Electrodeposition of black chromium from Cr(III)-ionic liquid solution

Sónia EUGÉNIO[1], Carmen M. RANGEL[1,2], Rui VILAR[1]

[1] Departamento de Engenharia de Materiais, Instituto Superior Técnico, Universidade Técnica de Lisboa, Portugal, E-mail:s.eugenio@ist.utl.pt, rui.vilar@ ist.utl.pt
[2] Fuel Cells and Hydrogen, Instituto Nacional de Energia e Geologia; Estrada do Paço do Lumiar, 1649-038 Lisboa, Portugal
E-mail: carmen.rangel@lneg.pt

Abstract:

Black chromium is an important coating material used in solar thermal systems as a spectrally selective surface. This coating is usually obtained by electrodeposition from sulphate free chromium (VI) aqueous solutions which represent a health and environmental hazard due to the presence of Cr(VI), a known toxic and carcinogenic agent. Recent developments in green chemistry have shown that ionic liquids can be used as electrolytes, allowing the deposition of a wide range of materials with negligible environmental and health impacts.

In the present study, the electrodeposition of black chromium films from a solution of ionic liquid containing chromium (III) has been investigated by cyclic voltammetry and chronoamperometry. Homogeneous and well adherent black Cr films have been obtained on several substrates, by potentiostatic electrodeposition. The films morphology and composition have been characterised by SEM/EDS and GI-XRD.

Keywords: ionic liquids, black chromium, electrodeposition

1. Introduction

Chromium and chromium oxides are important coating materials. Chromium is widely used as a decorative or functional coating, depending on its thickness. Decorative chromium is up to 0.8 µm thick and is usually applied over a nickel undercoat to increase corrosion resistance. Thicker chromium coatings, up to 500 µm, also called hard-chromium, are applied in wear resistant surfaces in aerospace, oil and gas, heavy equipment and a range of general industrial applications [1, 2].
Another type of chromium-based coating is black chromium, a mixture of metallic chromium and its oxides, which has its main application as absorbing coating in solar thermal panels [1-3].
Usually, chromium coatings are electrodeposited from aqueous solutions containing hexavalent chromium (Cr(VI)). Cr(VI) poses serious health and environmental concerns: is sharply irritating to the mucous membranes of the nose and throat and potentially carcinogenic, so contact with these solutions as well as inhalation of the mist formed during electrodeposition must be avoided. Moreover, due to its toxicity, treatment of waste waters before disposal is mandatory. These drawbacks have acted as an incentive for the development of alternative chromium plating electrolytes. The most obvious choice would be to use aqueous solutions of the less toxic trivalent chromium (Cr(III)). These electrolyes have been extensively studied, but their formulation is quite complex and often proprietary [2].
A less explored alternative for the electrodeposition of chromium is the application of Cr(III) ionic liquid solutions. Ionic liquids have several characteristics that make them interesting for electrochemical applications: high thermal stability, good conductivity, recyclability and low toxicity [4]. Another important feature is their large electrochemical window when compared to water which allows the electrodeposition of a range of metals impossible to deposit from aqueous solutions due to hydrolysis, such as aluminium and titanium [5]. First generation ionic liquids are chloroaluminate-based ionic liquids and have been extensively studied has electrolytes for the electrodeposition of aluminium and its alloys [5]. More recently, air and water stable ionic liquids have proven to be suitable for the electrodeposition of a wide range of materials [5].
Up to now only very few papers have been published on this subject. Abbott et al. [6-8] reported the electrodeposition of chromium from an ionic liquid analogue solution consisting of choline chloride and hexahydrated chromium salt. In the present paper, we report the electrodeposition of black chromium thin films from a solution of Cr(III) ions in 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm][BF_4]).

2. Materials and Methods

Cr(III) solutions in 1-n-butyl-3-methylimidazolium tetrafluoroborate [BMIm][BF_4] (Merck) -0.4 M were prepared by adding $CrCl_3.6H_2O$ (Merck) to the ionic liquid and mixing both components for several hours under vacuum. The resulting solution was reddish-purple in colour.
Electrochemical characterisation of the ionic liquid solutions and electrodeposition experiments were carried out inside a glove box with Ar controlled atmosphere (O_2 and H_2O< 2 ppm), using a conventional three-electrode cell setup and an Autolab PGSTAT100 potentiostat. A platinum plate (A= 1 cm^2) was used as counter electrode and a wire of the same material as quasi-reference electrode (QRE), to which all potentials are referred. The working electrode was one of the following materials:

glassy carbon (GC), AISI 304 austenitic stainless steel, Ck-45 carbon steel, copper (Cu) and nickel (Ni). Prior to electrochemical experiments, the counter and reference electrodes were immersed in diluted nitric acid for at least 15 minutes, thoroughly rinsed with distilled water and dried with hot air. The working electrode was subjected to a pre-treatment, as described in Table 1, rinsed with distilled water and dried with hot air.

