Obtaining and Structural Characterization of the Electrodeposited Metallic Copper from Ionic Liquids

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The present study deals with electrodeposition of copper from four different choline chlorides (ChCl) based ionic liquids (IL) as environmentally friendly electrolytes. Firstly, we prepared the ChCl-A (1:2 and 1:1) M based ionic liquids (A=Urea, Malonic acid, Oxalic acid, Ethylene glycol) and then measured the density, viscosity and conductivity of these mixtures. These ionic liquids have the great advantage of air and moisture stability in time. The solubility of $CuCl_{2(anh)}$ *and electrodeposition of Cu in these mixtures were performed. The working parameters along with the time and appearance of the obtained copper deposits were followed during the electrolysis process. Finally, the best deposits were studied by micrographic techniques. By X-ray method in* CuK_α*-radiation at room temperature is studied the crystal structure features of the cooper deposited on substrate from industrial steel using the method described in works. The thickness of the coating is determined. The unit crystalline cell values of thin cooper layers on steel are determined. The influence of the elecrodeposition conditions on crystalline ordering is also studied. Of the four electrolytes studied it was found that better deposits (fine, homogenous and adherent) were obtained in ChCl-Oxalic acid and ChCl-Ethylen glycol.*

Keywords: copper electrodeposition, XRD, ionic liquids, choline chlorine

The development of different areas of technology increases requirements for the chemical and electrochemical coatings needed for the ecological safety of obtaining such coatings. Electrodeposition of copper is essential for a variety of industrial and decorative purposes. Commercial copper electroplating is based on aqueous solutions which have high solubility for electrolytes and metal salts resulting in highly conducting solutions. Metal electrodeposition represents a significant domain for various industries. In the actual industrial practice, electrochemical surface treatments are based on aqueous solutions. The interest for the investigation of electrolysis in nonaqueous, organic media has risen in the last years. Moreover, the possibility to use media with melting temperature below 110° C has led to employing ionic liquids (ILs) for electro-deposition [1,2]. The advantages of ILs are: low cost, easy to prepare, stable to water attack and high solubility for metals compounds.Metal electrodepositions in ILs are divided after the ILs used as such ionic liquids stable against air and water and deep eutectic solvents (DES) which are ILs based on usual products like choline chloride (ChCl) that are easily handled even in the air. Electrodeposition in a special class of eutectic solvents/ionic liquids based on low cost products, such as choline chloride, is now of great interest. Ionic liquids based on ChCl have the advantage that this compound is a non-toxic and biodegradable one (also called vitamin B4) which is produced on an industrial scale at a low cost. As many ILs are environmentally friendly, they are considered as suitable alternatives for the poisonous plating baths.

In the present work, we present a study on copper electrodeposition from some ChCl-based ionic liquids. This technique is one ecological enough as the ILs used are non- or just a little toxic: ChCl, urea, malonic acid, oxalic acid and ethylene glycol. These Ils have the great advantage of a good stability against air and humidity for a long time. Purpose of the work is the study of obtaining and characterization of the layers crystal structure of different thickness of copper deposited from the ionic liquids to the substrate of electrotechnical steel.The copper electrodeposition was studied in the following four ionic liquids: ChCl-A (A=urea, malonic acid, oxalic acid, ethylene glycol) of composition (1:1) and (1:2) M. $CuCl_{2(anh)}$.

Experimental part

The ionic liquid is obtained relatively easy by mixing the two salts (pre-weighed for the corresponding compositions): ChCl-urea(1:2) M and ChCl-A(A=malonic acid, oxalic acid, ethylene glycol) (1:1) M under a slight heating at approximately 353 K. As our interest was to obtain some results which could be transferred to industrial practice, we used reagents of purity >98% as they come from the producers without other supplementary purification. All three ionic liquids ChCl-A (A=urea, malonic acid, ethylene glycol) were colorless, transparent liquids. We mention that ChCl-oxalic acid liquid has a higher consistency and ChCl-etylene glycol was very fluid and was prepared at a temperature <353 K. $CuCl_2$ (anhydrous) was added to the obtained ILs and solutions were homogenized with a glass rod under a slight heating at <353 K.The experimental set-up for copper electrodeposition from the above mentioned ILs was made of a stabilized power source (with current and tension displays), a multimeter for a precise current measurement, a glass cell (Berzelius flask) thermostated at ~353 K by means of magnetic heater provided with thermovertex (the cell was introduced in a glass with silicon oil). ChCl-A-$CuCl_2$ mixture was prepared in the glass electrolysis cell and the two electrodes were introduced: one made of high purity graphite (plate) of dimension comparable those of

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Table 1
DENSITY, ELECTRICAL CONDUCTIVITY AND VISCOSITY DATA OF THE STUDIED IONIC LIQUIDS AT 353 K.

