

## Electrodeposition of Co-Cr Black Coatings on Steel in an Ionic Liquid, For Solar Collection Applications

Gregorio Vargas, Ana P. García, Juanita Cerda and Jorge López

CINVESTAV-IPN, Unidad Saltillo, Calle Industria Metalúrgica No. 1062, Parque Industrial Saltillo - Ramos Arizpe, Ramos Arizpe, Coahuila, México, CP 25900

### Abstract

The electrodeposition of Co-Cr black coatings on AISI 304 stainless steel substrates was studied using a solution of Co and Cr salts in an ionic liquid as electrolyte. The electrolyte was prepared employing choline chloride (ChCl) and ethylene glycol (EG) in molar ratios of 1:2, 1:8 and 1:16, as well as Co and Cr salts in molar ratios of 1:1, 2:1 and 4:1. The electrodeposition times were 30, 45 and 60 min. Cyclic voltammetry was used in order to define the potential window in an interval from -1.93 to 1.12 V. The electrodeposition was carried out by chronoamperometry. Scanning Electron Microscopy (SEM) was used to characterize the microstructure and chemical composition of the coatings. Their optical properties were characterized by using UV-Vis spectroscopy and Fourier-Transform Infrared spectroscopy (FT-IR). Homogeneous black coatings having absorptivities ( $\alpha$ ) of 0.98 and emissivities ( $\epsilon$ ) of 0.03 were obtained, which were suitable for their application in solar thermal collectors.

Keywords: *Black Co-Cr coatings, deep eutectic solvents, optical properties.*

---

### 1. Introduction

Spectrally selective surfaces for applications in solar thermal collectors must have high absorptivity ( $\alpha$ ) and low emissivity ( $\epsilon$ ) values. Electrodeposition of black Cr has been widely studied for applications in solar collectors due to their good optical properties ( $\alpha = 0.97$  and  $\epsilon = 0.19$ ) (Grimmer and Collier, 1981; Eugenio et al., 2011). The toxicity of Cr (VI) has incentivized the study of systems using instead Cr (III) in less toxic water-based electrolytes (Eugenio et al., 2011). However, the success of such systems has been limited by the chemical complexity of the Cr (III) ions in such solutions (Ferreira et al., 2013), as well as due to the hydrogen embrittlement underwent by the coatings (Saravanan and Mohan, 2012). Recently, a new family of ionic liquids, including Deep Eutectic Solvents (DES), has been developed (Abbott, 2006). These liquids are generally composed by two or more environmentally friendly components that are able to associate freely, often through hydrogen bonds (Abbott, 2006). The aim of the present work is to show that the electrodeposition of Co-Cr black coatings on stainless steels, using Co-Cr salts and an ionic liquid as electrolyte, allowed us to obtain spectrally selective coatings that are suitable for applications in solar thermal collectors.

### 2. Experimental Method

The electrolyte was prepared employing ethylene glycol (EG), choline chloride (ChCl), chromium chloride hexahydrate ( $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ ) and cobalt chloride hexahydrate ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ). ChCl and EG mixtures (ethaline) were used in molar ratios of 1:2, 1:8 and 1:16, and the Co and Cr salts were used in molar ratios of 1:1, 2:1 and 4:1. The electrodeposition times were 30, 45 and 60 min. Cyclic voltammetry was used in order to define the potential window. The electrolyte was kept at a constant temperature of 60 °C. The studies were carried

out using a three-electrode electrochemical cell, employing a vitreous carbon electrode ( $A = 0.007 \text{ cm}^2$ ), a stainless steel counter electrode ( $A = 0.785 \text{ cm}^2$ ) and an Ag/AgCl reference electrode. The electrodeposition was carried out on AISI 304 stainless steel substrates. Both, the electrochemical studies and the electrodeposition were carried out using a PARSTAT 4000 potentiostat/galvanostat, controlled by the Versa Studio 2.43 software. The employed electrochemical techniques were voltammetry and chronoamperometry. The optical properties of the coatings were characterized using a LAMBDA 850 UV/Vis spectrophotometer, fitted with a 150 mm integrating sphere for the determination of the absorptivity ( $\alpha$ ). The emissivity ( $\varepsilon$ ) was determined employing a Frontier FT-IR spectroscopy fitted with an accessory for diffuse reflectance spectroscopy, which allowed us to obtain the spectral reflectance curves (reflectance vs. wavelength) for the studied coatings.

