

The Study of Surface Texture of Electroplated Ni from Deep Eutectic Solvents Type (II) Reline without Brighteners and With Brighteners Ethylene Diamine and Acetyl Acetone Using AFM Technique

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Abstract: The surface texture of the deposited nickel films with and without brightener agent ethylene diamine and acac from urea/ choline chloride (reline), based ionic liquid on copper substrate, have been studied by AFM. The surface has been depicted by atomic force microscopy in relation to RMS in terms of roughness, power spectral density (PSD), section, depth and width. The results obtained are very important and valuable, which revealed that the addition of the leveling agents have remarkably influence on the topology and the morphology of the coated surfaces.

Key words: reline, Ni deposits, ionic liquids, leveling agents, surface roughness and morphology

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I. Introduction

Salts that are liquids below 100°C[1]. are called ionic liquids. Generally one of the constituents is organic, most commonly the positive ion. The ions have a low degree of symmetry and considerably large size, these two factors are the main driving force for decreasing the intermolecular forces between molecules. By careful choice of the components it is possible to tune the properties of the ionic liquid. Ionic liquids can dissolve inorganic, organic substances or even macro molecules such as cellulose. One of the key advantages of these types of ionic liquids is the ease of manufacture. The liquid formation is generally mildly endothermic and requires simply mixing the two components with gentle heating. Another key advantage in favour is that the ionic liquids are water insensitive which is very important for practical electroplating systems. Ionic Liquids have clearly been reported to be green solvents and are most notably known for their low vapour pressure compared to the molecular alternatives. In the application of ionic liquids to metal deposition the green credentials of this methodology could also come from a significant reduction in the volume of low level aqueous streams that would need to deal with it. Generally, in today's world it is recognized that the only part of the picture of their applications in electroplating industries since many ionic liquids do have significant toxicity. However, some ionic liquids have been designed to contain ions which are known to have lower toxicity and these include functionalized imidazoles,[2], lactams,[3] amino acids,[4] and choline,[5] although it is only the last of these which have been extensively applied to metal deposition.

Why are ionic liquids used in electroplating?

As ionic liquids have developed the key advantages of liquids they have become; i- the wide potential windows, ii- high solubility of metal salts, iii- avoidance of water and metal/water chemistry iv- high conductivity compared to non-aqueous solvents. The utility of ionic liquids precursors not only have the potential to electrodeposit metals, but yet it has been impossible to reduce them in aqueous solutions, however they have the capability to engineer the redox chemistry and control metal nucleation characteristics. It is the latter area that is now being addressed and will no doubt be the focus of research over the forthcoming decade. The main utilization for using ionic liquids for metal plating is the ability to obtain wide potential windows, whereas the potential range of which the electrolyte is neither oxidized nor reduced at the electrode surface. Some ionic liquids have a very large potential window of up to 4.15 V for [Bmim][PF₆] at a Pt electrode[6], 5.5 V for [BMP](TF₂N) at a glassy carbon electrode[7]. The importance of potential windows is well known from aqueous processes where hydrogen evolution can be hazardous and lead to brittle electrodeposits (hydrogen embrittlement). Ionic liquids may even be chemically altered and hence destroyed if potential limits are not considered. The wide potential window of ionic liquids makes it possible to electrodeposit elements with low redox potentials, which cannot be reduced in other media such as Al,[8] Mg,[9], Ge,[10], and Si[11]. The relevant aspects of metal deposition using ionic liquids with discrete anions are reviewed[12,13]. The metals deposited to date are shown schematically in **Figure 1**.

Figure 1

I	2												13	14	15	16	17	18
H	He												B	C	N	O	F	Ne
Li	Be												Al	Si	P	S	Cl	Ar
Na	Mg	3	4	5	6	7	8	9	10	11	12	Ga	Ge	As	Se	Br	Kr	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	In	Sn	Sb	Te	I	Xe	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	Tl	Pb	Bi	Po	At	Rn	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg							
Fr	Ra	Ac																

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

As Metal
As Alloy
As Metal and Alloy

Deep Eutectic Solvents

The demand for ionic liquids to be applied on an industrial scale for metal deposition need to be low cost, non-toxic, pre-registered for reachandwater insensitive.

Based on the nature of the complexing agent applied, four types of deep eutectic solvents can be categorized [1]. Such classification is presented in Table 1.

