



ELECTROPLATING IN NOVEL DEEP EUTECTIC SOLVENT ELECTROLYTES



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Abstract: The electrolytic depositions of zinc (Zn), nickel (Ni) and Zn/Ni alloy on copper substrates from two novel deep eutectic solvents (Reline and Ethaline) have been carried out. Using cyclic voltammetry, the electrochemical stripping response of the metal ions in the eutectic solvents at different temperatures and scan rates were recorded. In both solvents, the voltammograms results revealed that the deposition of Zn and Ni were both temperature and scan rate dependent. It was observed that the onset of voltage deposition and dissolution of the two metals were different in the solvents. However, more deposition occurred in ethaline deep eutectic solvent than reline due to high viscosity of the latter. The morphological analysis of the metal deposit using scanning electron microscopy (SEM) revealed bright images of Ni metal coating on the substrate compared to Zn coated surfaces. SEM micrograph of metal deposit in the presence of additives was found to produce cracks on the surface of the substrates.

Keywords: Alloy, deep eutectic solvent, electrodeposition, ionic liquid

Introduction

Electrodeposition also referred to as electroplating is an economic technology that is used in protecting and enhancing the functionality of metallic materials. The process produces a thick, uniform, and adherent coating, commonly of metal or mixed metals (alloy), upon a surface by the act of passing an electric current (Kulkarni *et al.* 2013). Metal to be plated is made the cathode of the electrochemical cell through which a direct electric current is passed in an aqueous solution containing the required metal in an oxidized form, either as an aquated cation or as a complex ion. Generally, materials that have been electroplated have enhanced surface properties in terms of their appearance, resistance to corrosion, hardness and engineering properties. Use of aqueous solution in plating experience some major setback principally due to the narrow potential windows so metals with large negative reduction potentials, for instance Cr and Zn, are deposited with poor current efficiencies and suffer from hydrogen embrittlement (Abbott and McKenzie, 2006). Furthermore, due to health and environmental issues arising from some plating bath especially the use of chromic acid as electrolytes have necessitated search for a less toxic solvent for metals deposition. One of the options that have received widespread attention is ionic liquids.

The term ionic liquids (ILs) arbitrarily referred to ionic materials that are liquid below 100°C (Welton, 1999). A typical IL contains a large organic cation as well as an inorganic or an organic anion. Due to their robust physicochemical properties, ILs have emerged as a “green” and environmentally friendly solvents for use in the industrial manufacture of chemicals with a diverse applications in a variety of fields including chemical synthesis, catalysis, electrochemistry, engineering, mineral processing and biology, etc. (Plechkova and Seddon, 2008; Zhao, 2006; Werner *et al.*, 2010). As at June 2016, a search through the Web of Science citation indicates that there are about 63,437 publications with the words “ionic liquids”. Such a huge number of published scientific articles reveal high interest in this area among the

academia. ILs distinguish themselves from traditional molecular liquids in many ways as solvents. Some of their outstanding properties have been summarized by Liu *et al.* (2016). They have low toxicity and are difficult to volatilize, in most cases ILs are non-flammable and can be used over a wide temperature range. They have wide electrochemical window between 2 - 6 V. This allows the deposition of metals with very negative redox potentials.

More than a decade ago, Abbott and co-workers have demonstrated an alternative approach to making ionic liquids which they coined as “Deep Eutectic Solvent, (DES)” (Abbott *et al.*, 2003). DESs are eutectic mixtures of simple salts with either Lewis acidic or Brønsted acidic complexing agents. The Leicester group have extensively used the combination of quaternary ammonium salts with urea (melting point 133°C) and 2-hydroxy-ethyl trimethylammonium chloride (choline chloride, ChCl, melting point 302 °C) as starting materials to produce eutectic mixtures that is liquid at ambient temperature (melting point 12°C, for a molar ratio of 2:1) with a wide range of interesting properties (Abbott *et al.*, 2004). Although nearly all of DESs are prepared from ChCl as an ionic species, they cannot be considered as ILs because they are not entirely composed of ionic species and can also be obtained from non-ionic species (Zhang *et al.*, 2012). As compared to the traditional ILs, DESs have many advantages such as (i) low price, (ii) chemical inertness with water (i.e. easy storage), (iii) easy to prepare since DESs are obtained by simply mixing two components, thus by-passing all problems of purification and waste disposal generally encountered with ILs.