The values of  $\alpha$  were calculated employing equation 1 (Li, 2000):

$$\alpha = \frac{\int_{0.3\mu\text{m}}^{2.5\mu\text{m}} (1 - R) I_{sol} d\lambda}{\int_{0.3\mu\text{m}}^{2.5\mu\text{m}} I_{sol} d\lambda} \quad (\text{eq. 1})$$

where  $I_{sol}$  is the solar radiation taken from the ASTM AM1.5 standard (ASTM AM1.5, 2012), while  $R$  and  $\lambda$  are reflectivity and total hemispherical wavelength, respectively.

The values of  $\varepsilon$  were calculated at 100 °C employing equations 2 and 3 (Li, 2000):

$$\varepsilon = \frac{\int_{2.5\mu\text{m}}^{25\mu\text{m}} (1 - R) I_p d\lambda}{\int_{2.5\mu\text{m}}^{25\mu\text{m}} I_p d\lambda} \quad (\text{eq. 2})$$

$$I_p = \frac{2 \times 10^{-24} hc^2}{\lambda^5} \frac{1}{e^{\frac{10^6 hc}{\lambda kT}} - 1} \quad (\text{eq. 3})$$

where  $I_p$  is the black body radiation at 100 °C,  $c$  is the speed of light ( $2.998 \times 10^8 \text{ m s}^{-1}$ ),  $h$  is Planck's constant ( $6.628 \times 10^{-34} \text{ J s} = 4.136 \times 10^{-15} \text{ eV s}$ ), and  $k$  is Boltzmann's constant ( $1.381 \times 10^{-23} \text{ J K}^{-1} = 8.617 \times 10^{-5} \text{ eV K}^{-1}$ ).

Scanning Electron Microscopy (SEM) was used to characterize the microstructure and chemical composition of the coatings. This was carried out using a PHILIPS XL30ESEM apparatus, with a voltage of 20 KeV and a working distance of 10 mm.

### 3. Results and Discussion

Cyclic voltammetry allowed us to define the potential window (electrochemical stability range for the electrolyte) in an interval from -1.93 to 1.12 V (see Figure 1). At potential values higher than 1.15 V (anodic side), current density is rapidly increased, which is attributed to the decomposition of the medium, i.e., oxidation of Cl<sup>-</sup>. At potential values smaller than -1.5 V (cathodic side), a reduction process is observed with a decrement in the current density, which indicates a reduction of hydrogen (Souza et al., 2007). An additional event occurring at 0.72 V, corresponding to the reduction of ethaline, was also identified. The potential window determined in this work agrees with previously published research (Binder, 2010) for ethaline.

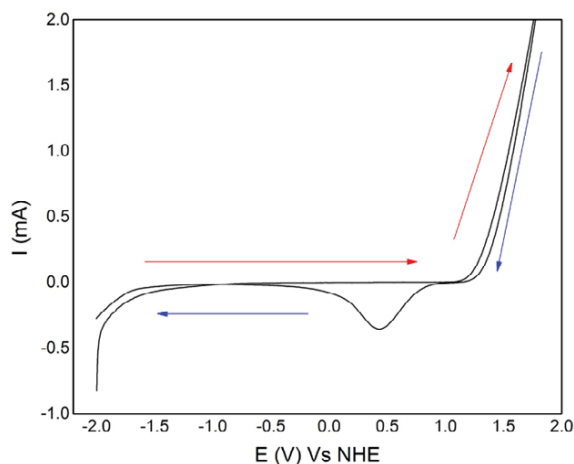


Fig. 1: Cyclic voltammety curve of Ethaline obtained at 65 °C and  $V = 25 \text{ mVs}^{-1}$  in vitreous carbon.

