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Electrodeposition of Zinc From Low Temperature Molten Salt Electrolyte: Part I-Imidazole And Zinc-Chloride Electrolyte

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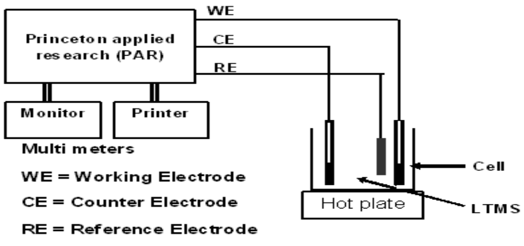
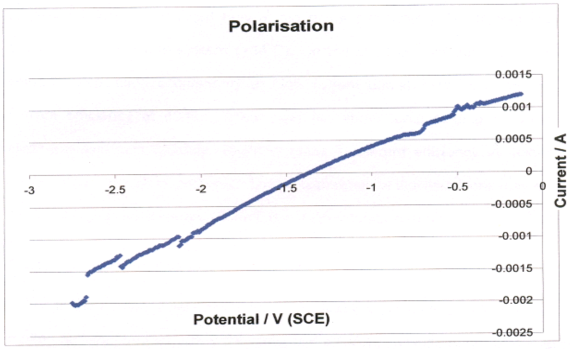
Abstract: Our R & D work was focused on the electro deposition of Zinc from imidazole as low temperature molten salt (LTMS) electrolyte with zinc chloride as a supporting salt at <100° C., without required controls from the previous existing non aqueous baths as well additive free system for the zinc deposition. Surface morphological studies and crystallographic orientation results were evaluated.

Graphical abstract



(imidazole : $ZnCl_2$ 1 : 0.31 at 40^{0}C)



Keywords: Low temperature Molten salt (LTMS), Imidazole, Zinc electrodeposition, Surface Characterization, Cathode current efficiency, Anode current efficiency.

1.0 Introduction

Electroplating of metals could be done either from aqueous or from non-aqueous solution. Non-aqueous baths are two types, based on organic solvents and molten salt electrolytes. Selective metal salts could be added to organic solvents along with supporting salts and electrolysed in specified atmosphere. Organic solvents require stringent control systems like inert atmosphere. Where as, molten salt electrolytes are fused salts i.e., the metal salts which are heated to melt and kept at that temperature to keep the formed melt as liquid. Addition of other supporting salts facilitates to lower the melting temperature at its eutectic points. Under this molten state, electrolysis could be carried out to deposit metals at the cathode. Conventional molten salt electrolytes operate normally at higher temperatures >350°C [1-10]. The reactive metals such as aluminium, magnesium and titanium that cannot be deposited from aqueous solutions, since its electrodeposition occurs at electrode potentials at more negative values. Conventional Hall – Heroult electrolysis process for the aluminium production usually operates at very high temperature (950 - 1000°C) and shows inevitable high energy consumption, complicated operation and emission of pollutant. Over the last decades, development in ionic liquids resulted is another potential approach for aluminium extraction and refining that offers peculiar advantages such as low energy consumption, low pollutant emission and low operating cost. Normally molten salt electrolytes such as imidazole and pyridinium groups are operated at temperature <100°C [10]. However, proper selection of suitable supporting salt can considerably reduce the temperature to low level. 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 $AlCl_3$ – imidazolium ionic liquids as potential electrolytes for the plating of aluminium for decorative and functional applications [11-19].

Electrodeposited Zinc coatings have been widespread use as sacrificial protection for steel substrates [20]. Zinc can be electrodeposited from acid and alkaline bath. The compositions of the acid and alkaline electrolytes are given in the table 1. Acid sulphate and chloride baths are reported earlier [21-5]. These baths have been widely used for coating sheet, wire and pipes where good throwing power is not required and where higher current densities can be used to produce coatings for industrial and functional applications. Alkaline baths are two types i.e., Cyanide and non cyanide. Alkaline cyanide baths are hazardous to health and disposal to effluent was complicated as well as costlier. Hence alkaline non cyanide zinc was formulated as an effective suitable electrolyte to avoid the inevitable effluent treatment procedures as well to meet the cost factor. But alkaline non cyanide baths lead to hydrogen embrittlement due to hydrogen evolution. Zinc could not be plated satisfactorily without addition agents in aqueous solvents [26-9]. In molten salt electrolysis good deposits can be obtained without any addition agents even at low temperature <100º C.

