# Nanostructure and Properties of Cr-C Coatings

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#### Abstract

Chromium plating from the trivalent state has gained increasing attention in the electroplating industry because it is relatively environmentally friendly as compared to the more common hexavalent chromium bath. However, the trivalent chromium process has several drawbacks such as low current efficiency and solution instability. Furthermore, results on coating structure, composition and properties reported in the literature have been inconsistent. In this paper we discuss in more detail the relationship between processing, structure, and properties of annealed Cr-C layers electrodeposited from carbon-containing trivalent baths. Our results show that these coatings are amorphous in the as-deposited state, but when they are subjected to thermal treatments such as could be encountered in practice, chromium nanocrystallization and carbide precipitation occurs. This structural evolution leads to substantial changes in coating properties.

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### **1. Introduction**

Electrodeposited chromium has been extensively employed in many industries and can be plated from either hexavalent or trivalent baths to produce functional or decorative coatings<sup>1</sup>. For many years the hexavalent bath has been employed to produce hard coatings with good wear and corrosion resistance<sup>2-4</sup>. However, chemical baths based on hexavalent chromium have deleterious effects on the environment and on the health of those working with it <sup>5</sup>. Chromium plating from the trivalent state has acquired increasing attention in the electroplating industry because it is more environmentally friendly than the hexavalent chromium process, but it has several drawbacks including low current efficiency (below 15%) and solution instability<sup>6-9</sup>. There is additionally a known difficulty in depositing thick coatings from trivalent baths due to the increase of pH near the cathode, even with organic additives which prevent hydrolysis of the chromium ion<sup>10</sup>. Uni-Polar Pulse Plating (UPP) and Periodic Pulse Reverse Plating (PPRP) have been developed to overcome some of the practical limitations of Direct Current (DC)<sup>7, 8, 9, 11-13</sup>. However, as noted recently by Baral et al.<sup>14</sup>, pulsed current plating yields generally thinner coatings than DC plating.

It has been reported that carbon-containing chromium coatings show an increase in hardness when subjected to thermal treatments<sup>14-18</sup>, an issue with clear practical implications for applications involving elevated service temperatures. In this paper we discuss the relationship between processing conditions, structure, and properties of Cr-C layers electrodeposited from carbon-containing trivalent baths. The effect of annealing on structure and properties is also explored.

## **2. Experimental methods**

## 2.1. Electrodeposition and thermal treatment

The electrolytic bath employed in this study is based on trivalent chromium, and has a complex composition as shown in Table  $1^{7, 8, 10, 11}$ . Each bath was prepared using reagent grade chemicals and deionized water. In order to attain a quasi-equilibrium state with Cr<sup>3+</sup> organic complexes, the bath was heated to 90°C for 20 min, and subsequently stirred for 24 h before use<sup>14, 19</sup>. The pH of the solution was adjusted to between 2 and 2.5 by adding HCl or NaOH prior to each plating experiment.

| Constituent                          | Concentration [g/L] | Function                                 |
|--------------------------------------|---------------------|--|
| CrCl <sub>3</sub> .6H <sub>2</sub> O | 107                 | Source of Cr <sup>3+</sup>               |
| NH <sub>4</sub> Cl                   | 80                  | Electrolyte support and complexing agent |
| HCOO(NH <sub>4</sub> )               | 38                  | Organic complexing agent                 |
| NaCH <sub>3</sub> COO                | 16                  | Organic complexing agent                 |
| NH <sub>4</sub> Br                   | 10                  | Antioxidizing agent                      |
| H <sub>3</sub> BO <sub>3</sub>       | 43                  | Buffer agent                             |
| KCl                                  | 37                  | Electrolyte support                      |
| Dodecyl NaSO <sub>4</sub>            | 0.2                 | Wetting agent                            |

**Table 1.** Composition and role of chemicals present in the electrolytic bath.

The plating experiments were carried out in a custom glass cell (2000 mL) with dielectric masks around the cathode to promote an even current density distribution; a platinum mesh was used as an anode. The cathode was either a copper or steel panel with an exposed surface area of  $8 \text{ cm}^2$ . The cathode was degreased with acetone, mechanically polished to 4000 grit, and electropolished to a mirror-like surface just before plating. All the plating experiments were conducted at room temperature (20-25°C), and the electrolytic bath was agitated using a magnetic stirrer and a recirculating pump (5000 mL/min). Direct or pulsed current was supplied by a Dynatronix DPR20-30-200 power supply; pulsed current was applied in either UPP or PPRP modes. The typical cathodic cycle pulse consisted of peak current density (J<sub>p</sub>) in the range of 5-40 A/dm<sup>2</sup>, and on- (T<sub>on</sub>) and off-time (T<sub>off</sub>) ranged from 5 to 40 ms. Optional anodic reverse pulses were employed by using cathodic (Q<sub>c</sub>) to anodic (Q<sub>a</sub>) charge density ratios between 20 and 40. Asdeposited samples were annealed in Ar for 30 min at a prescribed temperature, with a heating rate of ~40-50 K/min, and furnace cooling under an argon flow.

