

Electrodeposition of Cr coatings from a trivalent chromium plating bath based on deep eutectic solvent

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The electrodeposition of coatings from a trivalent chromium plating bath based on deep eutectic solvent was characterized in this work. The electrolyte contained chromium (III) chloride, choline chloride and the additive of extra water. The plating bath allowed electrodepositing chromium coatings with an amorphous type of microstructure, which contain some carbon and oxygen. The influence of the coatings thickness on a surface morphology was established by means of SEM technique. The polarization measurements confirmed the stepwise reduction of Cr(III) to Cr(0). The current efficiency of chromium electrodeposition reaction was stated to increase with increasing current density and decreasing temperature. The microhardness of deposits reached ca. 550–600 HV. The coatings obtained using plating bath based on DES showed electrocatalytic activity towards the hydrogen evolution reaction in acidic medium.

1. Introduction

Chromium coatings are widely used in up-to-date industry, because they ensure high microhardness, wear and corrosion resistance, attractive surface appearance, etc. [1]. Commonly, chromium coatings are electrodeposited from aqueous plating baths containing compounds of hexavalent chromium, which are extremely dangerous to the environment and people's health. It is known that EU adopted Regulation No 1907/2006 which forbade or severely limited the use of Cr(VI) compounds in functional and decorative electroplating. Therefore, the development of effective alternatives to hexavalent chromium electroplating is considered as a very important problem in the surface engineering and applied electrochemistry [2]. Trivalent

chromium electrodeposition is a possible and attractive option to resolve this problem [2–9]. Although some attempts have been made to replace Cr(VI) plating processes by trivalent chromium ones, there are still a number of problems which are mainly related to a very intricate solution chemistry of Cr(III) complexes in aqueous solutions [10]. In this context, chromium electroplating baths on the basis of deep eutectic solvents seem to be a promising alternative to "common" technologies.

Deep eutectic solvents (DESs) are fluids consisting of a eutectic mixture of some organic and inorganic components [11]. The melting point of a DES is lower than those of individual constituents due to the formation of hydrogen bonds between molecules and ions in the liquid mixture. DESs have an ionic character with respect to their transport properties [12–15]. The physicochemical and service properties of DESs are similar to those of "common" ionic liquids, while DESs are cheaper, more available and environmentally friendlier [11].

DESs can be successfully used in various electrochemical processes, especially in electrodeposition and electroplating [16–19].

A number of works have been published to date, in which some aspects of chromium electrodeposition from DESs based electrolytes were considered [20–27]. Nevertheless, some important questions remain practically unrevealed. For instance, published works reported the physicochemical properties of Cr(III)-containing DESs [21, 24, 27], electrocrystallization behavior [23] and electrochemical mechanism of Cr(III) electroreduction [21, 23, 25, 26]. However, the effect of electrodeposition conditions on current efficiency has not been systematically investigated. In addition, some properties of the coatings obtained from DESs based electrolytes are poorly studied. For example, the effects of electrolysis duration on the current efficiency and surface morphology of deposits have not been described yet. The microhardness of coatings deposited from choline chloride based Cr(III) plating bath has not been determined.

This work was aimed to summarize the main results of our study on the electrodeposition of chromium coatings prepared from a deep eutectic solvent with the addition of extra water. We characterized the surface morphology of Cr coatings

with different thickness, determined the microstructure and composition of deposits, defined voltammetry responses in the Cr(III) electrolyte based on DES and established the effects of current density and bath temperature on the current efficiency of chromium deposition. In addition, we measured the microhardness values of deposits and evaluated the electrochemical behavior of Cr coatings in an acidic medium in a wide range of electrode potentials.

The main results of this work have been published in our previous paper [28].

2. Experimental

Chromium coatings were electrodeposited using an electrolyte prepared 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 deep eutectic solvent was synthesized by mixing choline chloride (ChCl) and $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ in the molar ratio of 2.5:1, respectively [29]. The mixture was kept in a thermostatic heater at the temperature of 70 °C and continuously stirred until a homogenous, dark green fluid had formed. A required amount of bidistillate water was further added to the DES and the mixture was stirred at the same temperature to obtain a homogenous fluid.

