

# J E P T

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## 1. Introduction

The electrodeposition of chrome from  $\text{Cr}^{+6}$  electrolytes has been one of the most widely used electroplating systems in the plating industry during the last decades. The usual direct current processes are based on chromic acid solutions with the addition of a catalyst, being sulfuric acid, fluoride compounds or a mix of them the most common ones [1-3]. The Sargent type electrolyte [4] is still being used in the plating industry in spite of the actual efforts to change to more friendly electrolytes based on  $\text{Cr}^{+3}$  formulations [2, 5-7]. The  $\text{Cr}^{+6}$  based electrolytes are mainly used for producing metallic chromium deposits of different hardness and brightness that fulfills a vast number of practical applications [2, 3, 8, 9]. Different chromium species, such as  $\text{Cr}_2\text{O}_3$  and

$\text{Cr}(\text{OH})_3$ , can be electrodeposited modifying bath formulations through the addition of nitrates, carbonates, fluorides or organic additives to the chromic acid solution. In that way it has been possible to obtain solar selective black chromium deposits on copper substrates for solar energy absorbing systems [10-13]. In last decades, the use of pulsed current and pulse reverse current techniques has been increasing because they improve coating quality and process performance [14-16]. In this work, systematic investigation of SWPO electrolysis of a  $\text{CrO}_3/\text{H}_2\text{SO}_4$  electrolyte without levelling or brightening additives is presented. Preliminary cyclic voltammetry (CV), potentiostatic deposits (PD), potential steps and capacitance ( $C_E$ ) vs. potential curves were done to characterize this rather complex electrochemical system and to establish the limiting values of the

parameters of the SWPO signal. The morphology and chemical composition of the electrodeposits was controlled selecting the SWPO perturbation parameters. It was possible to obtain classic cracked metallic chromium films, crack free chromium deposits, layers of faceted  $\text{Cr}_2\text{O}_3$  crystals and leaf type morphologies of  $\text{Cr}(\text{OH})_3$ . The oxidation number of chromium, the oxygen content and the hardness of the coatings varied markedly with the SWPO signal parameters. As a result of this investigation a new method to obtain chrome deposits with different chemical compositions and morphologies from the same  $\text{Cr}^{+6}$  electrolyte without additives has been developed. The resulting morphologies of the metallic chromium, chromium hydroxide and mixtures of chromium oxides are well characterized and some insight into the possible mechanism of coating growth is given.

## 2. Experimental

The electrolyte used was a conventional chrome plating bath containing  $250 \text{ g L}^{-1} \text{ CrO}_3$  and  $2.5 \text{ g L}^{-1} \text{ H}_2\text{SO}_4$  ( $S_{\text{CR}}$ ). The working electrodes were  $0.3 \text{ cm}^2$  surface area flat copper sheets cut from virgin circuit board plates, and the counter electrode was made of Pb-5%Sb alloy as is usually referred in the literature [2] with anode to cathode areas ratio of 20:1 [5] and the electrolyte volume was 100 ml. CV were done at a sweep rate of  $20 \text{ mVs}^{-1}$  at  $50 \pm 0.1^\circ\text{C}$ . PD were obtained on the copper cathodes under free convection at  $50 \pm 0.1^\circ\text{C}$  during 120 s. Short duration potential steps were applied to the copper cathodes in the plating electrolyte and 1 s current density (CD) transients were analyzed.  $C_E$  vs. potential curves were recorded for the copper electrodes in the chrome plating bath at  $50 \pm 0.1^\circ\text{C}$  considering a simple RC series equivalent circuit. A frequency of 1.5 kHz was chosen for the ac signal because the capacity readings were stable and reproducible in a frequency range

from 0.5 to 3 kHz. A potential scan rate of  $2 \text{ mVs}^{-1}$  was applied and  $C_E$  was measured each 25 mV. The SWPO treatments were carried out cycling the electrode potential between an upper potential ( $E_U$ , during  $\tau_U$  seconds) and a lower potential ( $E_L$ , during  $\tau_L$  seconds) at  $50 \pm 0.1^\circ\text{C}$  in an open cell under potentiostatic control. A schematic of the SWPO function is shown in figure 1. The shape of the square wave was always symmetric ( $\tau_U = \tau_L$ ) and the frequency ( $f$ ) was fixed at 5 Hz ( $\tau = 0.2 \text{ s}$ ). In all the experiments the time of treatment was 10 minutes (3000 cycles).

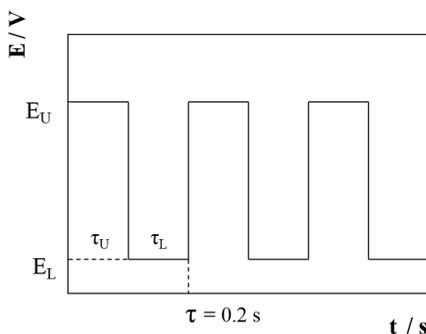


Fig. 1: Sketch showing a SWPO signal, alternating between  $E_L$  and  $E_U$  at a frequency  $f = 1/(\tau_U + \tau_L)$

CV, PD and SWPO treatments were applied with a potentiostat-galvanostat Princeton Applied Research Mod. 273 with in-built signal generator and controlled by the SoftCorr 2 software. The ac electrochemical technique was applied with a frequency response analyzer Solartron 1255 connected with a potentiostat-galvanostat Solartron 1287 controlled with the Z-plot for Windows v 3.0 software.

