UDC 544.65:621.357

V.S. Protsenko, L.S. Bobrova

ELECTRODE PROCESSES IN A DEEP EUTECTIC SOLVENT CONTAINING DISSOLVED CHROMIUM(III) CHLORIDE

Ukrainian State University of Chemical Technology, Dnipro, Ukraine

We considered the kinetics of electrochemical processes occurring during electrodeposition of coatings from a low-temperature ionic liquid based on a eutectic mixture of choline chloride and ethylene glycol, in which a trivalent chromium salt is dissolved. Irreversible current waves of Cr(III) ions discharge on a glassy carbon electrode in the electrolytes of studied compositions are not described by the «classical» equations of linear and cyclic voltammetry, which is due to both the presence of the migration component of the current and the cathodic passivation of the electrode. It has been established that the introduction of additional water into the electrolyte leads to an increase in the current density of the wave of irreversible discharge of Cr(III) ions on the glassy carbon electrode, which is caused by a significant decrease in the viscosity of the solution. The current efficiency of the chromium deposition reaction decreases when water is introduced into the ionic liquid. The X-ray amorphous coatings electrodeposited from the electrolyte under study, along with chromium, contain carbon and oxygen, the inclusion of which is due to the electrocatalytic properties of the freshly deposited chromium surface.

Keywords: electrodeposition, chromium, deep eutectic solvent, kinetics, current efficiency.

Introduction

The development of new processes for the electrolytic deposition of chromium and its alloys using electrolytes based on trivalent chromium compounds is one of the most urgent problems of up-to-date surface engineering [1]. The currently known chromium plating processes based on Cr(III) salts mainly involve «classical» aqueous electrolytes [1−3], which, along with some obvious advantages, also have a number of serious disadvantages [4]. In this regard, over the past decades, considerable attention has been paid to the development of processes for the deposition of chromium and its alloys from solutions of Cr(III) salts in non-aqueous solvents. One of the most promising directions should be considered the use of a new type of ionic liquids, the so-called deep eutectic solvents (DESs).

Deep eutectic solvents are a kind of room-temperature ionic liquids obtained by mixing of some organic and inorganic components in a eutectic ratio. The main advantages of DESs are a wide range of electrode potentials of electrochemical stability (a wide «electrochemical window» of the solvent), almost zero saturation vapor pressure, availability, low cost, and nontoxicity [5]. Another advantage that distinguishes these systems from «classical» low-temperature ionic liquids is their tolerance to water impurity [6]. Moreover, the introduction of water additives into the DESs often improves the physicochemical properties of electrolytes used for metal deposition [7].

One of the most well-known and widespread DES at present is the so-called ethaline, a eutectic mixture of ethylene glycol and choline chloride. Previously, the kinetics and mechanism of chromium deposition, the patterns of electrocrystallization, and some properties of coatings electrodeposited from an electrolyte containing chromium(III) chloride in ethaline were characterized [8−10]. In particular, it has been shown that coatings prepared in electrolytes based on a Cr(III) salt dissolved in an eutectic ionic liquid exhibit an increased electrocatalytic activity

in the reaction of cathodic hydrogen evolution in 1 M NaOH in comparison with a «pure» chromium electrodeposit [11]. At the same time, questions important for the theory and practice of chromium plating, concerning the effect of deposition conditions (among other things, the effect of water additives) on the current efficiency of the chromium deposition reaction, and features of the surface morphology of the resulting coatings, remain practically unexplored. Therefore, the purpose of this study was to establish the main kinetic patterns of the electrochemical processes that occur during the electrodeposition of coatings from an electrolyte based on a DES containing a dissolved Cr(III) salt.

Experimental

The ethaline solvent was prepared by mixing ethylene glycol and choline chloride in a molar ratio of 2:1, respectively, and then stirring the resulting mixture on a magnetic stirrer at a temperature of 70°C until a clear, colorless homogeneous fluid was formed. A chromium-containing electrolyte was prepared by dissolving a certain weighed portion of chromium(III) chloride hexahydrate in ethaline, followed by stirring at 70°C until a homogeneous dark green fluid was formed. In some cases, an additive of water was introduced into the electrolyte composition in such an amount that systems of the following compositions were formed: $1ChCl:2EG:0.5CrCl_3:xH_2O$, where the numbers in front of the chemical formulae indicate the corresponding molar ratios of the components (ChCl and EG stand for choline chloride and ethylene glycol, respectively), and x characterizes the total water content in the system. In our experiments, x was equal to 3, 5, 7.5, 10, and 12.5. Obviously, x=3 corresponds to a system without additionally introduced water (i.e., we are talking about a system containing only water of crystallization originated from chromium(III) chloride hexahydrate).

Voltammetric studies of the kinetics of electrode processes in the obtained electrolytes were carried out using a Potentiostat/Galvanostat/ZRAReference 3000 (Gamry, USA) on the end surface of a glassy carbon cylinder ($\varnothing$ 5 mm) pressed into a Teflon jacket. Before recording the polarization curve, the working electrode was polished, washed successively with an aqueous solution of HCl (1:1) and bidistilled water, and then dried in an air stream. A platinum plate was used as an auxiliary electrode. A silver wire was used as a quasi-reference electrode. To compensate for the ohmic drop, an automatic compensator built into the potentiostat was used. A glass three-electrode cell, in which voltammetric measurements were carried out, was thermostated

(40±0.1°C). In all cases, the electrode potential sweep was started from the steady-state potential value in the cathode direction, and then the potential sweep direction was changed to the anodic one.

Coatings were electrodeposited on the surface of a gold or copper plate placed in a plastic cassette. The surface area of the working electrode was 1 cm². The surface of the working electrode (substrate for the coating deposition) was degreased by treatment with an aqueous MgO suspension, etched in an HCl solution (1:1), thoroughly washed with bidistilled water, and dried. Electrodeposition was conducted in the galvanostatic mode using a stabilized current source in a glass thermostated cell with a volume of 100 cm³ according to a two-electrode scheme. A platinized titanium plate served as the anode in these experiments. The duration of electrolysis was chosen so that the thickness of the deposit was approximately 10 μm.