Thus, the ionic liquid containing $\text{CrCl}_3 + 2.5\text{ChCl} + 15\text{H}_2\text{O}$ was under consideration, where numbers denotes the molar proportions between the components.

It should be noted that extra water was introduced into ionic fluids containing CrCl_3 and ChCl to increase their electrical conductivity and decrease viscosity to the values which are acceptable to perform electrolysis under laboratory conditions [27–29]. Table 1 gives literature data on the effect of extra water on the viscosity and conductivity. Note that the value $x = 6$ in Table 1 is related to the liquid system without the addition of extra water (all water originates from hexahydrate salt $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$).

Table 1. The influence of water content on conductivity and viscosity of the $\text{CrCl}_3 + 2.5\text{ChCl} + x\text{H}_2\text{O}$ liquid mixtures at 40 °C [28, 29].

x	Conductivity ($\Omega^{-1} \text{ m}^{-1}$)	Viscosity (mPa s)
6	0.058	1958.7
15	1.301	77.2

In electrodeposition experiments, a thermostatted two-electrode cell was used. Chromium was deposited on a disk-shaped sample of copper foil ($S = 1.77 \text{ cm}^2$) placed in a plastic holder. Prior to each experiment, the surface of Cu foil was polished using 0.05 μm alumina slurry and then rinsed with hydrochloric acid solution (1:1 vol.) and distillate water. Platinized titanium was used as an anode without separation of anodic and cathodic compartments.

Voltammetric responses were recorded by means of Potentiostat Reference 3000 (Gamry). The ohmic potential drop was measured and automatically compensated using the built-in IR-compensator of the potentiostat. Electrochemical measurements were carried out in a common glass three-electrode cell. The electrochemical cell was thermostatted with an accuracy of $\pm 0.01 \text{ }^\circ\text{C}$. A platinum disk ($\varnothing 5 \text{ mm}$) in a glass holder was used as a working electrode in these experiments. A Pt wire was used as a counter electrode and the electrode potentials were measured relative to Ag pseudo-reference electrode.

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

The composition of coatings has been also evaluated by means of chemical analysis. In these experiments, a weighed electrodeposited coating was completely dissolved from the substrate in aqueous solution of HCl (1:1 vol.). A further complexation of Cr(III) ions with EDTA yielded stable colored complex, the concentration of which was determined by UV-vis spectroscopy technique (UV/vis spectrophotometer SF-46, $\lambda = 540 \text{ nm}$).

X-ray diffraction analysis was performed by means of an X-ray diffractometer DRON-3.0 in the monochromatized Co-K α radiation.

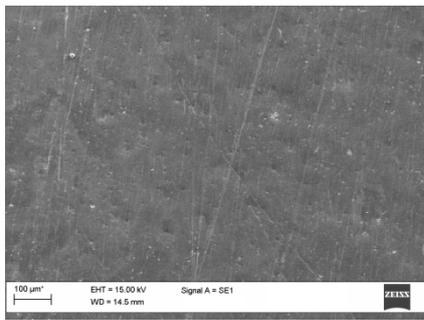
Vickers microhardness test was conducted using PMT-3 device at a 100 g load, and the coatings thickness was not less than 20 μm . The average microhardness of the deposits was calculated based on five separate measurements.

To estimate the corrosion-electrochemical behavior of obtained chromium coatings, the potentiodynamic polarization curves were recorded. An aqueous solution of 0.5 M H $_2$ SO $_4$ was used as a corrosive medium. Dissolved atmospheric oxygen was removed by purging purified electrolytic hydrogen. The coatings were electrodeposited on the gold disc electrode. The counter electrode was made of porous graphite. The potentials were measured towards the saturated Ag/AgCl reference electrode. The scan rate was 50 mV s $^{-1}$.

