



A Comparative Study of Nickel Electrodeposition Using Deep Eutectic Solvents and Aqueous Solutions



Andrew P. Abbott^a, Andrew Ballantyne^a, Robert C. Harris^a, Jamil A. Juma^{a,b},
Karl S. Ryder^{a,*}

^a Materials Centre, Department of Chemistry, University of Leicester, Leicester, LE1 7RH, UK

^b Chemistry Department, University of Koya, Erbil, Iraq

ARTICLE INFO

Article history:

Received 19 May 2015

Received in revised form 7 July 2015

Accepted 9 July 2015

Available online 18 July 2015

Keywords:

Electroplating

nickel

deep eutectic solvents

speciation

ABSTRACT

Metal electrodeposition using ionic liquid electrolytes and deep eutectic solvents is now well known but to our knowledge for electrolytic deposition of metals such as nickel no direct comparison has thus far been drawn between deposition using aqueous solutions and DES under otherwise identical conditions. In the current study it is shown that nickel deposition can be carried out with similar deposition rates in aqueous and ionic media despite the significant differences in viscosity and conductivity. It is, however, shown that in ionic media the morphology of the deposits is markedly different from that achieved using a Watts nickel bath and that one aspect of these differences manifests itself in significant increase in the coating hardness. It is proposed that the observed morphology differences occur due to the variations of nickel speciation in each electrolyte environment.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Nickel electrodeposits are used extensively for corrosion resistance, decorative applications and in the fabrication of printed electronic circuitry [1–3]. Oliver P. Watts formulated a general purpose nickel bath composition in 1916 (nickel sulfate, nickel chloride, and boric acid) [4] that has since been widely used and adopted for commercial processes [5–7]. The Watts nickel bath has been extensively applied and modified to produce a range of functional and decorative nickel finishes [8,9]. The variation in coating morphology and other physical properties is achieved using a variety of organic and inorganic additives to brighten and level the nickel deposit [10,11]. On the other hand the Watts bath has to be operated under close and attentive process control. Small variations in composition and pH can influence the deposit morphology, coating properties and adhesion.

In a general drive to overcome some of the drawbacks of electroplating in aqueous solutions (for example low current efficiency, stringent process control, complexity of bath and additives) the electrodeposition of metals using ionic liquids and deep eutectic solvents (DES) is a topic which is currently gaining significant attention due to the ability to deposit reactive metals and metal-alloys that are otherwise not attainable in

aqueous solution and to access novel architectures. There are, however, fundamental differences between molecular solvent and ionic DES electrolytes and these undoubtedly change the way in which metals nucleate and grow on surfaces. In the context of our current work there have been several recent studies of the electrochemical deposition of nickel and nickel alloys (with for example Zn, Sn, Co or P) from DES [2,12–17]. These studies have all uniquely focused on the electrochemical deposition of the metal or alloy system from a single electrolyte, DES, system. To our knowledge no work has been carried out to compare directly the properties of metals deposited from aqueous solutions with those from ionic liquids under exactly the same conditions of concentration and temperature [18–21]. As a result of such a comparative study we seek to understand the influence of the electrolyte on deposition rate, current efficiency and deposit morphology as well as metal ion speciation.

It has previously been shown that deep-eutectic solvents (DES), which are mixtures of quaternary ammonium salts with either hydrogen bond donors or metal salts, can be used for metal deposition [22]. One of the most effective of these DES electrolytes is a stoichiometric mix of ethylene glycol and choline chloride in a ratio of 2:1. This DES is known by the trivial (commercial) name of *Ethaline*. Electrodeposition of Zn, Cr, Ag, Ni, Zn–Sn alloys and Cu composites from *Ethaline* have been demonstrated [23]. The deposit morphology differs markedly in most cases from that obtained during electrodeposition of the same metal in aqueous solutions and is significantly affected by the content (electrolyte

* Corresponding author: Fax: +44 116 252 3789.