In all the experiments a Cu-CuSO<sub>4</sub> (sat) reference electrode was used ( $E^0 = 0.316 \text{ V}$  vs normal hydrogen electrode) and all the electrochemical potentials in this work are expressed in this

scale. SEM micrographs were recorded with a Quanta200 FEI equipment (Tungsten filament source). The composition of the coatings was evaluated using EDS. The detector scan mode with a step size of  $0.05^\circ$  and a sampling time of 3 s was used (scan rate  $0.0167^\circ/\text{s}$ ). X-ray photoemission spectroscopy (XPS) measurements were performed exciting with a radiation of 1253.6 eV (non-monochromatized X-ray Mg Ka source, 13 kV anode voltage and a power of 300 W). A two-point calibration of the energy scale was performed using sputtered gold and copper samples (Au 4f7/2 binding energy (BE) = 84.00 eV; Cu 2p3/2 BE = 932.67 eV). C 1s at 285 eV was used as charging reference. The hardness of each coating was determined averaging eight readings on its surface with a Shimadzu micro hardness tester with 15g loading during 5s.

### 3. Results

#### 3.1 Cyclic voltammetry

In figure 2 it is shown the first CV cycle of a copper cathode in  $S_{\text{CR}}$  solution from 0.00 V to -1.20 V. During the forward scan two peaks were detected, marked as A and B. The cathodic processes occurring from -0.20 V to the CD minimum at -0.82 V

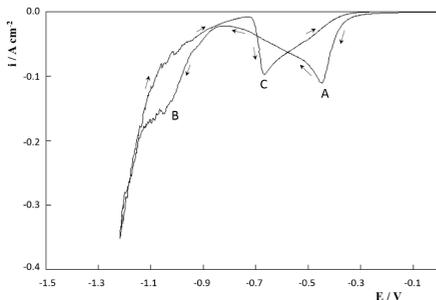
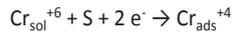


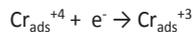
Fig. 2: First CV scan of a copper cathode in  $S_{\text{CR}}$  electrolyte at  $20 \text{ mVs}^{-1}$  and  $50^\circ \text{C}$

are usually ascribed [17-21] to the formation of a  $\text{Cr}^{+3}$  oxide adsorbed film, formed by the reduction products of the reactions underlying peak A. R. Giovanardi et al [17] proposed an adsorption-desorption mechanism involving chromium species of different oxidation states partially covering the electrode surface:

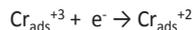
Equation 1:



Equation 2:



Equation 3:



Where S stands for copper electrode free surface area with its characteristic surface density of electroactive sites.  $\text{Cr}_{\text{sol}}^{+6}$  is the concentration of  $\text{Cr}^{+6}$  in solution and  $\text{Cr}_{\text{ads}}^{+n}$  represent de chromium species adsorbed on the copper active sites ( $n=2, 3, 4$ ). When the copper electrode potential is more cathodic than -0.82 V peak B start to grow, related to equation (3) [17] and also to the start of bulk chromium deposition [19, 21].  $\text{H}_2$  evolution is negligible on copper cathodes but at sufficiently cathodic potentials it is combined with metallic chromium as unstable hydrides [22]. The decomposition of this hydrides during chrome plating are responsible of the cracking of the coating during electrodeposition [23].

The first backward scan in figure 2 shows one peak (C) at -0.74 V ( $E_c$ ). CD is cathodic for forward and backward scans, indicating that the electrochemical reactions involved are irreversible [17, 24].  $E_c$  was measured for switching potentials (SP) between -1.0 V and -1.3 V and the cathodic charge resulting from the integration of the area of peak C ( $Q_c$ ) was calculated. As can be seen

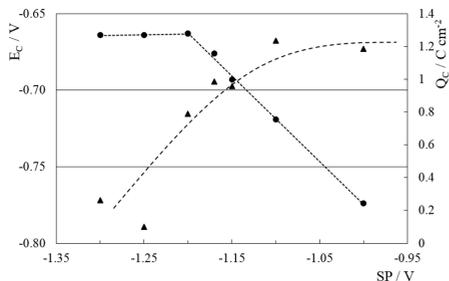


Fig. 3:  $Q_C$  ( $\blacktriangle$ ) and  $E_C$  ( $\bullet$ ) dependence with switching potential (SP)

in figure 3,  $E_C$  and  $Q_C$  both strongly depend on SP value. The shape of the backward scan on a metallic chromium surface in  $S_{CR}$  electrolyte is known to be a flat response [2, 3, 8, 9, 24]. For SP more cathodic than -1.25 V peak C practically disappears ( $Q_C \approx 0$ ) indicating that the entire copper surface is covered with metallic chromium, thus inhibiting equations (1), (2) and (3) due to the absence of free S sites. This behavior indicates that the coverage of the Cu surface with metallic Cr increases with more cathodic SP values. It is important to remark here that for SP more anodic than -0.80 V peak C does not show up, and this will be addressed again in section 3.3.