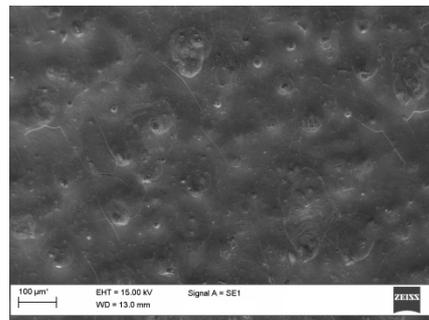
3. Results and discussion

3.1. Surface morphology, microstructure and chemical composition of coatings

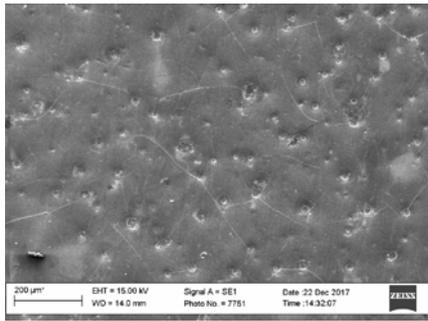
Figure 1 shows typical SEM images characterizing the surface morphology of coatings deposited from the plating bath based on DES. As can be seen, the surface morphology appreciably changes with thickness of coatings. At relatively small thickness (ca. 2.5 μm), the surface is smooth and there are some defects (micropores and microcracks). When the thickness of coatings increases, the cracks on the surface grow and crateriform cavities appear. The depth of these cavities seems to be increased with deposits thickness. Such evolution of the surface morphology is typical of chromium coatings obtained from plating baths on the basis of Cr(III) salts [5, 30].



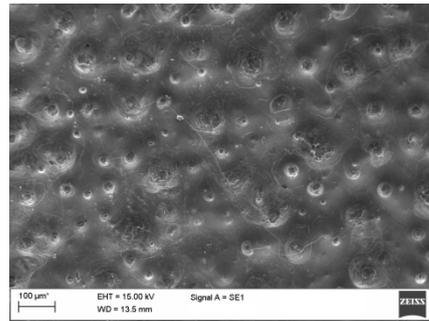
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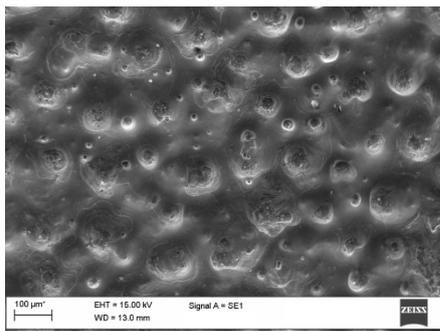
b



c



d



e

Fig. 1. SEM images of the surface of coatings deposited from the electrolyte based on DES with different average thickness (μm): (a) 2.5, (b) 5, (c) 10, (d) 15 and (e) 20 [28].

It is known that the electrodeposition of chromium is accompanied by simultaneous hydrogen evolution reaction (HER) both in aqueous electrolytes and in those prepared using DESs [5, 27]. The bubbles of hydrogen evolved remain on the surface for some time and partially block it. When chromium layers are grown around a hydrogen bubble attached to the surface, a cavity is formed. The plating electrolytes on the basis of DES are relatively viscous, therefore, the withdrawal of hydrogen gas bubbles is hindered in this case. Evidently, the longer the electrolysis

duration (that means an increase in average deposits thickness), the deeper are the cavities formed on the surface.

The X-ray diffraction patterns revealed the amorphous structure of the coatings (Fig. 2). The formation of X-ray amorphous or nanocrystalline structures of deposited coatings is commonly observed for Cr(III) electroplating baths [4, 5, 30, 31].