Different metal depositions have been carried out using DESs and the results have proven excellent as a substitute for conventional electrolytes in metal coating. Among industrial metals of interest that have been successfully deposited in DESs include Al, Cu, Sn, Zn, Ni, Cr, Al and Co (Endres *et al.*, 2008). The electrode position of corrosion- and wear-resistant coatings is an extremely important manufacturing process, particularly in the automotive and aerospace sectors. Zn and its alloys are used as anti-corrosion coatings for ferrous substrates,

particularly in the automotive industry while nickel electrodeposits are used for electroforming printing plates, phonograph stampers, sheet, tube, screen and many other articles (Schubert *et al.*, 2008).

In this current work, electrodeposition of zinc, nickel and zinc-nickel alloys on copper substrate was carried out using bulk electroplating method in a novel deep eutectic solvent (DES) type electrolytes. Electrochemical properties of the metal ions (Zn and Ni) with and without additives in DES were examined using cyclic voltammetry. The morphology of the coated substrates has been characterized using microscopic technique.

Materials and Methods

Chemicals

Choline chloride ($\text{HOC}_2\text{H}_4\text{N}(\text{CH}_3)_3\text{Cl}$, Aldrich, $\geq 99\%$), Ethylene glycol (EG, Aldrich $>99\%$), nickel salt ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, Aldrich $>98\%$), zinc salt (ZnCl_2 , Aldrich $>98\%$), sodiumbromide and boric acid (BDH Chemical, 99.8%) were used as received.

Methods

Preparation of deep eutectic solvents

The two DESs (Ethaline 200 and Reline 200) used in this study were prepared using the method of Abbott *et al.* (2007). According to this method, ethaline 200 DES was formed by heating a mixture of choline chloride (ChCl) with ethylene glycol (EG) in a molar ratio of 2 ChCl:EG at about 343 K with gentle stirring until a homogeneous colourless liquid was formed. In a similar way, Reline 200 DES was formed by mixing 139.6 g ChCl and 120 g of urea and heated at 343 K for about 8 h until homogeneous liquid was obtained. 50 mL of 0.6M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 50 mL of 0.5M ZnCl_2 were made up in both Ethaline and Reline. Boric acid (0.2M) and sodium bromide (0.1M) were used as additive to study their effect on the electrodeposition process as well as on the morphology of the coated metal.

Cyclic voltammetry (CV)

Cyclic voltammetry measurements on the solution of Ni^{2+} and Zn^{2+} ions both in Ethaline and reline DESs were carried out using an Autolab/PGSTAT12 potentiostat controlled with GPES/FRA version 4.9 software. A three-electrode system consisting of a platinum working electrode, a platinum counter electrode and a silver wire reference electrode was used. The working electrode was polished with 1 μm alumina paste prior to all measurements. All voltammograms were taken at temperatures 25, 50, 70 and 90°C with a scan rate of between 10 and 50 mV/s.

Electroplating

25 mL glass beaker was filled with DES containing 0.6M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.5M of ZnCl_2 . The content was then placed on a thermostatically controlled hot plate. Electrodeposition of Ni & Zn metals from DES (Reline and Ethaline) onto copper substrates were performed using bulk electrolysis as described by Abbott *et al.* (2007). Prior to deposition experiments, copper substrates (50 x 42 x 1 mm) were prepared by washing with deionised water and dried, then degreased by placing in dichloromethane (DCM) for 2 min and was removed and allowed to dry. The copper substrates were then immersed in the DES containing a known concentration of the metal ions solution. Copper substrate served as the cathode and was

connected to the negative terminal of a power supply while two oppositely clipped titanium mesh electrode, 40 x 50 mm, was used as an anode and connected to the positive terminal of power supply. The mesh was also rinsed with distilled water and DCM prior to use. After a fixed deposition time period (10 min for individual metal and 1 h for mixed metals alloy with additives) at 2V, the coated samples were removed from the electrolytic cell and subsequently rinsed with deionised water and in acetone then was air dried with proper labeling. Deposition experiments were conducted at temperatures of 50, 70, and 90°C.

