

# Communications

## Strategy to Improve the High-Temperature Mechanical Properties of Cr-Alloy Coatings

M.J.L. GINES, F.J. WILLIAMS, and C.A. SCHUH

Electroplated Cr-C alloy coatings exhibit significant increases in hardness and strength when exposed to elevated temperatures up to about 600 °C, owing to the evolution of their nanostructure. In this article, we describe a strategy by which this evolution can be shifted to even higher temperatures (approaching 850 °C), through a ternary addition of phosphorus. The resulting Cr-C-P coatings may be suitable for applications at higher service temperatures, where more conventional Cr-based coatings soften rapidly.

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Electrodeposited chromium coatings are extensively employed across many industries and can be plated from either hexavalent or trivalent baths.<sup>[1]</sup> For many years, the hexavalent bath has been used to produce “hard chromium” coatings with good wear and corrosion resistance;<sup>[2,3,4]</sup> however, these are quite temperature sensitive, and their contact and wear properties decline rapidly at elevated service temperatures.<sup>[5,6,7]</sup> In contrast, chromium plated from the trivalent state frequently contains metalloid alloying elements, which fundamentally change the evolution of the coating microstructure upon heating;<sup>[6–9]</sup> unlike “hard chromium” coatings, such alloy deposits harden considerably upon heating. In particular, carbon incorporation from a trivalent bath increases hardness after annealing by suppressing chromium crystallization and by precipitation of carbides that contribute to grain boundary pinning. We have recently proposed that Cr-C coatings derived from a trivalent bath may have broad applications in elevated-temperature environments.<sup>[10,11]</sup> As an added benefit, the health and environmental concerns about trivalent baths are dramatically lower than for hexavalent ones.<sup>[12]</sup>

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In spite of the advantages of Cr-C alloy deposits, the range of temperatures for which these coatings are suitable remains limited (<600 °C). This range is useful for some machine or engine applications, but is insufficient for, *e.g.*, hot metalwork tooling surfaces. For this reason, it is desirable to develop new coatings with advantageous hardness and surface properties even after heating to ~800 °C or 900 °C. It is our purpose in this article to introduce a strategy to improve upon Cr-C derived from a trivalent bath, through the addition of P to the coating. While the addition of phosphorus to such coatings has been discussed from an electrochemical point of view in prior literature,<sup>[13,14]</sup> we report here the ability of P additions to promote strengthening of such coatings after high-temperature exposure for the first time. By properly tuning the deposition bath chemistry, the temperature at which maximum hardness is achieved can be intentionally manipulated.

The electrolyte employed in this study was based on a trivalent chromium bath containing organic complexing agents<sup>[10,11,15]</sup> and sodium hypophosphite as the source of phosphorus<sup>[14]</sup> (Table I). It should be noted that carbon is incorporated into the coating as a result of organic compound reduction and/or the extremely high electrical field, which leads to the decomposition and adhesion of organic compounds as the coating is formed. All plating experiments were carried out at room temperature (20 °C to 25 °C) using a custom cylindrical cathode of either copper or steel, which was rotated at 400 rpm during deposition to promote an even current density distribution and a controlled turbulent flow. Platinum mesh was used as the anode, and pulsed current was supplied by a Dynatronix (Amery, WI) DPR20-30-200 power supply (generally 30 A/cm<sup>2</sup>, with on-time of 5 ms, off-time of 5 ms, and total time of 80 minutes). The surface morphology and metallographically prepared cross sections of each sample were characterized by scanning electron microscopy (SEM) using LEO (Cambridge, UK) 438VP equipment. The chemical composition was assessed using energy-dispersive spectroscopy (EDS) as well as electron spectroscopy for chemical analysis (ESCA). X-ray diffraction (XRD) was employed to evaluate the phases in the coatings, using a Rigaku (Tokyo, Japan) RU300 diffractometer with Cu K<sub>α</sub> radiation. Microhardness tests were conducted on polished cross sections of the electrodeposits using a Vickers indenter with 10-g load; in all cases, the hardness impression was much smaller than the film thickness, ensuring a clean measurement of the coating properties. To examine the effect of thermal exposure on the structure and properties of the coatings, annealing treatments were carried out in argon at various temperatures up to 900 °C, with a constant time-at-temperature of 30 minutes.

