

ELECTRODEPOSITION OF CHROMIUM COATINGS FROM A CHOLINE CHLORIDE BASED IONIC LIQUID WITH THE ADDITION OF WATER

Vyacheslav S. Protsenko¹, Lina S. Bobrova¹, Alexander S. Baskevich¹,
Sergey A. Korniy², Felix I. Danilov¹

¹Ukrainian State University of Chemical Technology
Gagarin Ave. 8, Dnipro, 49005, Ukraine
E-mail: Vprotsenko7@gmail.com

Received 13 June 2017
Accepted 20 December 2017

²Karpenko Physico-Mechanical Institute of the NAS of Ukraine
Naukova St. 5, Lviv, 79060 Ukraine

ABSTRACT

Chromium electrodeposition process was studied using a trivalent chromium plating bath on the basis of ionic liquid which consists of choline chloride, chromium (III) chloride and water additive in 2.5:1:x molar ratio, where $x = 6, 9, 12, 15$ or 18 . Cyclic voltammetry revealed that the increasing extra water content in the liquid mixtures causes the acceleration of hydrogen evolution reaction, and, consequently, the reduction of current efficiency of chromium electrodeposition. The favorable effect of extra water addition is associated with an increase in conductivity and a decrease in the electrolyte viscosity. The most suitable water content in ionic liquids seems to be in the range of $x = 9$ to $x = 15$. The current efficiency of chromium deposition increases with increasing the current density and decreasing the temperature, thus reaching 40 - 50 % in some cases. The choline chloride based ionic liquids with the addition of extra water allow obtaining uniform and bright chromium coatings with an amorphous type microstructure and nodular structure of the surface. The chromium plating baths under consideration can be used for the production of relatively thick chromium deposits (with a thickness of several tens microns) with microhardness close to the values required for industrial "hard chrome".

Keywords: trivalent chromium, electroplating, electrodeposits, ionic liquids, deep eutectic solvent, water addition.

INTRODUCTION

The electrodeposition of metal coatings using electrochemical systems containing deep eutectic solvents (DESs) is nowadays considered as a promising alternative to "usual" electroplating baths on the basis of both aqueous solutions and organic solvents [1 - 3]. DES is a special type of room temperature ionic liquids (ILs) which consists of a eutectic mixture of choline chloride (2-hydroxy-ethyl-trimethyl ammonium chloride, ChCl) and a metal salt or hydrogen bond donor species such as amides, glycols or carboxylic acids [2 - 4]. The charge delocalization occurring through hydrogen bonding between Cl⁻ anion and hydrogen donor molecules results in a decrease in the melting point of the liquid mixture as compared with the melting points of the individual constituents of DESs [1, 4 - 6].

Similarly to most ILs, deep eutectic solvents have wide electrochemical windows, negligible vapor pressure, high ionic conductivity, relatively high solubility of metal salts, thermal stability and inflammability compared to water electrolyte and non-aqueous solvents. At the same time, in contrast to most of the common room temperature ILs, DESs are relatively cheap, easily available and environmentally friendly [1 - 3]. All these favorable features make them very promising in various fields of application, especially, in electrochemistry and electroplating.

Among a great number of various metals which can be electrodeposited from DESs based electrolytes, chromium has a special place due to its wide application as a decorative, hard, anti-wear and protective coating [7 - 10].

The development of eco-friendly trivalent chromium electroplating baths as an alternative to highly toxic industrial hexavalent chromium electroplating is a key problem in modern surface engineering [10]. Thus, the European Union has issued the WEEE and RoHS directives to restrict Cr(VI) in electrical and electronic equipment. However, chromium is difficult to deposit from aqueous solutions based on trivalent chromium salts due to the complex aqueous solution chemistry of Cr(III) ions compounds [8, 11]. In this context, DESs based Cr(III) plating baths look very promisingly, although there have been only a few papers reported chromium electrodeposition using these type of ILs.

Abbott et al. used the eutectic mixture of ChCl and $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (in a 1:2 molar ratio) to electrodeposit chromium [3, 12]. The amorphous pale blue/grey coatings were crack-free but relatively soft (242 Vickers [12]), they could easily be removed from the substrate during wear test. Amorphous dark grey coatings with enhanced microhardness were also obtained from the DES based bath containing urea and hydrated chromium (III) chloride [13].

An important paper by Ferreira et al. [14] reported the electrochemical behavior of an ionic liquid formed between choline chloride and chromium chloride hexahydrate (2.5:1) containing 20 mass % of added water. Bright chromium deposits were obtained from this Cr(III) ionic liquid. However, the choice of the accepted water content (20 mass %) was not justified and the influence of water content in the bath on physicochemical properties of electrolyte and chromium electrodeposition was not investigated.

In a number of recent publications [15 - 19] a beneficial effect of extra water addition on some physicochemical properties of chromium baths containing DESs has been shown. Thus, McCalman et al. [16] reported the effect of water addition on speciation, conductivities and diffusivities in the mixtures of $\text{CrCl}_3/x\text{H}_2\text{O}/y\text{ChCl}$ ($y = 0.5$ or 2.5). The values of x in the range 9 - 18 showed good reduction in cyclic voltammograms experiments. However, the effect of water content on current efficiency and deposit properties has not been studied.

The influence of water upon density, viscosity, conductivity, and surface tension of ionic liquids was established for the ionic liquids containing chromium chloride (as hexahydrate salt), choline chloride and water in the molar ratios of 1:0.5: x and 1:2.5: x where

x is equal to 6, 9, 12, 15 or 18 in the temperature range of 25 to 80°C [17 - 19]. An increase in water content was shown to result in decreasing density, viscosity and surface tension and increasing conductivity, which is very important for the practical implementation of metal electrodeposition processes.