Ionic Liquid	Density ρ(g×cm^{-3})	Electrical conductivity κ(mS×cm^{-1})	Viscosity η(cP)
ChCl-urea	1.172	6.135	33.570
ChCl-malonic acid	1.500	2.210	69.069
ChCl-oxalic acid	1.133	12.812	13.804
ChCl-etylene glycol	1.029	15.165	9.139

Table 2
WORKING PARAMETERS FOR THE ELECTROLYSIS AT 353 K TOGETHER WITH TIME AND DEPOSIT ASPECT OF SAMPLES X1, X2.

Sample	i (A×cm^{-2})	t (min)	Aspect of the deposit
X1	200	30	The deposit is obtained with a large grain size and uneven, very little sticky, scratchy and dull.
X2	100	30	The deposit is rough, dull, but more homogeneous

i=current density; t= time

the working electrode (metal plate with high Si content).The current density was calculated for each experiment. Micrographic studied by means of a Hund microscope provided with a videocamera generating the images (magnification x 100 ÷ x 400) was connected to a PC for automatic acquisition. The thickness of copper coatings is determined with the aid of compact inverted metallurgical microscope GX41 with the accuracy of ±0,1 mcm on the polished end face of the substrate from sheet electrotechnical steel and substituted layer.The study of the copper coatings crystal structure is executed in CuK$_\alpha$-radiation by the modified diffractometer DRON-2 in the survey X-ray photographs regime by the points. For X-ray photographs obtaining of all samples is used survey regime: the information collection time at the point $\Delta\tau = 3$ s, the angle scanning step $\Delta 2\theta = 0.03$ degree. With the determination of the elementary crystalline cell parameters for obtaining the clearer reflexes profiles for the purpose of an increase in the accuracy of the determination of their angular positions was used the next survey regime: $\Delta\tau = 5$ s, $\Delta 2\theta = 0.01°$.

Results and discussions

Metal salt solubility in IL is very important for the electrodeposition process. The anions and cations have weak coordination properties in ILs and therefore the salvation energy is not high enough to break the electrostatic interactions between ions or between metallic atoms from the metal salt. It is then to be expected that ILs to have a low solubility for metals and metallic salts. A good solubility for metallic oxides and salts has been noticed in the case of ChCl-based ionic liquids. We solubilized 0.05-0.5 M divalent copper as $CuCl_2$ (anhydrous) in the formed ILs. The copper chloride solubilized quite easily in all cases when a brown-yellow pale liquid was obtained for ChCl-A (A=urea, malonic acid, oxalic acid) and a green pale for ChCl-Etylene glycol. We mention that $CuCl_2$ solubilization in IL with ethylene glycol was easiest to achieve.The knowledge of a physical transport properties of these ionic liquids is very useful for employing them as electrochemical media. As such data were not available in literature for the studied systems we had to determine these properties at 353 K which was the chosen temperature for electrodeposition process [1,7]. The values for density, viscosity and electrical conductivity obtained for the studied systems are listed in table1 [8] and found to be in good correlation with other literature data [9].

The electrolitic process working conditions and aspect along with the X-ray measurements of the obtained copper deposits are dealt with in the following.

ChCl-Urea-$CuCl_2$ system

Working parameters for the electrolysis at 353K together with time, deposit aspect and sample images are listed in table 2. As the electrolyte foams abundantly during electrolysis the copper deposit is not homogenous.

