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PRELIMINARY STUDIES OF SILVER COATINGS FORMATION FROM CHOLINE CHLORIDE BASED IONIC LIQUIDS

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Lucrarea prezintă o serie de rezultate experimentale preliminare referitoare la formarea acoperirilor de Ag pe substrat din cupru prin procedee electrochimice şi chimice din lichide ionice pe bază de clorură de colină şi săruri de Ag(I). De asemenea, sunt abordate şi câteva aspecte privind sinteza şi caracterizarea fizică (culoarea, aspectul, conductivitatea electrică) ale unor lichide ionice de diferite tipuri, cu conţinut de argint. Voltamogramele ciclice au arătat un domeniu larg de potenţiale pentru depunerea de Ag. Depunerile de Ag pe substrat de Cu obţinute electrochimic sau chimic (fără curent) din lichide ionice au culoarea gri deschis şi o bună aderenţă şi uniformitate. Aceste depuneri din lichide ionice pot fi folosite în industria electronică (de exemplu: tehnologiile de fabricare a circuitelor imprimate) şi reprezintă alternative ecologice deoarece se înlocuiesc electroliţii apoşi cianurici, care prezintă toxicitate ridicată.

This paper presents some preliminary experimental results regarding the formation of Ag coatings on Cu substrate using electrochemical and chemical procedures from choline chloride based ionic liquids containing Ag(I) salts. Some aspects regarding synthesis and characterization (color, appearance, electrical conductivity) of different types of silver containing ionic liquids are also discussed. Cyclic voltammograms have shown a large potential domain for Ag electrodeposition. Ag coatings on Cu substrate obtained both electrochemically and chemically (electroless deposition) from ionic liquids have light grey color and a good adherence and uniformity. These coatings obtained from ionic liquids could be used in the electronic industry (e.g. PCB technologies) and represent environmentally friendly alternatives as the cyanides baths which are very toxic are replaced.

Keywords: silver coating, ionic liquid, electro- and electroless deposition

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1. Introduction

Silver coatings are among the most used deposits at industrial scale in high performance technological fields belonging to electronics, electrical engineering, aeronautics, as well as in food industry or artistic design of jewels and art objects. Traditionally, Ag layers are obtained either electrochemically using cyanide aqueous electrolytes or chemically from very concentrated HNO_3 aqueous solutions. Ag layers are mainly applied in printed circuits boards (PCB) manufacturing to prevent the exposed Cu tracks degradation (which usually occurs in several months), before the final assembling of electronic devices. Silver metal has also a high solubility in welding flows based on tin or tin-lead alloys. However, the usual coating procedures in aqueous solutions require the use of strong inorganic acids which produce a chemical attack of Cu tracks. This is a significant disadvantage in the application of this procedure in electronic industry.

According to the trends of identification and development of cleaner technological alternatives and taking into account the environmental and human health protection, the ionic liquids (ILs) represent attractive electrolyte media for a large range of metallic coatings which recently has included the silver, involving both electrochemical and chemical procedures [1-7].

He *et al.* [2] investigated the electrochemical deposition of Ag from either hydrophobic 1-n-butyl-3-methylimidazole hexaphluorophosphate ($BMIMPF_6$) or hydrophilic 1-n-butyl-3-methylimidazole tetrafluoborate ($BMIMBF_4$) as ionic liquid media. These authors used cyclic voltammetry and potentiostatic transient techniques, working with glassy carbon electrodes. From the recorded transients, the electrochemical process of Ag deposition from the above ionic liquids has been found to take place through a 3D nucleation with diffusion controlled semispherical growth. It has been proved that the viscosity of ILs, as well as miscibility with water, may influence the properties of obtained Ag coating. From morphological point of view, the AFM microscopy investigations [2] showed that the Ag deposit is bright and dense, having clusters less than 100 nm; these findings correspond to the islands growth model.