However, the effect of extra water addition on the characteristics of chromium electrodeposition has not been studied yet. The effects of water content in the ionic liquid containing the mixture of CrCl_3 , ChCl and H_2O on the current efficiency of chromium electrodeposition and on the properties of coatings obtained remain unexplored. This work is aimed to consider these important issues.

EXPERIMENTAL

Ionic liquids investigated in this work were formed from choline chloride (Aldrich, purity > 98 %), which was recrystallized from isopropanol, filtered and dried under vacuum, and chromium (III) chloride hexahydrate (Aldrich, purity > 98 %), which was used as received. The liquid mixture was prepared by mixing choline chloride and $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ in 2.5:1 molar ratio [19]. The mixture was kept in a thermostatic heater at 70°C and stirred until a homogenous, dark green liquid had formed. Then a required amount of bidistilled water was added to the mixture and stirred at the same elevated temperature to obtain a homogenous liquid mixture.

Thus, the ionic liquids $\text{CrCl}_3 + 2.5\text{ChCl} + x\text{H}_2\text{O}$ were investigated in this work, where x denotes the amount of water in the system (in molar ratio). It should be emphasized that x in our study denominates the total amount of water in the system, both originating from hexahydrate salt $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ and specially added to the mixture. The value $x = 6$ corresponds to the system without extra water.

The procedures of measurement of viscosity and conductivity have been described in previous works [17, 19]. Voltammetry measurements were performed by using Potentiostat Reference 3000 (Gamry). The ohmic potential drop was measured and automatically compensated by means of the built-in IR-compensator of the potentiostat.

Electrochemical experiments were carried out in a conventional glass three-electrode cell. The electrochemical cell was thermostated by a thermostat

Flüssigkeitsthermostate Baureihe U/UH8 (Prüfgeräte-Werk Medingen GmbH). The temperature was measured with an accuracy of $\pm 0.01^\circ\text{C}$.

A platinum disk ($\varnothing 5\text{ mm}$) in a glass holder was used as working electrode. A Pt wire was served as counter electrode and Ag pseudo-reference electrode was used.

In electrodeposition experiments, a common thermostated two-electrode cell was used. Chromium was deposited on a disk-shaped sample of copper foil ($S = 1.77\text{ cm}^2$) fixed in a plastic holder. Prior to each experiment, the surface of copper foil was polished by $0.05\text{ }\mu\text{m}$ alumina slurry and then thoroughly rinsed with HCl solution (1:1 vol.) and distilled water. Electrodeposition was performed at a constant value of current density. Platinum gauze was used in all experiments as an anode without separation of anodic and cathodic compartments. The current efficiency of chromium deposition reaction was calculated by comparing the weight gain of the cathode placed in the plating bath with that of a copper coulometer connected in series.

The surface morphology of Cr coatings was investigated by scanning electron microscopy (Zeiss EVO 40XVP) in secondary electron (SE) regimes. The chemical composition of the surface layers was determined by energy dispersive X-ray spectroscopy (EDX) coupled with SEM microscope (Oxford INCA Energy 350).

Chemical composition of chromium coatings has been also determined by means of common chemical analysis. To this end a weighted electrodeposited coating was completely dissolved from the substrate in aqueous

solution of hydrochloric acid (1:1 vol.). A further complexation of Cr(III) ions with EDTA formed extremely stable coloured complex, its concentration was determined by UV-Vis spectrophotometry (UV/Vis spectrophotometer SF-46, $\lambda = 540\text{ nm}$).

X-ray diffraction (XRD) analysis was carried out by means of an X-ray diffractometer DRON-3.0 in the monochromatized Co-K_α radiation.

Vickers microhardness (HV) test was performed by PMT-3 apparatus at a 100 g load, the coating thickness being not less than $20\text{ }\mu\text{m}$. The average value of the electrodeposits microhardness was calculated as a result of five separate measurements.

RESULTS AND DISCUSSION

A beneficial effect of water introduction into ionic fluids containing CrCl_3 and ChCl is illustrated in Tables 1 and 2 [19]. As can be seen, there is an appreciable increase in electrical conductivity and a decrease in viscosity when the content of H_2O grows. A possible explanation for this behavior has been provided in our previous works [17 - 19] in terms of hole theory that is used to explain the mobility of particles in ionic liquids [1, 12, 13]. The changes of conductivity and viscosity reported in Tables 1 and 2 are caused by an increase in the average hole size in ionic fluid with increasing water content in the mixture, which makes ionic motion considerably easier.

Meanwhile, extra water can remarkably affect the electrochemical processes occurring in these systems.

Table 1. Effect of temperature and water content on viscosity for $\text{CrCl}_3 + 2.5\text{ChCl} + x\text{H}_2\text{O}$ liquid mixtures [19].

Temperature, $^\circ\text{C}$	Viscosity, mPa s				
	$x = 6$	$x = 9$	$x = 12$	$x = 15$	$x = 18$
25	-	881.8	209.9	169.8	57.9
30	-	650.8	148.6	130.3	47.5
40	1958.7	336.9	86.9	77.2	31.0
50	959.5	170.8	54.6	47.8	21.0
60	396.2	100.6	34.8	31.6	15.0
70	209.3	58.6	23.8	22.0	10.7
80	118.7	39.8	17.0	16.0	8.5

Table 2. Effect of temperature and water content on conductivity for $\text{CrCl}_3 + 2.5\text{ChCl} + x\text{H}_2\text{O}$ liquid mixtures [19].