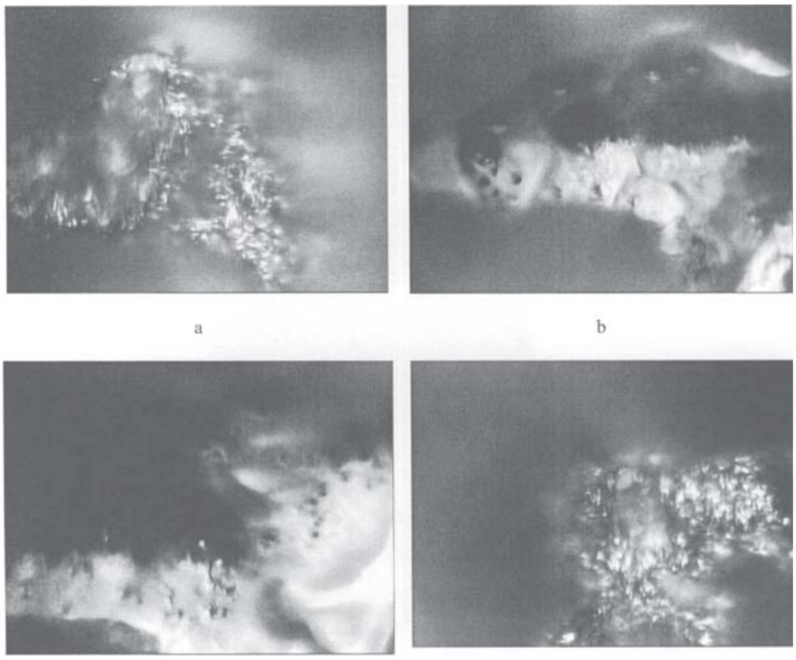
Micrographic studied (magnification x 400) for several sites on the copper deposit of sample X2 are presented in figure 1 and confirm the fact that copper deposit is not homogenous.

Besides electrolysis working parameters (c.d, t, time), preparation of the deposition substrate has a major importance. This is confirmed by the fact that micrographic image (x100) of the metallic substrate reveals much too many striations and nonhomogenities. Some thorough studies on metallic surface preparation are therefore to be made in the next stage of the study on Cu deposition from these ILs.

ChCl-Malonic acid-$CuCl_2$system

Electrolysis working parameters together with time, shape and image of the obtained Cu deposits are given in table 3.The following conclusion can be drawn from the above data: as current density and Cu^{2+} content in ChCl-malonic acid-$CuCl_2$ mixture are lower the copper deposit is finer and more homogenous. The deposit aspect changes on drying. The deposit is not uniform and nonadherent on a copper plate.

The way the samples are washed after electrodeposition is also important. If washing is done with distilled water the deposits oxidize in time, but if washing is done with distilled water and then acetone, they are less oxidized and remain clear. The sample P3 presented the best behavior as it maintaines the deposit aspect in time. A preliminary micrographic study was carried out in order in order to characterize the surface. The result is represented by the images in figure 2, taken on sample P3 (magnification x 40, x 100, x 400) in a single spot of the deposit chosen after a thorough microscopic investigation of the copper deposit on the metallic plate. These images show that copper deposit on the plate is not really homogenous.