According to Figure 2, when  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  were present in a molar ratio of 2:1 in ethaline, a displacement was observed in reduction peak I (dotted line), which corresponds to reduction of ethaline, towards more anodic potentials (from 0.72 to 0.88 V), which was due to the presence of Cr (III) and Co (II) ions in the solution.

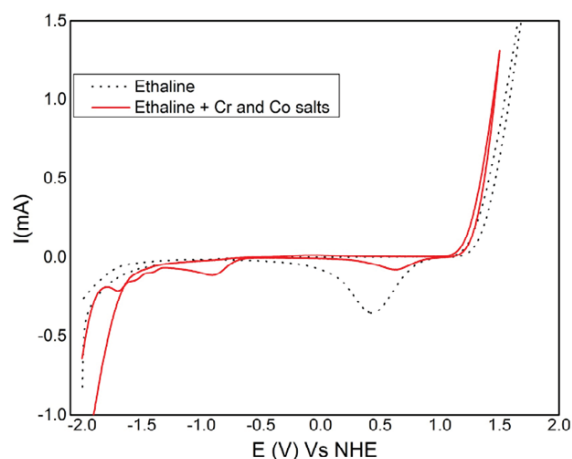


Fig. 2: Cyclic voltammety curves of ethaline and ethaline +  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  +  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  obtained at 65 °C and  $V = 25 \text{ mVs}^{-1}$  in vitreous carbon.

In this case, three reduction processes were observed in the potential window, which were located at -1.05, -1.38 and -1.6 V. The first one corresponded to the reduction of Cr (III) to Cr (II), the second one to the reduction of Cr (II) to Cr (0), and the third one to hydrogen embrittlement underwent by the coatings. These results are consistent with those reported by Eugenio et al. (2011).

To confirm the existence of the reduction processes observed when the electroactive species were added to ethaline, linear-sweep voltammety tests were carried out at more electronegative potentials. Figure 3 shows the corresponding voltammety curve in which three different processes can be appreciated: the first one was located at -1.06 V & Ag/ AgCl (1), the second one appeared at -1.38 V & Ag/ AgCl (2), and the third one was found at -1.6 V & Ag/ AgCl (3).

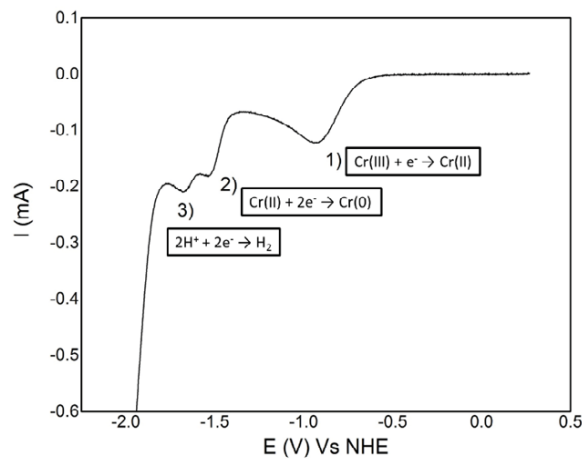


Fig. 3: Linear-sweep voltammetry curve of ethaline +  $\text{CrCl}_2 \cdot 6\text{H}_2\text{O}$  +  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  obtained at  $T = 65^\circ\text{C}$  with a sweep speed of  $25 \text{ mVs}^{-1}$ .

Chronoamperometric runs were carried out at the potentials identified in the voltammetric studies in order to select the working potential, which was based on the observation that uniform black deposits were obtained only at the potentials of  $-1.06$  and  $-1.38$  V. In contrast, black deposits were not obtained at a potential of  $-1.6$  V due to the evolution of hydrogen at the metal surface. Furthermore, an excessive formation of bubbles was visible in the electrolytic solution in the cell, which apparently caused that the deposit layers became fractured, and thus, the electrodeposition was hindered, resulting in a damaged electrode.

Table 1 shows the factors and levels used to study the effect of the processing variables on the optical properties of the coatings.

Tab. 1. Factors and levels used in the employed L9 orthogonal array Taguchi experimental design.