#### 2.2. Composition and structure

Chemical composition was determined by Glow Discharge Optical Emission Spectroscopy (GDS) with quantitative depth profiling, using LECO GDS-750A equipment. Additional information about chemical composition was obtained by X-Ray Photoelectron Spectroscopy (XPS) by employing an Axis Ultra X-ray Photoelectron Spectrometer (from Kratos Analytical) with a monochromatic Al- $K_{\alpha}$  X-ray source (1486.6 eV), operated at 150W.

Surface morphology and cross section of the as deposited and annealed samples were characterized by Scanning Electron Microscopy (SEM) using LEO 438VP equipment. Semiquantitative chemical composition was determined by calibrated Energy Dispersive X-ray Spectroscopy (EDS) with an electron probe attached to the SEM. X-Ray Diffraction (XRD) was employed to determine the structure of the electrodeposits as well as to estimate the average crystallite size from Cr (110) line-broadening using the Scherrer equation. The XRD patterns were collected in a Rigaku RU300 diffractometer, using Cu-K<sub> $\alpha$ </sub> radiation.

#### 2.3. Mechanical properties

Micro-hardness tests were conducted on polished cross sections of the electrodeposits using a Vickers indenter with 10, 25, and 50 g load, using a Clark micro-indenter model DMH2. Ten measurements were made for each load and the average is reported.

## 3. Results and discussion

## 3.1. Characterization of the as-deposited samples

The coating morphology was examined on both cross-sectional and plan views, using scanning electron microscopy. Figure 1a shows a plan view and Figure 1b a cross-sectional view of a typical coating. All deposits showed a nodular morphology for both UPP and PPRP, with a nodular size ranging between 5 and 20  $\mu$ m. The thickness of the chromium deposits was

homogeneous, and generally ranged from 5 to 60  $\mu$ m depending on the transferred charge. For the same transferred charge, the thickness depended strongly on peak current density.

Some small cracks were observed in both the plan and cross sectional views, although only very few of them reached the substrate (Fig. 1b). These cracks are presumably related to the evolution of hydrogen on the cathode, which is the most prevalent reaction during the trivalent chromium plating process<sup>10</sup>. Hydrogen is incorporated into the deposit forming chromium hydrides that are partially decomposed to metallic chromium and hydrogen gas; the attendant volume change produces cracking <sup>20, 21</sup>. EDS spectra acquired on the coating surface (not shown here) revealed the presence of C, O, Cl, N, and Cr, while of these elements only Cr and small amounts of C and O appeared in the cross sectional view. This suggests that only the latter elements are incorporated into the deposit, with Cl and N appearing predominantly as surface contaminants. Because light elements like C are not well quantified by EDS, GDS with depth profiling was performed.



**Figure 1.** SEM micrograph of chromium coating obtained by UPP  $(J_p=20 \text{ A/dm}^2, T_{on}=T_{off}=5 \text{ ms})$ . (a) Plan view. (b) Cross sectional view.

Figure 2 shows the composition as a function of depth from the coating surface, obtained by GDS for two coatings, one prepared by UPP, and one by PRPP; the transition to the underlying Cu substrate can also be observed. These plots indicate that carbon, nitrogen and oxygen are distributed uniformly inside the coating, with slightly higher concentrations at the surface. Carbon and oxygen are incorporated into the coating as a result of formate reduction <sup>22</sup> and/or the extremely high electrical field, which leads to the decomposition and adhesion of the organic compound as the coating is formed. Nitrogen, in lesser amounts, comes from the extremely high quantity of ammonium salts present in the bath (Table 1). Several experiments were performed in an effort to change the amount of carbon in the coating, but the carbon content remained almost constant in the range 4-5 wt.% (Table 2). This observation agrees with the results reported by Kim et al.<sup>16, 17</sup>, who has previously studied the effect of electrodeposition parameters on the chemical composition of similar coatings. They found that carbon content

varied only between 1.7 and 3.0 wt.% when the pH, bath temperature and current density were varied over the ranges 1.6-3.2, 30-60°C and 20-36 A/dm<sup>2</sup>, respectively. Our results are in general agreement with these, and with other literature data <sup>14, 16, 17, 22</sup>.