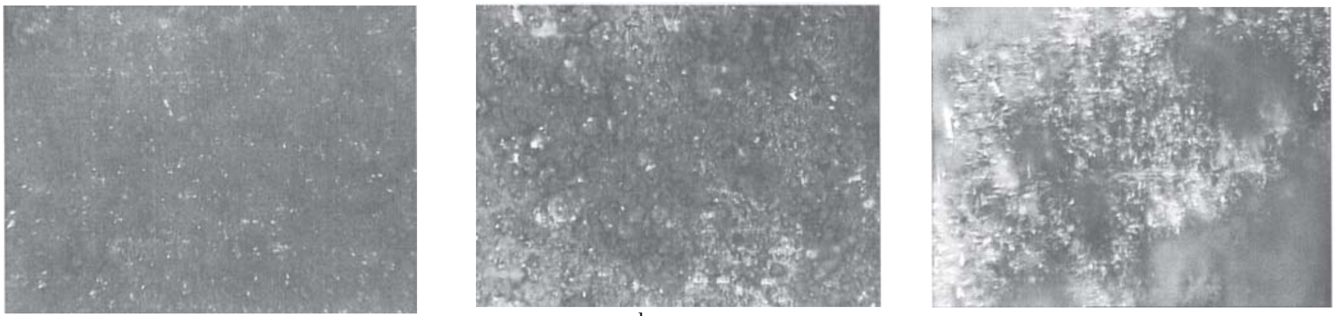
a b

Fig. 1. Micrographique images (x400) on different points of the sample X2

Table 3
ELECTROLYSIS PARAMETERS, DEPOSITS SHAPE AND IMAGE FOR THE SYSTEM ChCl-MALONIC ACID-$CuCl_2$ AT 353 K

Sample	$CuCl_2$ (M)	U (V)	i ($A \times cm^{-2}$)	t (min)	Aspect of the deposit
P1	0,5	10	0,1	35	Semi-adherent redish colour deposit, thick, falls off easily. Due to the intense foaming process,2 zones are noticed, one darker and the other lighter (at the upper part of the sample).In a thick layer, the deposit falls off in time.
P3	0,2	5	0,05	20	Adherent and uniform deposit with a small granulation. Two zones (one lighter at the upper part at the electrolyte interface) are present due to foaming.

i=current density; t= time; U=potential



a b c

Fig.2 Micrographic images on sample P3

a b c

Fig.3 Micrographic images on sample A4

Table 4
ELECTROLYSIS PARAMETERS, DEPOSITS SHAPE AND IMAGE FOR THE SYSTEM CHCL-OXALIC ACID-$CuCl_2$ AT 353 K

Sample	$CuCl_2$ (M)	U (V)	i ($A\times cm^{-2}$)	t (min)	Deposit aspect
A1	0,5	20	0,1	40	Nice deposit.(wet/dry), with small granulation and adherent to support. Liquid foams is forming during electrolysis.
A4	0,1	2,5	0,0125	50	Homogenous deposit (wet) and good enough even after drying. The color is due to the plate surface which was not uniformerly prepared prior to deposition.

i=current density; t= time; U=potential

Table 5
ELECTROLYSIS PARAMETERS, DEPOSITS SHAPE AND IMAGE FOR THE SYSTEM ChCl-OXALIC ACID-$CuCl_2$ AT 353 K.

Sample	$CuCl_2$ (M)	U (V)	i (Acm^{-2})	t (min)	Deposit aspect
E1	0,5	12	0,1	30	Deposit on both sides of the plate, spongious and abundant which fell off partially into the electrolyte. Liquid foams less than in the previous cases. Deposit which remained on the support is compact and maintains its shape and aspect after drying.
E2	0,5	2	0,005	40	Deposit with a very good adherence, glossy, thin (fine) and homogenous enough.

ChCl-Oxalic acid-$CuCl_2$ system

Working parameters of electrolysis together with time and aspect of the obtained deposits are listed in table 4, along with net and dry images of samples A1 and A4.

A preliminary micrographic investigation was carried out on A4 in order to characterize the deposit surface. The images in figure 3 were obtained at magnifications x 40, x 100, x 400 in a single spot of the copper deposit. All three images of sample A4 indicated a better homogeneity of the copper deposit which, in this case, proved to be more stable in time as well.

ChCl-Ethylene glycol-$CuCl_2$ system

The first thing noticed for this system was that the electrolyte is more fluid, fact confirmed by the above presented viscosity measurements. As it has also high electrical conductivity, it is to be expected that the electrolytic process proceeds more effectively in this medium.Table 5 summarizes the working conditions for electrodepositions, observations on the obtained deposits and sample images.