Other authors [25, 26] consider that peak A corresponds to  $Cr^{+6}$  to  $Cr^{+3}$  reduction and that its slight

shoulder corresponds to incipient  $H^+$  reduction, followed by a second passive region before the onset of  $Cr^{+6}$  to  $Cr^0$  reduction and  $H_2$  evolution at peak B potentials. L. C. Jiang and D. Pletcher [24, 27] instead, postulated that peak B corresponds to  $Cr^{+3}$  to  $Cr^0$  reduction together with  $H_2$  evolution. Survilene found that  $Cr^{+2}$  and hydrogen atoms are involved in the reaction mechanism [28]. There are some discrepancies between different investigators but most of them coincides on the formation of a thin layer very close to the electrode surface, made of  $Cr^{+6}$  reduction products, prior to bulk chromium deposition and that this process is responsible of peak A [29, 30]. The other common issue is that once this layer is formed, there is some evidence of passivation or at least a current reduction between peaks A and B [31, 32].

### 3.2 Potentiostatic deposits

PD were done on flat copper electrodes in  $S_{CR}$  electrolyte at selected potential values corresponding to some of the SP studied in 3.1. In figure 4 a) it is shown the SEM image of the electrode surface for  $E = -1.10$  V. It was confirmed by EDS analysis that isolated chromium crystals of 2  $\mu m$  average diameter size are obtained over the copper substrate. In figure 4 b) it is shown the SEM image of a deposit obtained at  $E = -1.20$  V were an almost complete layer of chromium deposit is formed.

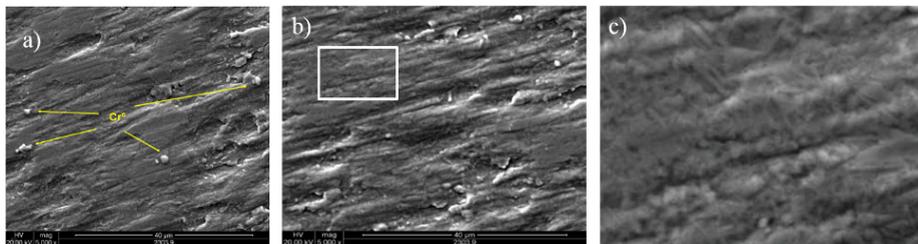


Fig. 4: SEM images of potentiostatic deposits on a copper cathode in  $S_{CR}$  electrolyte (50 $^\circ$  C during 120 s) at a) -1.10 V, arrows indicate the isolated metallic chromium crystals, b) -1.20 V (5000X). c) zoom of rectangle in b) showing geometric details on the coating (15000X)

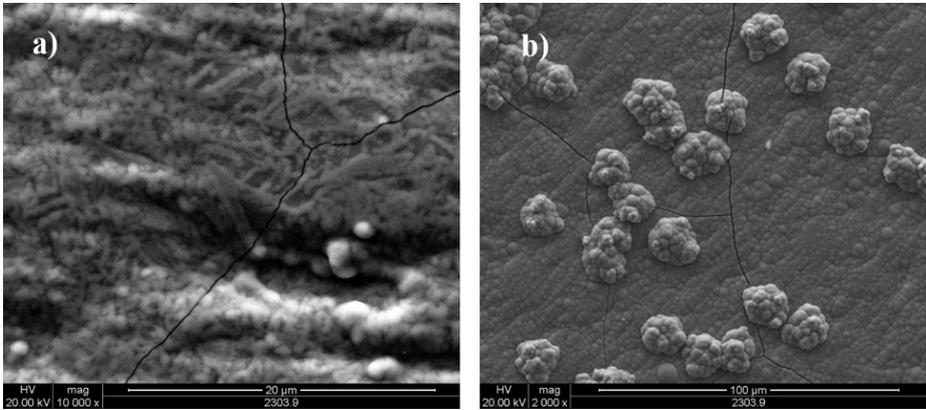


Fig. 5: SEM images of potentiostatic deposits on a copper cathode in  $S_{CR}$  electrolyte (50° C during 120 s) at a) -1.25 V (10000X), showing a network of crystals and the first cracks on the coating, b) SEM image representative of metallic chrome deposits for electrode potentials  $\leq -1.35$  V (2000X)

Very small geometric morphologies are observed at higher magnifications (figure 4 c)). The SEM image of figure 5 a) shows the coating obtained at  $E = -1.25$  V, where the minimum of  $Q_C$  is observed (figure 3). In this case the very thin chromium layer is cracked and the entire electrode surface is covered by the metallic chromium deposit and a network of crystals is observed. The SEM pictures of the PDs are consistent with what was inferred from the CV analysis in 3.1. For PDs at more cathodic potentials ( $-1.25$  V  $> E > -1.35$  V) the classic cracked smooth chromium plated surface is obtained (not shown). At higher cathodic

overpotentials ( $E \leq -1.35$  V) globular structures develop, like the “cauliflower” type described elsewhere [33] (figure 5 b)). It is clear from this picture that the cracks of the metallic coating are produced during the buildup of the film because some of the globular structures were grown over previously opened cracks and others are divided by the underlying fissures.