**Figure 2.** GDS depth profile of chromium coating obtained by (a) UPP ( $J_p=20 \text{ A/dm}^2$ ,  $T_{on}=T_{off}=5 \text{ ms}$ ) and (b) PPRP ( $J_p=20.9 \text{ A/dm}^2$ ,  $T_{on}=36.4 \text{ ms}$ ,  $T_{off}=0.2 \text{ ms}$ ).

| Wave | Charge transferred | Efficiency | Elemental composition [ wt.% ] |               |               |                |
|------|--------------------|------------|--------------------------------|---------------|---------------|----------------|
| form | $[C / dm^{2}]$     | [%]        | С                              | 0             | Ν             | Cr             |
| DC   | 36000              | 4.0        | $5.7 \pm 0.3$                  | $2.6 \pm 0.1$ | $0.8\pm0.1$   | $90.9\pm0.3$   |
| UPP  | 54000              | 17.3       | $4.0\pm0.2$                    | $4.9 \pm 0.3$ | $1.2\pm0.1$   | $89.9 \pm 1.3$ |
| UPP  | 54000              | 17.8       | $4.3 \pm 0.2$                  | $4.4 \pm 0.2$ | $1.2 \pm 0.1$ | $90.1 \pm 1.1$ |
| UPP  | 54000              | 5.4        | $4.4 \pm 0.2$                  | $4.7 \pm 0.4$ | $1.2 \pm 0.1$ | $89.7 \pm 1.5$ |
| UPP  | 108000             | 15.2       | $3.9\pm0.1$                    | $4.3\pm0.2$   | $1.1 \pm 0.1$ | $90.7\pm0.5$   |
| PPRP | 125000             | 15.0       | $5.0 \pm 0.2$                  | $3.0 \pm 0.2$ | $0.7 \pm 0.1$ | $91.3 \pm 0.3$ |
| PPRP | 125000             | 15.3       | $4.7 \pm 0.1$                  | $3.3 \pm 0.1$ | $0.9\pm0.1$   | $91.1 \pm 0.1$ |
| PPRP | 125000             | 17.2       | $4.9\pm0.2$                    | $2.8\pm0.3$   | $0.6 \pm 0.1$ | $91.7\pm0.3$   |

**Table 2.** Elemental composition (measured by GDS) of coatings obtained with different deposition conditions.

In order to determine the chemical state of the elements that formed the coating, XPS analysis was performed on the samples, first without any surface cleaning process, and then after 10 and 30 min of sputtering. Figure 3 shows XPS spectra for the Cr 2p, O 1s, and C 1s peaks, and the concentration of these elements as a function of sputtering time. On the first survey large amounts of carbon, oxygen, chlorine, nitrogen, sodium, calcium, and chromium were detected, but following sputtering only carbon, oxygen and chromium were observed. This result is consistent with the more qualitative EDS measurements reported above.

A detailed analysis of the Cr 2p peaks shows three components in the surface layer namely, metallic chromium (574.0 eV),  $Cr_2O_3$  (576.0 eV) and  $CrCl_3$  (576.8 eV)<sup>22, 23</sup>. The spectra of Cr 2p for deeper layers only show metallic chromium. As regards the carbon and oxygen content, the species observed in the surface layer cannot be taken as indicative of the deposit, due

to surface contamination of the samples. In deeper layers graphite C-C content (284.3 eV) clearly decreases while C-Cr increases (282.8 eV). With increasing sputtering time, the chromium concentration increases and the carbon and oxygen concentrations decrease, tending to the value measured by GDS. However, the carbon content inside the coating as determined by XPS (5.8 wt.%) is slightly higher than measured by GDS (3.6 wt.%). This difference may be attributed to the different characteristic sampling depths of the two methods.



**Figure 3.** XPS analysis of chromium coating obtained by UPP ( $J_p=20 \text{ A/dm}^2$ ,  $T_{on}=T_{off}=5 \text{ ms}$ ). XPS spectra as a function of sputtering time of the (a) Cr 2p peaks, (b) C 1s peaks, and (c) O 1s peaks. (d) Depth profiling concentration analysis for the components of the coating, with general trendlines added for visual clarity.