Table 1 shows the types of deep eutectic solvents

Type	General formula	Examples
Type I	$Cat^+ X^- zMCl_x$	M = Zn, Sn, Fe, Al, Ga, In
Type II	$Cat^+ X^- zMCl_x y H_2O$	M = Cr, Co, Cu, Ni, Fe
Type III*	$Cat^+ X^- zRZ$	Z = CONH ₂ , COOH, OH
Type IV**	$MCl_x + RZ = MCl_{x-1}^+ \cdot RZ + MCl_{x+1}^-$	M = Al, Zn and Z = CONH ₂ , OH

The novelty of Type III eutectics utilize a simple hydrogen bond donor to complex the simple anion (usually chloride). The majority of the work to date has focused on simple amides, alcohols and carboxylic acids. The first reports on eutectics were those formed between choline chloride and amides such as urea and acetamide[14]. These materials have been called Deep Eutectic Solvents to differentiate them from ionic liquids with discrete anions. However, the eutectic forms interaction between the two species in the mixture. An example of this is the choline chloride: urea mixture. They have freezing points of 303°C and 135°C respectively. By combining these two compounds in a ratio of 1:2 (choline chloride: urea), the product formed has a freezing point of 12°C which has a depression of freezing point of 168 °C. In comparison to the freezing point depression for the choline chloride-zinc chloride system was much larger (272 °C)[15]. due to the covalent bonds formed in the metal chloride case. The main reason behind choline chloride being such a useful quaternary ammonium salt is to do with the fact that it is an asymmetric quaternary ammonium salt, with a polar functional group, but it is also small. The asymmetric nature of this molecule reduces the freezing point of the ionic-molecular liquid, as does the polar functional group. The group of Abbott has published extensively on the subject of choline chloride HOC₂H₄N⁺(CH₃)₃Cl⁻ (ChCl) because it is non-toxic and readily available as a bulk commodity chemical. Its common usage stems a part from its simple manufacture; an efficient gas phase reaction between trimethylamine, ethylene oxide and HCl. This means that the Sheldon E factor[16] for this salt is close to zero because almost no waste products are formed during this reaction. Type IV**eutectics are very interesting due to the production of cationic metal complexes, guaranteeing a high metal ion concentration close to the electrode surface [17]. A noteworthy example is ZnCl₂, which forms eutectic compounds with different substances such as urea, acetamide, ethylene glycol and 1,6-hexanediol [18]. The demand of nickel plating in the market and industries is large, because of its excellent mechanical properties like wear resistance, heat resistance and shiny decorative films that can be obtained and as well as its corrosion resistance.[19,25].

The aim of this work is to focus on eutectic based ionic liquids which are closer to the market and in general are probably the most easily adopted by the metal finishing industry from a cost, registration and handling perspective, in addition to the investigation of surface roughness, topology and morphology of different nickel coating obtained in the presence and absence of additives.

II. Experimental

Choline chloride [$\text{HOC}_2\text{H}_4\text{N}(\text{CH}_3)_3\text{Cl}$] (ChCl) (Aldrich 99%) was recrystallised from absolute ethanol, filtered and dried under the vacuum. Urea (Aldrich .99%) was dried under the vacuum before use., nickel chloride dihydrate, ethylenediamine (en) and acetylacetonate (acac) (all Aldrich) were all used as received.

2.1 Preparation of Reline

Reline is prepared by mixing one mole equivalent of Choline chloride with two mole equivalents Urea and stirring the mixtures together at 100°C until a homogeneous, colourless liquid is formed

2.2 Atomic Force Microscopy (AFM) Surface Nano-characterization

AFM is a very-high-resolution type of scanning probe microscopy (SPM), with demonstrated resolution on the order of fractions of a nanometer, more than 1000 times better than the optical diffraction limit. Studying the topology and morphology of variety of surfaces by AFM. It can provide very valuable and important information about mechanical mass production and [26], tribological properties [27, 28], where tribology field of active research deals with, for example, friction and wearing and thin film surfaces [29, 30]. This tool can show the detail of surface texture better than other microscopic methods. Using appropriate software it is possible to assess features such as roughness, porosity, average size, and particle size distribution, which have great effect on the optical, mechanical, surface, magnetic and electrical properties of thin films. The goal of this work is to examine the surface topology and morphology of the nickel deposits on copper substrate from deep eutectic solvent reline, compared with the deposits of added leveling agents ethylene diamine and acetylacetonate (acac). The properties of deposits films and their nature have been investigated by parameters such as the average roughness, maximum peak to valley height, root mean square roughness, ten-point mean height roughness, surface skewness and surface kurtosis. However, surface analysis was carried out using a nanoscope IV Dimension 300 (Veeco) atomic force microscope with a $100\ \mu\text{m}$ scanning head and using both contact and tapping (resonant) modes. Images were acquired in air.