Table 1. Surface treatment performed on working electrodes before electrochemical and electrodeposition experiments.

Working electrodes	**Surface preparation**			
	Polishing	**Degreasing**	**Chemical pre-treatment**	
			Solution	Time (s)
GC	Al_2O_3 suspension	Acetone ultrasonic bath	-	
AISI 304 stainless steel	SiC paper 1000 grit	NaOH solution ultrasonic bath	1:1 HNO_3:H_2O	15
Ck45 carbon steel	Sand blasted		-	
Cu	SiC paper 1000 grit		1:1 HNO_3:H_2O	15
Ni	SiC paper 1000 and 2400 grit; 3 µm diamond paste		20% vol. H_2SO_4	180

The temperature of the electrolyte solution was maintained constant using a thermostated bath.
Cyclic voltammetry was performed by scanning the applied potential from -2 V, in the anodic direction to an anodic limit of +2 V at a scan rate of 50 mVs^{-1}. At this point, the scan was reversed to the cathodic direction, to stop at the starting potential.
Electrodeposition experiments were carried out under potentiostatic conditions. During the experiments, the solution was agitated using a magnetic stirrer and the temperature was maintained at 85ºC. After deposition, the samples were thoroughly rinsed with deionized water and acetone and dried using hot air. Their surface morphology and chemical composition were characterised by scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDS) and glancing-incidence X-ray diffraction (GI-XRD) (Siemens D5000) analysis.

3. Results and discussion

The ionic liquid used in the present study, [BMIm][BF_4], was chosen due to its ability to dissolve the chromium salt and relatively low viscosity. Also, this ionic liquid has been used as solvent for electrodeposition of several metals, such as magnesium [9], silver [10, 11] and platinum [12].

3.1. Cyclic voltammetry

The cyclic voltammograms of pure [BMIm][BF_4] and of the Cr(III) solution in this ionic liquid using a GC electrode are presented in Fig. 1.

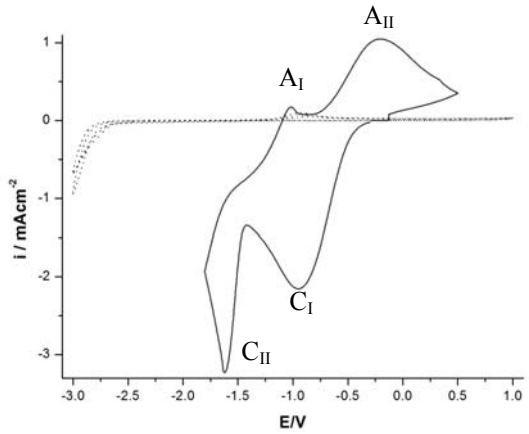

Fig. 1. Cyclic voltammogram of pure [BMIm][BF4] (dotted line) and [BMIm][BF4]+Cr(III) solution (solid line) at room temperature on a GC electrode. Scan rate: 50 mVs-1

The presence of Cr(III) ions in solution significantly changes its electrochemical behaviour. In the forward scan, two cathodic peaks, C_I and C_{II}, appear at -0.9 and -1.6 V respectively, which can be ascribed to the reduction of the Cr electroactive species in solution. The peak C_{II} corresponds to the formation of a solid phase at the electrode surface. In the reverse scan, two anodic peaks, A_I and A_{II}, are observed at -1 and -0.2 V respectively. The first peak can be attributed to the partial dissolution of the solid phase formed during the forward scan, while the second one corresponds to the oxidation of the intermediate Cr-species which was formed by the reduction reaction at -0.9 V during the forward scan.

When the temperature of the electrolyte increases the current density increases and the peaks shift to less negative (more anodic) potentials (Fig. 2). This is probably due to a decrease in the liquid's viscosity, which enhances the mobility of the active species in solution and the deposition rate. This effect is frequently observed in metal salt-ionic liquid electrolytic systems [10].