The current efficiency was calculated for the partial three-electron reaction $Cr(III)+3e^-=Cr(0)$ according to the Faraday law based on the data on the cathode weight gain and the chromium content in the coatings obtained. Since the coating also contains other elements besides metallic chromium, a chemical analysis was carried out to determine the mass of deposited chromium. To do this, the coating obtained on a gold substrate was quantitatively dissolved in hydrochloric acid solution, and the content of chromium(III) ions was determined according to the standard method (photometry of Cr(III) complexes with EDTA). For control, the obtained results were compared with the data on the determination of the chromium content in the coatings, obtained by energy-dispersive X-ray microanalysis. The discrepancies in the determination of the chromium content in the coatings, obtained by these two independent methods, did not exceed 0.9 wt.%.

The density of electrolytes was measured using a pycnometer with a volume of 5 ml, and the viscosity was measured using a VPZh-1 viscometer.

The surface morphology of the coatings was studied by scanning electron microscopy (SEM) using a Zeiss EVO 40XVP electron microscope with an Oxford INCA Energy 350 built-in attachment for chemical analysis by energy-dispersive X-ray microanalysis (EDX). X-ray diffraction studies of the coatings were carried out using a DRON-3.0 X-ray diffractometer in monochromatized CuK$_\alpha$ radiation.

Results and discussion

Voltammetric study of Cr(III)-containing electrolytes based on DES

Figure 1 shows voltammograms (VAGs) characterizing the electrochemical behavior of the solvent ethaline containing various amounts of water. It can be seen that anhydrous ethaline is characterized by a relatively wide electrochemical window (from ~-2 V in the cathode region to $\sim+1.3$ V in the anode region with respect to the scale of the Ag quasi reference electrode). The corresponding cathodic and anodic currents recorded on the VAG when the indicated potential values are exceeded are due to the processes of electrochemical reduction and oxidation of the DES components, the nature of which is still poorly understood [12]. It should be noted that the cathodic current wave at ~1 V, detected on the reverse cathode scan, is due to the reduction of the oxidation products of the ethaline components formed on the previous anodic potential scan [12]. As shown below, the discharge of Cr(III) ions proceeds at much more negative potentials; therefore, this peak of the cathode current is not discussed further in our work.

The introduction of water somewhat narrows the region of electrochemical stability of the DES (Fig. 1), although the electrochemical window remains rather wide (more than 2.5 V). It is logical to assume that the cathode and anode currents on the voltammograms are associated with the electrochemical transformation of water molecules (hydrogen and oxygen evolution reactions) occurring together with the transformations of the main components of the deep eutectic solvent.

The introduction of a Cr(III) salt into the electrolyte leads to the appearance of a cathode current wave C1 on the VAG (Fig. 2), which corresponds to the following one-electron reduction process [9]:

$$Cr(III)+e^-\rightarrow Cr(II). \qquad (1)$$

On the cathode potential scan, after the passage of the maximum current C1, an increase in the current density is observed; this can be associated with the achievement of the electrode potentials corresponding to the beginning of the deposition of metallic chromium according to the following two-electron reaction:

$$Cr(II)+e^-\rightarrow Cr(0). \qquad (2)$$

The formation of a metal phase on the surface of the glassy carbon electrode is indicated by the presence of a loop on the cathode section of the VAG after the change in the direction of the potential sweep to the anodic one (a characteristic criterion for the appearance of a new phase during electrocrystallization on a foreign substrate). Obviously, in this case, the reaction of hydrogen evolution on freshly formed chromium crystals, which play the role of the corresponding catalytic active sites, is also not excluded.

The anodic scan shows the appearance of a current peak A1, which apparently corresponds to the electrochemical oxidation of Cr(II) ions accumulated in the near-electrode layer (the reverse process of reaction (1)). The potentials of the peaks of the cathode and anode waves C1 and A1 differ by almost 2 V, which unambiguously indicates the irreversible nature of the process of the discharge of Cr(III) ions [9]. Note that the VAG does not detect
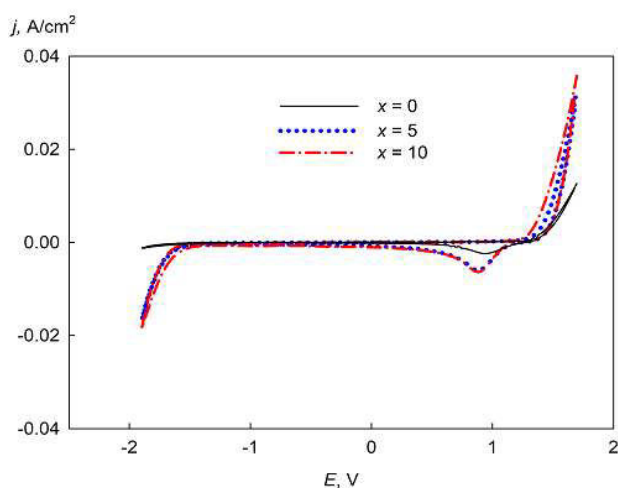

Fig. 1. Voltammograms of a glassy carbon electrode in ethaline at various contents of introduced water. Potential sweep rate is 50 mV/s, temperature is 40^{0}C
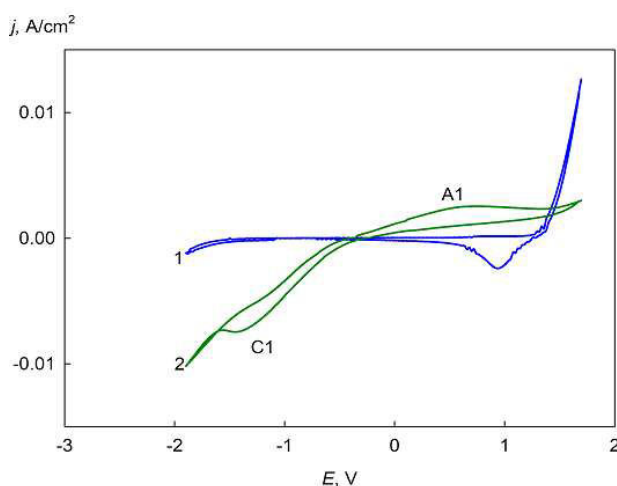

