

Electrodeposition of black chromium thin films from trivalent chromium-ionic liquid solution

S. Eugénio⁽¹⁾, R. Vilar^{(1)*}, C. M. Rangel⁽²⁾ and I. Baskaran⁽¹⁾

(1) Departamento de Engenharia de Materiais, Instituto Superior Técnico, Universidade Técnica de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal. E-mail: s.eugenio@ist.utl.pt, rui.vilar@ist.utl.pt, iruson.baskaran@ist.utl.pt.

(2) Unidade de Electroquímica de Materiais, Instituto Nacional de Engenharia, Tecnologia e Inovação, Paço do Lumiar, 22 1648-039 Lisboa, Portugal. E-mail: carmen.rangel@ineti.pt.

* Corresponding author.

Abstract – In the present study, black chromium thin films were electrodeposited from a solution of 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm][BF₄]) ionic liquid containing trivalent chromium (Cr(III)). Homogeneous and well adherent coatings have been obtained on nickel, copper and stainless steel substrates. The nucleation and growth of the films were investigated by cyclic voltammetry and current-density/time transient techniques. SEM/EDS, XPS and XRD were used to study the morphology, chemical composition and structure of the films. The coatings consist of a mixture of metallic chromium and chromium oxides (black chromium) and present a sub-micrometric granular structure.

Black chromium is an important coating material used in solar thermal systems as a spectrally selective surface and is usually produced by electrodeposition from hexavalent chromium (Cr(VI)) aqueous solutions. However, these electrolytes raise serious health and environmental concerns, and their replacement has been long pursued. Developments in green chemistry have shown that ionic liquids can be used as electrolytes, due to their wide electrochemical window and enhanced chemical stability when compared to water [1]. These characteristics allow the electrodeposition of a wide range of materials including aluminium and titanium, which are impossible to deposit from aqueous solutions [1].

In the present study, black chromium thin films were electrodeposited from solutions of 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm][BF₄]) containing trivalent chromium (Cr(III)). Cyclic voltammetry and current-density/time transient techniques were used to study the nucleation and growth of the films. Electrodeposition was carried out on copper, nickel and austenitic stainless steel substrates, by a potentiostatic method. The coatings were characterized by SEM/EDS, XPS and XRD.

Cyclic voltammetry allows the identification of the potential range at which the reduction reaction corresponding to the formation of black chromium occurs. Current-density/time transients were recorded on stainless steel substrates and fitted the Scharifker–Hills model equations. This analysis indicates that the formation of black chromium on this substrate occurs by an instantaneous nucleation process with diffusion controlled three-dimensional growth.

Homogeneous and well adherent black chromium coatings were obtained on all substrate materials. The films present a sub-micrometric granular structure (Fig.1). EDS chemical analysis showed that the main elements present in the coating are Cr and O. XPS analysis confirmed the presence of Cr oxides and metallic Cr. XRD results suggest that the coating material is amorphous.

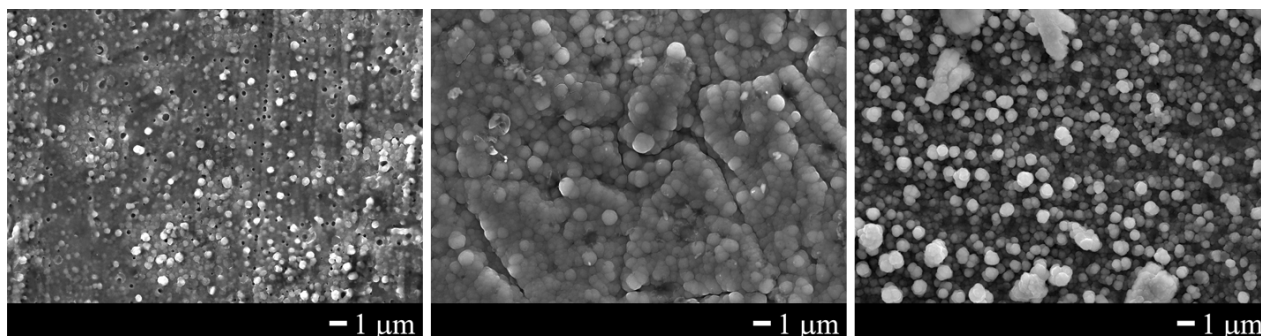


Figure 1: Scanning electron micrographs of black Cr coatings electrodeposited from [BMIm][BF₄]-Cr(III) solution on (a) nickel, (b) copper and (c) stainless steel.

References

[1] F. Endres, D. MacFarlane, A. Abbott (eds), *Electrodeposition from Ionic Liquids*, Wiley-VCH (2008).