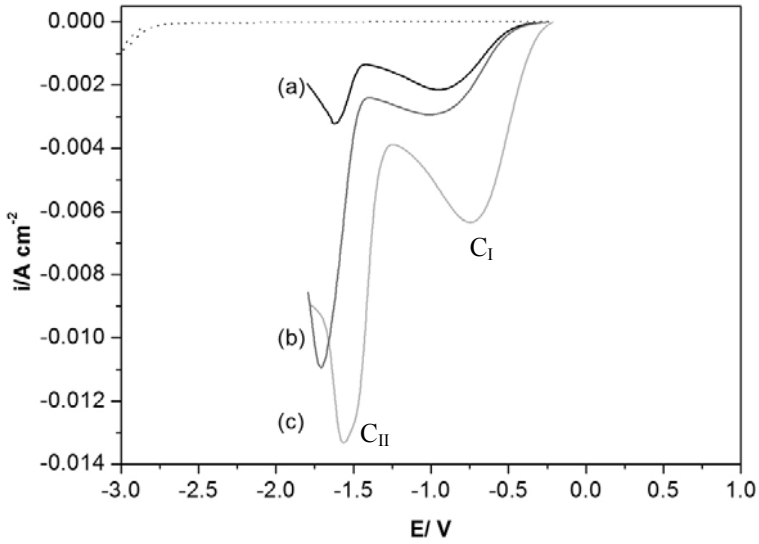

Fig. 2. Cathodic branch of voltammograms obtained in [BMIm][BF_4]+Cr(III) solution at: (a) 30 ºC, (b) 50 ºC and (c) 85 ºC, on a GC electrode. Scan rate: 50 mVs^{-1}

3.2. Electrodeposition of black chromium

Electrodeposition experiments were carried out on AIS 304 stainless steel, Ck-45 carbon steel, Cu and Ni substrates. The potentiostatic deposition experiments were performed using a range of applied potentials (-1 to -2 V), deposition times (300 to 3600 s) and electrolyte solution temperatures (30 to 95ºC) in order to find the optimum deposition parameters. The adhesion of the deposits depends strongly on the pre-treatment performed on the substrates, and the topography of the films is determined by the final topography of the substrates.

3.2.1. AISI 304 stainless steel

SEM micrographs of black chromium films deposited on AISI 304 stainless steel substrates by potentiostatic deposition are presented in Fig. 3. Continuous and homogenous films are obtained for a deposition time of 3600 s. The effect of the applied potential in the morphology of the films is shown in Fig. 3. When the applied potential is more cathodic than -1.5V, the deposited films becomes more fractured and less homogeneous. The films obtained by electrodeposition at -1.5 V present a granular morphology (Fig. 3a), the average size of the constituting particles varying between 0.3 and 0.5 μm.