Temperature, °C	Conductivity, $\Omega^{-1} \text{m}^{-1}$				
	$x = 6$	$x = 9$	$x = 12$	$x = 15$	$x = 18$
25	0.022	0.174	0.553	0.804	2.107
30	0.028	0.211	0.660	0.983	2.681
40	0.058	0.360	0.983	1.301	3.456
50	0.111	0.632	1.500	2.158	4.254
60	0.192	1.053	2.158	2.949	5.600
70	0.369	1.361	3.160	3.687	7.373
80	0.575	1.843	3.814	5.027	9.029

To estimate this influence, the voltammetric curves recorded in $\text{CrCl}_3 + 2.5\text{ChCl} + x\text{H}_2\text{O}$ liquid mixtures have been examined. Fig. 1 shows the effect of water content on voltammograms of a Pt electrode in ionic liquids under consideration. The potential scan was started from open circuit potential (about 0 V vs. Ag quasi-reference electrode) in the negative potential direction, then reversed towards more anodic values and, finally, reversed in the direction of more negative potential values.

Earlier cyclic voltammetric responses in the mixture containing CrCl_3 , ChCl and H_2O have been investigated in works [14 - 16], where the nature of the current peaks in voltammograms was characterized. It was shown that

the reduction of Cr(III) ions occurs in two steps, Cr(III) to Cr(II) and Cr(II) to Cr(0), respectively [14], in much the same way as in aqueous Cr(III) electrolytes [8].

Taking into account all those findings, one can assert that the cathodic current peak at around -0.5 ... -0.9 V corresponds to the reduction of Cr(III) to Cr(II). Further increasing negative potential leads to a growth of current which can be attributed to the simultaneous processes of chromium deposition (via the discharge of Cr(II) intermediates) and hydrogen evolution reaction (HER).

After reversing the potential scan to the direction of more positive values, a crossover in i , E – curves is observed which is typical of nucleation and growth processes at metal electrodeposition reactions [14].

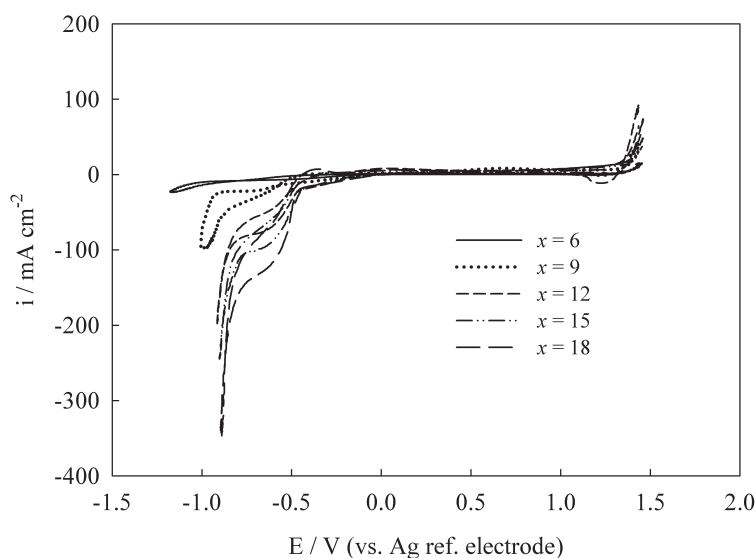


Fig. 1. Cyclic voltammograms recorded on Pt electrode in liquid mixtures $\text{CrCl}_3 + 2.5\text{ChCl} + x\text{H}_2\text{O}$. Scan rate 100 mV s^{-1} , temperature 70°C .

In addition, the recorded voltammograms revealed the presence of two weakly distinguishable broad reduction waves at ca. -0.4 V and ca. 0 V, which are related to the oxidation/stripping of metallic chromium formed during the forward (cathodic) scan and the oxidation of Cr(II) ions, respectively [14].

After complete stripping of the Cr deposit from Pt substrate continuous sweep to more positive potential values results in the growth of anode current at $E > \text{ca. } 1.2 \text{ V}$ which can be associated with oxygen evolution reaction on platinum. The successive potential reverse in the direction of more negative potentials shows the electrochemical behavior which is typical of Pt-electrode in choline chloride based DESs [20]: the reduction peak around +1.1 ... +1.2 V which is connected with the reduction of some components of DES.

It should be observed that each polarization curve in Fig. 1 was recorded using Ag pseudo-reference electrode placed in the same electrolyte as the working electrode and at the same temperature. Since the studied electrolytes contained different contents of water and, consequently, different concentrations of chloride ions, the equilibrium potential of Ag pseudo-reference electrode might somewhat change which would introduce the error in the measurements and result in incomparability of these i, E - curves. In order to clarify this issue, the potentials of Ag electrode in DESs with different contents of extra water were measured with respect to the Ag/AgCl-electrode saturated with KCl. The obtained results showed that the values of potential of Ag pseudo-reference electrode in ionic liquids containing various water concentrations are highly reproducible. The observed anodic shift of electrode potential with increasing x proved to be moderate (the change in equilibrium potential of about 50 mV when x increases from 6 to 18). Such a change is relatively small as compared with the corresponding influence of water addition on the position of the current waves of Cr(III) electroreduction. Therefore, as a first approximation, one may neglect these slight changes when analyzing the voltammetric responses.