E-mail address: k.s.ryder@le.ac.uk (K.S. Ryder).

formulation) and operating conditions of the process [24]. The nucleation and growth of metal coatings from solution depends clearly upon the physical conditions of temperature and applied potential and current but it also is strongly affected by metal speciation, mass transport and double layer properties. In this manuscript we describe a study of nickel electrodeposition from three comparable nickel solutions, these are;

- Watts nickel bath: $1.14 \text{ mol dm}^{-3} \text{ NiSO}_4$, $0.51 \text{ mol dm}^{-3} \text{ NaCl}$, $0.65 \text{ mol dm}^{-3} \text{ B(OH)}_3$ in water.
- Aqueous solution: $1.14 \text{ mol dm}^{-3} \text{ NiCl}_2 \cdot 6\text{H}_2\text{O}$ in water.
- Ethaline: $1.14 \text{ mol dm}^{-3} \text{ NiCl}_2 \cdot 6\text{H}_2\text{O}$ in 1ChCl: 2 ethylene glycol.

The effects of speciation and mass transport were studied while maintaining constant temperature, concentration and electrochemical control. Using the Watts nickel bath as a standard the operating conditions of 1.14 mol dm^{-3} and 80°C were used throughout the electrochemical experiments. This leaves the speciation, mass transport and double layer structure as the remaining significant variables between the systems.

2. Experimental

Choline chloride, $[\text{HOC}_2\text{H}_4\text{N}(\text{CH}_3)_3\text{Cl}]$ (ChCl) (Aldrich 99 %) was recrystallized from absolute ethanol, filtered and dried under vacuum. Ethylene glycol (EG) (Aldrich + 99 %), was used as received. The two components have been mixed together by stirring (in a 1: 2 molar ratio of ChCl: hydrogen bond donor) at 60°C until a homogeneous, colourless liquid formed. The nickel salts; $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (Aldrich $\geq 98\%$), sodium chloride and boric acid (BDH Chemical, 99.8%) were used as purchased. The concentration of nickel salts in all liquids was 1.14 mol dm^{-3} (except where explicitly stated).

The conductivity of the liquids was measured as function of temperature using a Jenway 4510 conductivity meter fitted with an inherent temperature probe (cell constant = 1.01 cm^{-1}). Cyclic voltammetry investigations were carried out using an Autolab PGSTAT12 potentiostat controlled with GPES2 software. A three-electrode system was used, consisting of a platinum working-electrode (0.12 cm^2 area), a platinum flag counter-electrode and a silver wire pseudo-reference electrode. The working electrode was polished with $0.05 \mu\text{m}$ γ -alumina paste and cleaned by rinsing with deionised water followed by acetone prior to each experiment. All cyclic voltammograms were recorded at 80°C and at a scan rate of $5\text{--}10 \text{ mV s}^{-1}$. Quartz crystal microbalance (QCM) was used to determine current efficiency. An electrochemical quartz crystal microbalance consisting of an Agilent HPE5061A network analyser with a 10 MHz AT-cut gold quartz crystal (International Crystal Manufacturing Co., Oklahoma City, USA) was used. A three-electrode compartment cell was constructed from PTFE, with a polished gold coated crystal working electrode, a silver wire reference electrode and a Pt flag counter electrode. The electrodes were connected to a potentiostat (Autolab 263A) in order to record voltammetric data. The quartz crystal had a piezoelectrically active area of 0.23 cm^2 .

Bulk electrolysis was carried out using cathodic plates (nickel and mild steel, $50 \text{ mm} \times 42 \text{ mm} \times 1 \text{ mm}$) which were mechanically polished and cleaned with acetone and rinsed with water and dried. An iridium oxide-coated titanium mesh electrode, $40 \text{ mm} \times 50 \text{ mm}$, was used as an anode. In all of the experiments the solution temperature was 80°C and deposition was carried out using a constant current for 3 to 9 hours, after which the substrates were removed from solution and washed with water and acetone.

Surface microstructure analysis: The surface morphology was characterised using scanning electron microscopy (SEM) and

elemental analysis of the deposit compositions was carried out by energy dispersive X-ray spectroscopy (EDX), using a Phillips XL30 ESEM instrument with an accelerating voltage between 15 and 20 keV, giving an average beam current of $ca. 120 \mu\text{A}$.