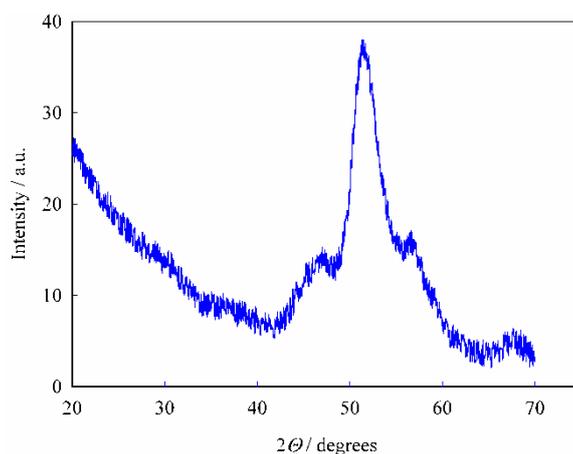


Fig. 2. Typical X-ray diffraction pattern of a coating deposited from the bath containing $\text{CrCl}_3 + 2.5\text{ChCl} + 15\text{H}_2\text{O}$ at 7 A dm^{-2} and $40 \text{ }^\circ\text{C}$ [28].

The results of EDX analysis showed the presence of such elements as Cr, C, Cl and O on the coatings surface (Fig. 3, Table 2). As expected, chromium is a dominant element. The oxygen spectra may be originated as a result of the formation of a thin oxide passive film on a chromium surface. Additionally, oxygen can be incorporated into coatings in the form of poorly soluble hydroxide compounds of Cr(III), which are always formed in the near-electrode layer during chromium electrodeposition [3]. Chlorine (a very weak signal) may be detected due to the capture of some chloride ions from the plating electrolyte. As concerns the presence of carbon in coatings, it can be explained by interaction of a part of active chromium ad-atoms with adsorbed organic bath constituents by the so-called "chemical" mechanism [32]. The incorporation of carbon into the electrodeposits hinders surface diffusion of chromium ad-atoms that ensures the formation of amorphous or nanocrystalline structure, and chromium can exist as nanocrystalline phases of chromium carbides [4, 7, 31, 32]. The identification of the phases of chromium carbides in the obtained

X-ray diffraction patterns (Fig. 2) is complicated by the fact that the diffraction peaks of amorphous chromium is relatively broad, and they can overlap the responses from other phases.

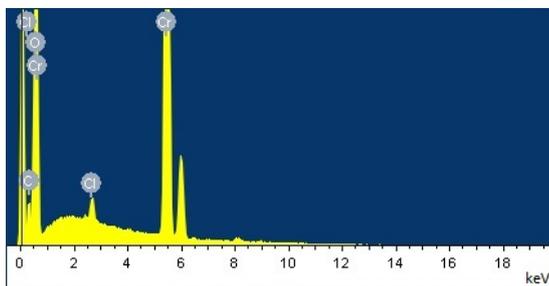


Fig. 3. Typical EDX spectrum of the surface of a coating deposited from the bath containing $\text{CrCl}_3 + 2.5\text{ChCl} + 12\text{H}_2\text{O}$ at 7 A dm^{-2} and $40 \text{ }^\circ\text{C}$ [28].

Table 2. Chemical composition of the coating surface according to the results of EDX analysis [28].

Element	Content (wt.%)
Cr	83.04
O	10.52
Cl	0.97
C	5.74

It should be observed that EDX may provide ambiguous and uncertain information on the content of light elements (like O and C). In order to confirm the presence of carbon in electrodeposits obtained from the DES based plating bath, we annealed the coatings and perform the X-ray diffraction analysis of the heat-treated material. Earlier, Zeng et al. [33] and Huang et al. [34] have stated that the annealing of amorphous Cr–C layers at the temperatures of $400\text{--}600 \text{ }^\circ\text{C}$ leads to the their crystallization and the peaks originated from chromium carbide can be easily observed in XRD patterns.

As follows from the data shown in Fig. 4, pronounced diffraction peaks corresponding to Cr_2O_3 and Cr_{23}C_6 are seen in the XRD patterns of the coatings annealed at $500 \text{ }^\circ\text{C}$. This confirms the presence of carbon in as-deposited coatings.