### 3.3 Potential steps

Copper cathodes were stabilized during 10 seconds at +0.50 V, then the potential was stepped to  $E_p$  and the CD transient was registered during 1 second.  $E_p$  was varied from -0.50 V to -1.15 V covering the potential zone between peaks A and B.

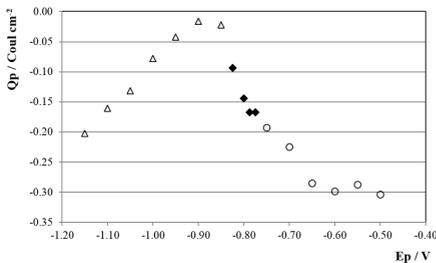


Fig. 6:  $Q_p$  vs.  $E_p$  dependence for potential steps on copper cathodes in  $S_{CR}$  electrolyte at 50° C ( $\circ$  diffusion,  $\blacklozenge$  nucleation and growth and  $\Delta$  flat transient behavior).

CD was integrated for each transient during 1 s and the charge density ( $Q_p$ ) was obtained for each  $E_p$ , showing the results in figure 6. For  $E_p$  between -0.50 and -0.75 V the transients show diffusion like behavior and the CD transients presented lineal  $i$  vs.  $t^{-1/2}$  responses with  $i \approx 0$  for  $t=0$  (not shown), indicating that a diffusion process is involved and that the following relation holds:

Equation 4:

$$i = n F D_0^{1/2} C^* / \pi^{1/2} t^{1/2}$$

were all the variables and constants have their usual meaning. The slope was in average  $-0.14 \pm 0.01$ . Considering  $D_0 \approx 1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  and  $C^* \approx 1/3 C_{\text{CrO}_3}$  because of polymerization of  $\text{H}_2\text{CrO}_4$  [17, 34], we get from equation (4) an estimate of  $n \approx 3$ . This is consistent with  $\text{Cr}^{+6}$  to  $\text{Cr}^{+3}$  reduction previously described. For  $E_p$  between  $-0.78$  and  $-0.83 \text{ V}$  the CD transients show a characteristic nucleation and growth curve (figure 7).

This type of behavior has been assigned by Pletcher et al [24, 27] to the nucleation and growth of holes in a passive layer. This narrow potential range matches quite well with the electrochemical potential of the direct reduction of  $\text{Cr}_2\text{O}_3$  to metallic chromium equilibria [35] (Equation (14) in section 4.2). If we consider  $\text{pH} \approx -1$  and make the temperature correction to  $50^\circ\text{C}$  [36] we get, from (15),  $E^{50} \approx -0.82 \text{ V}$ . This suggests that the nucleation and growth process could correspond to the reduction of the oxide layer and the birth of new metallic chromium nucleus, living "holes" in the previous passive layer. As was stated in 3.1 the fact that peak C does not appear for SP more anodic than  $-0.80 \text{ V}$  is related with this phenomena. For  $E_p$  more cathodic than  $-0.83 \text{ V}$  the CD transients show a flat response characteristic of the PD at short times (figure 7) and  $Q_p$  is 95% smaller than for  $E_p \leq -0.75 \text{ V}$ , indicating that a new slow kinetic process starts. As it was shown in the previous section, this corresponds to the growth of the metallic chromium deposit. The direct  $\text{Cr}^{+6}$  reduction to bulk metallic chromium starts on the new born chromium phase, through the usually accepted mechanism [24, 25, 27, 31, 34], with the corresponding lower CD at this low cathodic overpotential for this reaction (3.2). When  $E_p$  reaches more cathodic values,  $\text{Cr}^{+6}$  reduction gets more important and CD and  $Q_p$  grow again.

### 3.4 Capacitance vs. potential curves

Figure 8 shows the  $C_E$  vs. potential response for the copper cathodes in the  $S_{\text{CR}}$  solution at  $50 \pm 0.1^\circ\text{C}$ . There is a very low  $C_E$  zone between  $+0.60 \text{ V}$  and  $+0.15 \text{ V}$  because of Cu passivation through the formation of an insoluble  $\text{CuCrO}_4$  film. Near  $+0.10 \text{ V}$  the corresponding Cu active to passive pseudo  $C_E$  maximum is observed. For  $E > +0.60 \text{ V}$  transpassivity is reached.

From  $E = 0 \text{ V}$  to  $-0.30 \text{ V}$  a new  $C_E$  plateau is shown, with a minimum at  $\approx -0.20 \text{ V}$  indicating that this could be the potential of zero charge (pzc) of the cathode [37].