Factors	Level 1	Level 2	Level 3
ChCl: EG molar ratio in the electrolyte	1:2	1:8	1:16
Co:Cr salt molar ratio	1:1	2:1	4:1
Voltage (V)	-1.06	-1.22	-1.38
Time (min)	30	45	60

Table 2 shows the employed L9 orthogonal array Taguchi experimental design, as well as the  $\alpha$  and  $\epsilon$  values obtained for the coatings deposited on the AISI 304 stainless steel substrates.

Tab. 2. L9 orthogonal array Taguchi experimental design.

Experiment	Independent variables				Dependent variables	
	Electrolyte	Co:Cr salt molar ratio	Voltage (V)	Time (min)	$\alpha$	$\epsilon$
1	1:2	1:1	-1.06	30	0.59	0.07
2	1:2	2:1	-1.22	45	0.55	--
3	1:2	4:1	-1.38	60	0.85	0.08
4	1:8	1:1	-1.22	60	0.90	0.16
5	1:8	2:1	-1.38	30	0.97	0.19
6	1:8	4:1	-1.06	45	0.95	0.18
7	1:16	1:1	-1.38	45	0.77	0.03
8	1:16	2:1	-1.06	60	0.98	0.03
9	1:16	4:1	-1.22	30	0.94	0.09

As it can be seen, the stainless steel substrates without electrochemical treatment showed an  $\alpha$  value of 0.55, while the substrates with electrodeposited coatings achieved  $\alpha$  values of up to 0.98. The best  $\alpha$  values were achieved employing a deposition potential of  $-1.06$  V for 60 min, with a ChCl:EG molar ratio of 1:16 and a

$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}:\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  molar ratio of 2:1. Sample 8 showed a value of  $\alpha = 0.98$  and a value of  $\varepsilon = 0.035$ . The lowest  $\varepsilon$  value obtained corresponded to sample 7 ( $\varepsilon = 0.0309$ ). This sample was coated using a deposition potential of  $-1.38\text{ V}$  & Ag/AgCl for 45 min, with a ChCl:EG molar ratio of 1:16 and a  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}:\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  molar ratio of 1:1. However, this sample showed a value of  $\alpha = 0.77$ . According to Malhotra and Chopra (1986), an increment in the value of  $\alpha$  is considerably more favorable than a reduction in the value of  $\varepsilon$ . Mar et. al. (1976), in a similar previous work, reported values of  $\alpha = 0.91$  and  $\varepsilon = 0.07$  ( $T = 100\text{ }^\circ\text{C}$ ). In this work, higher values of  $\alpha$  and  $\varepsilon$  were achieved.

Sample 8, which showed the best optical properties, was characterized by SEM/EDS in order to identify and quantify the composition of the areas of interest. The SEM studies revealed that the black deposits were composed of Cr and Co oxide particles, whose chemical composition and morphology varied in the sample's cross section (Tab. 3. Results of the SEM/EDS analysis carried out in the cross-section of sample 8.3).

Tab. 3. Results of the SEM/EDS analysis carried out in the cross-section of sample 8.

Sample	Analyzed zone	Elemental Composition (wt.%)				
		O	Cr	Co	Cu	Fe
8	I	15.97	20.3	56.28	-	7.45
	II	17.58	19.68	60.93	-	1.81

The SEM micrograph and photograph of Figure 4 correspond to sample 8. At a glance, it can be observed that the formed coating was uniformly distributed throughout the substrate surface, showing a black coloration.

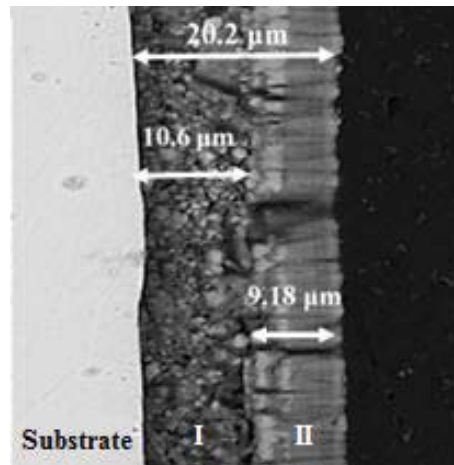


Fig. 4: SEM micrograph and photograph taken for the sample for which the best coating was obtained (sample 8).