Surface analysis

In order to explore the crystal structures of the deposit, the surface morphology and compositions of coated substrates were characterized by means of Scanning Electron Microscopy (SEM) acquired with a Phillips XL30 ESEM instrument.

Results and Discussion

Cyclic voltammetry studies

The cyclic voltammograms recorded on platinum electrode of Zn (II) in ethaline and reline ionic liquids as a function of potential scan rate (20 mVs^{-1}) at different temperatures are shown in Fig. 1(a and b). Data for the cyclic voltammetry of Ni (II) in Ethaline and Reline DESs are presented in Fig. 1(c and d). From both voltammograms, the anodic portions of the scans show well defined oxidation peaks compared to the cathodic portions indicating fast relative nucleation rate in the anodic region. In all cases, the voltammograms (Fig. 1) with exception of ZnCl_2 in Ethaline at 70°C, showed single reduction and oxidation peaks, arising from the reduction of Zn^{2+} to Zn metal and the metal being oxidised back to Zn^{2+} . In the same way, Ni^{2+} being reduced to Ni atom and oxidised back to Ni^{2+} again. Possible explanation for the double oxidation peak occurring for ZnCl_2 in Ethaline at 70°C would suggest two separate Zn phases, i.e. Zn metal undergoing oxidation to Zn^+ and later to Zn^{2+} . The reduction peak potentials for the two metal complexes are different (about -1.15 V for Zn and -0.55 V for Ni).

Clearly, it can also be observed from the cyclic voltammetry (Fig. 1) that the magnitudes of oxidation current peaks increase with increase in temperature, indicating increase in deposition of both Zn and Ni with rise in temperature over the applied deposition potential. As temperature increases, viscosity of the solution decreases and this results in faster rate of mass transfer reaction of ions in the reaction system. At 90°C, the voltammograms are well defined (sharp) and clear. It is also evident from Fig. 1(a and b) that the magnitude of oxidation currents of zinc in Ethaline are higher in reline despite having similar concentrations. This behaviour can be explained based on the difference in viscosities of the two liquids with the urea based liquid being more viscous ($\eta_{\text{urea}} = 1072$ cP at 20°C) than the ethylene glycol based liquid ($\eta_{\text{EG}} = 50$ cP at 20°C) (Abbott *et al.*, 2003; Abbott *et al.*, 2005). Thus, rate of conductivity is faster in ethaline (with low viscosity) and slow in reline (with high viscosity). Similar trend has been observed for nickel in ethaline and reline (Fig. 1 c and d).