From  $-0.30 \text{ V}$  to  $-0.78 \text{ V}$  there is a new pseudo  $C_E$  loop corresponding to the diffusion transients described in 3.3. It is highly probable that this corresponds to

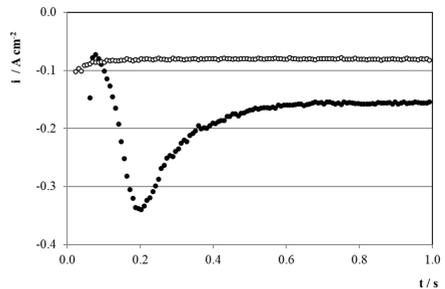


Fig. 7: Characteristic CD transients for  $E_p = -0.80 \text{ V}$  (●) and  $E_p = -1.00 \text{ V}$  (○)

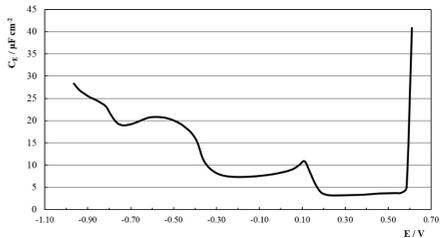


Fig. 8:  $C_E$  vs. potential curve for a copper cathode in  $S_{\text{CR}}$  electrolyte at  $50^\circ\text{C}$  and  $1.5 \text{ kHz}$

the film formation described elsewhere [26, 29, 30, 34]. Although thermodynamically feasible, the reduction of  $\text{Cr}^{+6}$  to  $\text{Cr}^{+3}$  is kinetically inhibited until  $E = -0.30$  V generating the pre-plating cathodic film which is widely accepted as high  $\text{Cr}^{+3}$  content. For  $-0.83$  V  $\leq E \leq -0.78$  V after another  $C_E$  arrest, a different process start, associated to the nucleation and growth depicted in 3.3. For  $E < -0.83$  V  $C_E$  continues to grow after a slight shoulder, probably related to equation (3) [17, 28].

### 3.5 Square wave pulsating overpotential treatment

Based on the preceding results a relatively fast periodic SWPO was applied to the copper cathodes.  $E_L$  was fixed at  $-1.30$  V, value sufficiently cathodic to obtain the reduced chromium species after peak A and B, but just before diffusion effects become important (3.2 and figure 5). Also from the curves of figure 3, at this  $E_L$  it is expected to obtain a complete coverage of the copper substrate. The  $E_U$  values were selected between  $-0.70$  V and  $+0.50$  V to vary the electrode potential through the different capacity plateaus in the

anodic direction. Different types of deposits were obtained depending on  $E_U$  values.

For  $-0.70$  V  $\leq E_U < -0.40$  V the deposits look very similar to the standard bright cracked metallic chromium coatings as in potentiostatic or galvanostatic electrolysis [2, 15]. In the case of setting  $-0.4$  V  $\leq E_U < -0.2$  V the coatings morphology and their metallic luster are almost the same but cracks are absent. It is very interesting to remark that the cracks disappear when  $E_U$  is more anodic than  $E_A$ .

Moving to more anodic  $E_U$  values, a new type of deposit is obtained, shown in figure 9 a). In these cases the coatings are matt gray and their morphologies are faceted and exhibit a very peculiar structure that is maintained for  $-0.20$  V  $\leq E_U < +0.30$  V, with slight changes in faceting. The average particle size is around  $0.5$   $\mu\text{m}$ .

When  $E_U$  reaches  $+0.40$  V and  $+0.50$  V a new coating morphology appears, shown in figure 9 b). This type of coating, matt black, resembles the black coatings prepared with modified electrolytes reported elsewhere [12, 13].

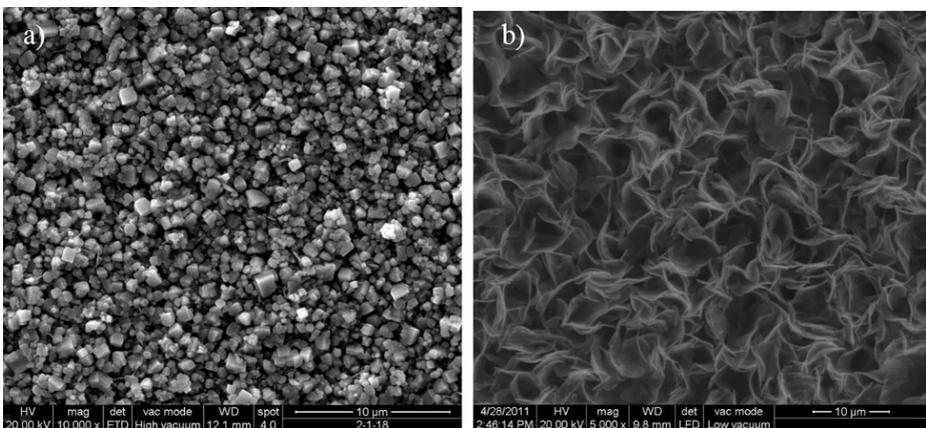


Fig. 9: SEM images of deposits obtained with SWPO treatment on the copper cathodes in  $S_{CR}$  electrolyte at a)  $E_U = -0.10$  V and b)  $E_U = +0.50$  V.