Bomparola *et al.* [7] reported the electrochemical formation of Ag deposits from $BMIMBF_4$ ionic liquid, at low overvoltages or currents. Decorative thin coating layers of about 0.3 μm thickness were obtained using a commercial Cu substrate. Although this IL is considered as water stable one, the long time exposure at atmospheric humidity determines its partial decomposition and the formation of aggressive HF acid.

Other ionic liquids with more stable anions, such as trifluoromethylsulfonate ($CF_3SO_3^-$), bis(trifluoromethylsulphonyl)amide [$(CF_3SO_2)_2N^-$] or tris(trifluoromethylsulphonyl)metide [$(CF_3SO_2)3C^-$] were also investigated. Thus, Zein El Abedin and Endres [4] reported the electrodeposition of Ag nano-crystalline films from stable ionic liquids based on 1-ethyl-3-methyl-imidazole trimethylsulphonate [EMIm]TfO, with Ag trimethylsulfonate as sourse of cations. Porous Ag deposits of about 4 µm, with a nodular morphology constituted by nano-crystallites agglomerations have been obtained after 2 hours electrolysis on glassy carbon under potentiostatic conditions.

Abbott *et al.* [1,3] reported for the first time the electroless Ag deposition on Cu from choline chloride – ethylene glycol ionic liquid containing Ag^+ ions. This is a technological procedure with reduced impact on environment. The choline chloride – ethylene glycol mixture has good stability vs. air and water and does not require additional manipulation measures. Ag deposition on Cu takes place due to: (a) the thermodynamic reduction of Ag^+ ion, and (b) Cu dissolution (resulting Cu^+ ion). These processes are determined by the difference in the redox potentials of the two involved couples. $Ag(CH_3COO)$, $AgNO_3$, Ag_2SO_4 and AgCl have been tested as silver salts at similar concentrations of about 10 mM. The best results have been obtained when AgCl was used, when bright and adherent Ag deposits resulted. The authors found that the nucleation and crystal growth mechanisms for Ag on copper are fundamentally different in ionic liquids in comparison to aqueous solutions. Thus, the deposition of up to 5 µm Ag layers in ionic liquids became possible because the deposit was porous and Cu^+ ions could diffuse from the substrate surface through pores or channels of the silver coating. The obtained experimental results supported a deposition mechanism involving a rapid nucleation followed by a slower growth step, that suggests a mass transport limitation. The adherence of Ag layer was adequate to prevent Cu substrate corrosion, thus the welding procedures on printed circuits tracks being successfully tested.

Preliminary investigations regarding the growth of Ag layers onto Cu substrates from choline chloride based ionic liquids involving either electrochemical or chemical procedures are reported in the present paper. Some aspects regarding the synthesis of different types of Ag based ILs and their physical characterization are also discussed.

2. Experimental

All chemical reagents (choline chloride, urea, triethanolamine, ethylene glycol, silver nitrate and silver chloride) were of p.a. quality (Aldrich) have been used without any additional purification for synthesis of ionic liquids. A homogeneous colorless ionic liquid was obtained by mixing choline chloride (a quaternary ammonium salt, 2 hydroxy-ethyl-trimethyl-ammonium chloride, $C_5H_{14}NOCl$) with hydrogen bond donor species such as urea, triethanolamine or ethylene glycol and heating at above 90^0C for 30 min. In these ILs, silver salts ($AgNO_3$, AgCl) were easily dissolved by stirring.

The composition of IL systems is shown in Table 1.