Fig. 2. Voltammograms of a glassy carbon electrode in ethaline (1) and in an electrolyte containing chromium(III) chloride without additionally introduced water (x=3) (2) at a potential sweep rate of 50 mV/s. Temperature is 40^{0}C

V.S. Protsenko, L.S. Bobrova

a separate current wave associated with the anodic dissolution of metallic chromium. Apparently, this process proceeds at very positive potentials together with the anodic decomposition of the ethaline components (>1.5 V).

An increase in the potential scan rate in the electrolyte without additionally introduced water leads to a regular increase in the height of the C1 current wave (Fig. 3,a). However, the dependence of the C1 peak height on the square root of the potential scan rate (v) is not a straight line, as it follows from the well-known Delahay equation for the current peak of an irreversible electrode process (see inset in Fig. 3,a). Moreover, when additional water is introduced into the electrolyte, some unexpected effects are observed (Fig. 3,b−d). Firstly, the current peak typical of linear voltammetry practically disappears (it is clearly visible on the voltammograms only at two of the lowest scan rates

used, 10 and 25 mV/s). Secondly, the current density at each fixed value of the potential decreases with increasing v, and, accordingly, the height of the Cr(II) anodic oxidation current on the anodic scan noticeably decreases.

Thus, as a general trend, a decrease in the cathode current on the VAG with an increase in the potential scan rate should be noted. Dependences of this kind, in general, are not typical of linear voltammetry. Moreover, in our previous work [9], we observed strictly linear dependences in the coordinates j_p vs. $v^{1/2}$ and E_p vs. $\ln v$ (where j_p and E_p are the current density and potential of the peak on the VAG, respectively) quite typical of linear voltammetry on the same glassy carbon electrode for an electrolyte containing chromium(III) chloride dissolved in ethaline and water additives. The only difference between the conditions for obtaining VAG in work [9] and in the present study is a significant
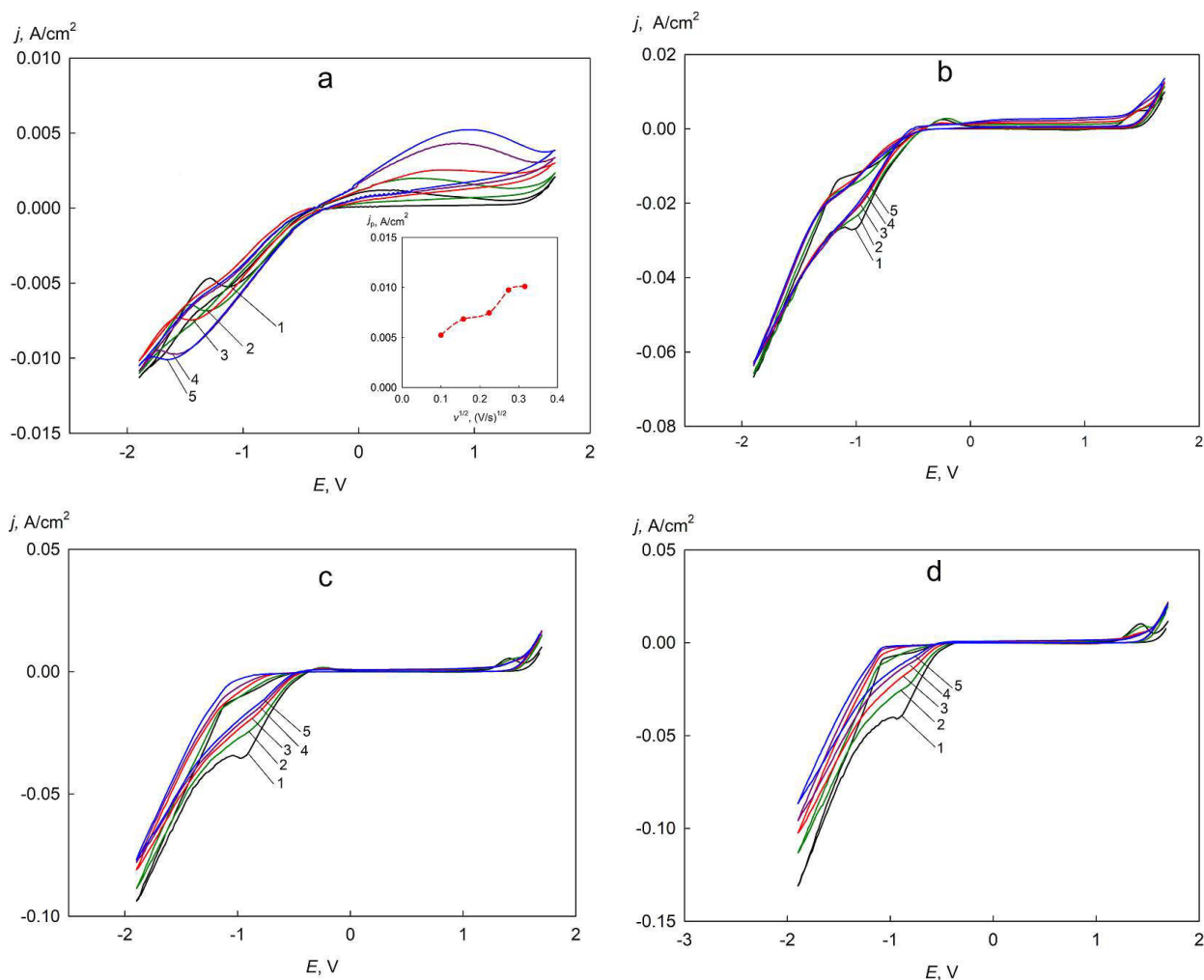