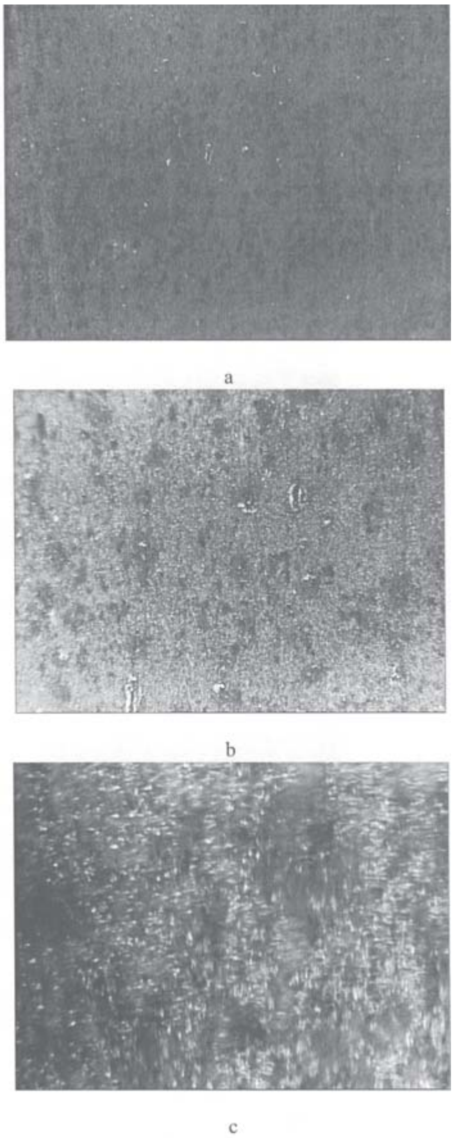
We mention here that sample E2 was obtained at 343-353 K, while for E1 the temperature was raised up to 373 K. The deposit on sample E1 is good on the well prepared side of the plate but coarse/nonadherent on the other, not thoroughly polished, side.In the case of sample E1, although current density was similar to that for samples P1 and A1, due to a higher current and during on electrolysis of only 30 min all copper in the electrolyte was consumed and this was why the deposit is was coarse and pulverulent and the electrolyte perfectly clear in the end. This electrolyte foams less than in other cases but leads to formation of a consistent and pulverulent copper deposit which is not adherent and falls off into the electrolyte.As electrolysis comes to an end all copper from electrolyte is consumed and deposited on the cell bottom and electrolyte is clearly seen. Sample E1 present a reddish adherent deposit on the surface parallel to the graphite anode which maintains its configuration after drying. A more adherent and glossy deposit is observed for sample E2, aspect formed also after drying. Both sample images on the deposition day after 5 days maintained their aspect in time even they got dried. Moreover, sample E2 is very adherent and quite glossy. Preliminary micrographic studies were performed on the E2 sample under the same conditions as those for the other samples and the obtained images are depicted in figure 4.

We conclude that sample E2 looks as being the most homogeneous and similar to other samples obtained in this ionic liquid, but glossier than them.

As a find conclusion we must conclude, after the micrographic study made after more then six month on the samples (A1, A3, P1, P3, E1 and E2) obtained by deposition from the ionic liquids ChCl-A (A=malonic acid, oxalic acid, ethylene glycol), that the best deposits obtained with a good stability in time were for samples P3, A4 and E1.

X-ray characterization of the copper deposits

The thickness of the copper layer, obtained under the different conditions during the deposition on electro-



a

b

c

Fig.4 Micrographic images on sample E2

technical sheet by the green technology method, was determined by the average value of ten measurements. The reason for the needed measurement results averaging is caused by the fact that the measurements of the coating thickness even in the close adjacent sections are distinguished on 0.2-0.5 mcm because of the dissimilarity of the “lobes” and “needles” sizes of Cu surface layers on the substrate plane. Depending on the regimes of synthesis and time of the reactions flow on the steel substrates the layers of copper of different thickness are synthesized. The measurements results of the thickness in three series A, E and P of the Cu coatings are given in table 6.

The X-ray photographs of the copper layers with a thickness of $d \approx 6.5$ mcm and $d \approx 2.2$ mcm are represented in figure 6.

The X-ray photograph of the sample A_1 in the angles range of $40° \leq 2\theta \leq 100°$ contains two series of the *hkl* reflexes. The large intensity (111), (200), (220), (311), (222), which correspond to the cubic crystal structure of the copper layer with the unit cell of space group S.G.: Fm $\overline{3}$ m [10], and also the reflexes of weak intensity (110), (200), (110), (211), (220), which correspond to the crystal structure of the Fe substrate with the unit cell of space group S.G.: Im 3 m [11]. The X-ray photograph of the A_4 model with the thickness of the copper layer $d \approx 2{,}2$ mcm in the angles range $40° \leq 2\theta \leq 100°$ also contains these two series of reflexes, but with completely different relationship of the *hkl* intensities. The decrease of the thickness of the copper layer from ~ 6.5 mcm to ~ 2.2 mcm leads to the sharp decrease of the reflexes intensity of Cu and the clearer manifestation of the substrate Fe reflexes. The analysis of the reflexes angular positions of the X-ray photographs on figure 6 showed that all *hkl* of the X-ray photographs for the A_4 composition were moved to the side of large angles in comparison with 2θ of the reflexes on the X-ray photograph for the A_1 sample. This makes it possible to draw the conclusion that the unit cell of the thinner copper layer has smaller volume, i.e., it is compressed with the decreasing of layer thickness. The reason for the compression of unit cell can be explained