The imidazolium or pyridinuim types of ions are the starting point for the development of low temperature molten salt for the electrodeposition of metals. Imidazole is a pale white salt of having molecular formula of $C_3H_4N_2$, molecular weight of 68, melting point of 88-90º C and boiling point of 255-258º C. The structure of imidazole used in the present study is given in fig1. It is a five numbered organic compound containing two nitrogen atoms. Whenever it is converted into imidazolium ions one of nitrogen consists of positive charge is delocalized with the neighboring nitrogen in the ring which is the basic characteristic requirement to form liquid at low temperature (<100º C).

Table 1. composition of acid zinc bath and alkaline zinc bath

Chloride bath **(g.l^{-1})**	**Fluoborate bath** **(g.l^{-1})**	**Cyanide bath** **(g.l^{-1})**	**Non cyanide bath** **(g.l^{-1})**
$ZnCl_2$ 100 $NaCl_2$ 150 pH 3.0 - 4.0 C D 5 A.dm^{-2} Temp 20 – 60º C C E 96 – 100%	$Zn(BF_4)_2$ 300 NH_4BF_4 35 NH_4Cl 30 pH 3.5 – 4.0 CD 2.5– 4.0 A.dm^{-2} Temp Room C E 96 – 100%	Zinc cyanide 60 – 90 NaCN 23 – 37.5 NaOH 53 pH 12 – 13 CD 1 – 11 A.dm^{-2} Temp: Room C E 100%	Zn oxide 9 – 12 NaOH 90 – 120 pH 12 – 13 C D 2 A.dm^{-2} Temp: Room C E 70%

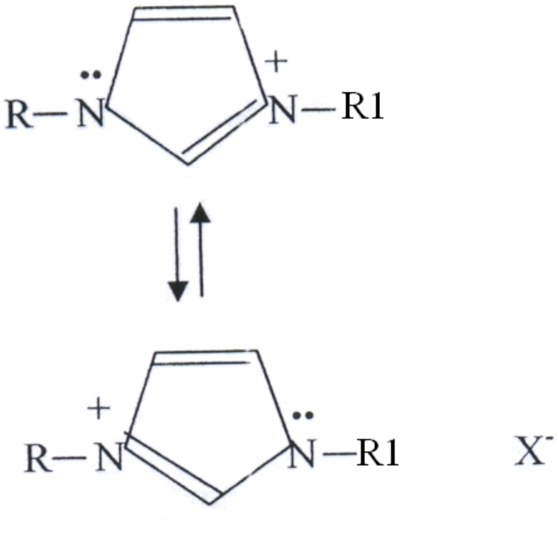


Figure 1: The structure of imidazolium ions

Zinc coatings were deposited from imidazolium - zinc chloride eutectic mixtures using imidazole at the temperature of slightly higher than crystallization temperature and various parameters such as current density, current efficiency were optimized. Surface Characterisation studies such as SEM and XRD of the deposited zinc coatings were carried out.

2.0 Methods and materials

2.1 Electrode preparation

Copper of 10 mm × 60 mm and plating grade zinc of 5mm × 60 mm were used as cathode and anode respectively for electrodeposition. This copper sheet was subjected to mechanical polishing, degreasing using trichloroethylene, cathodic cleaning in an alkaline solution, washed, and neutralized with 5% sulfuric acid. After cleaning it was chemically polished in 1:1:1 phosphoric, nitric and acetic acid for 2 minutes, washed, rinsed with demineralised water, dried and weighed. Except the 1 Cm^2 other areas are masked using with adhesive tape. Zinc anode was subjected to scrub cleaning, acid treatment in 1% nitric acid washed, rinsed with demineralised water, dried and weighed.

2.2 Electrolyte preparation

All chemicals used were laboratory reagents only. Known amount of Imidazole was weighed and heated in a hot water bath to melt and melting temperature (~90ºC) was noted and then supporting salt i.e.; Zinc chloride was added in a particular mole ratio with imidazole and heated to get clear homogenous liquid. This liquid was allowed to cool slowly and noted its minimum temperature to be in liquid form. Zinc chloride facilitate the formation of imidazolium chloride type of ion and thus formed imidazolium chloride prevents the formation of crystalline even at low temperature, So, Zinc was deposited by using this molten salt electrolyte in the temperature range of 40 -100ºC.