Fig. 3. Voltammograms of a glassy carbon electrode in 1ChCl:2EG:0.5CrCl$_3$:xH$_2$O electrolytes at different water content: x=3 (a), x=7.5 (b), x=10 (c), and x=12.5 (d). Potential scan rate (mV/s): 1 − 10, 2 − 25, 3 − 50, 4 − 75, and 5 − 100. Temperature is 40^{0}C. Inset in Fig. 3a shows the dependence of the peak current C1 on the square root of the potential scan rate

difference in the concentration of Cr(III) ions in solution. The concentration was varied in the range from 0.05 to 0.20 mol/dm³ in work [9], while the concentration of Cr(III) ions in the present study, calculated on the basis of the measured solution density, turned out to be much larger (Table 1): about 1−1.5 mol/dm³.

Table 1

Calculated molar concentration of Cr(III) ions in electrolytes 1ChCl:2EG:0.5CrCl₃:xH₂O and measured viscosity of solutions (η) at the temperature of 40⁰C and various water content

x	C(Cr(III)), mol/dm³	η, mPa·s
3	1.60	229.4
5	1.44	86.6
7.5	1.28	31.5
10	1.15	29.7
12.5	1.04	14.4

We assume that under conditions of such a high concentration of Cr(III) ions, it becomes impossible to neglect the migration component of the mass transfer and take into account only the diffusion component, as is customary in deriving the classical equations of linear and cyclic voltammetry. It should be noted that deviations from the simple well-known equations of «classical» voltammetry in systems based on DESs at a relatively high content of metal ions were observed earlier [13]. For a quantitative description of VAGs obtained in systems of this kind, where migration transfer cannot be neglected and where diffusion, in principle, may not obey the Stokes-Einstein equation [14], it is necessary to develop adequate mathematical models. However, this task is far beyond the scope of the present study.

One more specific feature of the obtained VAGs should be pointed out, which is that the currents of the anodic peaks are much lower than the currents of the corresponding cathodic peaks of reaction (1), while in the «classical» cyclic voltammetry, the heights of the current waves on the anode and cathode scans, as a rule, are close, and their ratio is determined by the ratio of the diffusion coefficients of the oxidized and reduced forms, which usually do not differ much from each other. In our case, a noticeable depression of the wave of the anodic current of Cr(II) oxidation on VAG can be associated with the low solubility of complex Cr(II) salts in the DES and the formation of a layer of poorly soluble Cr(II) compounds that partially block the electrode surface [15].

For the convenience of analyzing the effect of adding water on the kinetics of electroreduction of

Cr(III) ions in an ethaline-based solution, Figure 4 summarizes the corresponding VAGs registered at different H₂O contents and the same electrode potential scan rate. It can be seen that with an increase in the H₂O concentration, in general, there is a tendency to an increase in the cathode current density, although at a sufficiently high water content (x=7.5, 10 and 12.5) there is no significant difference in the current values in the initial section of the VAG. Such an ambiguous dependence, apparently, is a consequence of the manifestation of several oppositely acting effects. On the one hand, when adding water and maintaining a constant molar ratio of electrolyte components, the concentration of discharged chromium(III) ions decreases (Table 1), which should result in a decrease in the currents on the VAG. In addition, changes in the composition of complex chromium ions (gradual replacement of chloride ions in the inner sphere by water molecules [16]) should also lead to deceleration of charge transfer in the Cr(III)/Cr(II) system [9]. On the other hand, the introduction of water contributes to a decrease in the viscosity of the electrolyte (Table 1), and hence to an increase in the rate of diffusion mass transfer in the electrolyte, which leads to a regular increase in the diffusion component of the currents on the VAG.

Discussing the voltammetric curves shown in Fig. 4, one should keep in mind the fact that for each curve the potentials were measured with respect to a silver quasi-reference electrode immersed in an electrolyte with different water content (the same as in the solution where the working electrode was
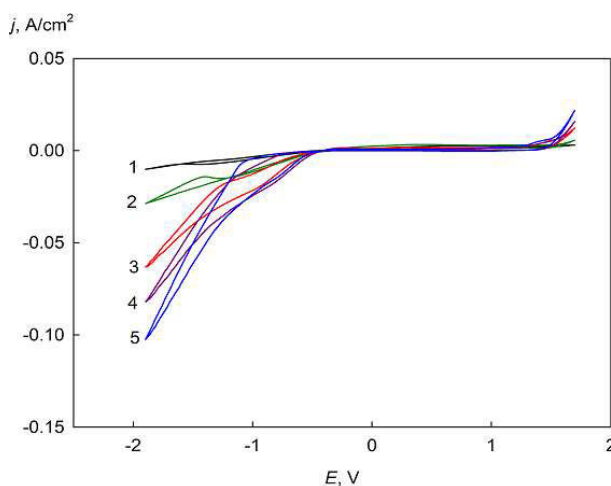

Fig. 4. Voltammograms of a glassy carbon electrode in 1ChCl:2EG:0.5CrCl₃:xH₂O electrolytes at different water content: 1 − x=3, 2 − x=5, 3 − x=7.5, 4 − x=10, and 5 − x=12.5. Potential scan rate is 50 mV/s. Temperature is 40⁰C

V.S. Protsenko, L.S. Bobrova

located). This was done in order to prevent the occurrence of an additional uncontrolled component of the interfacial potential at the contact boundary «working electrolyte−electrolyte of the reference electrode». Thus, the potentials on the VAG in Fig. 4 are measured in principle against differing reference electrodes. In order to assess how serious these differences might be, open circuit voltages (OCV) were measured for circuits composed of a silver reference electrode immersed in an ethaline-based electrolyte with various water contents, and a saturated silver chloride electrode placed in an aqueous electrolyte (Table 2). As can be seen, the change in OCV when adding the largest amount of water used in the work (x=12.5) does not exceed 200 mV. Such relatively small changes in the first approximation can be neglected.