Table 1

Ionic liquids systems based on choline chloride for silver deposition

Deposition method	Symbol and system type	Ag salt concentration (mol/L)	IL appearance
Electro-chemical	**(ILAN)** choline chloride–urea (1:2 molar ratio) + $AgNO_3$	0.03	colorless transparent liquid above 25^0C
		0.07	colorless transparent liquid above 35^0C
	(ILA) choline chloride–urea (1:2 molar ratio) + $AgNO_3$	0.11-0.47	colorless transparent liquid above 50^0C
	(ILAC) choline chloride–urea (1:2 molar ratio) + AgCl	0.03	yellowish transparent liquid above 25^0C
		0.07	
		0.10	yellowish transparent liquid above 30^0C
		0.20	
	(ILA – ILT) choline chloride–urea (1:2 molar ratio) mixed with choline chloride-triethanolamine (1:1 molar ratio) in various volume ratios: 2.5:1; 5:1; 25:1 + $AgNO_3$	0.08-0.33 (2.5:1)	colorless transparent liquid above 25^0C
		0.09-0.39 (5:1)	
		0.10-0.46 (25:1)	
Chemical (Electroless)	**(ILAC)** choline chloride–urea (1:2 molar ratio) + AgCl	0.03	yellowish transparent liquid above 30^0C
		0.07	
		0.10	
		0.20	
	(ILEG-AC) choline chloride– ethylene glycol (1:2 molar ratio) + AgCl	0.03	yellowish transparent liquid above 25^0C
		0.07	

The following physical properties of ILs from Table 1 have been determined: melting and freezing temperature, consistency, stability in time. Temperature dependence of their electrical conductivity, using a WTW 340i model conductometer probe with the cell constant K=0.469 cm^{-1}, was also investigated.

To investigate the electrochemical behavior of IL, cyclic voltammograms have been recorded at scan rates in 10-200 mV/s range, using a Autolab PGSTAT 302 EcoChemie equipment. The electrochemical cell (50 cm^3) contained a Pt foil (0.5 cm^2) as working electrode, a large platinum plate (4 cm^2) as auxiliary electrode, and a Ag wire as quasi reference electrode.

In order to obtain Ag deposits, Cu sheets of 35x70 mm and electrolytic purity were used as metallic substrates. Their initial surface treatment involved a chemical pickling in 1:1 (vol.) HNO_3:H_2O solution for 10-30 s at 25^0C, followed by rinsing with water and drying. In case of electrochemical deposition a graphite counter electrode was used. Chemical (electroless) deposition was acomplished for periods of 10-30 min. immersion.

The quality of Ag coatings obtained from the investigated ILs has been evaluated from adherence and appearance points of view. XRD measurements were also performed in some cases using a Brucker AXS D8 ADVANCE equipment under Cu K_{α} radiation. Optical microscopy investigations using OPTIKA B-253 equipment with a digital EverFocus Model EQ250 video color camera have been made to analyze the layers morphology. The influence of ILs temperature has been investigated between 20 ^{0}C and 80 ^{0}C.

3. Results and discussion

3.1. Synthesis and characterization of ionic liquids systems containing Ag salts

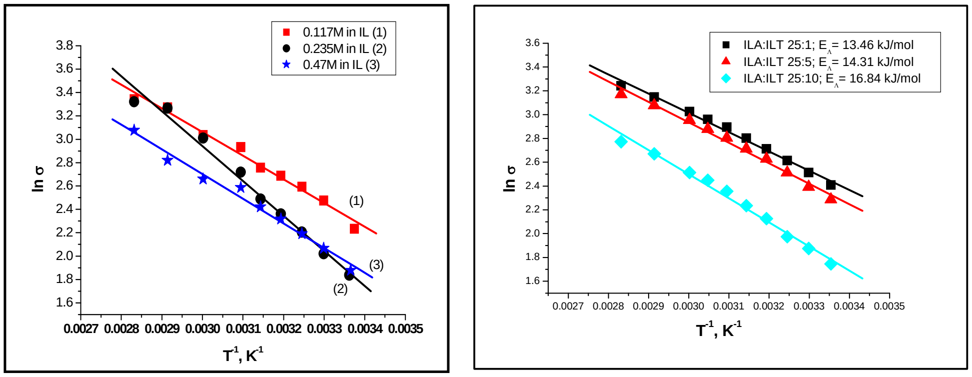
The deep eutectic of choline chloride : urea mixture in 1:2 molar ratio has been prepared as ionic liquid medium (solvent, IL) and then various $AgNO_3$ or AgCl amounts have been added, in the concentration range 0.03M – 0.47M (Table 1). When the silver salt is added in the ionic liquid the color varies from white to light violet at air-solution interface. As the mixture is further heated for several minutes at 60-80^{0}C and with continuous stirring, the salt dissolves with a slight ammonia release. Finally, the obtained ionic liquid is transparent and keeps its liquid state at room temperature. The electrolytes prepared with $AgNO_3$ (ILAN, ILA and ILA-ILT) have a colorless appearance whereas the electrolytes prepared with AgCl additions (ILAC and ILEG-AC) are yellow. If the content of added salt is relatively high, of about 0.47-0.5M, the formed ionic liquid shows a high time instability materialized through the formation of a grey-black precipitate at the bottom of the vessel; this precipitate is then dissolved during heating and stirring leading again to a transparent liquid. Equimolar mixtures of choline chloride : $AgNO_3$ have proved to be very instable and with explosion hazard on heating.