2.3 Current efficiency studies

Current efficiency is the ratio of the actual weight of the deposit to the theoretical weight. Actual weight could be found out by either weight gain at the cathode or weight loss at the anode. Anode and cathode current efficiencies are calculated from the weight loss or weight gain of the anode and cathode plates respectively and the charge passed for the deposition. In the present system total charge was found out using a coulometer connected in series to the circuit. Theoretical weight was calculated from the electrochemical equivalent weight and the charge passed

3.0 Results and discussion

3.1 Effect of mole ratio of Imidazole/ Zinc chloride on crystallization temperature

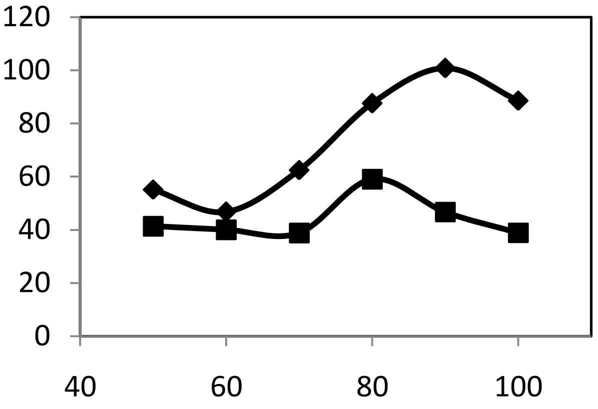
The mole ratio of Imidazole to Zinc chloride was varied between 1:0.08 and 1:0.12 and found out the minimum temperature required to keep the mixture in clear liquid form. Mole ratio of Imidazole/ Zinc chloride on crystallization temperature is given in Table 2. Beyond the ratio of 1:0.12 the liquid become more viscous and turbid. The mole ratio of 1:0.12 shows a lowest temperature of 40^0C than other ratios. For further studies 1:0.12 was used.

Table II: Mole ratio of Imidazole/ Zinc chloride on crystallization temperature

Imidazole Mole	Zinc chloride Mole	Temperature (º C)
1	0.08	60
1	0.12	40
1	0.33	57

3.2 Effect of temperature on anode and cathode current efficiencies

Temperature of the imidazole/zinc chloride (1:0.12 mole ratio) liquid was varied between 50^0C and 100^0C by keeping a constant current density of 5 A.dm^{-2}. Effect of temperature on anode and cathode current efficiency is given in figure 2. It shows that increasing liquid temperature increases both anode current efficiency (ACE) and cathode current efficiency (CCE) and reaches a maximum of 100% at 90^0C and 60% at 80^0C respectively. However, the CCE is <100% only. Further studies were carried out at 80^0C.



X – AXIS Current efficiency in (%)

Y – AXIS Temperature in (^{0}C)

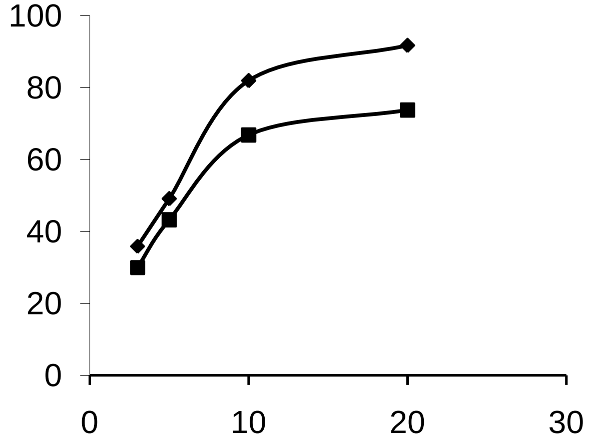
Figure 2 Effect of temperature on anodic and cathodic current efficiency (at 5 A.dm^{-2})

Anodic ◆—◆

Cathodic ■—■

3.3 Effect of current density on anode and cathode current efficiencies

Current density was varied between 3 and 20 A.dm^{-2} in the imidazole/zinc chloride liquid (1:0.12 mole ratio) at 80^0C. Effect of current density on anode and cathode current efficiency is given in figure 3. It shows that ACE is always higher than the CCE. ACE reaches a maximum of ~85 % at 20 A.dm^{-2} whereas CCE is about 75% only for the above said current density. Lower CCE (<100%) is mainly due to the dissociation of moisture present in the liquid since the deposition was carried out in an open atmosphere.