The cyclic voltammetric curves recorded on Pt electrode in ionic liquids containing mixtures $\text{CrCl}_3 + 2.5\text{ChCl} + x\text{H}_2\text{O}$ revealed that the limiting current density of incomplete reduction of Cr(III) to Cr(II) increases with increasing water content which can be associated with a proper decrease in electrolyte

viscosity (see above). In principle, this feature might be favorable for acceleration of chromium electrodeposition reaction since increasing content of Cr(II) intermediates in the near electrode layer provides an increase in the rate of metal electrodeposition process [8]. However, one has to take into account that the cathodic current wave corresponding to the simultaneous processes of chromium deposition and hydrogen evolution reaction obviously moves towards the positive direction with increasing extra water content in the liquid mixtures (see Fig. 1). The acceleration of hydrogen evolution reaction is extremely undesirable as this leads to a decrease in current efficiency of chromium electrodeposition reaction and induces the processes of oxidation and formation of insoluble Cr(III) hydroxides blocking the electrode surface and deteriorating the coatings properties [8].

Thus, the introduction of water has both positive and negative effects. The results of the study of current efficiency and surface appearance of coatings corroborate this conclusion. Indeed, Fig. 2 shows that the current efficiency of chromium electrodeposition reaction drastically falls with an increase in water content in ionic liquid. This behavior is evidently due to appreciable acceleration of hydrogen evolution reaction with increasing H_2O content in electrolyte.

It should be noted that Fig. 2 as well as all following Figures does not contain the data concerning the current efficiency in the chromium plating bath with $x = 6$ (i.e. without added extra water). The problem is that using this electrolyte with a relatively low conductivity (see Table 2) is attended with a very high ohmic drop. Consequently, this will result in an inadmissibly high cell voltage which can reach 80 - 100 V, depending on the applied current density, temperature and distance between the electrodes. Evidently, such high cell voltages cannot be implemented by means of common commercial power supplies. Even if one applied high voltage power supply, local overheating due to intensive Joule heat would result in the impossibility of maintaining a required stationary bath temperature. Additionally, low electrical conductivity indicates reduced covering power of the plating bath, which is extremely undesirable for chromium electroplating [7, 10].

Taking into account these issues, we do not give any results of electrodeposition experiments for the system with $x = 6$ (without extra water addition). We think that the electroplating chromium baths based on DESs have no prospects of practical application if they

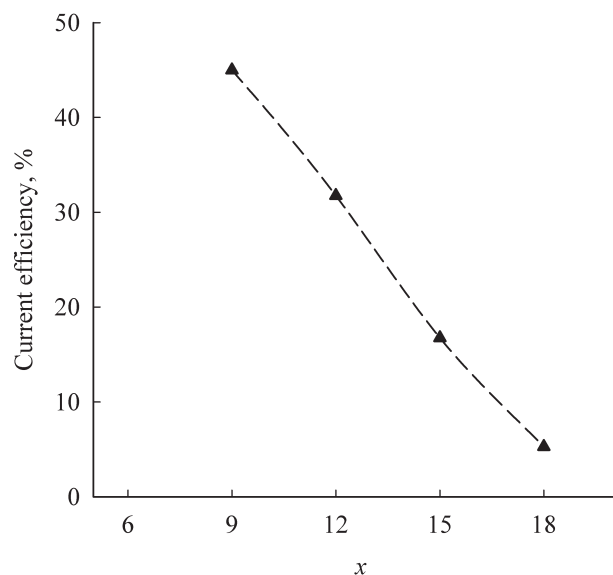


Fig. 2. Effect of water content in liquid mixtures $\text{CrCl}_3 + 2.5\text{ChCl} + x\text{H}_2\text{O}$ on current efficiency of chromium electrodeposition. Current density 3 A dm^{-2} , temperature 40°C , electrolysis duration 20 min.

do not contain some water addition.

At the same time, when the electrolyte contains a relatively high amount of water ($x = 18$), the current efficiency of metal deposition becomes too low ($< 10\%$). In addition, dark deposits with poor adhesion to the substrate are formed from the electrolyte with $x = 18$. This may be due to intensive formation of hydroxocompounds of Cr(III) caused by the HER. Traces of dark green films of Cr(III) hydroxides can be easily recognized visually on the electrode surface after deposition experiment, however, they can be removed from the surface by thorough rinsing with water. Thus, uniform Cr coatings with good adhesion to the substrate and relatively high current efficiency can be produced from the liquid mixtures of CrCl_3 , ChCl and H_2O only at some “intermediate” values of x in the range of about 9 to 15. Therefore, in all further experiments, chromium electrodeposition has been performed only from the electrolyte with $x = 9, 12$ or 15 .

The dependences of current efficiency of chromium deposition on the electrolyte temperature are shown in Fig. 3. The values of current efficiency diminish with electrolyte temperature which is typical of Cr electroplating baths [7, 9, 10]. It should be observed that temperature has no appreciable effect on the surface appearance of deposits: the coatings remain bright and

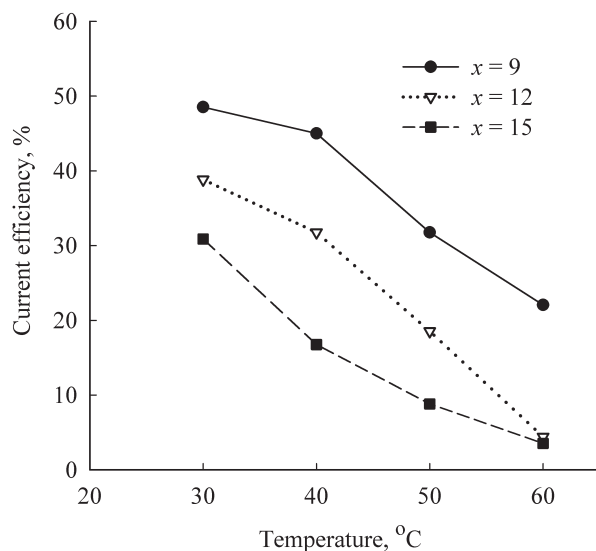


Fig. 3. Effect of temperature on current efficiency of chromium electrodeposition in liquid mixtures $\text{CrCl}_3 + 2.5\text{ChCl} + x\text{H}_2\text{O}$ with various content of water. Current density 3 A dm^{-2} , electrolysis duration 20 min.

uniform and have a good adhesion to the substrate when temperature increases from 30 to 70°C . Taking into consideration a favorable effect of temperature on viscosity and electrical conductivity on the one hand and a decrease in current efficiency with increasing temperature on the other, one can conclude that the most advantageous value of temperature should be about $40 - 50^\circ\text{C}$.