Table 2

Open circuit voltages of circuits consisting of an aqueous saturated silver chloride electrode and a silver electrode placed in ethaline with different water contents. Temperature 40^{0}C

x	OCV, mV
0	−275
3	−180
5	−145
7.5	−121
10	−106
12.5	−112

Current efficiency of chromium deposition reaction, coating composition and surface morphology

The current efficiency of the reaction of chromium deposition increases with a decrease in the electrolyte temperature and with an increase in the cathode current density (Fig. 5, a, b). This trend is typical not only of the processes of chromium electrodeposition from electrolytes of various compositions based on Cr(III) salts dissolved in DES, but also of aqueous chromium plating electrolytes both based on Cr(III) and Cr(VI) [1]. An increase in the water concentration in the electrolyte leads to a decrease in the current efficiency of the chromium deposition reaction, all other things being equal (Fig. 5,c), which, apparently, is a consequence of an increase in the rate of the competing hydrogen evolution reaction at the cathode. The decrease in current efficiency with the addition of water becomes especially noticeable at x≥7.5.

It should be noted that the current efficiency of chromium electrodeposition in some cases reaches 25−28%, which is significantly higher than the value characteristic of industrial chromic acid electrolytes

(13−15%). This is an important advantage of environmentally friendly chromium plating electrolytes based on trivalent chromium compounds.

Taking into account the fact that an increase in temperature leads to a decrease in viscosity and an increase in the electrical conductivity of the considered ionic liquids, although it is accompanied by a decrease in the current efficiency, it is reasonable to perform the deposition at the temperature of about 40^{0}C. In this case, the highest current density (20 A/dm^2) should be used, which ensures a high current efficiency while maintaining a satisfactory quality of the resulting electrodeposits.

It is well known that chromium plating electrolytes based on trivalent chromium salts allow producing coatings that do not consist of «pure» chromium, but alloys and/or composites containing a sufficiently large amount of metalloids [1]. The results of EDX microanalysis show that the coatings deposited from the DES-based electrolyte include three elements: chromium, carbon and oxygen (Table 3).

Table 3

Chemical composition of coatings deposited from the electrolytes 1ChCl:2EG:0.5CrCl$_3$:xH$_2$O at the current density of 20 A/dm^2, temperature of 40^{0}C and various water content

x	Content of chemical elements, wt.%		
	Cr	C	O
3	84.56	3.61	11.83
5	82.16	4.15	13.69
7.5	81.85	4.27	13.88
10	80.71	4.84	14.45
12.5	76.38	6.55	17.07

With an increase in the amount of water added to the electrolyte, the content of carbon and oxygen in the coating increases, which may be due to the formation of chromium oxide-hydroxide compounds on the electrode surface and their inclusion in the growing deposit, accompanied by partial occlusion of the molecules of the organic components of the electrolyte. The incorporation of carbon into the deposit can also be the result of chemical or electrochemical reduction of organic molecules on the electrode surface [1,7].

The surface morphology of the coating deposited from the Cr(III) electrolytes based on the DES without the addition of water is characterized by a inhomogeneous microstructure, consisting mainly of spheroids of different sizes (Fig. 6,a). In addition, individual cracks and hollows (caverns) are found on the surface. The introduction of additional
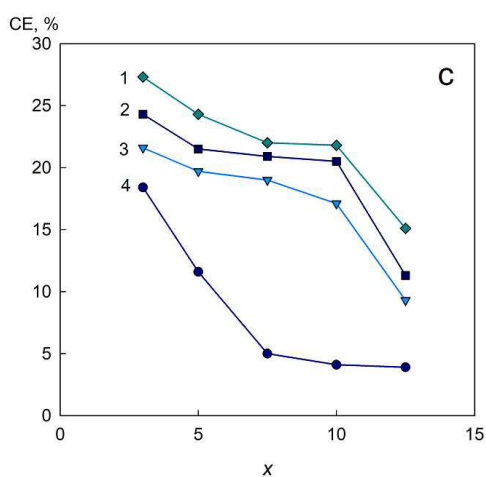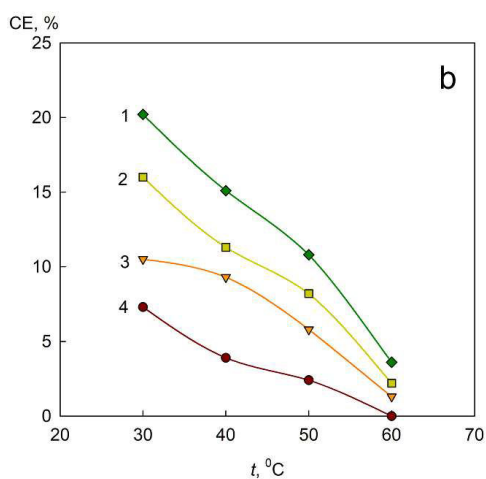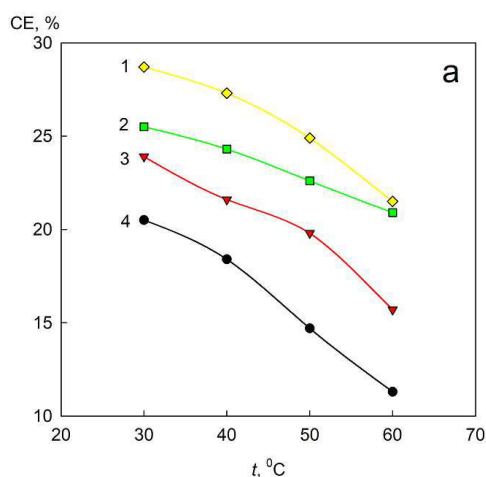
Fig. 6. Micrographs of the surface of coatings deposited from 1ChCl:2EG:0.5CrCl$_3$:xH$_2$O electrolytes at different water contents: x=3 (a), x=10 (b), and x=12.5 (c) at the temperature of 40⁰C and the current density of 20 A/dm^2