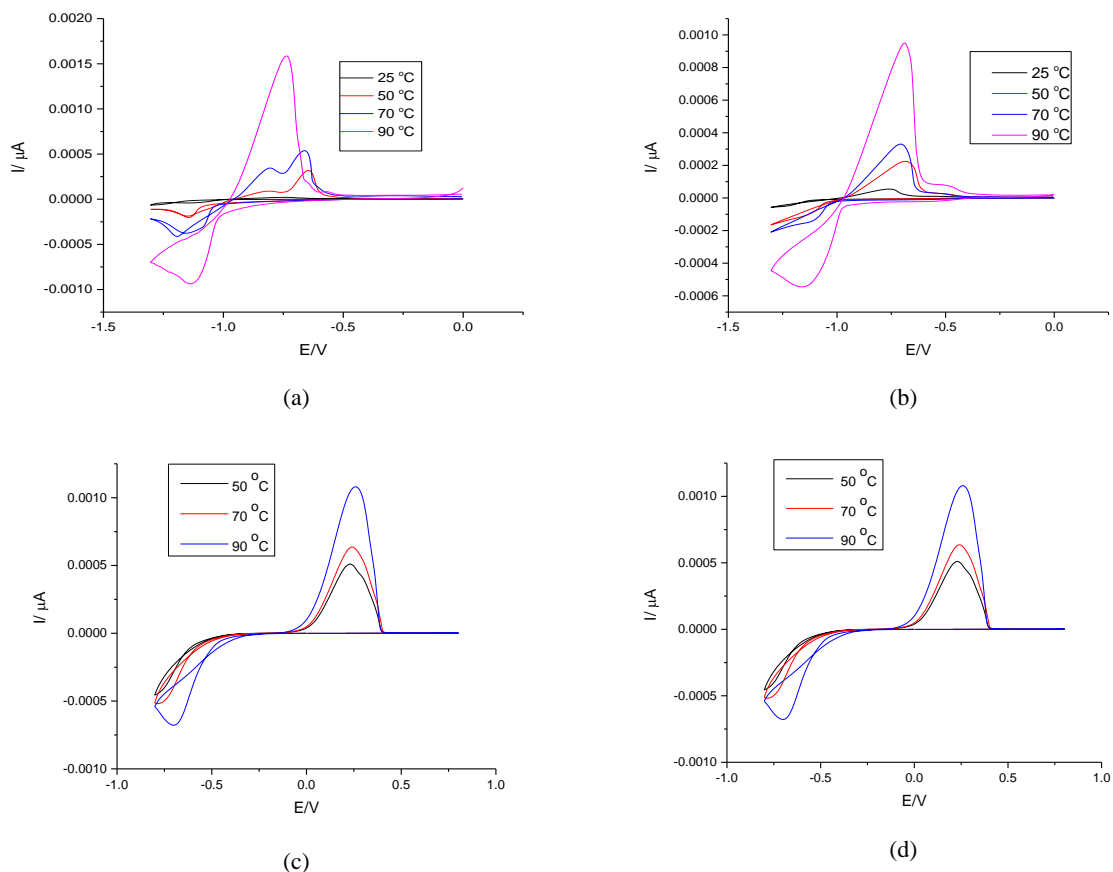


Fig. 1: Effects of temperature on the cyclic voltmetry of: 0.5 M ZnCl₂ in ethaline (a) and reline (b); 0.6 M Ni (II) in ethaline (c) and reline (d); on Pt electrode at sweep rate of 20 mVs⁻¹.