It is very interesting that for  $E_U$  just in the intermediate zone between the faceted type morphologies and the black coatings, an intermediate mixed coating is obtained (figure 10). In this case it is possible to distinguish both types of structures. This behavior is observed for  $E_U$  values between +0.30 V and +0.40 V. Finally for  $E_U \geq +0.60$  V no Cr deposit is obtained.

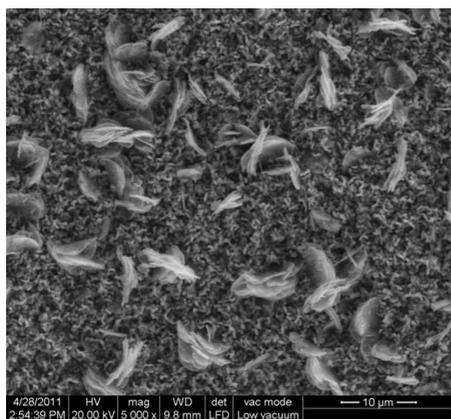


Fig. 10: SEM image of a deposit obtained with SWPO for  $E_U = +0.40$  V.

### 3.6 Characterization of SWPO deposits

All the coatings obtained with the SWPO treatments were exhaustively washed with double distilled water, fast air dried and micro hardness and EDS quantitative analysis was done. The only elements detected were Cr and O. In figure 11 it is shown the dependence of the oxygen content in weight per cent ( $O_{\%}$ ) with  $E_U$ . Based on the  $O_{\%}$  values, it is possible to distinguish three zones: A)  $-0.70$  V  $< E_U \leq -0.20$  V with  $O_{\%}$  near to 10%; B)  $-0.20$  V  $< E_U < +0.30$  V with increasing  $O_{\%}$  values almost reaching 30% and C)  $+0.30$  V  $\leq E_U \leq +0.50$  V, a very distinct zone where  $O_{\%}$  start to grow with a sharp positive slope, reaching 50%. If we make an estimation of the  $O_{\%}$  for  $Cr_2O_3$  and for  $Cr(OH)_3$

the approximate values are 30% and 50% correspondingly.

In order to correlate the  $O_{\%}$  behavior with chemical composition of the coating some XPS determinations were done. It was concluded that in zone B the main chromium species were  $Cr_2O_3$  and in zone C  $Cr(OH)_3$ . For the particular case of the coating obtained at  $E_U = +0.50$  V the composition was 71%  $Cr(OH)_3$  and 29%  $CrO_3$ . Accordingly for  $E_U \geq +0.60$  V no deposit was obtained indicating that all the chromium species formed at  $E_L$  during  $\tau_l$  are dissolved at  $E_U$  during  $\tau_u$ .

The surface Vickers micro hardness of the SWPO coatings shown in figure 11 varies with  $E_U$  from the same value as the substrate at  $E_U = +0.50$  V to three times this value at more cathodic  $E_U$  values. Here again the three different zones arises, A) with an average Hv between 200 and 300, B) with 150 constant value and a pronounced softening for C). The higher Hv values are found for  $E_U$  more cathodic than  $-0.20$  V, that is when the coating is metallic Cr. The micro hardness was not measured in the cross section of the coatings due to the small thickness of the samples produced in this work ( $\approx 3 - 4 \mu\text{m}$ ).

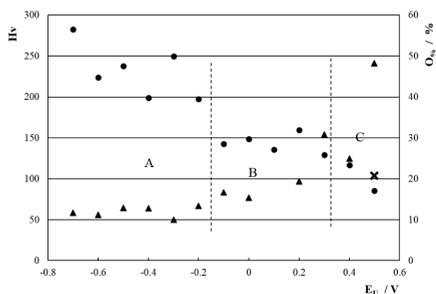


Fig. 11: Surface Vickers micro hardness (Hv; ●) and EDS oxygen content ( $O_{\%}$ ; ▲) of SWPO deposits as a function of  $E_U$ . X = Hv of substrate. Zones A, B and C are delimited with dashed lines.

## 4. Discussion

### 4.1 Current density transients during SWPO treatments

The average CD during application of  $E_U$  during  $\tau_u$ ,

Equation 5:

$$\langle i_{i_u} \rangle = \frac{1}{\tau_u} \int_{n\tau_u}^{(n+1)\tau_u} i dt$$

was calculated for  $n=2000$  (200 s), 4000 (400 s) and 6000 (600 s) for each SWPO treatment. The results are shown in figure 12. The dependence of  $\langle i_{i_u} \rangle$  with  $E_U$  shows that for  $E_U$  more cathodic than  $-0.20V$  the CD is always cathodic and that  $\langle i_{i_u} \rangle$  practically does not vary with time. This last behavior is probably related with the very smooth surface of the deposits obtained for these samples.