3.2. Potentiodynamic polarization study and current efficiency of chromium electrodeposition reaction

Figure 6 shows the cyclic voltammetry curve recorded on a Pt electrode in the chromium (III) plating electrolyte based on DES. The polarization curve looks like those described earlier for similar electrochemical systems [24–26]. In the cathodic branch, the reduction peak C_1 corresponds to the electrochemical reaction $\text{Cr(III)} + e^- \rightarrow \text{Cr(II)}$. At a further increase of cathode polarization, the current density starts to steeply rise (peak C_2) which can be attributed to both the formation of metallic chromium according to the reaction $\text{Cr(II)} + 2e^- \rightarrow \text{Cr(0)}$ and the hydrogen evolution reaction. The formation of metallic chromium as well as the evolution of H_2 bubbles in this range of electrode potential can be visually detected.

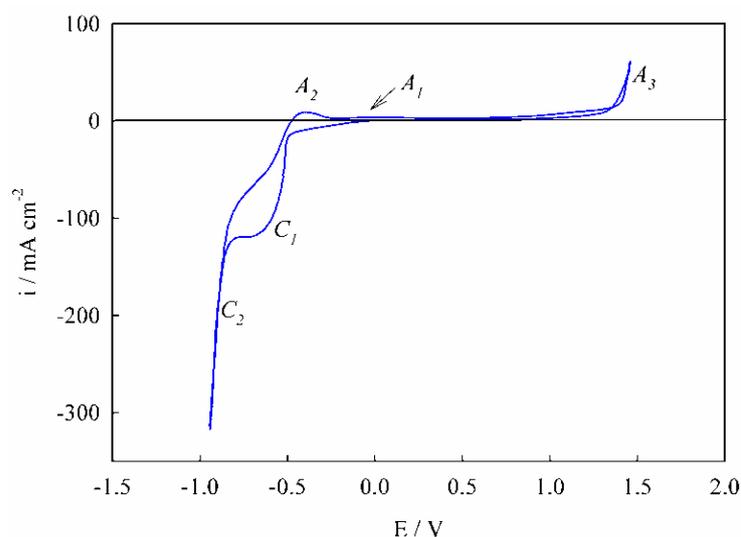


Fig. 6. Cyclic voltammetry curve recorded on platinum electrode in the electrolyte containing $\text{CrCl}_3 + 2.5\text{ChCl} + 15\text{H}_2\text{O}$. The scan rate was 125 mV s^{-1} and the temperature was $70 \text{ }^\circ\text{C}$ [28].

In the reverse anodic scan, three current peaks are observed. The current peak A_2 is associated with the oxidation of Cr(0) to Cr(II) (electrochemical dissolution of chromium). The peak A_1 (a weak signal) can be assigned to the oxidation of Cr(II) to Cr(III) . The current peak A_3 corresponds to the anodic evolution of gaseous chlorine. In general, the results of cyclic voltammetry study are in good agreement with the

concept of stepwise reduction of Cr(III) with the participation of Cr(II) complexes as intermediates [3, 35, 36].

The current efficiency of the partial reaction of chromium deposition reaction (Cr(III)→Cr(0)) 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 correction for the content of metallic chromium in the coatings (Fig. 5) was applied in these calculations. The current efficiency of chromium electrodeposition reaction increases with increasing current density and decreasing bath temperature (Table 3). Such behavior is typical of trivalent chromium electroplating baths [1, 2, 5]. It should be noted that the bath temperature has no effect on the surface appearance of coatings and semi-bright and uniform layers with a good adhesion to the substrate are obtained in the temperature range of 30 to 60 °C. The current density has more pronounced effect upon the surface appearance of coatings: the surface of deposits becomes relatively rough and not bright enough if the current density exceeds the value of about 10 A dm⁻². Therefore, we think that the most suitable current density is close to 3–7 A dm⁻².

Table 3. The effects of temperature and current density on the current efficiency of chromium electrodeposition reaction in the plating bath containing CrCl₃ + 2.5ChCl + 15H₂O. Electrolysis duration was 20 min [28].