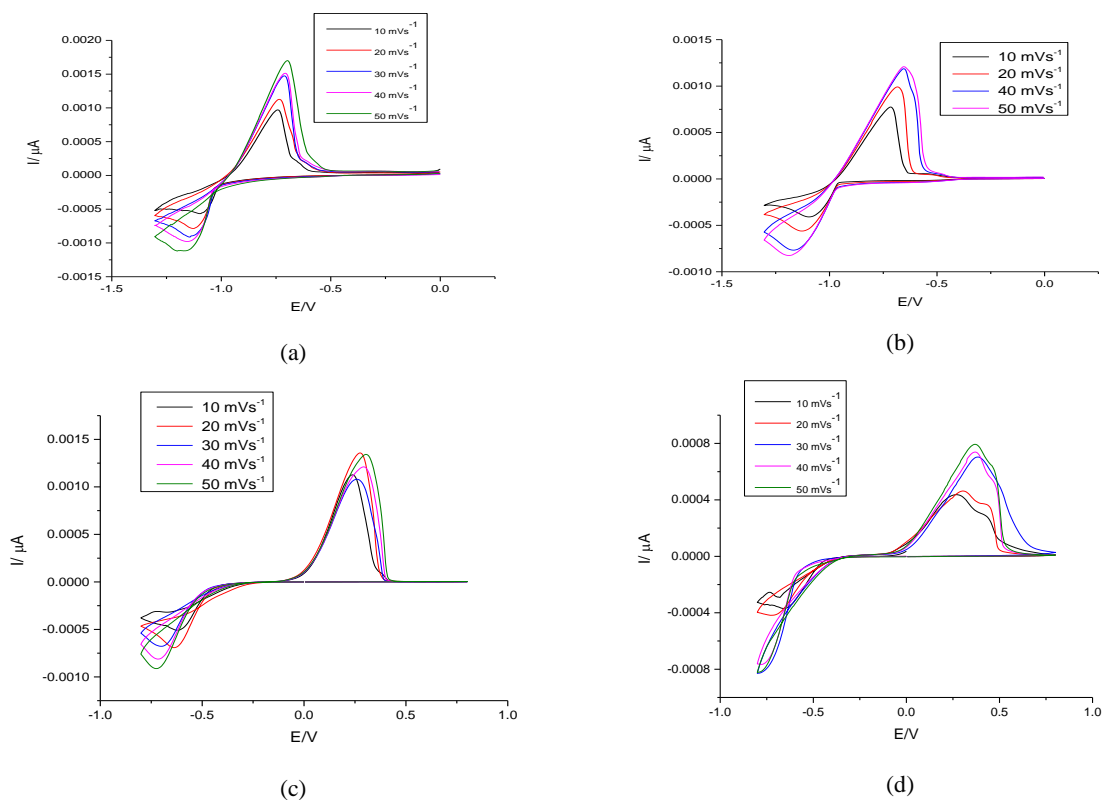


Fig. 2: Effects of different scan rates on the voltammograms of: 0.5 M ZnCl₂ in: (a) ethaline and (b) reline; 0.6 M NiCl₂ in: (c) ethaline and (d) reline; on Pt electrode at 90°C.

Effect of different scan rates on the cyclic voltammetry of Zn (II) and Ni (II) in Ethaline and Reline were recorded and Fig. 2(a–d) shows the results. The cyclic voltammetry reveals that the deposition of the metals increases with increase in scan rates. Thus it can be concluded that the best optimum range for deposition is at 50 mVs⁻¹ in both solvents.

Generally, the onsets of deposition process of a particular metal have been observed to vary in the two liquids. This can be explained in terms of the complex formed between a given pair of metal and solvent. It has been propounded by Abbott *et al.* (2008) that changes in speciation at the electrode surface or ligand activity in DES can cause such difference in the onset deposition of metals. For instance, in Ethaline DES, the hydrogen bond donor, ethylene glycol, is a relatively weak ligand and Reline DES contains urea which is a stronger ligand. As a consequence, free Cl⁻ activity in Ethaline will be relatively higher than in Reline. Therefore, the Cl⁻ ions in Ethaline liquid will rapidly diffuse to the electrode surface in preference to the bulkier [ZnCl₄]²⁻ anions, this will in effect reduce the concentration of Zn species in the electrochemical double layer and hence the rate of Zn nucleation. On the other hand, much faster Zn nucleation

will be expected to occur in Reline because its concentration in the double layer will be higher since the free Cl⁻ activity is much lower in this solvent.

Effect of mixed metal alloy and additives on the cyclic voltammetry of Zn (II) and Ni (II)

The cyclic voltammetry responses of mixed metal alloy of Ni/Zn and Ni + Zn + NaBr + BA all in ethaline DES are presented in Fig. 3. In contrast to the previous voltammograms of individual metal, it is obvious that the present voltammograms shows multiple peaks indicating many mixed phases due to presence of additives which might have cause the changes in the multiplenumbers of peaks of the voltammograms. Thus, in Fig. 3(a) there are about two reduction peaks, the more positive assigned to Ni²⁺ reduction and the more negative to the reduction of Zn²⁺. About three distinct oxidation peaks are observed suggesting multiple phases in the oxidation of this alloy. It can be also observed from Fig. 3(b) that the addition of additives tends to affect the cathodic deposition of these metals as with virtually absence of clear peaks in this portion.