A typical XRD spectrum from an as-deposited coating is shown in Figure 4. A very broad peak was detected in the vicinity of the Cr (110) reflection, as well as a broad secondary halo. This pattern has the general form expected of an amorphous structure, although the first peak in

this case is somewhat sharper than would be expected for a homogeneous amorphous solid. The peak is centered on  $2\theta$ =43.5°, slightly shifted from the (110) peak for pure Cr at  $2\theta$ =44.4° due to the significant lattice distortion from dissolved C and O, and possibly from residual stress in the coating<sup>8, 18</sup>. Prior researchers have observed that when carbon is incorporated into a chromium matrix from either trivalent<sup>14, 16-18</sup> or hexavalent<sup>24, 25</sup> baths, the resulting material is amorphous. We observed no relationship between the structure of the coating and the electrodeposition parameters used, because in all cases the chemical composition was quite similar.



Figure 4. Typical XRD pattern of as-deposited chromium coating obtained by PPRP.

Microhardness was measured on the cross-section of the deposits at different loads, but only the results at 10 g are reported. At this load the ratio between the mean indentation diagonal and coating thickness is close to 10 for all the samples, ensuring that the measurement reflects the property of the coating, without convolution with the substrate or surface properties. The results of microhardness measurements for coatings obtained at different electrodeposition conditions are listed in Table 3. Microhardness values ranged from 490 to 635 kgf/mm<sup>2</sup> (Table 3), and are close to the hardness of coatings obtained from hexavalent chromium at similar temperatures<sup>8</sup>  $(23^{\circ}C)$  but lower than those at higher temperatures  $(50^{\circ}C)^{8,9,16}$ .

| <b>Table 3.</b> Thickness and hardness measurements of chromium coatings. |  |                  |  |  |  |  |
|---|--|------------------|--|--|--|--|
| Wave form   | Average/Peak Current Density [ A / dm <sup>2</sup> ] | Thickness [ µm ] | Micro Hardness [ kgf / mm <sup>2</sup> ] |  |  |  |
| DC  | 10/10  | 4.0              | NM                                       |  |  |  |
| UPP   | 10/30  | 10.8             | $574 \pm 50$                             |  |  |  |
| UPP   | 10/30  | 22.2             | $489 \pm 44$                             |  |  |  |
| UPP   | 10/20  | 23.3             | $552 \pm 48$                             |  |  |  |
| UPP   | 10/20  | 24.0             | $554 \pm 47$                             |  |  |  |
| UPP   | 20/40  | 7.3              | $598 \pm 106$                            |  |  |  |
| UPP   | 10/20  | 21.5             | $615 \pm 55$                             |  |  |  |
| UPP   | 10/20  | 41.0             | $570 \pm 53$                             |  |  |  |
| PPRP  | 18/20  | 46.8             | $635 \pm 44$                             |  |  |  |
| PPRP  | 17/20  | 47.7             | $615 \pm 50$                             |  |  |  |
| PPRP  | 16/20  | 53.8             | $611 \pm 39$                             |  |  |  |

### 3.2. Characterization of the annealed samples

The evolution of the specimen morphology during annealing was studied by SEM, as was the diffusion of copper from the substrate into the coating. Figure 5 shows plan and cross-sectional micrographs of a typical specimen in the as-deposited state, and then after annealing for 30 minutes at 600°C. There was no obvious change in the nodular structure of the coatings, but annealing led to a remarkable degree of cracking. Further experimentation revealed that these cracks are initially formed at lower temperatures (300°C) and at least some of them reach the substrate. The width of the cracks suggests a volume change in the coating, and again, the evolution of hydrogen from the coating may be involved; hydrogen removal during annealing results in high internal tensile stresses that favors the formation of cracks<sup>22</sup>. This result is apparently not strongly influenced by the diffusion of copper from the substrate, as our measurements showed that copper diffused only a few microns into the chromium-carbon coating (less than 5  $\mu$ m at 600°C).



*Figure 5.* SEM micrographs of chromium-carbon coatings obtained by UPP. Plan and cross-sectional views of (a) as-deposited and (b) annealed sample at 600°C.