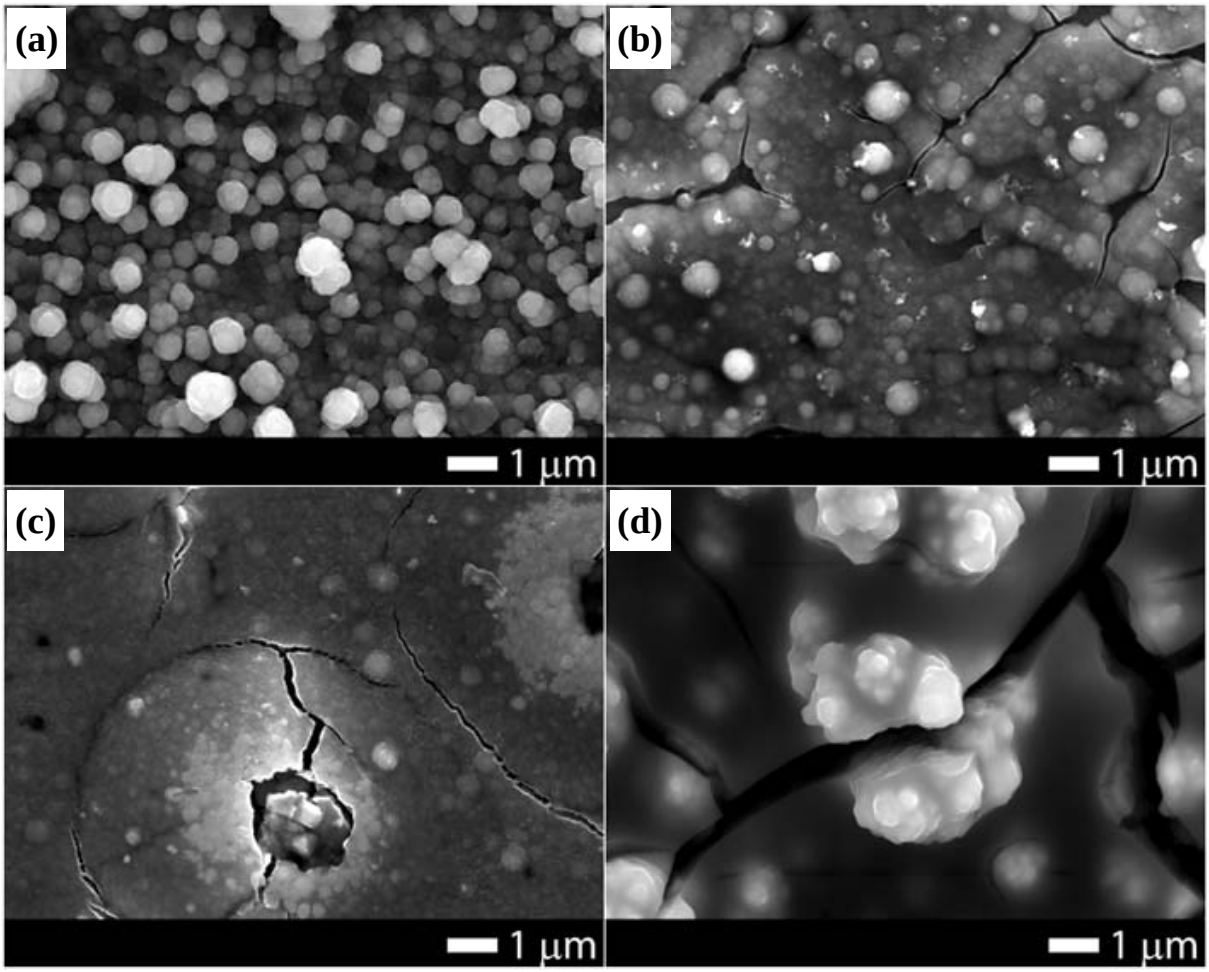

Fig. 3. SEM micrographs of black chromium on stainless steel substrate obtained by potentiostatic deposition for 3600 s at: (a) -1.5 V, (b) -1.7 V, (c) -1.8 V and (d) -2 V.

It was found that the typical cyclic voltammetry curve of Cr(III)-[BMIm][BF_4 solution] (Fig. 4) exhibits a crossover between consecutive scans which indicates that the film is deposited through a nucleation and growth mechanism [13]. The peak at -1.5 V in the cathodic scan is associated with the reduction of Cr(III) active species and electrodeposition of black chromium, while the anodic peak located at about +0.2 V is attributed to the dissolution of the black Cr thin film formed during the cathodic part of the scan.

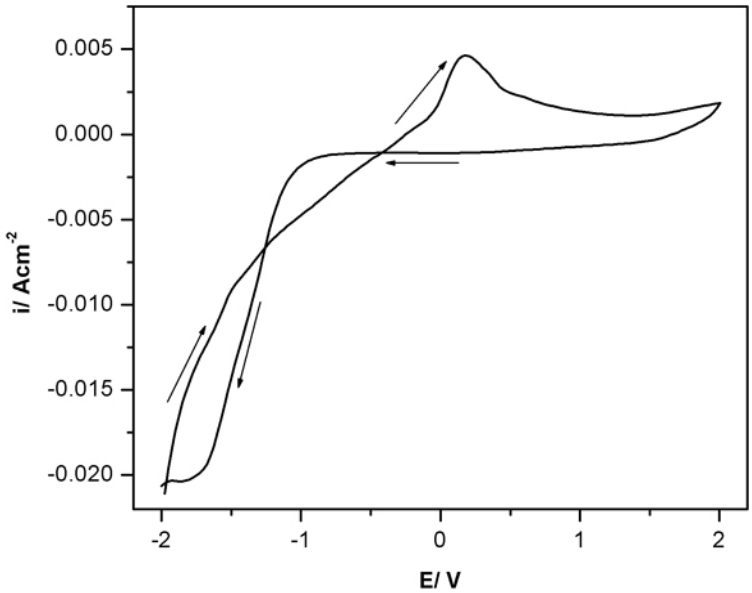

Fig. 4. Cyclic voltammograms of pure [BMIm][BF_4] (dotted line) and [BMIm][BF_4]- Cr(III) solution (solid line) on a 304 stainless steel electrode at 85°C. Scan rate: 50 mVs^{-1}.

The electrodeposition mechanism of the coatings can be identified by comparing experimental potentiostatic current-density time transients obtained by chronoamperometry with theoretical model predictions [13]. In chronoamperometric experiments, the working electrode potential is stepped from a value where no reduction of the active species (Cr(III) in the present case) occurs to a more negative potential which induces electrodeposition and the current density is measured as a function of time. The experimental chronoamperometric curves obtained on a stainless steel substrate are depicted in Fig. 5.