Table 6

RESULTS OF THE THICKNESS MEASUREMENTS OF THE COPPER LAYER AND OF THE ELEMENTARY CRYSTALLINE CELL PARAMETERS

Set of samples	A_1	A_4	E_1	E_2	P_3
d, mcm	~ 6.5	~ 2,2	~ 4,5	~ 3,9	~ 5,9
a, nm	$0.3622_{(6)}$	$0.3617_{(5)}$	$0.3618_{(6)}$	$0.3617_{(8)}$	$0.3619_{(5)}$

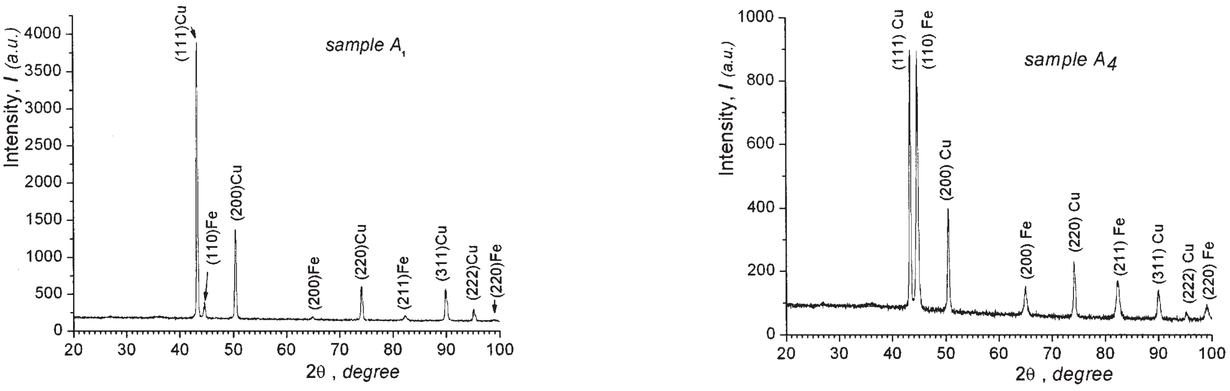
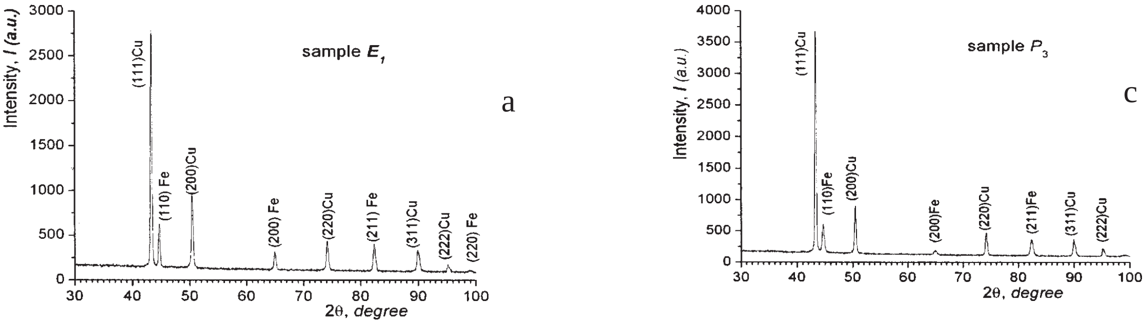


Fig.5 The X-ray photographs of the A series samples with the Cu layer coating thickness $d \approx$ 6,5 mcm (A_1) and $d \approx 2{,}2$ mcm (A_4) on the Fe substrate: a) A1; b)A4.