An increase in cathode current density leads to growing current efficiency of chromium deposition reaction (Fig. 4). This behavior is a characteristic feature of chromium plating processes both in hexavalent baths and in trivalent ones [7, 9, 10]. When the current density is more than ca. 10 A dm^{-2} , the deposits surface becomes rough and not bright enough. Additionally, the “burnings” occur on the coatings surface at higher current densities. Thus, the most suitable values of current density seem to be close to $3 - 7 \text{ A dm}^{-2}$.

The current efficiency of chromium electrodeposition and, hence, the rate of electroplating process only slightly diminish with electrolysis time (Fig. 5). It is a very important feature of the plating bath under consideration because it provides the possibility of obtaining not only thin “decorative” Cr layer (with a thickness of ca. $1 - 2 \mu\text{m}$) but also thicker metal films (with a thickness of several tens micrometers) which

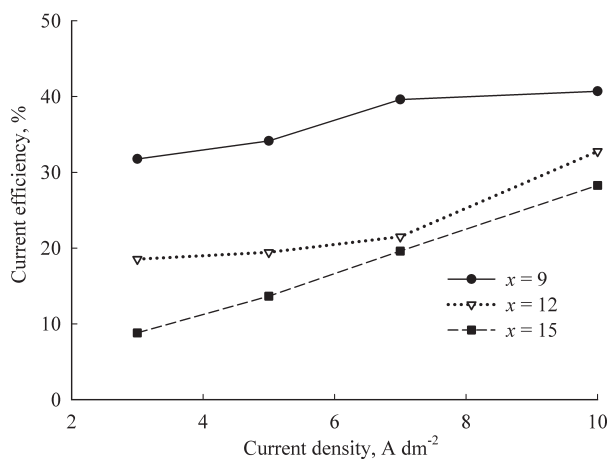


Fig. 4. Effect of current density on current efficiency of chromium electrodeposition in liquid mixtures $\text{CrCl}_3 + 2.5\text{ChCl} + x\text{H}_2\text{O}$ with various content of water. Temperature 50°C , electrolysis duration 20 min.

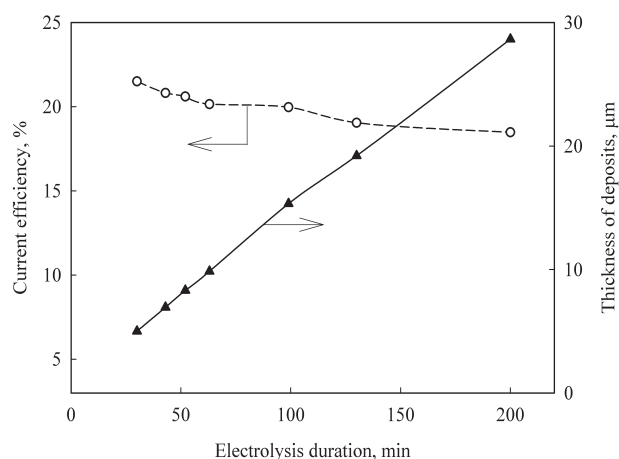


Fig. 5. Effect of electrolysis duration on current efficiency of chromium electrodeposition and thickness of deposits obtained from the bath containing $\text{CrCl}_3 + 2.5\text{ChCl} + 15\text{H}_2\text{O}$. Current density 5 A dm^{-2} , temperature 40°C .

can be used in “hard” chromium electroplating [7, 10].

Fig. 6 represents typical SEM images of Cr coatings obtained from choline chloride based plating bath. The deposits surface exhibits nodular structure and some microcracks on the coatings which is typical of chromium layer fabricated from Cr(III) plating baths [21, 22]. With increasing current density, the average nodule size increases somewhat (compare Fig. 6 A, B, and C). Let us stress that the nodules become indistinguishable if the coating was deposited at a higher temperature (70°C , see Fig. 6D). However, when Cr deposits were prepared at high temperature or at relatively high current density, some crater-like defects (cavities) can be observed on the surface (see Fig. 6 C and D). We think that the formation of craters is due to intensive hydrogen evolution occurring together with metal electrodepositing. Indeed, as stated above, current efficiency of chromium deposition is low under the conditions of higher temperatures and (or) current densities. This means a relatively high rate of the HER. Because of a comparatively high viscosity of the plating electrolyte, the withdrawal of hydrogen gas bubbles evolved on the cathode is hindered; they remain near the electrode surface for some time and block it. Overgrowing of chromium layer around hydrogen bubbles causes formation of cavities on the coating surface.

The results of local EDX analysis of the chromium coatings revealed that their surface mainly consists

of chromium (ca. 86 %), the presence of oxygen and chlorine has been also detected (Fig. 7, Table 3). The chlorine spectra (weak signal) seem to be originated from chloride ions in the plating bath which are entrapped into deposits obtained. The detection of oxygen is explained by the fact that chromium is easily passivated and a passive film that formed on chromium surface is commonly attributed to a hydrated form of Cr_2O_3 [23]. The change in current density and temperature has no pronounced effect on the chemical composition of surface determined by EDX study.