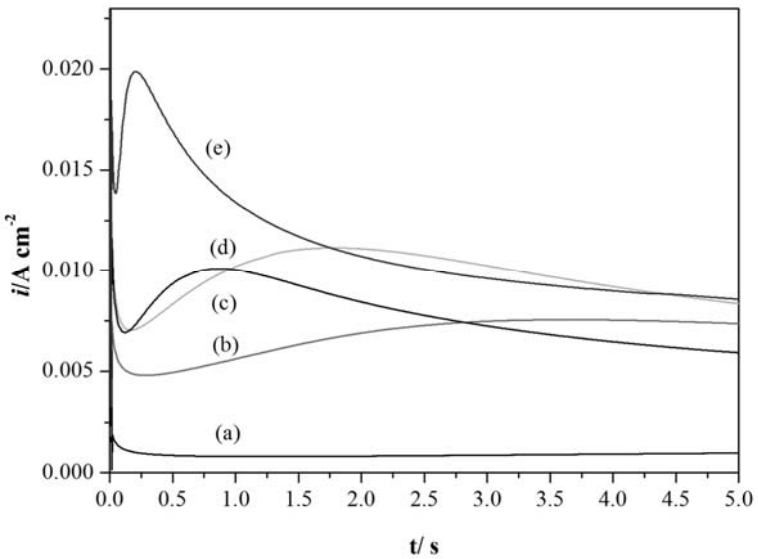

Fig. 5. Chronoamperometric curves at the constant final potential of (a) -0.5, (b) -0.75, (c) -1, (d) -1.25 and (e) -1.5 V.

The model proposed by Scharifker and Hills [14] describes the kinetics of nucleation and diffusion controlled growth of 3D nuclei taking into account the overlap of individual nuclei diffusion zones and the consequent development of nucleation exclusion areas around pre-existing nuclei. This model is widely accepted for electrochemical deposition from aqueous solutions [15] and has been successfully applied to the study of electrodeposition from ionic liquids solutions as well [10-12]. It leads to two non-dimensional equations for the current-density/time variation for two limiting cases of 3D nucleation with diffusion-controlled growth kinetics (Eq. 2 and 3, respectively):

$$\left(\frac{i}{i_{max}}\right)^2 = 1.9542\left(\frac{t_{max}}{t}\right)\left\{1-\exp\left[-1.2564\left(\frac{t}{t_{max}}\right)\right]\right\}^2 \quad (2)$$

$$\left(\frac{i}{i_{max}}\right)^2 = 1.2254\left(\frac{t_{max}}{t}\right)\left\{1-\exp\left[-2.3367\left(\frac{t}{t_{max}}\right)^2\right]\right\}^2 \quad (3)$$

In these equations i_{max} and t_{max} are the current density and the time coordinates of the I(t) curve maximum, respectively (Fig. 5).
The experimental data in Fig. are plotted as $(i/i_{max})^2$ versus (t/t_{max}) in Fig. 6 and compared with the theoretical curves calculated using equations (2) and (3) respectively. A good agreement is obtained between the experimental results and the theoretical values for the instantaneous nucleation according to eq. 2. This result confirms that the nucleation of black chromium films is instantaneous and diffusion-controlled and their growth is 3-dimensional and also diffusion-controlled.

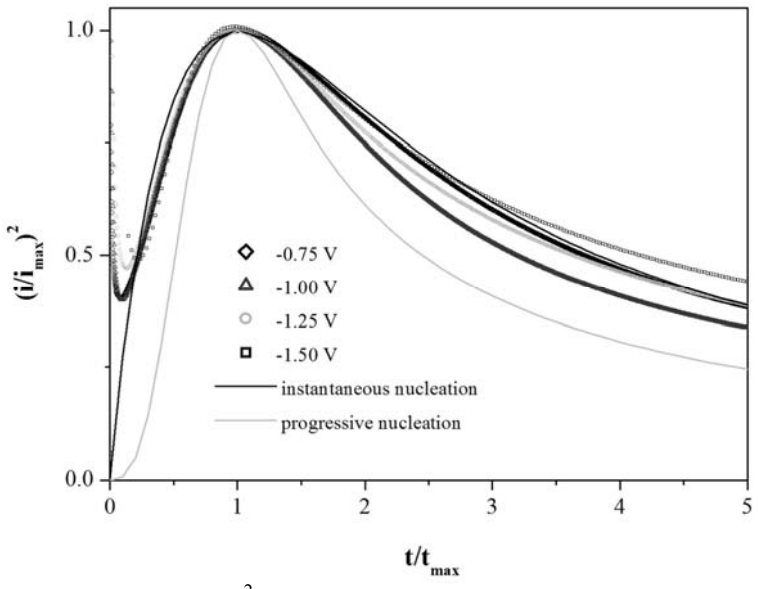

Fig. 6. Non-dimensional $(i/i_{max})^2$ vs t/t_{max} plots obtained from the experimental current-density/time transient for different final potentials. The solid lines represent the theoretical curves calculated on the basis of the Scharifker-Hills nucleation model.

3.2.2. Ck-45 carbon steel

Preliminary electrodeposition experiments on Ck-45 stainless steel show that it is also a suitable substrate for black chromium deposition. Dull black, homogenous coatings have been deposited by potentiostatic method, at -1.5V for 900s.
The substrate was sandblasted before electrodeposition and the surface topography originated by this pre-treatment is steel identified in the coating (Fig. 7). Nevertheless, as in stainless steel substrates, the film is formed of sub-micrometric particles.