X axis -Current Efficiency in (%)

Y axis - Current Density in (A.dm^{-2})

Figure 3 Effect of current density on anodic and cathodic current efficiency (at 80^{0}C)

Anodic ◆—◆

These effects of current density and temperature clearly indicates that when combining imidazole and zinc chloride and heated to form liquid there is a chance of formation of zinc imidazolium chloride of the following probable structure shown in figure 4.

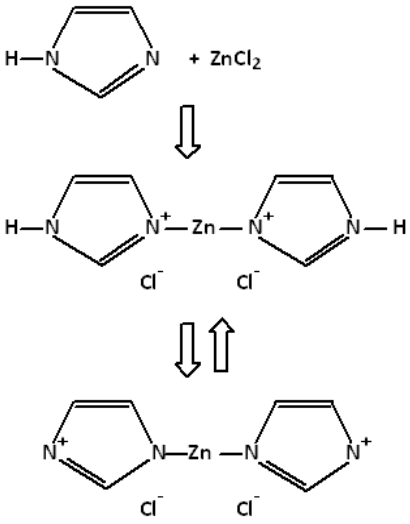


Figure 4 : Zinc imidazolium chloride

In this type of zinc imidazolium chloride there is no free zinc ions available to deposit easily as do with acid zinc baths. To drive the zinc ions to cathode and to reduce it as zinc metal it requires high energy similar to the cyanide or other complex baths. Further, the reduction in CCE may also due to the possible reduction of imidazolium ion of the zinc imidazolium chloride where the nitrogen atoms carry a positive charge. The positive charge carrier of the zinc imidazolium chloride attracted towards cathode where it gets reduced and release zinc ion. Thus released zinc ion gets reduced to metal zinc at the cathode. These are the reasons for the low CCE of zinc deposition from the LTMS electrolyte based on imidazole.

3.4 Polarization study: Polarization study of imidazole/zinc chloride system predicts that zinc deposition was started at about -1.8V vs Ag/Agcl. Polarisation was represented in graphical abstract. Zinc deposition occurs with simultaneous evolution of gas. Therefore imidazole/ zinc chloride molten salt at temperatures for 40^{0}C- 90^{0}C produces low cathode current efficiency. Zinc deposition occurs only at high current density with low cathode current efficiency at 40^{0}C.

3.5 SEM studies

Surface Characterization studies such as SEM (Model 3000H, Hitachi, Japan) of the deposited zinc coatings was carried out. For comparison purposes SEM of zinc deposits produced from alkaline and acid baths are given in figures 5a and 5b with the magnification of X1000. SEM of LTMS electrolytes shows microcrystalline structure as in fig: 5 c) even at higher magnification as compared to other two figs of 5 a & b i.e.; alkaline bath, acid bath at lower magnification. SEM structure at lower magnification of acid and alkaline bath in aqueous bath is more or less equivalent to Low temperature molten salt electrolyte at higher magnification. This shows the fine grained nature of deposits of zinc from LTMS (fig. 5c) on copper surface and it indicates its higher corrosion resistance of zinc from LTMS than obtained from any aqueous bath.

It shows Imidazole/zinc chloride system produces zinc deposits with smaller grain sizes than zinc deposits produced from acid chloride aqueous bath. Electrodeposited zinc from acid as well as alkaline bath without additives does not produce bright finish deposits where as LTMS bath without any addition agent it produces semi bright deposits.

Surface morphology is also comparable to pulsed electrodeposits of zinc. Due to 2nd nucleation growth it possesses uniform compact structure as compared to above alkaline and acid bath.