III. Results And Discussion

The dimensions of the sample parameters are described by data which gives the details and figures about the statistical average values, such as roughness, heights, shape of the histogram heights and properties. The average roughness (R_a) is the mean height calculated over the entire measured length/area. Root mean square (RMS) roughness (R_q) is the square root of the distribution of the surface height and is also used to evaluate the kurtosis and skew parameters.

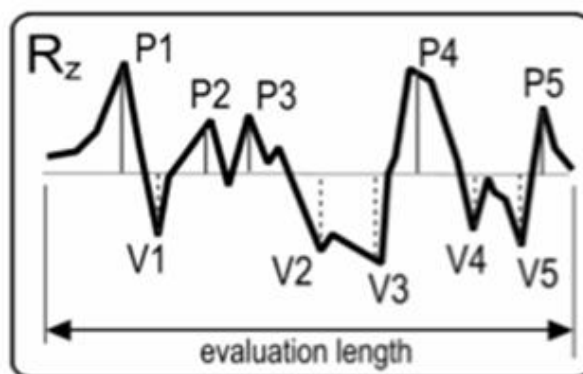
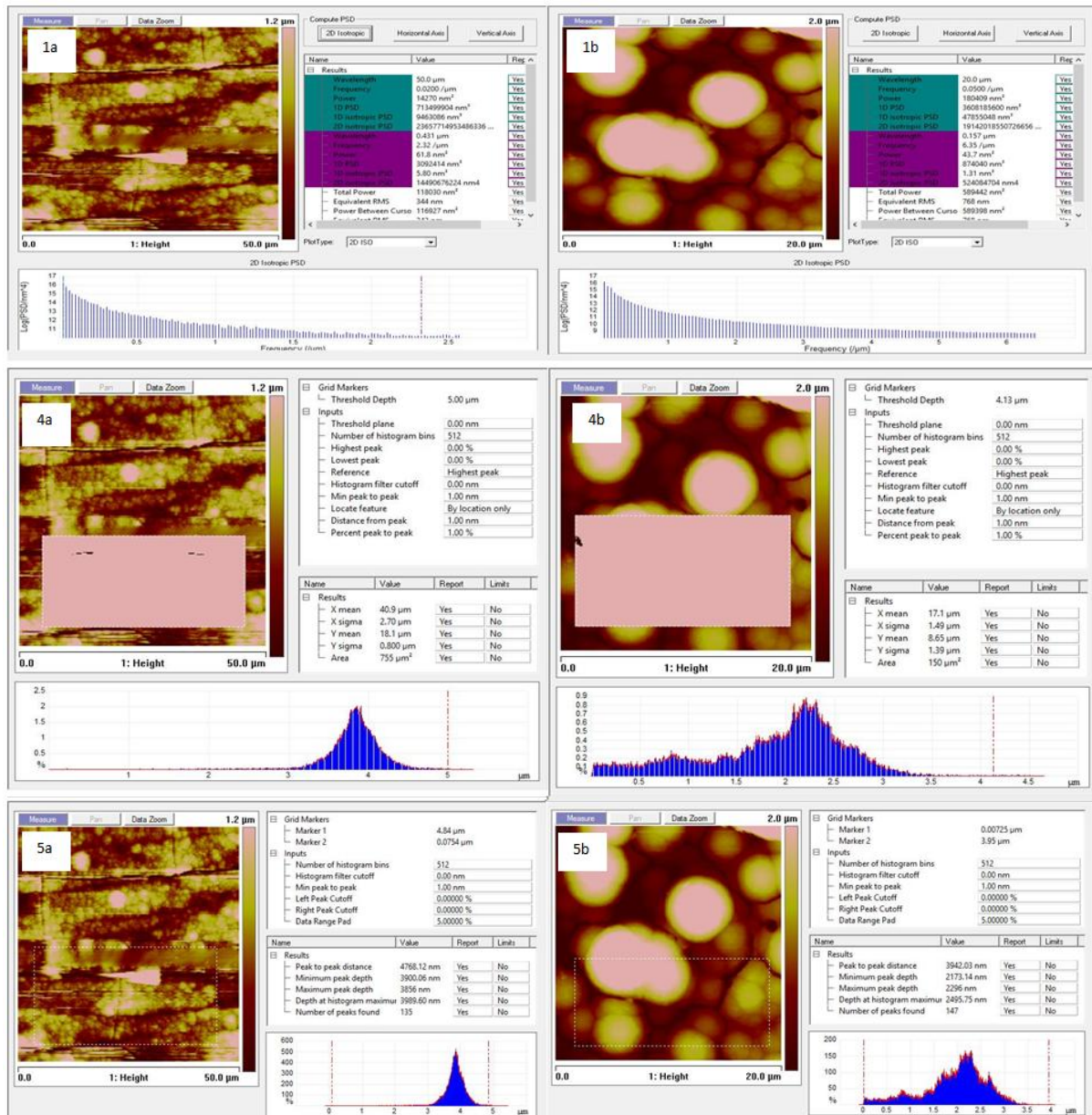