Cross-section microstructure: The samples were mounted in a resin using a Struers Labo Press 3. The samples were then polished first with 240 grit silicon carbide paper to make them flat, then with diamond abrasives of successively $9 \mu\text{m}$ and $3 \mu\text{m}$ size and finally with $0.5 \mu\text{m}$ colloidal silicon carbide paste.

UV visible spectrophotometer: A Shimadzu model UV-1601 spectrophotometer was used with the cell path length equal to 10 mm. Values for λ_{max} were determined using the spectrophotometer's built-in peak-pick feature, using UV- probe software.

Hardness: The hardness of the electrodeposits was evaluated as resistance to indentation, in the form of force of indentation and depth of indentation, for nickel deposits on copper and nickel with a Mitutoyo model MVK-G100 hardness meter. The specimens were indented using different forces and a loading rate of 0.1 mm s^{-1} for 10 s. The Vickers number is the number obtained by dividing the kg-force load by the square area of indentation of a standard probe.

3. Results and Discussion

Most studies of metal deposition in ionic liquids have been carried out at relatively low (10^{-3} molar) metal ion concentrations and at ambient temperatures. This is in stark contrast to the conditions commonly used for commercial metal electroplating in aqueous solutions which is generally performed at much higher concentration (molar) and higher temperatures. The electrodeposition of Ni has previously been studied in Ethaline using $0.2 \text{ mol dm}^{-3} \text{ NiCl}_2 \cdot 6\text{H}_2\text{O}$ at 20°C [24]. Black deposits were obtained from bulk deposition and metallic looking deposits could only be obtained using ethylene diamine as an additive [24]. The electrochemical behaviour previously reported showed a response which was poorly reversible with a large overpotential ($ca. >0.75 \text{ V}$) separating the deposition and stripping peaks in the voltammetry. In contrast to this Fig. 1 shows the cyclic voltammogram of a solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in Ethaline. In this case the concentration is increased to a 1.14 mol dm^{-3} which is the same as that used for $[\text{Ni}^{2+}]$ ion in the aqueous Watts nickel bath. At this higher concentration of Ni^{2+} a more reversible redox behaviour is observed in Ethaline than that previously reported and a clear

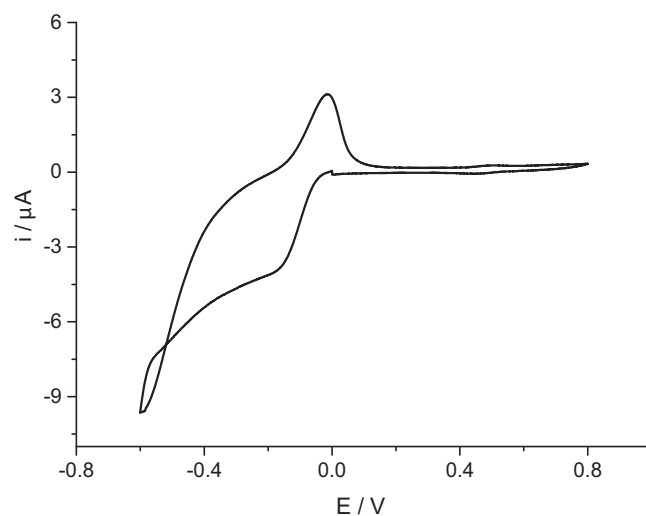


Fig. 1. Cyclic voltammogram of $1.14 \text{ mol dm}^{-3} \text{ NiCl}_2 \cdot 6\text{H}_2\text{O}$ in Ethaline at 25°C on a Pt electrode (1 mm disk), at a sweep rate of 10 mV s^{-1} vs $[\text{Fe}(\text{CN})_6]^{4+/3+}$.

Download English Version:

<https://daneshyari.com/en/article/6610997>

Download Persian Version:

<https://daneshyari.com/article/6610997>

[Daneshyari.com](https://daneshyari.com)