Usually, the electrical conductivity of both ILAN and ILA systems was in the range of 6-30 mS/cm (the ILA containing 0.23M $AgNO_3$ being slightly more conductive) for the investigated temperature domain, 20-80^{0}C. It was tested if the ionic liquid conductivity (σ) depends on temperature (T) according to an Arrhenius equation (1):

$$\ln\sigma = \ln\sigma_O - \frac{E_\Lambda}{RT} \tag{1}$$

where E_Λ is the activation energy for electrical conduction [8], σ_0 is a pre-exponential parameter, R – the ideal gas constant. Figure 1 shows some examples of ln σ *vs.* 1/T straight lines obtained for investigated systems of ILs containing

$AgNO_3$. Activation energies values between 13 – 25 kJ/mol have been determined from the slopes of these linear dependences.



(a) (b)

Fig.1 – Arrhenius semilogarithmic plots for $AgNO_3$ containing ionic liquids:
(a) ILA with $AgNO_3$ in different concentrations;
(b) ILA – ILT with 0.168M $AgNO_3$ (2.5:1), 0.196M $AgNO_3$ (5:1 and 25:1)

3.2. Electrodeposition of Ag layers from choline chloride based ionic liquids

There is a lack of information in literature regarding Ag electrochemistry in choline chloride-urea based ionic liquids. Several cyclic voltammetry experiments have been performed by us to illustrate the electrochemical reversibility of Ag/Ag^+ couple and most of the results have been reported in [9]. Figure 2 shows examples of cyclic voltammograms at different scan rates recorded for a Pt working electrode. Starting from the stationary potential (0 V *vs.* Ag quasi reference electrode), all curves show clearly the beginning of cathodic deposition process with a current peak located at electrode potentials in the range -0.1 ÷ -0.3V, followed by a quite large potential region of limiting currents.

By further polarizing of the Pt electrode (not shown here) a continuous increase of cathodic current at potentials more negative than -1.2V was recorded, proving a supplementary process of the ionic liquid solvent together with the massive deposition of Ag on working electrode. In all voltammograms, by returning the electrode potential in the anodic direction a single well pronounced peak was obtained, with a peak potential located at +0.2 ÷ +0.4 V. This clearly seen anodic peak having the increasing amplitude for higher concentrations and scan rates is surely due to the silver stripping process onto the platinum electrode. The increase of current at potentials more positively than +1.2V (not shown, too) was attributed to the anodic process of supporting electrolyte, being probably the chlorine evolution.