Temperature (°C)	Current density (A dm ⁻²)	Current efficiency (%)
30		24.6
40	3	12.7
50		6.7
60		2.5
	5	11.7
50	7	15.6
	10	24.1

It is important that the current efficiency only slightly diminishes with electrolysis time (by ca. 1–2% during several tens of minutes of electrolysis) which can be associated with a gradual development of the surface area in the course of electrodeposition process (see Fig. 1). However, thick layers can be obtained from the chromium plating bath under consideration, and hence these coatings can be used not only as thin "decorative" Cr (with a thickness of ca. 1 μm) but also in "hard" chromium electroplating where the thickness of deposits reaches several tens micrometers [1].

3.3. Microhardness and corrosion-electrochemical behavior of coatings

Microhardness is a very important characteristic of industrial chromium electrodeposits [1]. The measured values of microhardness of chromium coatings deposited from the DES based plating bath are shown in Fig. 7. Abbott et al. [21] established that soft chromium coatings with a microhardness of 242 HV are deposited from ionic liquids based on the mixture of choline chloride and CrCl_3 (without extra water addition). The use of special additives to the electrolyte allowed increasing the microhardness to ca. 600 HV.

It can be seen from the data given in Fig. 7 that the coatings with the microhardness of about 550–600 HV can be deposited using the deep eutectic solvent containing the addition of extra water, without any other special organic or inorganic additives. It should be observed that the microhardness of as-deposited coatings prepared in this work is close to that typical of industrial hard chrome (from hexavalent chromium bath) [1, 2].

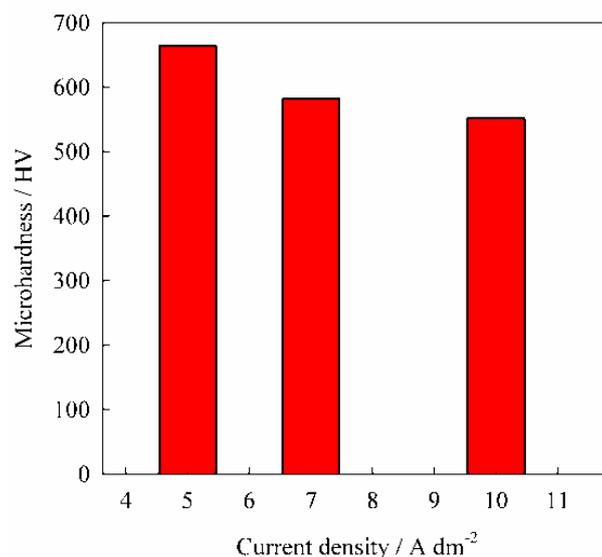


Fig. 7. Microhardness of deposits prepared from the bath containing $\text{CrCl}_3 + 2.5\text{ChCl} + 15\text{H}_2\text{O}$ at different current densities. The electrolyte temperature was $40\text{ }^\circ\text{C}$.

The corrosion-electrochemical behavior of the coatings was evaluated by the potentiodynamic polarization technique (Fig. 8). The polarization curve of "pure" chromium (obtained from common hexavalent chromium plating baths) is given for the sake of comparison (Fig. 8, curve 1). This curve exhibits all specific features typical of chromium in an acidic medium: the region of hydrogen evolution reaction, the active dissolution peak and the regions of passive and transpassive states [37]. However, the coating prepared from the DES shows quite a different electrochemical behavior: the active dissolution region disappears, and the open circuit potential increases (Fig. 8, curve 2).

The transpassive region shifts towards more negative potentials. It should be observed that the cathodic branch of the polarization curve corresponding to the HER shifts in the direction of more positive potentials indicating the electrocatalytic properties of the coatings deposited from the plating bath containing DES.