Table 7

ANGULAR POSITIONS AND THE INTENSITY OF THE Cu DIFFRACTION REFLEXES IN THE X-RAY PHOTOGRAPHS OF THE LAYERS OF DIFFERENT THICKNESS

Cu sample A_1			Cu sample A_4			Cu sample E_1			Cu sample E_2			Cu sample P_3		
2θ	I(*a.u.*)	*hkl*	2θ	I(*a.u.*)	*hkl*	2θ	I(*a.u.*)	*hkl*	2θ	I(*a.u.*)	*hkl*	2θ	I(*a.u.*)	*hkl*
43.25	3887	111	43.32	899	111	43.27	2890	111	43.31	2827	111	43.30	3627	111
50.39	1373	200	50.46	398	200	50.38	956	200	50.42	959	200	50.43	902	200
74.06	596	220	74.13	229	220	74.17	434	220	74.12	420	220	74.16	458	220
89.84	580	311	90.00	140	311	89.92	325	311	90.01	286	311	89.98	339	311
95.09	300	222	95.25	74	222	95.17	173	222	95.26	145	222	95.11	220	222



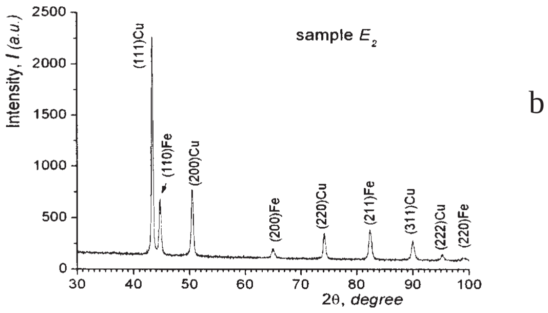


Fig.6 The X-ray photographs of the Cu layers of the samples of series E and P on Fe substrate: a) E1; b) E3; c) P3.

by the increase of quicker adhesion of Cu film to the substrate surface and by a difference in the space groups of the unit cells of the thin copper layers and Fe substrate. The parameters unit cells of copper of the layers A_1 and A_4 are given in table 7.

For determining the elementary crystalline cell parameter is used the expression for the cubic structure [12]:

$$\sin^2 \theta_{hkl} = \frac{\lambda^2}{4a^2}(h^2 + k^2 + l^2) \qquad (1)$$

where:

θ - the reflexes angular positions with *hkl* indices;

λ - for the CuK_α-radiation wave length.

On figure 7 are given the X-ray photographs of the Cu layers of the samples of series E and P, obtained with the varied synthesis conditions. The X-ray photographs analysis of all samples under investigation showed that the angular 2θ positions of the *hkl* reflexes of the Fe substrate are practically constant what cannot be said about the angular positions of *hkl* copper layers of different thickness of those obtained with different regimes of synthesis. Table 2 gives angular reflexes and *hkl* reflexes intensity of all investigated thin layers of copper coatings. .

X-ray studies showed that the composition of the coverings contains only copper, which is crystallized in the cubic structure of space group S.G.: F3m. This is confirmed by numerous studies of the Cu powders, performed earlier [7].

Conclusions

The method of metallic layers deposition (green of technology), proposed in the works corresponds to the high contemporary requirements of ecology. It is important to mention that this kind of study on copper electrodeposition from choline chloride based ionic liquids is the first presented in literature.Of the four electrolytes studied [ChCl-A(A= urea, malonic acid,oxalic acid and ethylene glycol)] for the electrodeposition of copper, it was found that the best deposits (fine, homogenous) and more adherent were obtained in ChCl-oxalic acid and especially in ChCl-ethylene glycol.It is also necessary to take a supplementary care of preparing of the metallic support of the process in all these mixtures of ionic liquids. Important information obtained from the X-ray study are the following: the thickness of the copper layer deposited from the ionic liquids on the substrate of electrotechnical sheet steel as a result of the varied conditions of synthesis and time of the flow of reactions are determined; the crystal structure of the Cu layers is studied. The results of X-ray studies make it possible to speak about the high quality both the cleanliness of copper layers in composition and crystalline ordering; the compression of the elementary crystalline cell of the structure of the copper layers with the decreasing of their thickness on Fe substrate is revealed. Our experiments have shown that it is possible to obtain good electrodeposits of copper on metallic substrate as a more or less adherent red-brown layer from choline chloride based ionic liquids as environmentally friendly electrolytes. Also we have to mention that this study is the first of this kind in literature on these ionic liquids.

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