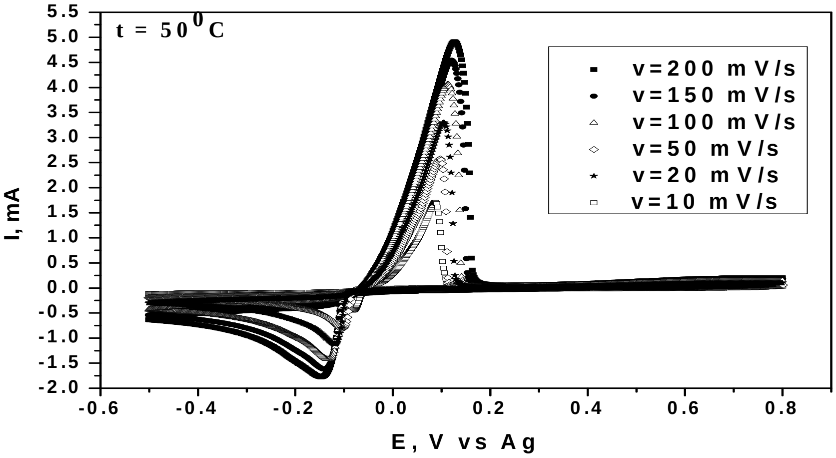


Fig.2 - Cyclic voltammograms for Pt electrode (0.5 cm^2) in ILA containing 0.03M $AgNO_3$ with various scan rates, 50^{0}C

The electrochemical deposition of Ag onto a Cu substrate has been tested for temperatures in the range 25-80^{0}C using various ionic liquids, as detailed in Table 1. Usually, the experiments showed a difficulty to electrodeposit the Ag layer, mainly due to the instantaneous nucleation process that determines the formation of a powdery deposit which further impedes a suitable adhesion. However, it should be mentioned that the ILA-ILT systems (ionic liquids containing supplementary triethanolamine, see Table 1) allowed the formation of light grey silver coatings, with a good adherence and uniformity. The operation parameters were: 70-80 ^{0}C working temperature, 30-60 min electrolysis time, 1 V voltage and about 25 mA/cm^2 current density. Figure 3 presents an example of optical microscopy image of the obtained silver deposit.

As Figure 3 shows, an ordered and uniform coating has been formed that entirely covers the metallic substrate. XRD measurements were carried out to get more information on composition and structure. According to the X-ray diffraction patterns the deposit is formed of pure Ag. However, owing to its small thickness there are also evidenced the characteristic peaks at angles (2θ) corresponding to the Cu substrate, as it can be seen in Figure 4.

Based on XRD measurements the average sizes of crystallites of 28-35 nm dimensions have been estimated for pure Ag deposits.

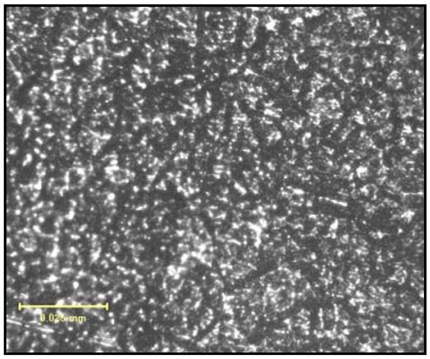


Fig. 3 – Optical micrography image of a silver coating electrodeposited onto Cu surface using ILA-ILT system for 5:1 volume ratio and 0.196 M $AgNO_3$, 80^0C, 25 mA/cm^2, 30 min.; x 50 magnification

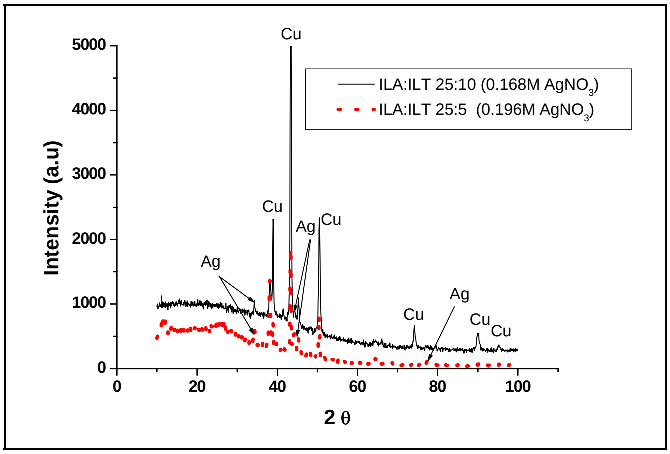


Fig. 4 – X-ray diffractograms for electrodeposited Ag from two ILA-ILT systems; electrolysis conditions: 25 mA/cm^2, 70 ^0C, 60 min.