For  $E_U$  more anodic than  $-0.20 V$ ,  $\langle i_{i_u} \rangle > 0$ , indicating that anodic processes prevails on the electrode during  $\tau_u$ . It is also evident that  $\langle i_{i_u} \rangle$  increases with time due to the surface roughening of the deposits during treatment (figures 9 and 10). Finally for  $E_U = -0.20 V$ ,  $\langle i_{i_u} \rangle = 0$ , indicating that no net faradaic process occurs during  $\tau_u$  and that it is invariant with time of treatment. The SEM images of figure 13 shows the morphology

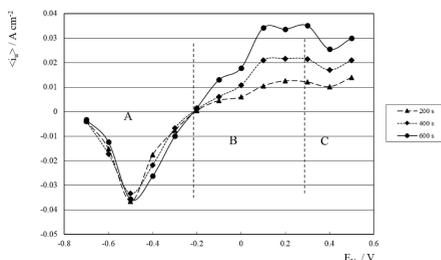


Fig. 12: Average CD  $\langle i_{i_u} \rangle$  for 200, 400 and 600 s of SWPO treatment as a function of  $E_U$ . Zones A, B and C are delimited with dashed lines.

of this coating where it is possible to see a cubic structure with very well faceted crystals. It is interesting to remark that this point coincides with the possible pzc of the system as seen on  $C_E$  vs.  $E$  curve (figure 8). This  $E_U$  value is a transition point from which to more cathodic values the deposits are metallic chromium and to more anodic values the coatings are faceted structures with high oxygen content. As was observed on data of figure 11 we can differentiate zone A, B and C on  $\langle i_{i_u} \rangle$  vs.  $E_U$  dependence on figure 12.

When we analyze the complementary average CD during the cathodic hemicycle of the SWPO treatment,  $\langle i_{i_c} \rangle$ , with integration limits in (5) from  $(n+1)\tau_i$  to  $(n+2)\tau_i$  for  $n = 2000, 4000$  and  $6000$  at  $E_L = -1.30 V$ , we find that  $(\langle i_{i_c} \rangle / \langle i_{i_u} \rangle)_i \approx 10$ . This is consistent with the asymmetric efficiencies of the deposition and dissolution processes in chrome plating [2, 5, 38]. Based on this, we can consider that practically all the reduced chromium species obtained at  $E_L$  during each  $\tau_i$ , are electrochemically modified during next  $\tau_u$  depending on  $E_U$  value. W. R. Rosas and A. Robin showed that for very short times the thin layer necessary to obtain metallic Cr during chrome plating is not formed [31], so during the SWPO treatment the formation of this type of deposit will depend on  $E_U$ . In that way, for  $E_U$  values more cathodic than  $-0.20 V$  (cathodic  $\langle i_{i_u} \rangle$ ) it is possible to keep intact or even to build up the film during  $\tau_u$ . As previously depicted in 3.5 the deposits obtained in this range of  $E_U$  values are all metallic chromium, with the lowest oxygen content. The fact that for  $E_U$  between  $-0.40$  and  $-0.20 V$  the deposits are crack free is associated with the elimination of chromium hydride as in pulse reverse chrome plating [23].

For  $E_U$  values more anodic than  $-0.20 V$  the morphology and composition of deposits change abruptly and faceted crystallites are clearly seen.

It is also verified that for gradually more anodic  $E_U$  values the chromium oxides composition moves from  $\text{Cr}_2\text{O}_3$  towards  $\text{Cr}(\text{OH})_3 \cdot n\text{H}_2\text{O}$ . This was confirmed by EDS and XPS measurements. This evidence is also consistent with the oxygen content and the softening of the coatings (figure 11).

#### 4.2 Thermodynamic considerations

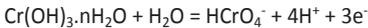
From a thermodynamic point of view, the possible processes that can occur on the electrode during SWPO treatment, depending on the electrochemical potential and based on the chemical species found after the SWPO treatment are:

Equation 6:



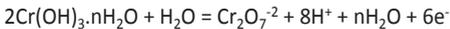
$$E_0 = 1.034 + 0.138 \text{ pH} + 0.0197 \log(\text{HCrO}_4^- / \text{Cr}^{+3})$$

Equation 7:



$$E_0 = 0.801 - 0.0788 \text{ pH} + 0.0197 \log(\text{HCrO}_4^-)$$

Equation 8:



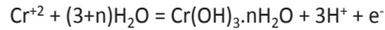
$$E_0 = 0.785 - 0.0788 \text{ pH} + 0.0098 \log(\text{Cr}_2\text{O}_7^{2-})$$

Equation 9:



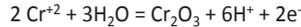
$$E_0 = 0.311 + 0.1379 \text{ pH} + 0.0147 \log(\text{HCrO}_4^- / \text{Cr}^{+2})$$

Equation 10:



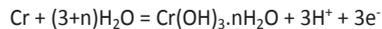
$$E_0 = -0.027 - 0.1773 \text{ pH} - 0.0591 \log(\text{Cr}^{+2})$$

Equation 11:



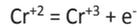
$$E_0 = -0.228 - 0.1773 \text{ pH} - 0.0591 \log(\text{Cr}^{+2})\#$$

Equation 12:



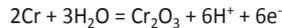
$$E_0 = -0.676 - 0.0591 \text{ pH}$$

Equation 13:



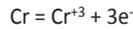
$$E_0 = -0.723 + 0.0591 \log(\text{Cr}^{+3} / \text{Cr}^{+2})$$