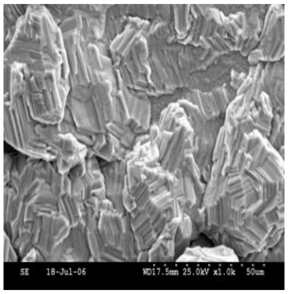


FIG: 5a)Zinc deposits from alkaline bath (J appl electrochem 36 (2006) 315-321) FIG:5 b) Zinc deposits from acid bath

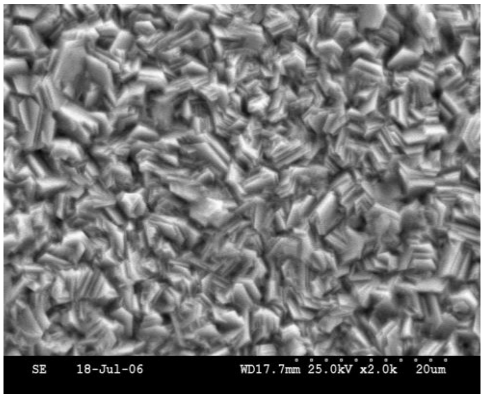
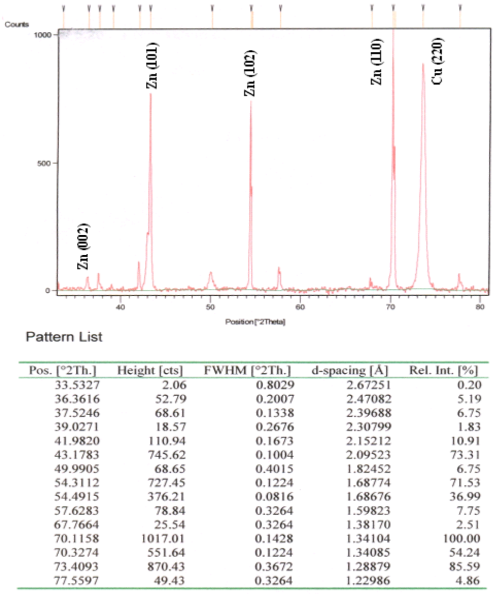


FIG: 5 c) Zinc deposits from low temp molten salt

3.6 XRD ANALYSIS

XRD (PANALITICAL ,X"PERT Model) of the deposited zinc coatings was carried out. The XRD pattern of zinc deposit produced from LTMS electrolyte is shown in Fig. 6. It shows the occurrence of multi higher and lower peaks at different wave length implicit its multifaceted structure. The presence of basal plane (002) indicates its compactness [30] as well hcp crystal structure. From the basal plane pyramidal growth of parallel planes (101,102) with higher intensity peak was observed. Preferentially oriented crystal growth plane of (110) with maximum highest intensity peak was investigated which explains the reaction associated with low rate of zinc ions discharge and hence higher potential is needed to dissociate the metal ions in turn lower cathodic efficiency was observed.



Pattern List

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
33.5327	2.06	0.8029	2.67251	0.20
36.3616	52.79	0.2007	2.47082	5.19
37.5246	68.61	0.1338	2.39688	6.75
39.0271	18.57	0.2676	2.30799	1.83
41.9820	110.94	0.1673	2.15212	10.91
43.1783	745.62	0.1004	2.09523	73.31
49.9905	68.65	0.4015	1.82452	6.75
54.3112	727.45	0.1224	1.68774	71.53
54.4915	376.21	0.0816	1.68676	36.99
57.6283	78.84	0.3264	1.59823	7.75
67.7664	25.54	0.3264	1.38170	2.51
70.1158	1017.01	0.1428	1.34104	100.00
70.3274	551.64	0.1224	1.34085	54.24
73.4093	870.43	0.3672	1.28879	85.59
77.5597	49.43	0.3264	1.22986	4.86

Figure 6 : XRD data of Zinc deposited from LTMS electrolyte

From the XRD data the average crystalline size was calculated using the following Debye Scherer equation.

$$\text{Crystalline size} = \frac{0.9 \times \lambda \times 180}{\text{Fwhm} \times 3.14 \times \cos\theta}$$

The grain size was calculated from XRD pattern shows the average grain size of 40-70 nanometers and it indicates its nano crystallinity.

4.0 Conclusion:

Electrodeposited zinc coatings from alkaline and acid baths (aqueous) without addition agents produces grey deposits only whereas electrodeposits produced from low temperature molten salt produces semi bright deposits without any addition agent. If one required close values of ACE and CCE electrolyte temperature of 60^0C is preferable one to closely maintain the mole ratio of imidazole to zinc. SEM structure correlation shows uniform compact structure in low temperature molten salts than alkaline and acid electrolyte. Textural analysis of XRD confirmed its compactness. Of all, LTMS zinc deposition is eco- friendly and processing is easier with flexible temperature limits and the process is simple and low cost process without glove-box. No formation of chelating complexes during waste disposal due to non cyanide usage.

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