3.3 Chemical deposition of Ag coatings from choline chloride based ionic liquids

Electroless deposition procedure has been also used to obtain Ag coatings with a suitable quality, using ionic liquids based on either choline chloride – urea (ILAC) or choline chloride - ethylene glycol (ILEG-AC) as deep eutectics; Ag^+ ions have been provided from AgCl as Ag source. The coatings on Cu substrates from choline chloride - ethylene glycol were formed chemically at lower working temperatures than in electrochemical procedure.

Tables 2 and 3 present the tested operation parameters and the properties of formed deposits from ILAC and ILEG-AC ionic liquids systems (see also Table 1 for IL symbols).

Table 2

The operation parameters and Ag coatings appearance in chemical deposition procedure using ILAC ionic liquid

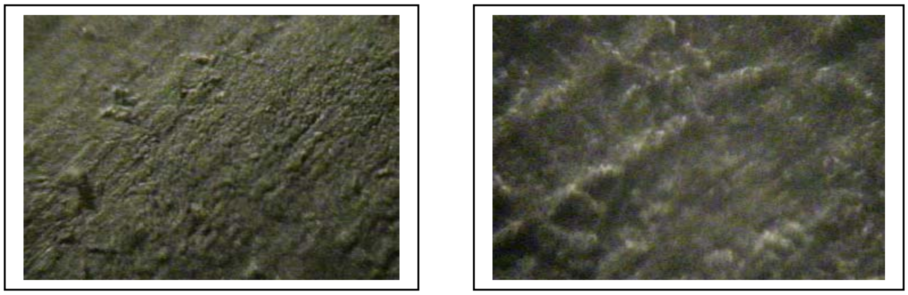
Components in ionic liquid and composition	Working temperature, ^{0}C	Immersion time period, min.	Appearance
choline chloride–urea (1:2 molar ratio) + 0.03M AgCl	30	10	Thin, adherent, uniform deposit, various shades of grey (silvery)
		20	
		30	
	40	10	Thin, adherent, uniform deposit, various shades of grey (silvery)
		20	
		30	
	60	10	Bright, thin, adherent, uniform deposit, light silvery
		20	
		30	
	70	10	Bright, thin, adherent, uniform deposit, light silvery
		20	
		30	
choline chloride–urea (1:2 molar ratio) + 0.07M AgCl	30	10	Thin, adherent, uniform deposit, mat white
		20	
		30	Bright, thin, adherent, uniform deposit, light silvery
	40	10	Bright, thin, adherent, uniform deposit, light silvery
		20	Thin, adherent, uniform deposit, mat white
		30	
	60	10	Bright, thin, adherent, uniform deposit, light silvery
		20	
		30	
	70	10	Bright, thin, adherent, uniform deposit, light silvery
		20	
		30	
choline chloride–urea (1:2 molar ratio) + 0.10M AgCl	30	10	Mat, thin, adherent, uniform deposit
		20	
		30	
	40	10	Mat, thin, adherent, uniform deposit
		20	
		30	
	60	10	Bright, thin, adherent, uniform deposit, light silvery
		20	
		30	
	70	10	Bright, thin, adherent, uniform deposit, light silvery
		20	
		30	

Table 3

The operation parameters and Ag coatings appearance in chemical deposition procedure using ILEG-AC ionic liquid

Components in ionic liquid and composition	Working temperature, ^{0}C	Immersion time period, min.	Appearance
choline chloride – ethylene glycol (1:2 molar ratio) + 0.03M AgCl	30	10	Very bright, dense, thin, adherent, uniform deposit, light silvery
		20	
		30	
	40	10	Very bright, dense, thin, adherent, uniform deposit, light silvery
		20	
		30	
choline chloride – ethylene glycol (1:2 molar ratio) + 0.07M AgCl	30	10	Very bright, dense, thin, adherent, uniform deposit, light silvery
		20	
		30	
	40	10	Very bright, dense, thin, adherent, uniform deposit, light silvery
		20	
		30	

As it can be seen from Tables 2 and 3 both investigated systems for electroless deposition led to uniform Ag coatings with a very good adherence to the Cu substrate. As regards the thickening rates, it should be mentioned that they are quite slow, up to 20-30 nm/min. It should be however evidenced the ILEG-AC system based on choline chloride-ethylene glycol eutectic as solvent that allows the formation of very bright, compact and uniform deposits at both working temperatures (30 and 40 ^{0}C). Figures 5 and 6 show some examples of optical micrographs for the obtained Ag layers using chemical deposition procedure.