Equation 14:



$$E_0 = -0.895 - 0.0591 \text{ pH}$$

Equation 15:



$$E_0 = -1.060 + 0.0197 \log(\text{Cr}^{+3})$$

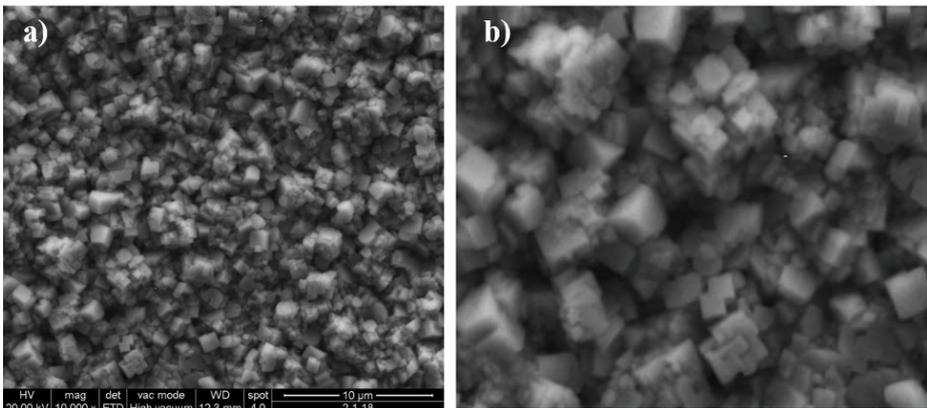
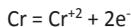


Fig. 13: SEM image of deposit obtained with SWPO treatment.  $E_U = -0.20 \text{ V}$ . a) 10000X; b) 25000X.

Equation 16:



$$E_0 = -1.229 + 0.0295 \log(\text{Cr}^{+2})$$

Based on the results obtained in 3.1 it is evident that some of these reactions are strongly inhibited on the Cu electrode (e.g. 6-8). During the cathodic hemicycle of the SWPO, species like  $\text{Cr}^{+3}$ ,  $\text{Cr}^{+2}$  and  $\text{Cr}^0$  will be formed on the electrode surface. The possible mechanisms could be quite complex and will be the result of a mix of some of the processes listed above. But considering the experimental evidence that for  $E_U$  more anodic than +0.60 V all these intermediate species are dissolved, suggests that  $\text{Cr}^{+2}$  could play a role on the processes occurring at  $E_L$ . This assertion can be postulated because the only equation that thermodynamically allows the direct oxidation of chromium species to a soluble compound at this potential value is (9), after correcting the right potential value at 50° C. If we assume that the main active chromium species generated during  $\tau_i$  is  $\text{Cr}^{+2}$  we can also understand through equations (10) and (11) how the deposits depicted in 3.5 for  $E_U$  between -0.20 and +0.30 V could be grown. The continuous build up of the gray and black chromium oxides/hydroxides films described in 4.1 suggests that the  $\text{Cr}_2\text{O}_3$  and  $\text{Cr}(\text{OH})_3 \cdot n\text{H}_2\text{O}$  are irreversibly formed on the cathode surface. That means that during each cycle of the SWPO signal  $\text{Cr}^{+2}$  is formed at  $E_L$  during  $\tau_i$ , and then this  $\text{Cr}^{+2}$  is oxidized at  $E_U$  during next  $\tau_u$  to the corresponding  $\text{Cr}^{+3}$  compound. As this is a dynamic model, not in equilibrium, the thermodynamic considerations has to be considered as feasibility limits.

For the metallic chromium deposits obtained for  $-0.70 \text{ V} \leq E_U < -0.20 \text{ V}$  it is clear that during  $\tau_u$  at this electrode potentials the pre plating layer necessary for obtaining metallic chromium is

not destroyed. In that way the usually accepted chrome plating mechanism will be possible during both hemicycles of the SWPO treatment ( $\tau_i + \tau_u$ ).

## 5. Conclusions

Based on preliminary cyclic voltammetry, potentiostatic deposits, potential steps and  $C_E$  vs. potential curves, it was designed a square wave pulsating overpotential treatment that allows the obtaining of coatings of different chrome species on copper substrate starting from a standard chrome plating bath. Properly adjusting the frequency and lower and upper potential values of the SWPO signal it was possible to obtain cracked and crack free metallic chromium coatings and chromium oxide and hydroxide mixtures films. The oxygen content and surface hardness of these coatings can be controlled as well. Different deposit morphologies were obtained: smooth metallic surfaces, very well faceted crystallites arrangements and leaf type structures. The color of each type of coating also varied from white bright metallic finish for the cracked and crack free metallic coatings, light gray for the faceted crystallites, dark gray for the mixed type coating and matt black for the high hydroxide content leaf type structure. This last type of coating was found to be very similar to the black deposits used for solar energy absorption panels.

Some thermodynamic considerations were made regarding the possible mechanism of coating build up during the SWPO treatment and some insight in deposition mechanism could be done.

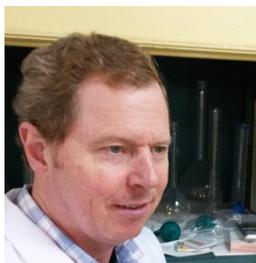
## 6. Acknowledgements

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