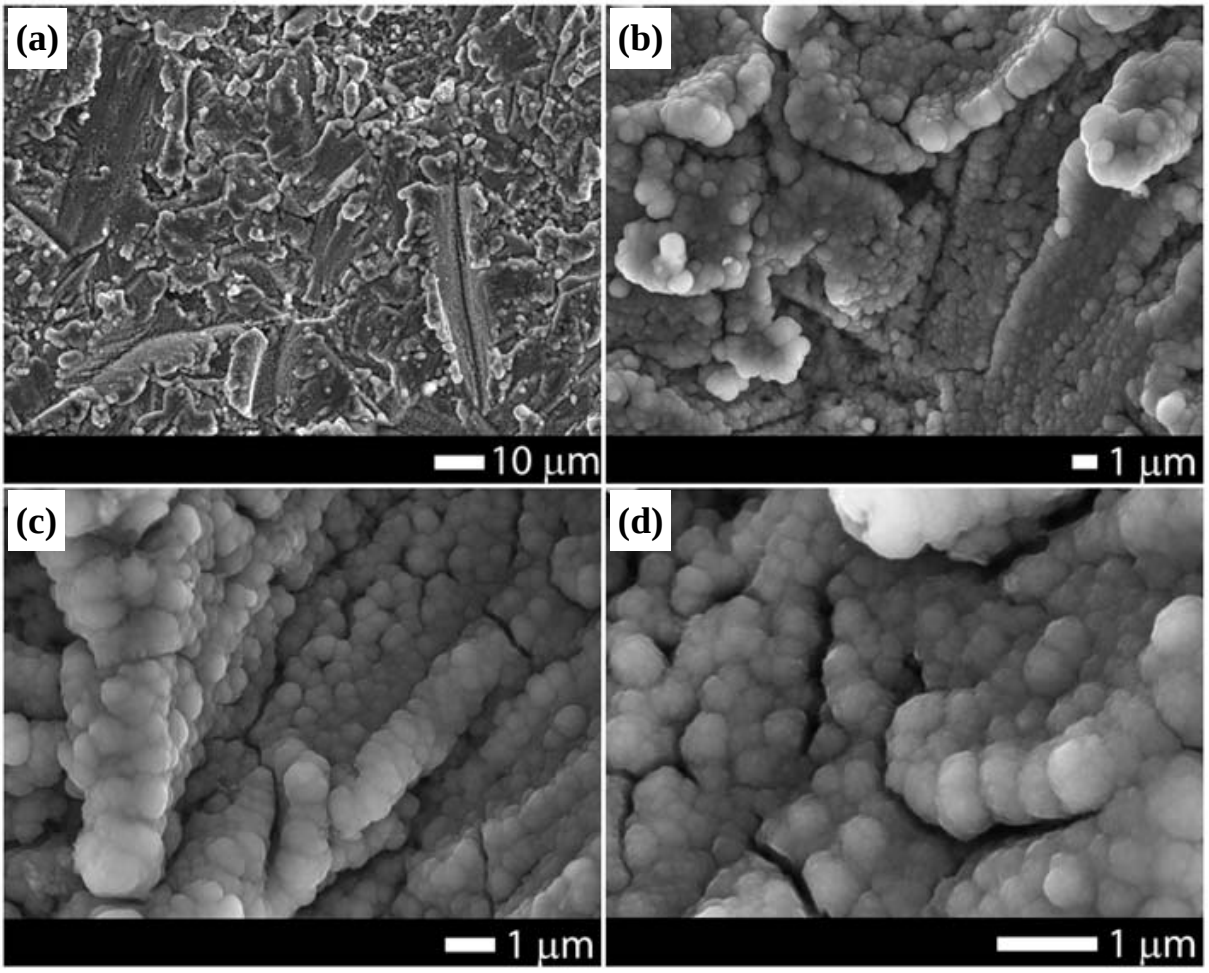

Fig. 7. SEM micrographs of black chromium on carbon steel substrate obtained by potentiostatic deposition at -1.8 V for 900 s.

3.2.3. Cu substrate

Black chromium films were deposited on Cu substrates by potentiostatic deposition at -1.5 V. The best results were obtained for deposition times between 900 and 1800 s. In these conditions, the films deposited are homogeneous, uniform and well adherent to the substrate and present a sub-micrometric granular structure. A further increase in deposition time leads to an increase in the number of microcracks of the film (Fig. 8 d).
The surface topography of the films reproduces the surface topography of the substrate; since the substrate was etched in nitric acid before electrodeposition it presents a surface relief showing the grain boundaries and twins existing in the material (Fig. 8 a, b and c). The surface defects are preferential nucleation sites for the thin film material.