It should be noted that EDX spectra are limited to semi-quantitative analysis of electrodeposited coatings, since the chemical composition of the surface layer can sufficiently differ from that in the bulk metal. Therefore, we performed a common chemical analysis of Cr deposits obtained from the DESs based plating bath under consideration. This analysis involved a full chemical dissolution (stripping) of a chromium layer in aqueous solution of HCl, a further formation of colored complex of Cr(III) with EDTA and the determination of Cr content by spectrophotometric method. The results of the chemical analysis showed that electrodeposited layers contained at least 98.5 mass % of chromium under the conditions of obtaining uniform bright coatings, irrespective of bath temperature and current density. Thus, the chromium plating baths based on the mixture of choline chloride, chromium (III) chloride and some

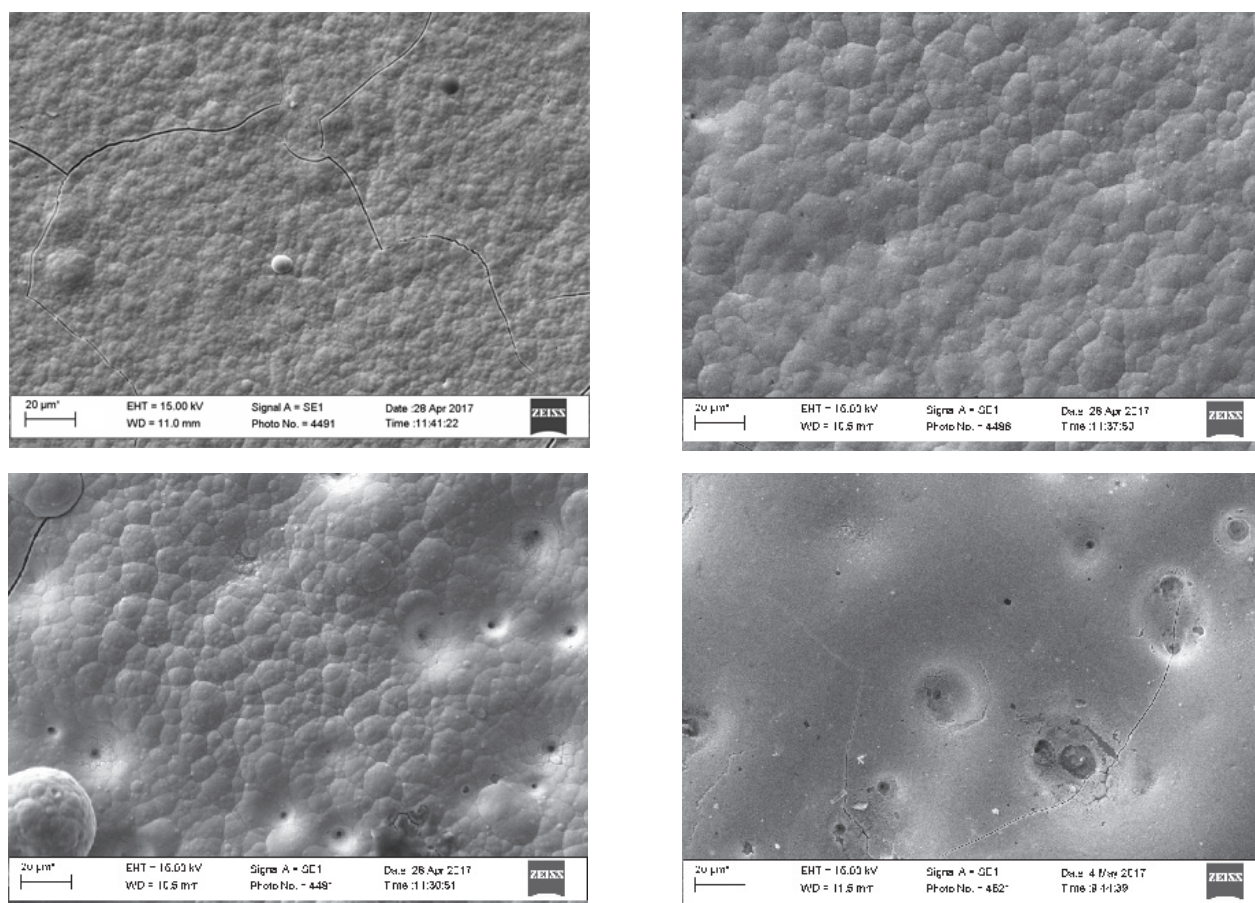


Fig. 6. Typical SEM images of chromium coatings deposited from the bath containing $\text{CrCl}_3 + 2.5\text{ChCl} + 15\text{H}_2\text{O}$ at various current densities and temperatures: (A) 5 A dm^{-2} and 40°C , (B) 7 A dm^{-2} and 40°C , (C) 10 A dm^{-2} and 40°C , (D) 10 A dm^{-2} and 70°C . Electrolysis duration 20 min.

water addition allow fabricating electrodeposits which consist of virtually pure chromium with an oxide film on its surface. X-ray spectra of Cr deposits prepared in the choline chloride based electroplating bath exhibited amorphous type microstructure (Fig. 8). The reflections of Cu foil substrate were also detected. The formation of amorphous deposits in Cr(III) plating electrolytes was earlier observed in a number of works [24, 25].

Table 4 demonstrates the influence of current

Table 3. Chemical composition of the coating surface according to the results of EDX analysis presented in Fig. 7.