We think that the particular corrosive and electrochemical behavior of Cr-deposits obtained in this work (an anomalous shape of polarization curves recorded in an acidic medium) can be presumably associated with the presence of some carbon in the coatings. Carbon incorporated into the film structure provides the formation of a

protective film on the surface of the coatings [4]. Edigaryan et al. [38] attributed a special electrochemical behavior of the chromium carbide electrodeposits obtained from a trivalent Cr-bath to the presence of chromium carbides in them. Chromium carbides can be peculiar "cathodic agents" that shift the open circuit potential to the passivity region. Apparently, these considerations can be extended to the electrodeposits prepared in this work. It should also be noted that the electrocatalytic activity of chromium carbides in the reaction of hydrogen evolution reaction has been detected in a number of works [39–41].

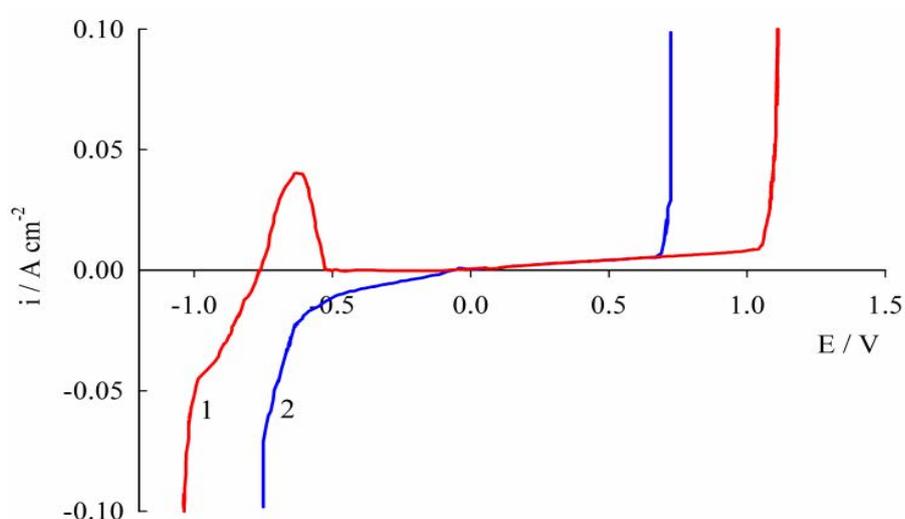


Fig. 8. Potentiodynamic polarization curves recorded on chromium deposits in 0.5 M H₂SO₄ at 25 °C. The coatings were electrodeposited from the bath containing 250 g dm⁻³ CrO₃ and 0.025 g dm⁻³ H₂SO₄ at 40 A dm⁻² and 45 °C (1) and from the bath containing CrCl₃ + 2.5ChCl + 15H₂O at 5 A dm⁻² and 40 °C (2). The scan rate was 50 mV s⁻¹ [28].

4. Conclusions

We reported in this work the electrodeposition of chromium coatings using environmentally friendly trivalent chromium plating bath on the basis of a deep eutectic solvent. The electrolyte contains the mixture of CrCl₃, choline chloride and some extra water. The obtained coatings have an amorphous type of microstructure which crystallized after the thermal treatment showing the presence of chromium carbide. Thus, as-deposited coatings included some carbon which was also confirmed by the results of EDX analysis. The polarization measurements displayed stepwise electroreduction of Cr(III) that is typical of chromium deposition from Cr(III) electrolytes. The electrodeposition is accompanied by the hydrogen evolution

reaction which affects the surface morphology (the formation of cavities on the surface) and results in the fact that the current efficiency of chromium deposition reaction is not more than 25%. The current efficiency grows both when increasing current density and decreasing electrolyte temperature. The microhardness of as-deposited Cr coatings prepared in this work is about 550–600 HV. The polarization curve characterizing the electrochemical behavior of the obtained coatings in 0.5 M H₂SO₄ differs from that of "usual" chromium: there is no region of active dissolution and the region corresponding to the HER shifts towards more positive potentials, indicating the electrocatalytic properties of the synthesized electrodeposits.

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