Fig. 5. Dependence of the current efficiency of the reaction of chromium deposition from electrolytes based on DES on temperature at x=3 (a) and x=12.5 (b) and on the water content in the electrolyte at the temperature of 40⁰C (c). Cathode current density (A/dm^2): 1 − 20, 2 − 15, 3 − 10, and 4 − 5
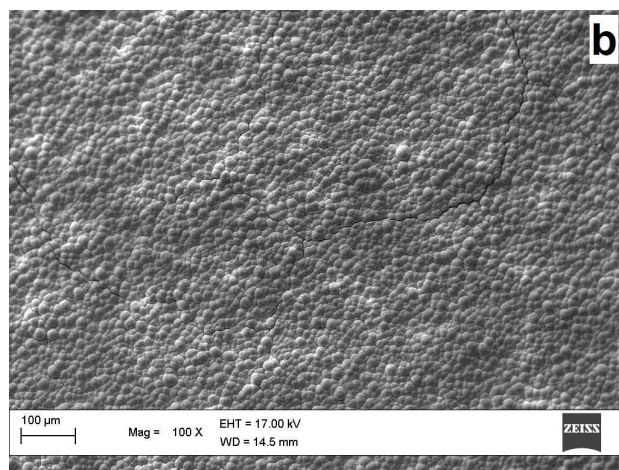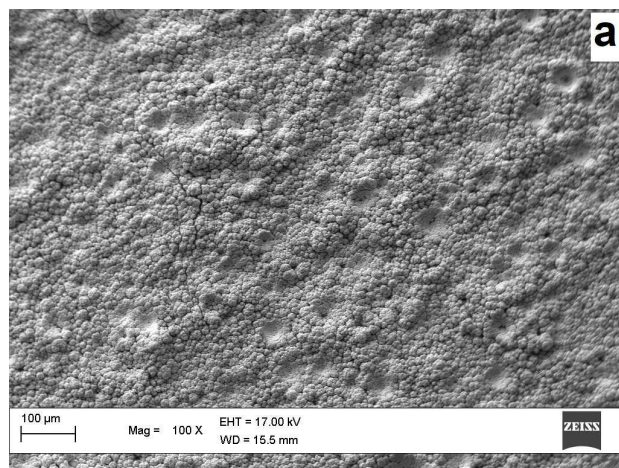
water into the ethaline-based electrolyte leads to a significant leveling the surface microprofile: cavities and microcracks practically disappear, and the surface is built from fairly symmetrical intergrown spheroids

V.S. Protsenko, L.S. Bobrova

with an average size of about 10 μm (Fig. 6,b,c). Note that the formation of a spheroid-type surface morphology is typical under conditions of strong inhibition of electrocrystallization, which is also evidenced by the formation of an X-ray amorphous microstructure of the coatings (Fig. 7). Variation in the water concentration in the DES-based electrolyte (x=3÷12.5) does not affect the type of microstructure of the resulting coating: it remains X-ray amorphous in all cases.
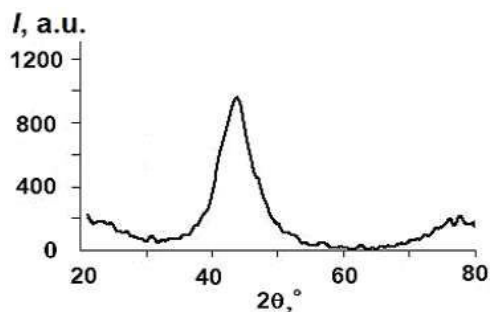

Fig. 7. Typical X-ray diffraction pattern of a coating deposited from $1ChCl:2EG:0.5CrCl_3:3H_2O$ electrolyte at the temperature of 40^0C and the current density of 20 A/dm^2

Conclusions

The patterns of electrodeposition of coatings from electrolytes based on a deep eutectic solvent (a liquid eutectic mixture of ethylene glycol and choline chloride) containing chromium(III) chloride and water additives have been systematically studied for the first time. It has been established that irreversible current waves of Cr(III) ions discharge on a glassy carbon electrode in electrolytes of the studied compositions are not described by the «classical» equations of linear and cyclic voltammetry, which is due to both the presence of the migration component of the current and the cathodic passivation of the electrode.

The current efficiency of the chromium deposition reaction decreases with increasing temperature, decreasing cathode current density and adding water to the plating bath. In a number of cases, the values of the current efficiency significantly exceed the values typical of industrial hexavalent chromium electrolytes. This feature is an important advantage of environmentally acceptable electrolytes based on Cr(III) salts dissolved in eutectic ionic liquids.

It is shown that X-ray amorphous deposits are formed on the cathode during deposition from the studied electrolytes, which do not consist of «pure» chromium, but include a significant amount of carbon and oxygen. The inclusion of a noticeable amount of carbon in the coatings is a consequence of the interaction of freshly deposited chromium with organic components of the electrolyte. Apparently, the increased electrocatalytic activity of the studied coatings in the hydrogen evolution reaction in 1 M NaOH [11] is caused by the incorporation of carbon into the composition of the electrodeposit and the corresponding change in the electronic structure of the metal. A change in the water content in the trivalent chromium plating electrolyte makes it possible to control the chemical composition and surface morphology of the coatings.

REFERENCES

1. *Danilov F.I., Protsenko V.S.* Chromium electrodeposition using electrolytes based on trivalent chromium compounds: a review // Voprosy Khimii i Khimicheskoi Tekhnologii. − 2020. − No. 2. − P.4-29.