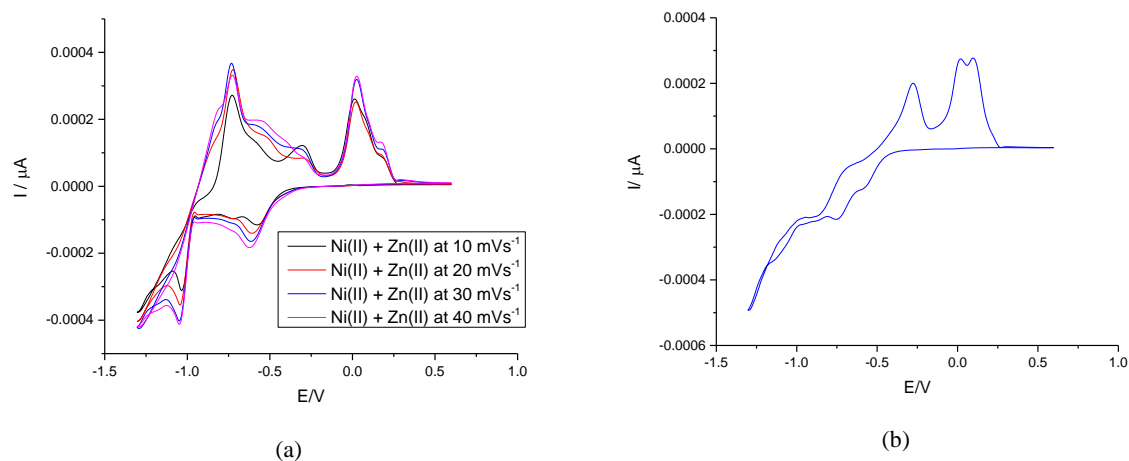


Fig. 3: (a) Effect of scan rate on the CV of mixed Zn and Ni alloy and (b) CV of metal alloy/additives

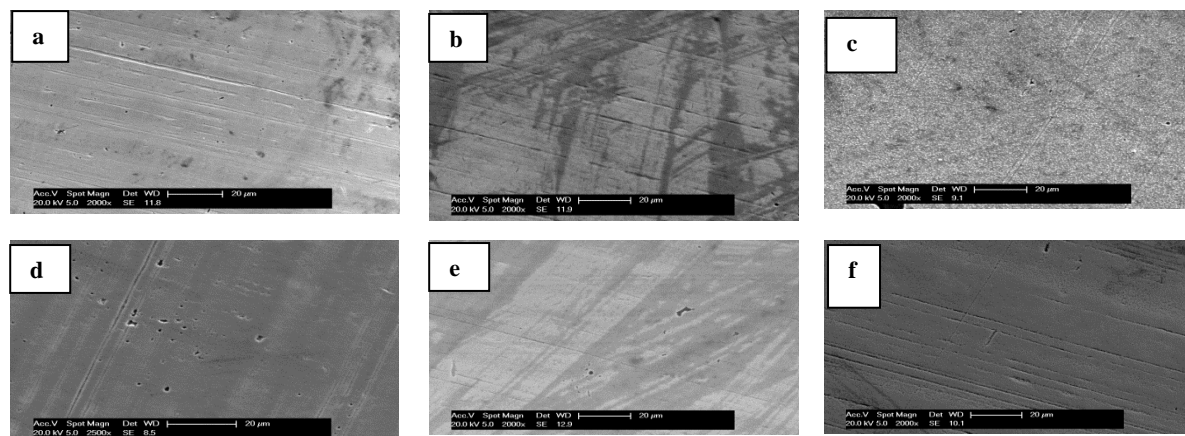


Fig. 4: SEM images of nickel deposit on copper substrate using Reline (a – c) and ethaline (d – f). (a - 50°C, 2 V, 35 mA; b -70°C, 2 V, 45 mA; c - 90°C, 2 V, 105 mA; d -50°C, 2 V, 55 mA; e -70°C, 2 V, 60 mA; f - 90°C, 2 V, 92 mA).