The structural evolution of the coatings was examined as a function of temperature by XRD, using in every case an annealing time of 30 minutes. The XRD patterns for a coating

prepared by UPP are shown in Figure 6. Structural analysis shows that chromium starts to form nanocrystals at around 350°C (10 nm) and the crystal size increases with annealing temperature. Upon annealing at 500°C, the crystal size reaches ~20 nm and there is no longer clear evidence for a co-existing amorphous phase. At temperatures above 600°C, the chromium crystal size is greater than 20 nm and chromium carbide ( $Cr_7C_3$ ) begins to precipitate. The temperature at which we observed the appearance of carbide agrees with the results published by Kim et al. <sup>16, 17</sup>, but not with those from Benaben <sup>18</sup>, who detected chromium carbide at annealing temperatures as low as 350°C. A possible explanation for this discrepancy might lie in the preparation of the coating; in Benaben's study the trivalent chromium solution was obtained by reduction of chromic acid with methanol. This may lead to a more carbon-rich coating than the present procedure, which would promote the evolution of carbides. Finally, at 800°C peaks ascribed to  $Cr_2O_3$  were detected, while the chromium crystal size increased to above 50 nm. Although  $Cr_{23}C_6$  was reported upon annealing of a similar coating in the literature<sup>16, 17</sup>, in our case no peak attributable to this carbide could be detected.



*Figure 6.* X-ray diffraction patterns illustrating evolution of the structure of Cr-C deposits as a function of annealing temperature.

The effect of annealing temperature on hardness is shown in Figure 7 for a coating obtained by UPP; the behavior of all the coatings prepared in this study was similar. In general, the values reported in Fig. 7 are slightly lower than those reported in the literature for similar coatings<sup>8, 11, 16-18</sup>. This is likely due to the use of different indentation loads; we have verified that as load increases the value of hardness increases somewhat. All of the values reported here are for 10 g loads.

Examining Fig.7, we see that hardness clearly increases when the coating is annealed at temperatures even as low as 300°C, despite the fact that no compound phases were formed. This behavior suggests that a dispersion of precipitated Cr nanocrystals in the amorphous matrix leads to strengthening, a result consistent with the existing literature on partially devitrified metallic glasses containing metalloids<sup>26,27</sup>. It is interesting to observe that at progressively higher annealing temperatures up to 600°C, hardness continues to increase, despite the fact that the Cr grain size is also increasing; the classical Hall-Petch relationship indicates that grain growth should promote softening. However, in the present coatings the growth of the Cr crystals is convoluted with an increasing volume fraction of the crystal phase within an amorphous matrix. The hardening we observe is most likely a consequence of the volume fraction increase. It is important to note that the Cr phase in this case is of BCC structure and likely heavily laden with interstitial impurities that promote extreme solid solution strengthening.

At around 600°C, the hardness evolves to a maximum value near 1400 kgf/mm<sup>2</sup>, and then decreases somewhat for higher annealing temperatures. Ironically, the emergence of carbide and oxide phases at 800° C does not correlate with increased hardness; it is possible that softening due to the increase in Cr grain size at this temperature offsets the hardening effects of those phases.



*Figure 7.* Effects of annealing temperature on hardness for a typical sample obtained by UPP. Each specimen was annealed for 30 minutes in an argon atmosphere.

As a final point of discussion, we examine a qualitative measure of coating toughness, the presence and prominence of cracks around the hardness indentations. We observed that when

indentation was performed on as-deposited samples, cracks appeared from the corners of the impression site regardless of the load employed (Fig. 8), but these cracks were not detected for the same indentation applied on annealed samples. Thus, annealing not only substantially improves the hardness of trivalent Cr-C coatings, but their toughness as well. This observation is important for industrial applications of thin coatings, where hardness and toughness are often of equal importance<sup>28</sup>. The physical origin of this effect may be associated with the evolution of hydrogen upon annealing.



As deposited  $-571 \pm 28 \text{ kgf / mm}^2$ Figure 8. SEM micrographs after 25 g load indentation, illustrating an apparent increase in coating toughness upon annealing.

#### 4. Conclusions

In the present work, semi-bright or dull coatings on copper and steel were obtained from a trivalent chromium bath, with an efficiency ranging from 15 to 22 %. Carbon and oxygen were present in the coatings and carbon content remained between approximately 4 and 5 wt. % for all of the applied current waveforms. Consequently, all of the deposits had the same structure, appearing amorphous in x-ray diffraction experiments.

Structural changes during annealing lead to very high hardness values (up to ~1400 kgf/mm<sup>2</sup>), which we attribute to the precipitation of interstitial-strengthened BCC Cr phase. At relatively high temperatures (> 600°C) the precipitation of carbides is observed, although without any additional strengthening.

#### Acknowledgements

This work made use of the Shared Experimental Facilities supported by the MRSEC Program of the National Science Foundation under award number DMR 02-13282. F. J. Williams is a research fellow from the National Research Council of Argentina (CONICET).

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