We found that the degree of phosphorus incorporation in the coating could be varied by simply changing the concentration of hypophosphite in the deposition bath, as illustrated in Figure 1. The morphology of our Cr-C-P coatings in the as-deposited state is shown in both cross-sectional and plan views in the SEM images of Figure 2. All deposits had the same nodular morphology (Figure 2(a)) regardless of the amount of

**Table I. Composition and Role of Chemicals Present in the Plating Bath Used in This Study for Cr-C-P Electrodeposition**

Constituent	Concentration (g/L)	Function
CrCl <sub>3</sub> ·6H <sub>2</sub> O	110	Source of Cr <sup>3+</sup>
NH <sub>4</sub> Cl	80	Electrolyte support and complexing agent
HCOO(NH <sub>4</sub> )	40	Organic complexing agent
NaCH <sub>3</sub> COO	15	Organic complexing agent
NH <sub>4</sub> Br	10	Antioxidizing agent
H <sub>3</sub> BO <sub>3</sub>	45	Buffer agent
KCl	40	Electrolyte support
Dodecyl NaSO <sub>4</sub>	0.2	Wetting agent
NaH <sub>2</sub> PO <sub>2</sub> ·H <sub>2</sub> O	0 to 20	Source of P

The pH of the bath was adjusted to 2.3 by adding HCl or NaOH prior each plating experiment.

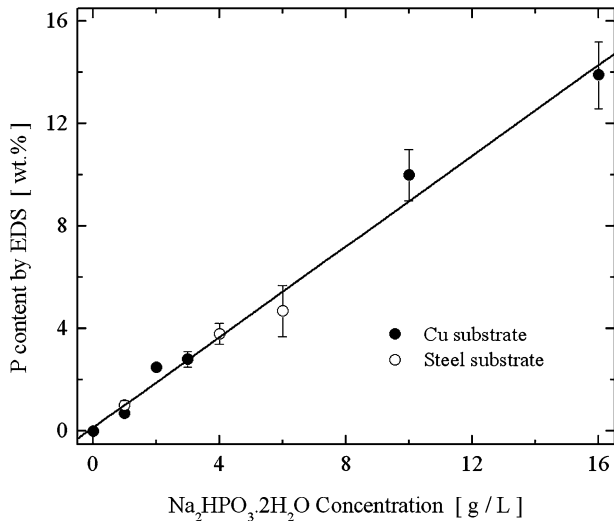


Fig. 1.—Phosphorus content in Cr-C-P coatings as a function of phosphorus in the electrolytic bath (Table I). Peak current density = 30 A/dm<sup>2</sup>;  $t_{\text{on}} = t_{\text{off}} = 5$  ms; total charge transferred = 72,000 C/dm<sup>2</sup>; and temperature = 20 °C to 25 °C.

phosphorus incorporated, with a similar form to those seen in binary Cr-C coatings.<sup>[10,11]</sup> A few small cracks were observed, but these rarely spanned the full film thickness in the as-deposited coatings (Figure 2(b)). The thickness of the Cr-C-P deposits was homogeneous across the substrate surface and ranged from 10 to 30 μm depending on the phosphorus content (*i.e.*, as phosphorus concentration increased, thickness decreased). All of the coatings were “X-ray amorphous” in the as-deposited state, as illustrated in Figure 3. Microhardness, measured on the cross section of the deposits, ranged from 5.4 to 6.4 GPa in the as-deposited condition.

Figure 3(a) shows a series of XRD patterns for a Cr-C sample without incorporated phosphorus, as a function of annealing temperature. The structural evolution documented here is in line with our previous research<sup>[10,11]</sup> on binary Cr-C coatings. The bcc chromium peaks from ~10-nm nanocrystals begin to appear at around 350 °C, and the crystal size increases with annealing temperature, up to about 50 nm, as estimated by conventional line-broadening measurements. Chro-