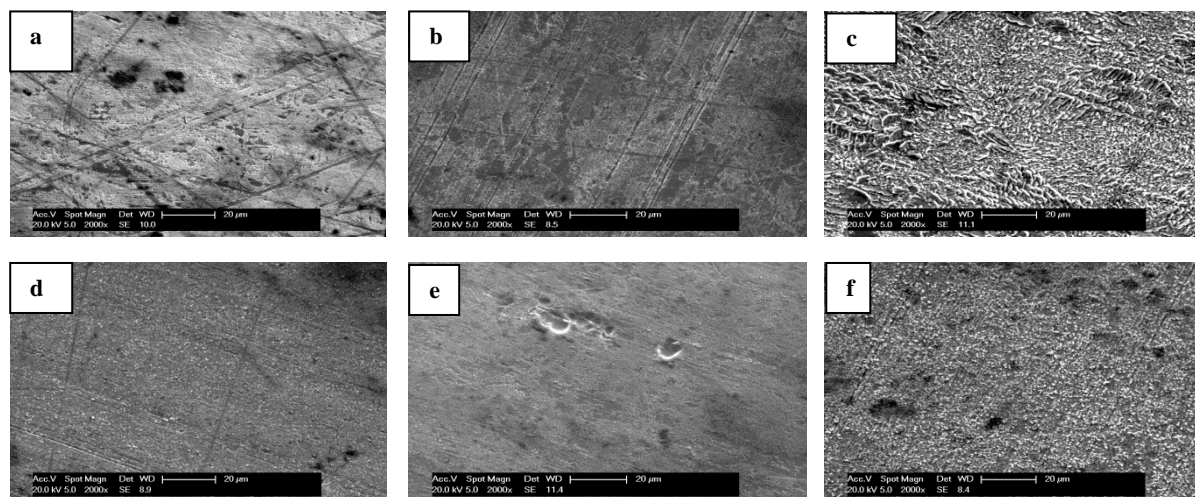


Fig. 5: SEM images of zinc deposit on copper substrate using Reline (a – c) and Ethaline (d – f). (a - 50°C, 2 V, 3 mA; b - 70°C, 2 V, 9 mA; c - 90°C, 2 V, 28 mA; d - 50°C, 2 V, 15 mA; e - 70°C, 2 V, 20 mA; f - 90 °C, 2 V, 50 mA).

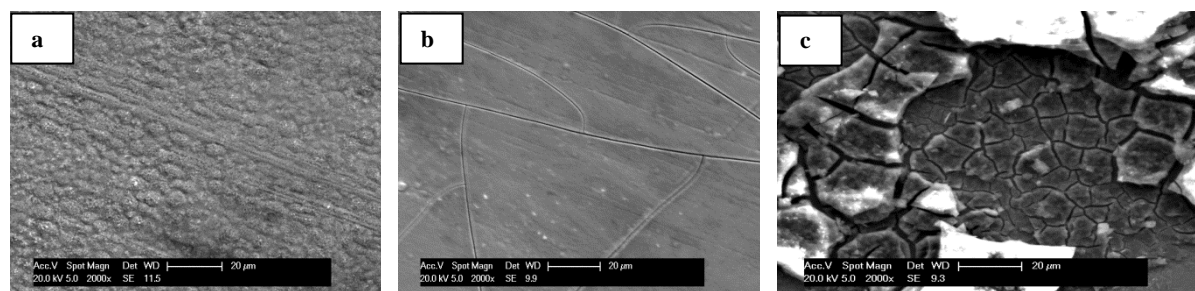


Fig. 6: SEM images (a) alloy of Zn and Ni with NaBr additive; (b) alloy of Zn and Ni with NaBr+ BA additives; (c) alloy of Zn and Ni only, all at 90°C in ethaline DES

SEM analysis

The micrograph images presented in Fig. 4 - 6 show the SEM analysis of nickel and zinc deposits from the two solvents under study at different temperature and at the stated conditions. The SEM images show that bright surfaces are obtained for Ni deposition in ethaline than in reline at the same experimental conditions. On comparing with SEM images of Zn in both solvents, Ni images show smooth and bright mirror surface shining. The SEM micrographs obtained for the metals mixed alloy and with additives (Fig. 6) clearly demonstrates changes in morphology with crack deposits observed in Zn/Ni alloy and Zn/Ni + NaBr + BA additives. The Zn/Ni alloy micrograph obtained at the stated experimental conditions shows a dull and crack surface coating probably could be due to high operating temperature. However, this cannot be confirmed since Zn/Ni alloy deposition at lower temperature was not conducted in this work. Thus, for a Zn-Ni alloy coating, good morphology can be obtained only by incorporating additives to it.

Conclusion

This study has shown that deep eutectic solvents of ethaline and reline can be used for Zn and Ni deposition both individually and as an alloy. A bright, smooth and crack free Zn and Ni deposit is possible from these solvents at temperatures ranging from 50 – 90°C. Also, a good surface morphology of Zn-Ni coating can be obtained by adding additives and selectively varying the experimental conditions. We have shown that both Zn and Ni deposition are temperature and scan rate dependent

from these solvents. We conclude, based on the results obtained from this study, that deposition of metals and alloys in these novel solvents can be possible, safer and cheaper route to the traditional use of ionic liquid solvent. However, investigations like hardness, thickness of the deposited metal on substrate and corrosion studies etc. are the short comings of the present study.

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