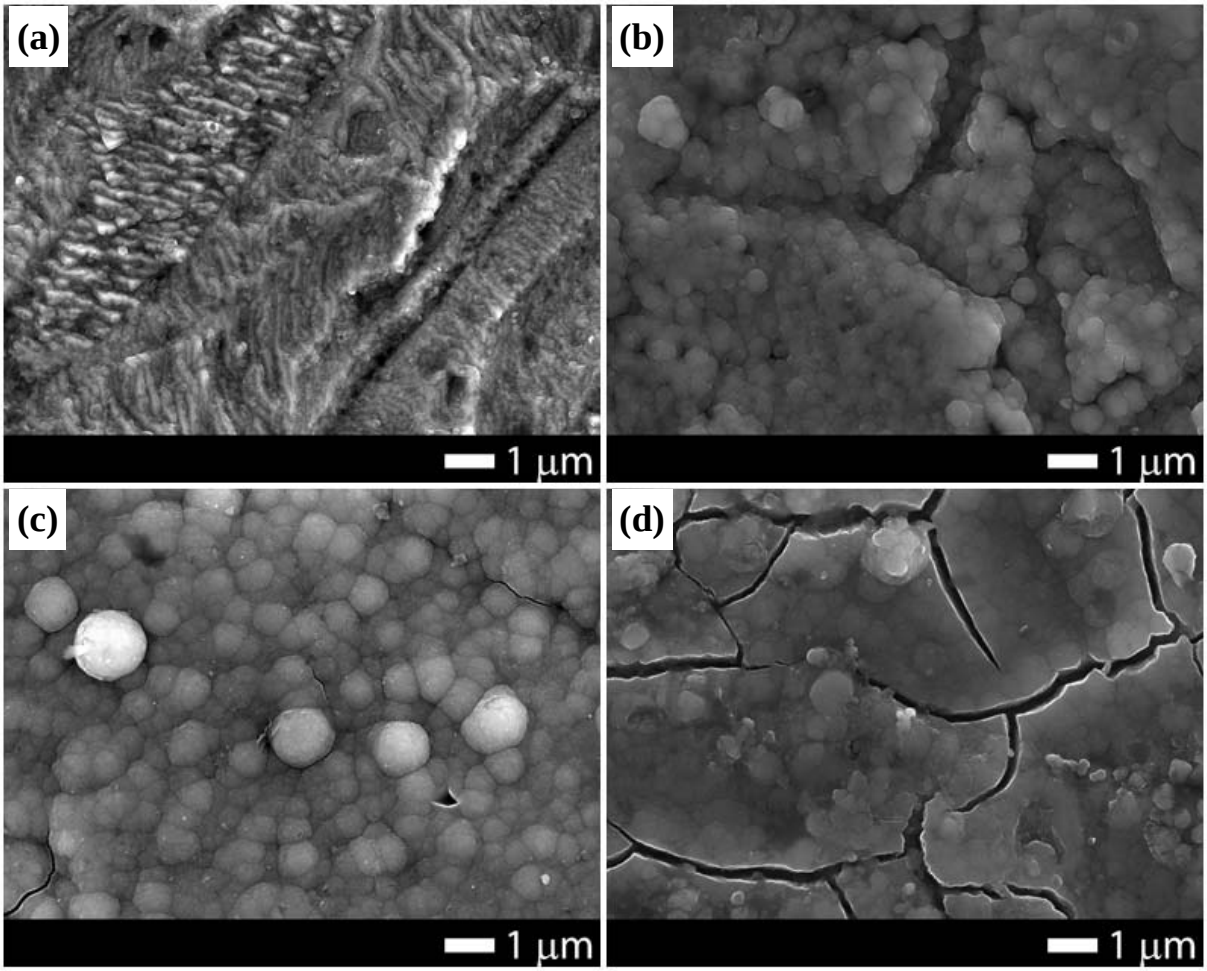

Fig. 8. SEM micrographs of black chromium on Cu substrate obtained by potentiostatic deposition at -1.5 V for: (a) 300s, (b) 900 s, (c) 1800 s and (d) 3600 s.

3.2.4. Nickel substrate

Black chromium films were deposited on Ni substrates by potentiostatic deposition at -1.5 V (Fig. 9). In this condition, black adherent films constituted by sub-micrometric particles were obtained. Just like in Cu substrates, the increase in deposition time leads to an increase of particle size, and for deposition times higher than 3600 s the films become highly fractured.