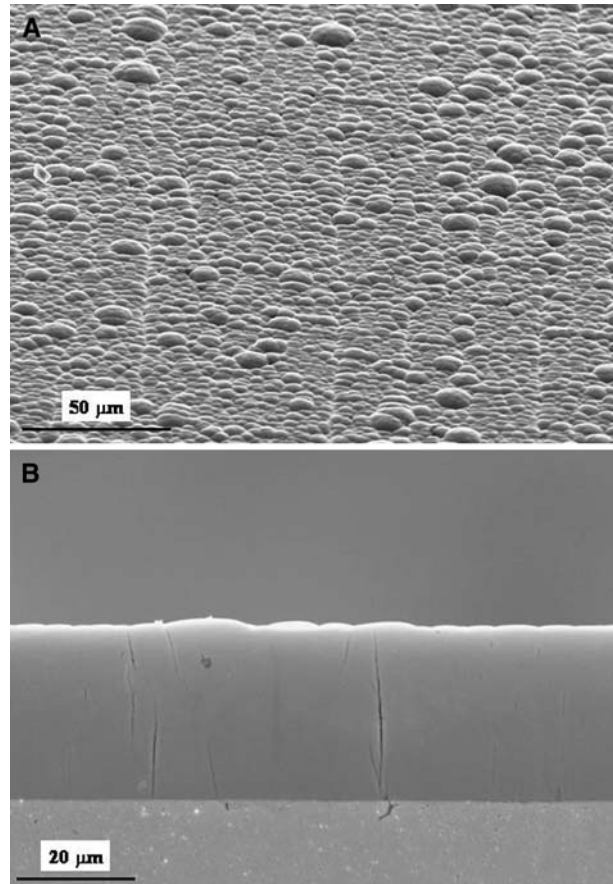


Fig. 2.—SEM micrograph of as-deposited Cr-C-P coating (2.8 wt pct P by EDS): (a) plan view and (b) cross-sectional view.

mium carbide (Cr<sub>7</sub>C<sub>3</sub>) begins to precipitate around 600 °C, while at 900 °C, Cr<sub>23</sub>C<sub>6</sub> forms at the expense of Cr<sub>7</sub>C<sub>3</sub>. When a small amount of phosphorus (0.7 wt pct) is introduced into the Cr-C coating, the same basic sequence of structural evolutions is seen (Figure 3(b)), but the onset of chromium crystallization is delayed to somewhat higher temperatures (from 335 °C to about 370 °C; not shown in Figure 3(b)). Also, several small peaks attributable to chromium phosphides (CrP and mainly Cr<sub>3</sub>P) begin to appear at 700 °C. For a somewhat higher content of phosphorus (2.8 wt pct),

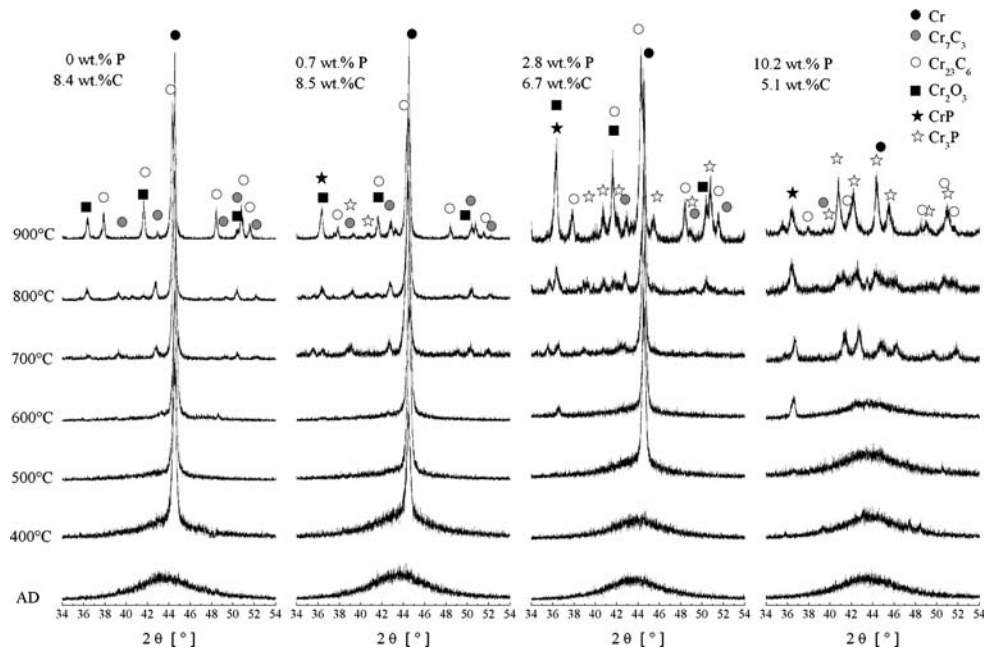


Fig. 3.—XRD patterns of the Cr-C-P coatings as a function of annealing temperature, for different levels of phosphorus addition determined by EDS. Carbon content determined by ESCA.