2. *Unusually* high current efficiency of nanocrystalline Cr electrodeposition process from trivalent chromium bath / Protsenko V.S., Gordiienko V.O., Danilov F.I., Kwon S.C., Kim M., Lee J.Y. // Surf. Eng. − 2011. − Vol.27. − P.690-692.

3. *Danilov F.I., Protsenko V.S., Butyrina T.E.* Chromium electrodeposition kinetics in solutions of Cr(III) complex ions // Russ. J. Electrochem. − 2001. − Vol.37. − P.704-709.

4. *Effect* of Cr(III) solution chemistry on electrodeposition of chromium / Surviliene S., Nivinskiene O., Cesuniene A., Selskis A. // J. Appl. Electrochem. − 2006. − Vol.36. − P.649-654.

5. *Smith E.L., Abbott A.P., Ryder K.S.* Deep eutectic solvents (DESs) and their applications // Chem. Rev. − 2014. − Vol.114. − P.11060-11082.

6. *Solvation* dynamics of wet ethaline: water is the magic component / Alfurayj I., Fraenza C.C., Zhang Y., Pandian R., Spittle S., Hansen B., Dean W., Gurkan B., Savinell R., Greenbaum S., Maginn E., Sangoro J., Burda C. // J. Phys. Chem. B. − 2021. − Vol.125. − P.8888-8901.

7. *Protsenko V., Bobrova L., Danilov F.* Trivalent chromium electrodeposition using a deep eutectic solvent // Anti-Corros.

Methods Mater. − 2018. − Vol.65. − P.499-505.

8. *Mechanism* and kinetics of chromium electrochemical nucleation and growth from a choline chloride/ethylene glycol deep eutectic solvent / Mejia-Caballero I., Aldana-Gonzalez J., Manh T.L., Romero-Romo M., Arce-Estrada E.M., Campos-Silva I., Ramirez-Silva M.T., Palomar-Pardave M. // J. Electrochem. Soc. − 2018. − Vol.165. − P.D393-D401.

9. *Kinetics* of Cr(III) ions discharge in solutions based on a deep eutectic solvent (ethaline): effect of water addition / Protsenko V.S., Bobrova L.S., Kityk A.A., Danilov F.I. // J. Electroanal. Chem. − 2020. − Vol.864. − Art. No. 114086.

10. *Electrochemical* mechanism of trivalent chromium reduction in ChCl-EG deep eutectic solvents containing trivalent chromium / Qian H., Sun J., Li Q., Sun H., Fu X. // J. Electrochem. Soc. − 2020. − Vol.167. − Art. No. 102511.

11. *Electrochemical* synthesis and characterization of electrocatalytic materials for hydrogen production using Cr(III) baths based on a deep eutectic solvent / Protsenko V.S., Bobrova L.S., Korniy S.A., Danilov F.I. // Mater. Lett. − 2022. − Vol.313. − Art. No. 131800.

12. *Electrochemical* decomposition of choline chloride based ionic liquid analogues / Haerens K., Matthijs E., Binnemans K., Van der Bruggen B. // Green Chem. − 2009. − Vol.11. − P.1357-1365.

13. *Choline* chloride based ionic liquids containing nickel chloride: physicochemical properties and kinetics of Ni(II) electroreduction / Kityk A.A., Shaiderov D.A., Vasil'eva E.A., Protsenko V.S., Danilov F.I. // Electrochim. Acta. − 2017. − Vol.245. − P.133-145.

14. *Taylor A.W., Licence P., Abbott A.P.* Non-classical diffusion in ionic liquids // Phys. Chem. Chem. Phys. − 2011. − Vol.13. − P.10147-10154.

15. *Ionic* liquid analogues formed from hydrated metal salts / Abbott A.P., Capper G., Davies D.L., Rasheed R.K. // Chem. Eur. J. − 2004. − Vol.10. − P.3769-3774.

16. *Combining* MCR-ALS and EXAFS as tools for speciation of highly chlorinated chromium(III) in mixtures of deep eutectic solvents and water / Verdonck T., Verpoort P., De Strycker J., De Cleene A., Banerjee D., Nockemann P., Van Deun R., Van Hecke K. // Dalton Trans. − 2019. − Vol.48. − P.2318-2327.

ЕЛЕКТРОДНІ ПРОЦЕСИ В НИЗЬКОТЕМПЕРАТУРНОМУ ЕВТЕКТИЧНОМУ РОЗЧИННИКУ, ЩО МІСТИТЬ РОЗЧИНЕНИЙ ХРОМ(III) ХЛОРИД

В.С. Проценко, Л.С. Боброва

Розглянуто закономірності кінетики електрохімічних процесів, що відбуваються при електроосадженні покриттів з низькотемпературної іонної рідини на основі евтектичної суміші холін хлориду і етиленгліколю, в якій розчинена сіль тривалентного хрому. Необоротні хвилі струму розряду іонів Cr(III) на скловуглецевому електроді в електролітах досліджуваного складу не описуються «класичними» рівняннями лінійної і циклічної вольтамперометрії, що обумовлено як наявністю міграційної складової струму, так і проявленням катодної пасивації електрода. Встановлено, що введення додаткової води до електроліту приводить до зростання густини струму хвилі необоротного розряду іонів Cr(III) на скловуглецевому електроді унаслідок суттєвого зниження в'язкості розчине. Вихід за струмом реакції осадження хрому зменшується при введені води до іонної рідини. Рентгеноаморфні осади, що осаджуються з дослідженого електроліту, окрім хрому, містять в своєму складі вуглець і кисень, впровадження яких викликано електрокаталітичними властивостями свіжеосадженої поверхні хрому.

Ключові слова: електроосадження, хром, низькотемпературний евтектичний розчинник, кінетика, вихід за струмом.