Element	Content, mass %
Cr	85.91
O	12.60
Cl	1.49

density and bath temperature on the microhardness of Cr electrodeposits. It is clearly seen that the microhardness of chromium coatings slightly decreases with current density and does not practically depend on temperature. Earlier, Abbott et al. [13] indicated that using a liquid mixture of choline chloride and chromium (III) chloride (without water addition) allowed obtaining relatively

Table 4. Microhardness of deposits prepared from the bath containing $\text{CrCl}_3 + 2.5\text{ChCl} + 15\text{H}_2\text{O}$ at different current densities and electrolyte temperatures.

Current density, A dm^{-2}	Temperature, $^\circ\text{C}$	Microhardness, HV
5	40	664
7	40	582
10	40	552
10	70	549

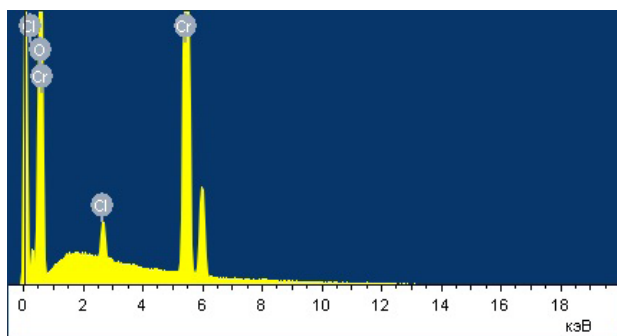


Fig. 7. Typical EDX spectrum of the surface of a coating deposited from the bath containing $\text{CrCl}_3 + 2.5\text{ChCl} + 15\text{H}_2\text{O}$ at 7 A dm^{-2} and 40°C .

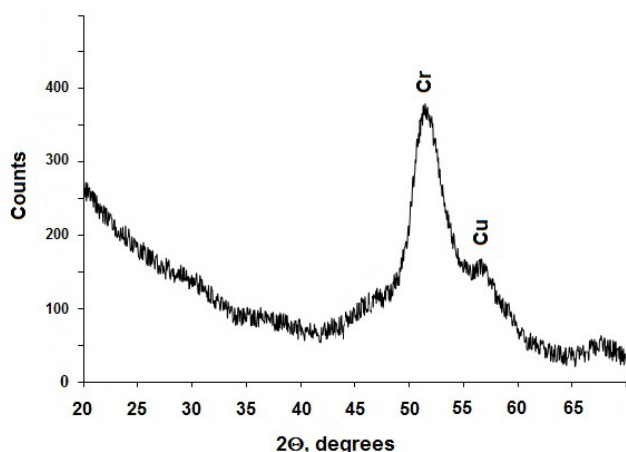


Fig. 8. Typical X-ray spectrum of a coating deposited from the bath containing $\text{CrCl}_3 + 2.5\text{ChCl} + 15\text{H}_2\text{O}$ at 7 A dm^{-2} and 40°C .

soft coatings with a microhardness of 242 Vickers. The application of proprietary additives enabled to increase the hardness to 600 Vickers. Our findings show that such values of microhardness can be achieved via a simple introduction of some extra water into the ionic liquids, without any other additives. The microhardness of obtained Cr coatings coincides with that measured for the deposits produced from the room-temperature deep eutectic solvents formed by mixing urea and chromium (III) chloride [13]. Evidently, the bulk-deposited Cr coatings have the microhardness which is close to the values required for industrial hard chrome [7, 13].

CONCLUSIONS

The addition of some extra water to the ionic liquids containing choline chloride and chromium (III) chloride opens the way for practical implementation of such type of chromium electroplating baths. Indeed, the electrolyte

without any extra water additive exhibits relatively high viscosity, unacceptably low conductivity and, therefore, extremely high cell voltage. With increasing water content, the electrical conductivity appreciably grows and the viscosity diminishes. However, an excessive concentration of water causes acceleration of hydrogen evolution reaction and, hence, decreasing current efficiency and deteriorating surface appearance of deposits. Thus, chromium electroplating should be performed at some intermediate water content in the bath ($x \approx 12\text{--}15$ for $1\text{CrCl}_3 + 2.5\text{ChCl} + x\text{H}_2\text{O}$ liquid mixtures where numbers designate molar ratio of constituents). We showed that the current efficiency of chromium electrodeposition reaches 40 – 50 % in some cases (depending on temperature and current density), which is appreciably higher than the values which are typical of “common” industrial chromium plating baths (ca. 13-18 %). Compact and bright chromium deposits with a good adhesion to the substrate and satisfactory microhardness can be obtained from ionic liquids containing chromium (III) chloride, choline chloride and water additives.

REFERENCES

1. E.L. Smith, A.P. Abbott, K.S. Ryder, Deep eutectic solvents (DESS) and their applications, *Chem. Rev.*, 114, 2014, 11060-11082.
2. A.P. Abbott, G. Frisch, K.S. Ryder, Electroplating using ionic liquids, *Annu. Rev. Mater. Res.*, 43, 2013, 335-358.
3. A.P. Abbott, K.S. Ryder, U. König, Electrofinishing of metals using eutectic based ionic liquids, *Trans. Inst. Met. Finish.*, 86, 2008, 196-204.
4. A.P. Abbott, G. Capper, D.L. Davies, R.K. Rasheed, V. Tambyrajah, Novel solvent properties of choline chloride/urea mixtures, *Chem. Commun.*, 2003, 70-71.
5. A.P. Abbott, G. Capper, D.L. Davies, R. Rasheed, Ionic liquids based upon metal halide/substituted quaternary ammonium salt mixtures, *Inorg. Chem.*, 43, 2004, 3447-3452.
6. A.P. Abbott, D. Boothby, G. Capper, D.L. Davies, R.K. Rasheed, Deep eutectic solvents formed between choline chloride and carboxylic acids: versatile alternatives to ionic liquids, *J. Am. Chem. Soc.*, 126, 2004, 9142-9147.
7. J.K. Dennis, T.E. Such, *Nickel and Chromium Plating*, Elsevier Science, 2013, 2015.