these differences are more pronounced (Figure 3(c)). In particular, phosphorus now notably delays the chromium crystallization, which in this case is not observed until about 500 °C. Furthermore, the prevalence of carbides at temperatures above 700 °C is substantially diminished, in favor of phosphides. At even higher phosphorus contents (10.2 wt pct), chromium crystallization is apparently completely inhibited even at temperatures as high as 900 °C (Figure 3(d)), and in fact clear evidence for the amorphous phase is retained to temperatures as high as 600 °C. Above 700 °C, Cr<sub>3</sub>P precipitates and becomes the main phase detected up to 900 °C; only small peaks corresponding to Cr<sub>23</sub>C<sub>6</sub> were found in these specimens.

The XRD data in Figure 3 demonstrate that the addition of P to Cr-C coatings generally shifts the crystallization and transformation sequence to higher temperatures. This effect is also mirrored in the evolution of the coating hardness, as illustrated in Figure 4. The structural evolution upon annealing of Cr-C (0 wt pct P) leads to very high hardness values (up to ~13.7 GPa), which we have previously attributed primarily to the precipitation of interstitial-strengthened bcc Cr phase.<sup>[10,11]</sup> The decline in strength at higher temperatures is related to structural coarsening, leading to a maximum in hardness after annealing near about 600 °C in the binary coating. As phosphorus is added to the deposits, the same trends are observed, but with a shift toward increasing temperatures that is commensurate with the shift in the structural evolution sequence of Figure 3. The role of phosphorus here is apparently to directly stabilize the near-amorphous phase against crystallization, and a contribution to grain boundary pinning at higher temperatures cannot be ruled out. In any event, the incorporation of a properly-selected amount of phosphorus can shift the maximum hardness

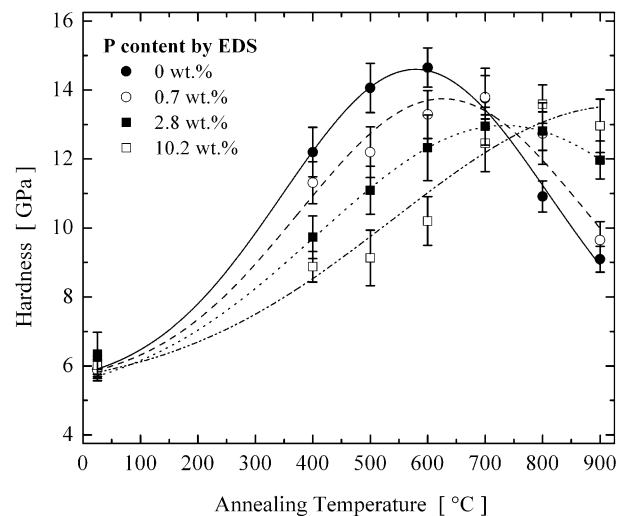


Fig. 4.—Effect of annealing temperature and phosphorus content on hardness of electrodeposited Cr-C-P coatings. Each specimen was annealed for 30 minutes in an argon atmosphere. Ten measurements were made for each load (10 g) and the average is reported.

peak to temperatures approaching 850 °C, substantially higher than the ~600 °C peak observed in the binary Cr-C system. Additionally, the hardness level attained after annealing at these temperatures (~13.0 GPa) is substantially above that reported for other metal-metalloid deposits such as electroless and electroplated Ni-P coatings, which generally exhibit maximum hardness values of at most ~8.8 GPa at substantially lower annealing temperatures ( $T < 500$  °C).<sup>[16-22]</sup> This strength enhancement after annealing suggests that ternary Cr-C-P coatings may find use in applications

where high hardness must be maintained after exposure to elevated service temperatures, such as for tooling surfaces in warm or hot metal forming operations.

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