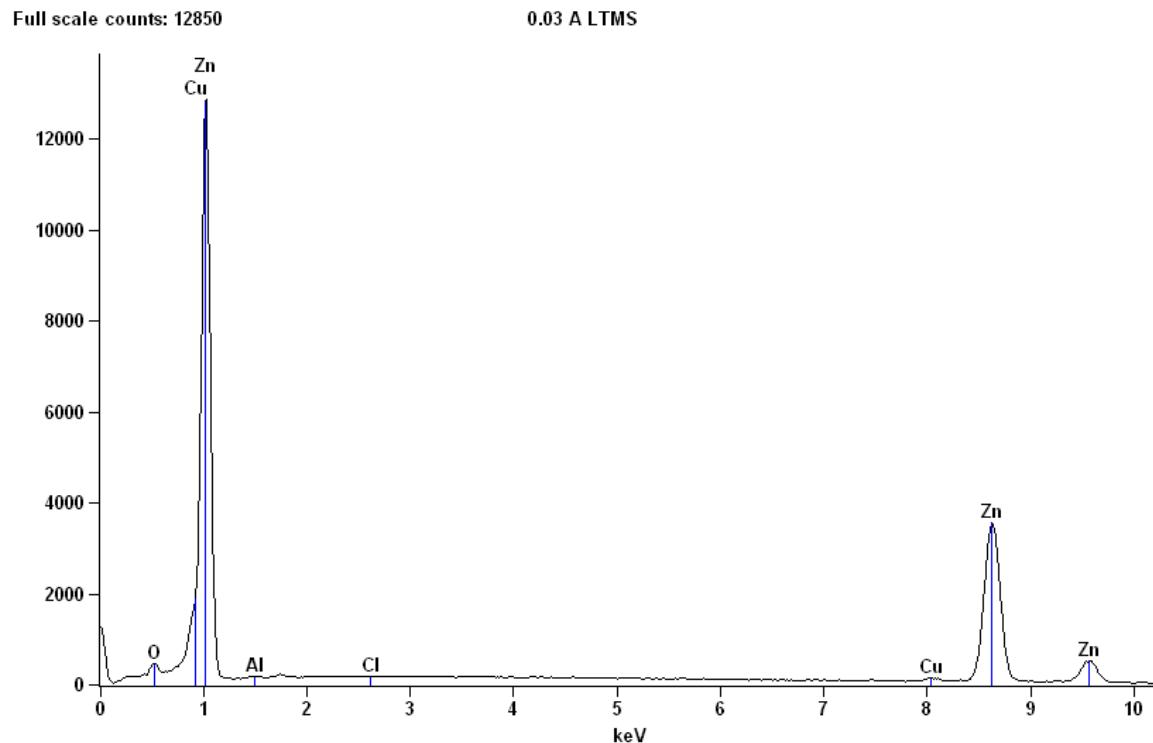


Figure 4c. SEM of zinc from imidazole +zinc chloride and aluminium chloride



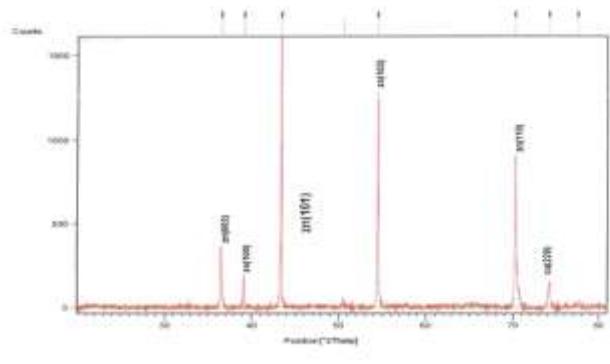
Element	Quantitative Results 0.03 A LTMS		
	Net Counts	Weight %	Atom %
O	1553	2.56	9.60
Al	941	0.67	1.50
Cl	406	0.16	0.26
Cu	1271	1.33	1.25
Zn	70150	95.28	87.39
Total		100.00	100.00

Figure 5: EDAX analysis of deposited Zinc from imidazole+Alcl₃ + Zinc chloride

6. XRD

XRD analysis revealed that zinc coatings obtained in the presence of AlCl₃ shows crystal lattice of zinc plane (101) with highest intensity predominant peak as reported earlier [19] and noticeable planes of (002), (100), (102) and (110) were observed in **Figure 6**. The addition of AlCl₃ to the imidazole enhances significant changes in the morphology and crystallographic orientation of the Zn coatings from LTMS. The texture component of the basal plane (002) is higher and it is observed by the high intensity peak than imidazole with zinc chloride LTMS. This is due to the deposits generated at some distance from the substrate and minimising the free energy which favours the grain growth in faster rate with non epitaxial growth which causing denser deposits. Substrate of copper (220) plane peak is minimized in this LTMS bath since the development of crystal in higher thickness was observed [20-24]. Partial

amount of zinc in free ionic was deposited without dissociation from its complex, since AlCl₃ mainly forms complex with imidazole and the rate of deposition is higher than imidazole with zinc chloride LTMS.