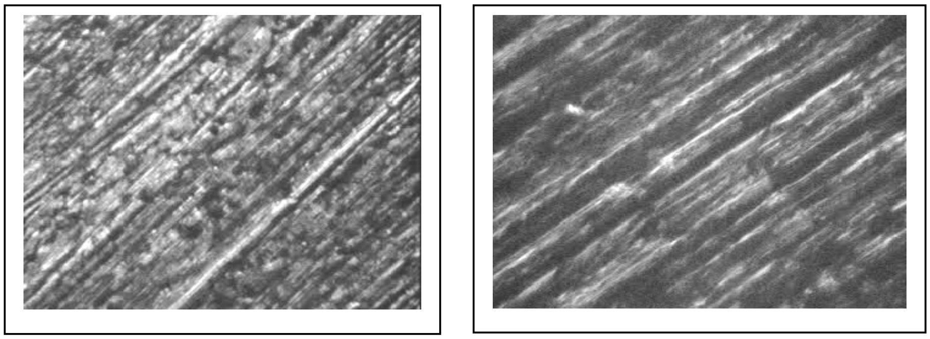
(a) (b)

Fig.5 - Optical micrographs for an Ag coating deposited chemically on Cu from ILAC system with 0.1M AgCl at 70^{0}C for 10 min.; magnifications: (a) x 200; (b) x 400

The growth of silver layer onto Cu surface suggests a process that takes into account a reversible chemical displacement reaction that may occur between the two metals according to the differences in their redox potentials. Thus, the following reaction may be written:

$$Ag_{IL}^{+} + Cu(s) \rightleftarrows Cu_{IL}^{+} + Ag(s) \qquad (2)$$

where Ag^{+}_{IL} , Cu^{+}_{IL} represent the solvated ions in the ionic liquid and Cu(s), Ag(s) are atoms in solid metallic phases.



(a) (b)

Fig.6 - Optical micrographs for an Ag coating deposited chemically on Cu from ILEG-AC system with 0.03M AgCl at 30 ^{0}C for 10 min.; magnifications: (a) x 200; (b) x 400

The electroless deposition process seems to be limited by mass transport within the Ag layer. When the entire metallic surface is covered by a compact Ag layer, there is no longer access of silver ions from ionic liquid towards Cu substrate and thus there is not possible for Ag^{+} ions to migrate within the layer. These findings are in good accordance with Abbott's data [1,3] who reported a similar mechanism; however, the reported deposition rates were improved due to a rough and porous nature of the silver layer that allowed to reach relatively higher thicknesses, up to several microns. Thus, future experiments need to be performed to optimize deposition efficiency and layer thickness as well.

4. Conclusions

Our preliminary investigations showed the possibility of preparation of various Ag containing ionic liquids using deep eutectics of choline chloride – urea (ILAN, ILA, ILAC) or choline chloride – ethylene glycol (ILEG-AC) mixtures; the formed low temperature ionic liquids are characterized by a good stability in time.

The ionic liquid system involving choline chloride, urea and triethanolamine (ILA-ILT system) allowed successful electrochemical deposition of Ag layers with good quality and adherence to the Cu substrate.

The chemical procedure applied to form Ag coatings facilitated formation of uniform, thin and adherent layers with an increased brightness and compactness in the case of choline chloride - ethylene glycol mixture (ILEG) used as solvent. The slow deposition rates, of *cca* 30 nm/min, are probably due to a limited mass transport of silver ions through the compact layer towards the metallic substrate. Further experiments to acquire more information on the deposit composition and deposition mechanism as well as to optimize the deposition procedures need to be performed.

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