The SEM micrograph of Figure 4 shows the morphology of the coating obtained on the surface of sample 8, in which the presence of equiaxed (zone I) and columnar (zone II) particles can be noticed. According to Table 3, it can be seen that both zones had a high content of Co and Cr, and thus, it was deduced that they were composed by a mixture of Co and Cr oxides. The main compositional difference among both zones was a higher Fe content in zone I and a higher Co content in zone II. Saravanan and Mohan (2012), who investigated a similar system, observed the formation of nodular particles. Probably in this study the variation in the composition of the used electrolyte and salts, as well as the applied potential, influenced the composition and morphology of the coatings. The coating formed on the surface of sample 8 was dense and compact, with zone I with a thickness of  $10.6\text{ }\mu\text{m}$ , and zone II with a thickness of  $9.18\text{ }\mu\text{m}$ . The coating thickness was dependent on the time of deposition.

#### 4. Conclusions

The electrochemical study of the system ethaline/Co-Cr chloride salts allowed us to establish the conditions required to obtain uniform and well-adhered black Co-Cr oxide coatings on AISI 304 stainless steel

substrates, with excellent optical properties suitable for their application in solar thermal collectors ( $\alpha = 0.98$  and  $\epsilon = 0.03$ ).

The efficiency of the process was controlled mainly by the molar composition of the electrolyte.

The conditions employed to obtain the electrochemical coating having the best optical properties were: a ChCl:EG molar ratio of 1:16, a Co:Cr salt molar ratio of 2:1, and a deposition potential of -1.06V.

The SEM characterization of the best deposited coating revealed that it was composed by two layers formed by particles with different morphologies, which probably consisted of a mixture of Co and Cr oxides. The total thickness of the coating was approximately 20  $\mu\text{m}$ .

## 5. References

Abbott, A.P., McKenzie, K.J., 2006. Application of ionic liquids to the electrodeposition of metals. *Phys. Chem. Chem. Phys.* 8, 4265-4279.

ASTM G173, 2012. Standard Tables for Reference Solar Spectral Irradiances: Direct Normal and Hemispherical on 37° Tilted Surface. American Society for Testing and Materials, West Conshocken, PA, USA.

Binder, Q.A.L., 2010. Synthesis and Characterization of Choline Chloride Based Binary Mixtures. *ECS Trans.* 33, 49-59.

Eugenio, S., Rangel, C.M., Vilar, R., Botelho do Rego, A.M., 2011. Electrodeposition of black chromium spectrally selective coatings from a Cr(III)-ionic liquid solution. *Thin Solid Films* 519, 1845-1850.

Ferreira, E.S.C., Pereira, C.M., Silva, A.F., 2013. Electrochemical studies of metallic chromium electrodeposition from a Cr(III) bath. *J. Electroanal. Chem.* 707, 52-58.

Grimmer, D.P., Collier R.K., 1981. Black-chrome solar-selective coatings electrodeposited on metallized glass tubes. *Sol. Energy* 26, 467-469.

Li, L., 2000. AC anodization of aluminum, electrodeposition of nickel and optical property examination. *Sol. Energy Mater. Sol. Cells* 64, 279-289.

Malhotra, L.K., and Chopra, K.L., 1986. Selective Coatings for Photothermal Conversion, in: Garg, H.P. (Eds), *Solar Water Heating Systems: Proceedings of the Workshop on Solar Water Heating Systems*, Springer Science & Business Media, New Delhi, pp. 169-178.

Mar, H.Y.B., Peterson, R.E., and Zimmer, P.B., 1976. Low cost coatings for flat plate solar collectors. *Thin Solid Films* 39, 95-103.

Saravanan, G., Mohan, S., 2012. Structure composition and corrosion resistance studies of Co-Cr alloy electrodeposited from deep eutectic solvent (DES). *J. Alloys Compd.* 522, 162-166.

Souza, R.F., Padilha, J.C., Gonçalves, R.S., de Souza M.O., Rault-Berthelot, J., 2007. Electrochemical hydrogen production from water electrolysis using ionic liquid as electrolytes: Towards the best device. *J. Power Sources* 164, 792-798.