Fig. 2 R_z average of the sum of the five highest peaks in the five deepest valleys of sample's profile (Zygo Corporation, 2011).

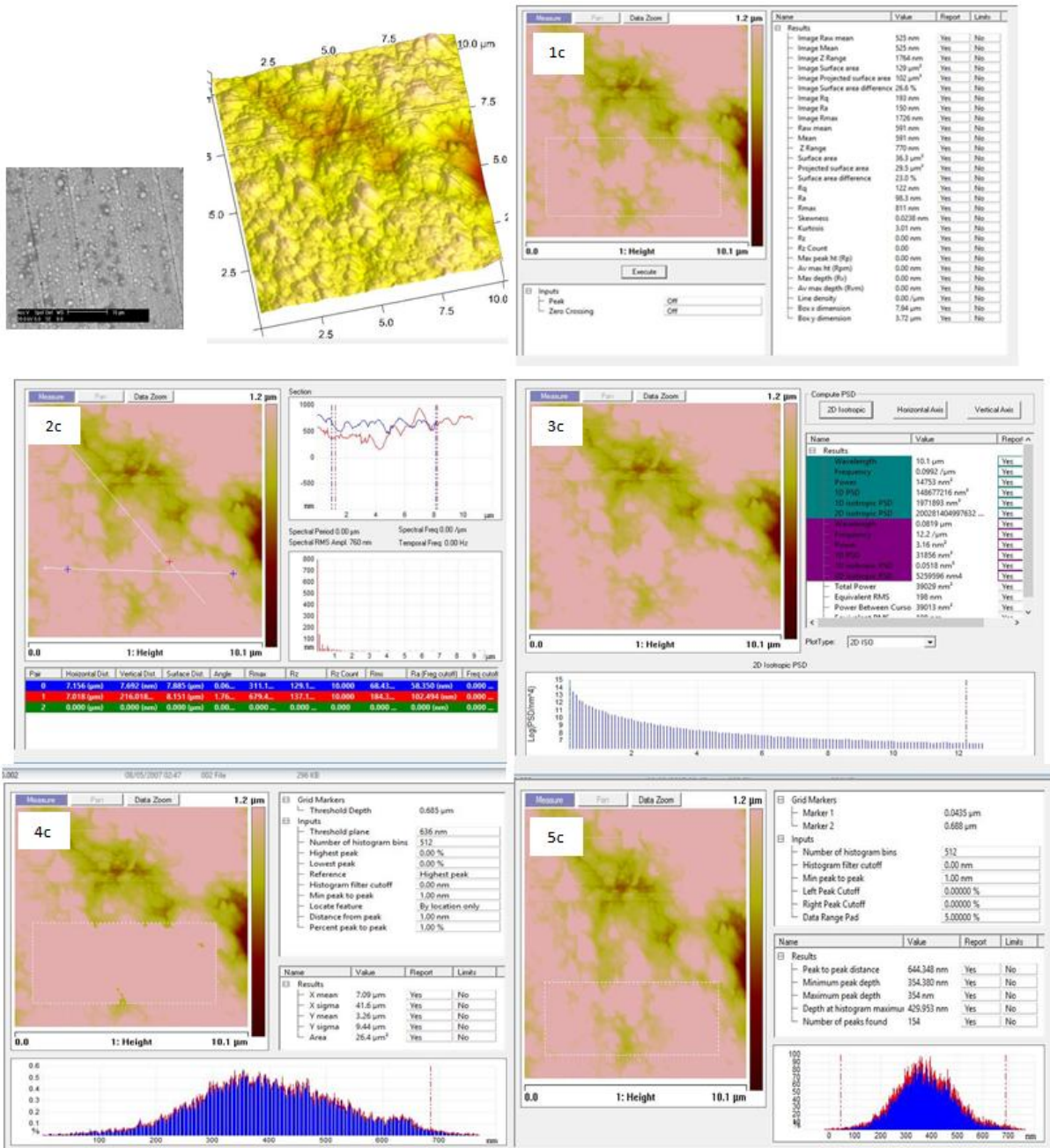
RMS roughness (R_q) refers to the finish of optical surfaces. It illustrates the standard deviation of the profile heights and is applied to figuring of skew and kurtosis values. Ten-points mean height roughness (R_z) as shown in the figure 2 is the difference in height between the average of five highest peaks, and five lowest valleys in the evaluation profile/surface and is more sensitive to occasional high peaks or deep valleys than R_z . Roughness skewness (R_{sk}) is used to measure the symmetry of the variations of a profile/surface about the mean line/plane and is more sensitive to occasional deep valleys or high peaks. R_{sk} illustrates the load carrying capacity, porosity, and characteristics of nonconventional machining processes.