Pattern List

Pos. [$^{\circ}$ 2Th]	Height [cts]	FWHM [$^{\circ}$ 2Th]	d-spacing [Å]	Rel. Int. [%]
36.3965	376.08	0.1428	2.46648	23.31
38.0579	192.03	0.2040	2.30433	11.90
43.2831	1613.38	0.1020	2.08857	100.00
50.4780	51.68	0.1832	1.80854	3.20
54.4076	1298.34	0.1428	1.68498	80.47
70.1042	803.05	0.1632	1.34023	49.77
74.1406	165.71	0.2856	1.27788	10.27
77.4993	12.16	0.9792	1.23067	0.75

Figure 6 : XRD of zinc from imidazole + AlCl₃ + Zinc chloride in the mole ratio of (1:(0.04:0.05)

The adsorption of aluminium activates important changes in the electro reduction mechanism of Zn (II) ions, and also in the morphology and crystallographic structure of the Zn coatings from LTMS electrolyte.

A single reduction process of Zn (II) process, yielded massive Zn deposition in dense as agglomerated clustered crystals were observed.

7. CONCLUSION

Inclusion of aluminium chloride in imidazole as supporting salt, acts as additive system for semi bright deposits. It forms complex with imidazole into imidazolium ion and induces zinc into free ions and made the zinc to deposit easily. Presence of aluminium indicates its non epitaxial growth of cauliflower structures. Crystallographic orientation shows less homogeneity than imidazole and zinc chloride LTMS. Pollution free, low cost, simple route without any glove box or inert atmosphere and bright deposits with higher cathode current efficiency were identified.

REFERENCES

- K. R. Seddon, J. Chem. Tech. Biotech. 68 (1997) 351.
- M. Freemantle, Chem. Eng. New. 76 (1998) 32.
- T. Welton, Chem. Rev. 99 (1999) 2071.
- Martyn J. Earle, Kenneth R. Seddon , Pure Appl. Chem. 72 (2000) 1391.
- C. A. Nieto de Castro, F. J. V. Santos, chem. Today, 25 (2007) 20.
- B. Wu, R.G. Reddy, R.D. Rogers, U.S. Pat. Appl. Publ. (2002) 15.
- R. Rogers and K. Seddon (Ed.), Ionic Liquids as Green Solvents Progress and Prospects, American Chemical Society, Boston (2003) p. 41
- S. Zein El Abedin, M. Polleth, S. A. Meiss, J. Janek and F. Endres, Green chemistry, 9 (2007) 549.
- M. C. Buzzo, R. G. Evans ,R. G. Compton, Chem.Phys. Chem, 5 (2004) 110.
- I Ivanov Hydrometallurgy, 72 (2004) 73.
- Shanmugasigamani Srinivasan and M.Selvam, "Electrodeposition of zinc from Low Temperature molten salt electrolyte: Part I:Imidazole and zinc chloride Electrolyte " – communicated to Appl. Surf. Sci.
- D. L. Wang, Y. Q. Wu, X. Y. Zhong, W. Q. Zhang, M. C. Li and J. N. Shen, Russ. J. Electrochem. 45 (2009) 291.
- D.J. Mackinnon J.M. Brannen, R.M. Morrison, J Appl. Electrochem., 18 (1988) 252.
- Ivan S.Ivanov, Yavor S.Stefanov, Stefan S.Rashkov, Bulg.Chem.Commun. 28 (1995) 600.
- A.Stankevičiute, K Leinartas, G Bikulcius, D,Virbalyte Sudavicius, A E Juzeliunas, J Appl. Electrochem., 28 (1998) 89.
- M.S..Chandrasekar, Shanmugasigamani Srinivasan, Malathy Pushpvanum, Mater. Chem. Phys. 115 (2009) 603.
- I.Ivanov and Y. Stefanov,, Hydrometallurgy 64 (2002) 111.
- M.S.Chandrasekar, Shanmugasigamani Srinivasan, Malathy Pushpvanum, J Mater. Sci., 45 (2010) 1160.
- L.E. Morón, Y. Meas, R. Ortega-Borges, J.J. Perez-Bueno, H. Ruiz, G. Trejo, Int. J. Electrochem. Sci. 4 (2009) 1735.
- Kh.M.S. Youssef, C.C Koch, P.S. Fedkiw, J. Electrochim. Soc. 151 (2004) C103.
- A. Gomes, M.I. da Silva Pereira, Electrochim. Acta 51 (2006) 1342.
- Mou Cheng Li , Li Li Jiang, Wen Qi Zhang ,Yu Hai Qian , Su Zhen Luo , Jia Nian Shen, J. Solid State Electrochem. 11 (2007) 549.
- J. H.Yang, J. H. Zheng, H.j. Zhai, L L Yang, Cryst. Res. Tech. 44 (2009) 87.
- Szu-Jung Pan,Wen-Ta Tsai,I-Wen Sun, Effects of Electrode position Charge and Heat Treatment on Material Characteristics Al-Zn Coatings on a Magnesium Alloy Formed in AlCl₃-EMIC-ZnCl₂ Ionic Liquids (National Cheng Kung University), presented at 3rd asian conference on molten salt and ionic liquids on 1-3-2011 , P.R. China