ELECTRODE PROCESSES IN A DEEP EUTECTIC SOLVENT CONTAINING DISSOLVED CHROMIUM(III) CHLORIDE

V.S. Protsenko *, L.S. Bobrova

Ukrainian State University of Chemical Technology, Dnipro, Ukraine

* **e-mail: Vprotsenko7@gmail.com**

We considered the kinetics of electrochemical processes occurring during electrodeposition of coatings from a low-temperature ionic liquid based on a eutectic mixture of choline chloride and ethylene glycol, in which a trivalent chromium salt is dissolved. Irreversible current waves of Cr(III) ions discharge on a glassy carbon electrode in the electrolytes of studied compositions are not described by the «classical» equations of linear and cyclic voltammetry, which is due to both the presence of the migration component of the current and the cathodic passivation of the electrode. It has been established that the introduction of additional water into the electrolyte leads to an increase in the current density of the wave of irreversible discharge of Cr(III) ions on the glassy carbon electrode, which is caused by a significant decrease in the viscosity of the solution. The current efficiency of the chromium deposition reaction decreases when water is introduced into the ionic liquid. The X-ray amorphous coatings electrodeposited from the electrolyte under study, along with chromium, contain carbon and oxygen, the inclusion of which is due to the electrocatalytic properties of the freshly deposited chromium surface.

Keywords: electrodeposition; chromium; deep eutectic solvent; kinetics; current efficiency.

REFERENCES

1. Danilov FI, Protsenko VS. Chromium electrodeposition using electrolytes based on trivalent chromium compounds: a review. *Voprosy Khimii i Khimicheskoi Tekhnologii.* 2020; (2): 4-29. doi: 10.32434/0321-4095-2020-129-2-4-29.

2. Protsenko VS, Gordiienko VO, Danilov FI, Kwon SC, Kim M, Lee JY. Unusually high current efficiency of nanocrystalline Cr electrodeposition process from trivalent chromium bath. *Surf Eng.* 2011; 27: 690-692. doi: 10.1179/1743294410Y.0000000019.

3. Danilov FI, Protsenko VS, Butyrina TE. Chromium electrodeposition kinetics in solutions of Cr(III) complex ions. *Russ J Electrochem.* 2001; 37: 704-709. doi: 10.1023/A:1016764600973.

4. Surviliene S, Nivinskiene O., Cesuniene A, Selskis A. Effect of Cr(III) solution chemistry on electrodeposition of chromium. *J Appl Electrochem.* 2006; 36: 649-654. doi: 10.1007/s10800-005-9105-8.

5. Smith EL, Abbott AP, Ryder KS. Deep eutectic solvents (DESs) and their applications. *Chem Rev.* 2014; 114: 11060-11082. doi: 10.1021/cr300162p.

6. Alfurayj I, Fraenza CC, Zhang Y, Pandian R, Spittle S, Hansen B, et al. Solvation dynamics of wet ethaline: water is the magic component. *J Phys Chem B.* 2021; 125: 8888-8901. doi: 10.1021/acs.jpcb.1c04629.

7. Protsenko V, Bobrova L, Danilov F. Trivalent chromium electrodeposition using a deep eutectic solvent. *Anti-Corros Methods Mater.* 2018; 65: 499-505. doi: 10.1108/ACMM-05-2018-1946.

8. Mejia-Caballero I, Aldana-Gonzalez J, Manh TL, Romero-Romo M, Arce-Estrada EM, Campos-Silva I, et al. Mechanism and kinetics of chromium electrochemical nucleation and growth from a choline chloride/ethylene glycol deep eutectic solvent. *J Electrochem Soc.* 2018; 165: D393-D401. doi: 10.1149/2.0851809jes.

9. Protsenko VS, Bobrova LS, Kityk AA, Danilov FI. Kinetics of Cr(III) ions discharge in solutions based on a deep eutectic solvent (ethaline): effect of water addition. *J Electroanal Chem.* 2020; 864: 114086. doi: 10.1016/j.jelechem.2020.114086.

10. Qian H, Sun J, Li Q, Sun H, Fu X. Electrochemical mechanism of trivalent chromium reduction in ChCl-EG deep eutectic solvents containing trivalent chromium. *J Electrochem Soc.* 2020; 167: 102511. doi: 10.1149/1945-7111/ab9c8b.

11. Protsenko VS, Bobrova LS, Korniy SA, Danilov FI. Electrochemical synthesis and characterization of electrocatalytic materials for hydrogen production using Cr(III) baths based on a deep eutectic solvent. *Mater Lett.* 2022; 313: 131800. doi: 10.1016/j.matlet.2022.131800.

12. Haerens K, Matthijs E, Binnemans K, Van der Bruggen B. Electrochemical decomposition of choline chloride based ionic liquid analogues. *Green Chem.* 2009; 11: 1357-1365. doi: 10.1039/b906318h.

13. Kityk AA, Shaiderov DA, Vasil'eva EA, Protsenko VS, Danilov FI. Choline chloride based ionic liquids containing nickel chloride: physicochemical properties and kinetics of Ni(II) electroreduction. *Electrochim Acta.* 2017; 245: 133-145. doi: 10.1016/j.electacta.2017.05.144.

14. Taylor AW, Licence P, Abbott AP. Non-classical diffusion in ionic liquids. *Phys Chem Chem Phys.* 2011; 13: 10147-10154. doi: 10.1039/c1cp20373h.

15. Abbott AP, Capper G, Davies DL, Rasheed RK. Ionic liquid analogues formed from hydrated metal salts. *Chem Eur J.* 2004; 10: 3769-3774. doi: 10.1002/chem.200400127.

16. Verdonck T, Verpoort P, De Strycker J, De Cleene A, Banerjee D, Nockemann P, et al. Combining MCR-ALS and EXAFS as tools for speciation of highly chlorinated chromium(III) in mixtures of deep eutectic solvents and water. *Dalton Trans.* 2019; 48: 2318-2327. doi: 10.1039/c8dt04292f.