Figure 1 represents a, b and c showing AFM and SEM images for Ni coatings in presence and absence of additives, 1a, 1b and 1c depict roughness data for Ni coatings in presence and absence of additives, 2a, 2b and 2c explain section graphs and data for Ni deposits in presence and absence of additives, 3a, 3b and 3c represent

power spectral density (PSD) information for Ni deposits in presence and absence of additives, 4,5a,4,5b and 4,5c represent the width and depth data for Ni deposits in presence and absence of additives respectively. Figure 3



(c)Plated Ni from reline with added acac



Usually, R_{sk} is used to distinguish two profiles of the same R_a or R_q values but of different shapes. Kurtosis is a measure of the distribution of spikes above and below the mean line. Kurtosis gives information about the machined surfaces. It is sometimes specified for the sway of stress fracture. Roughness kurtosis (R_{ku}) is applied to calculate the distribution of the spikes above and below the mean line/plane. For spiky surfaces, $R_{ku} > 3$; for

Table.2 Roughness parameters of Nickel deposits with and without brighteners

Ni deposits from reline	R_a nm	R_q nm	R_z nm	R_q / R_a	R_{sk} nm	R_{ku} nm	Distribution Of spikes
No brightener	240	372	542	1.55	2.41	19.9	Spiky
en	538	641	1859	1.19	-0.0962	2.56	bumpy
acac	98.3	122	00	1.24	0.0238	3.01	Perfectly random

bumpy surfaces, $R_{ku} < 3$; the ideally random surfaces have a value 3 of R_{ku} [31]. According to Gaussian distribution, from point view statistics the values R_q / R_a have to be 1.25. Ward [32], observed that asperity height distribution of most engineering surfaces (tribology) may be approximated by a Gaussian distribution with R_q/R_a values of up to 1.31. The data obtained in Table 2 from AFM images are significantly valuable and important as they show that the addition of brighteners modify the nucleation and the growth [32]. In Table 1 nickel deposits without leveling agents indicates, that the skewness has a negative value which reveals that the valleys are dominant over the scanned region. The positive values of skewness of both nickel deposits, with added ethylene diamine (en) and acetyl acetonate (acac), show that the peaks are dominant on the top of the plated area. The value of R_{ku} for nickel deposits from acac is equal 3.01, which is a significant result, while Ni deposits from Reline only has a large value which shows that the surface is spiky, this could be due to the difference in mechanism of growth deposition from both liquids [33,34]. Furthermore, it has been seen that the data represented in Table 2 is very much consistent with results obtained by section figures 2a, 2b and 2c.

Fig.3 Photograph of Ni plated onto mild steel substrate following electrolysis of reline containing 0.2M with added brightener en



Figure 3 shows the photograph of Ni deposits on a mild steel which was kept exposed to humidity and air for 8 years to assess the performance of the nickel coating. It is observed that the nickel coat protects the area coated while the uncoated area tarnished and became rusty.

IV. Conclusion

The investigation of the surfaces of deposits Ni with and without added brighteners ethylene diamine and acetyl acetonate have been studied by an AFM technique, the results obtained are very important and valuable, which reveal that the addition of the leveling agents have a great influence on the topology and the morphology of the coated surfaces. All of the three nickel deposits have different Kurtosis R_{ku} values the categorized nickel coating first the nickel deposits in absence of additives has a spiky surface, second nickel coating in the presence of ethylene diamine possesses bumpy surface, while the last with added acac has perfectly random spiky distribution and besides added complexing agents (en) suppresses under potential deposition (upd) of nickel and lead to smaller particles deposits.

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