8. V. Protsenko, F. Danilov, Kinetics and mechanism of chromium electrodeposition from formate and oxalate solutions of Cr(III) compounds, *Electrochim. Acta*, 54, 2009, 5666-5672.
9. F.I. Danilov, V.S. Protsenko, V.O. Gordiienko, S.C. Kwon, J.Y. Lee, M. Kim, Nanocrystalline hard chromium electrodeposition from trivalent chromium bath containing carbamide and formic acid: Structure, composition, electrochemical corrosion behavior, hardness and wear characteristics of deposits, *Appl. Surf. Sci.*, 257, 2011, 8048-8053.
10. V.S. Protsenko, F.I. Danilov, Chromium electroplating from trivalent chromium baths as an environmentally friendly alternative to hazardous hexavalent chromium baths: comparative study on advantages and disadvantages, *Clean Techn. Environ. Policy*, 16, 2014, 1201-1206.
11. S. Survilienė, O. Nivinskienė, A. Češūnienė, A. Selskis, Effect of Cr(III) solution chemistry on electrodeposition of chromium, *J. Appl. Electrochem.*, 36, 2006, 649-654.
12. A.P. Abbott, G. Capper, D.L. Davies, R.K. Rasheed, Ionic liquid analogues formed from hydrated metal salts, *Chem. A Europ. J.*, 10, 2004, 3769-3774.
13. A.P. Abbott, A.A. Al-Barzinjy, P.D. Abbott, G. Frish, R.C. Harris, J. Hartley, K.S. Ryder, Speciation, physical and electrolytic properties of eutectic mixtures based on $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ and urea, *Phys. Chem. Chem. Phys.*, 16, 2014, 9047-9055.
14. E.S.C. Ferreira, C.M. Pereira, A.F. Silva, Electrochemical studies of metallic chromium electrodeposition from a Cr(III) bath, *J. Electroanal. Chem.*, 707, 2013, 52-58.
15. M.L. Mares (Badea), O. Ciocirlan, A. Cojocaru, L. Anicai, Physico-chemical and electrochemical studies in choline chloride based ionic liquid analogues containing trivalent chromium chloride, *Rev. Chim. (Bucharest, Rom.)*, 64, 2013, 815-824.
16. D.C. McCalman, L. Sun, Y. Zhang, J.F. Brennecke, E.J. Maginn, W.F. Schneider, Speciation, conductivities, diffusivities, and electrochemical reduction as a function of water content in mixtures of hydrated chromium chloride/choline chloride, *J. Phys. Chem. B*, 119, 2015, 6018-6023.
17. L.S. Bobrova, F.I. Danilov, V.S. Protsenko, Effects of temperature and water content on physicochemical properties of ionic liquids containing $\text{CrCl}_3 \cdot x\text{H}_2\text{O}$ and choline chloride, *J. Mol. Liq.*, 223, 2016, 48-53.
18. V.S. Protsenko, L.S. Bobrova, K.S. Burmistrov, F.I. Danilov, The application of hole theory for the interpretation of data on conductivity of ionic liquids containing chromium(III) chloride, choline chloride and water additives, *Voprosy khimii i khimicheskoi tekhnologii*, 1, 2017, 27-35.
19. V.S. Protsenko, L.S. Bobrova, F.I. Danilov, Physicochemical properties of ionic liquid mixtures containing choline chloride, chromium (III) chloride and water: effects of temperature and water content, *Ionics*, 23, 2017, 637-643.
20. A.P. Abbott, K. El Ttaib, K.S. Ryder, E.L. Smith, Electrodeposition of nickel using eutectic based ionic liquids, *Trans. Inst. Met. Finish.*, 86, 2008, 234-240.
21. V.S. Protsenko, V.O. Gordiienko, F.I. Danilov, S.C. Kwon, M. Kim, J.Y. Lee, Unusually high current efficiency of nanocrystalline Cr electrodeposition process from trivalent chromium bath, *Surf. Eng.*, 27, 2011, 690-692.
22. V.S. Protsenko, V.O. Gordiienko, F.I. Danilov, S.C. Kwon, Thick chromium electrodeposition from trivalent chromium bath containing carbamide and formic acid: An investigation into current efficiency, electrodeposition rate and surface morphology, *Met. Finish.*, 109, 2011, 33-37.
23. T.P. Moffat, R.M. Latanision, An electrochemical and X-ray photoelectron spectroscopy study of the passive state of chromium, *J. Electrochem. Soc.*, 139, 1992, 1869-1879.
24. S.C. Kwon, M. Kim, S.U. Park, D.Y. Kim, D. Kim, K.S. Nam, Y. Choi, Characterization of intermediate Cr-C layer fabricated by electrodeposition in hexavalent and trivalent chromium baths, *Surf. Coat. Technol.*, 183, 2004, 151-156.
25. F.I. Danilov, V.S. Protsenko, T.E. Butyrina, E.A. Vasil'eva, A.S. Baskevich, Electroplating of chromium coatings from Cr(III)-based electrolytes containing water soluble polymer, *Prot. Met.*, 42, 2006, 560-569.