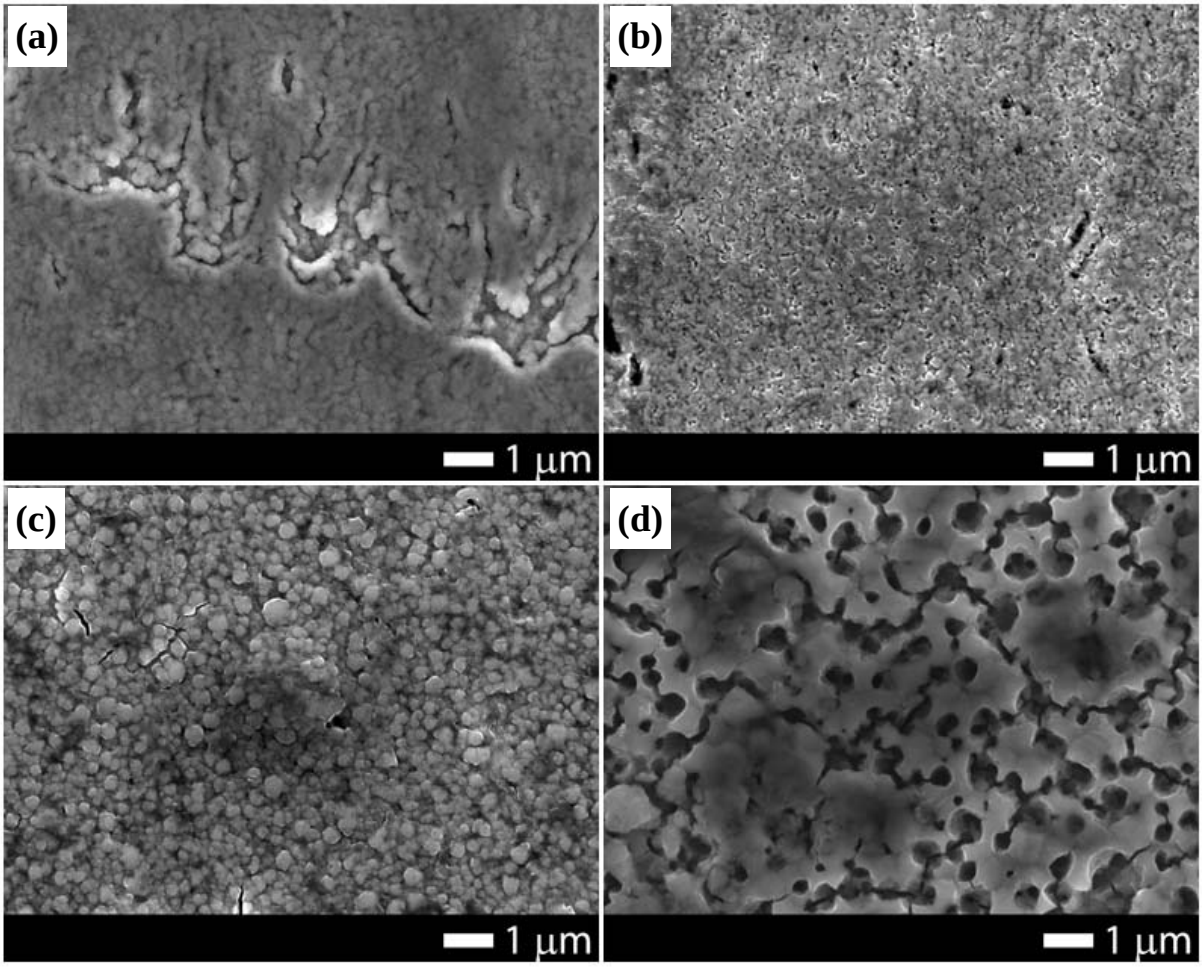

Fig. 9. SEM micrographs of black chromium on Ni substrate obtained by potentiostatic deposition at -1.5 V for: (a) 300s, (b) 900 s, (c) 1800 s and (d) 3600 s.

3.3. Chemical and phase composition

The chemical composition of the black chromium films was studied by EDS. The main elements present in the coatings are Cr and O. Small quantities of Cl and F are also detected, suggesting that some electrolyte is absorbed or trapped in the film during its formation. Moreover, peaks related to the substrate are often observed due to the small thickness of the deposits when compared to the penetration of the electron probe in the material.

The diffractograms of the coatings only show peaks that can be ascribed to the substrate. This result suggests that the coating material is amorphous, or nanocrystalline, with a particle size too small to produce coherent diffraction.

4. Conclusions

- It is possible to prepare a 0.4M solution of $CrCl_3.6H_2O$ in [BMIm][BF_4] ionic liquid. The voltammetric study of the solution allows the identification of the potential window where the electroreduction processes occur.
- The cyclic voltammograms of Cr^{3+} solutions in [BMIm][BF_4] ionic liquid using a stainless steel electrode present a crossover which indicates that the film grows by a

nucleation process. Analysis of the current density transients using the Scharifker–Hills nucleation model shows that the electrodeposition process occurs by instantaneous nucleation with 3D growth under diffusion control.
- Black Cr films electrodeposited have also been electrodeposited in carbon steel, copper, nickel. The films are homogeneous and well adherent, present a granular morphology and are formed of sub-micrometric particles.

5. References

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