



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>



Contents lists available at SciVerse ScienceDirect

## Int. Journal of Refractory Metals and Hard Materials

journal homepage: [www.elsevier.com/locate/IJRMHM](http://www.elsevier.com/locate/IJRMHM)

## Short communication

## Improving hardness and tribological characteristics of nanocrystalline Cr–C films obtained from Cr(III) plating bath using pulsed electrodeposition

V.S. Protsenko<sup>a,\*</sup>, F.I. Danilov<sup>a,\*</sup>, V.O. Gordienko<sup>a</sup>, A.S. Baskevich<sup>a</sup>, V.V. Artemchuk<sup>b</sup><sup>a</sup> Department of Physical Chemistry, Ukrainian State University of Chemical Technology, Gagarin Av. 8, Dnipropetrovsk, 49005, Ukraine<sup>b</sup> Dnipropetrovsk National University of Railway Transport named after Academician V. Lazaryan, Lazaryana St. 2, Dnipropetrovsk, 49010, Ukraine

## ARTICLE INFO

## Article history:

Received 21 August 2011

Accepted 14 October 2011

## Keywords:

Hard chromium

Pulsed electrodeposition

Nanocrystalline

Wear

Tribology

## ABSTRACT

Effect of pulsed electrodeposition on the nanocrystal size, composition, hardness, coefficient of friction and wear resistance was investigated for the Cr–C electrodeposits obtained from a trivalent chromium bath. The electrodeposits were shown to contain about 9% of carbon. Pulsed electrodeposition does not virtually affect the carbon content. At the same time, an increase in the off time duration leads to a decrease in the nanocrystals size. The hardness and wear parameters of the electrodeposits may be sufficiently improved when using pulsed current. For instance, at  $t_{on} = t_{off} = 1$  s, the hardness reaches the values of  $\sim 1200 \div 1300$  HV (meanwhile, it is close to  $850 \div 950$  HV at a steady-state electrolysis).

© 2011 Elsevier Ltd. All rights reserved.

## 1. Introduction

Hard chromium electroplating is widely used in modern industry for improving hardness, wear and corrosion resistance, decorative appearance of different tools and machines. Usually, chromium is deposited from solutions containing highly toxic compounds of Cr(VI). Because of the great toxicity and carcinogenicity, the Cr(VI) baths are now under pressure and numerous efforts have been made in order to develop eco-friendly processes based on Cr(III) compounds.

In recent years, a number of publications were devoted to Cr–C electrodeposition from Cr(III) baths [1–11]. Such chromium–carbon coatings were shown to distinguish by their valuable physicochemical and mechanical properties. It was established in our works [12,13] that the nanocrystalline Cr–C deposits may be obtained from sulfate trivalent chromium bath containing carbamide and formic acid. The hardness of these coatings does not differ substantially from the hardness of electrodeposits which are obtained in a Cr(VI)-based bath. Their wear characteristics are somewhat better than those obtained from the common Cr(VI)-bath. It is clear that further improvement of hardness and wear parameters of deposits under consideration is desirable.

Recently, the authors of study [14] showed that nanocrystalline Cr–C layers with excellent anti-wear performance can be prepared by electrodeposition in Cr(III) bath with subsequent annealing. However, annealing is a rather power-consuming procedure.

Improvement of different properties of Cr electrodeposits has also been reported using pulsed electrolysis [15–18]. Therefore, the aim of the present work was to study effect of pulsed current deposition on hardness and wear characteristics of Cr–C coatings from Cr(III) bath containing carbamide and formic acid.

## 2. Material and methods

A sulfate trivalent chromium bath with the following composition was applied ( $\text{mol L}^{-1}$ ): 1 Cr(III), 0.5 HCOOH, 0.5  $\text{CO}(\text{NH}_2)_2$ , 0.15  $\text{Al}_2(\text{SO}_4)_3$ , 18H<sub>2</sub>O, 0.3 Na<sub>2</sub>SO<sub>4</sub>, 0.5 H<sub>3</sub>BO<sub>3</sub> and 0.1 g L<sup>−1</sup> of sodium dodecyl sulfate [12,13]. Chromium was deposited at current densities of 30, 35, and 40 A dm<sup>−2</sup>; the temperature of the chromium bath was equal to 35 °C; the bath pH was 1.5.

Chromium electrodeposition was carried out both at a steady value of current density and at pulsed current with square wave in a usual thermostated glass cell. Prior to each experiment, the cathode surface was treated with magnesium oxide, etched for several minutes in 1:1 (vol) hydrochloric acid solution and then thoroughly rinsed with distillate water. The electrolysis was performed with titanium–manganese dioxide anodes without separation of anodic and cathodic compartments.

Small-angle X-ray scattering (SAXS) experiments were carried out by means of an X-ray diffractometer DRON-3.0–IBM with a small-angle X-ray camera KRM-1 in the monochromatized Mo- $K_\alpha$  radiation [12].

The surface morphology of deposits was investigated by scanning electron microscopy (SEM) utilizing scanning electron microscope EVO 40XVP (Carl Zeiss AG).

Vicker's microhardness (HV) was determined using a PMT-3 apparatus (manufactured in Russia) at a 100 g load, the coating thickness

\* Corresponding authors. Tel./fax: +380 562474586.

E-mail addresses: [Vprotsenko@smtp.ru](mailto:Vprotsenko@smtp.ru) (V.S. Protsenko), [fdanilov@optima.com.ua](mailto:fdanilov@optima.com.ua) (F.I. Danilov).

being not less than 20  $\mu\text{m}$ . The average value of deposits microhardness was calculated from more than 10 separate measurements.

The wear tests were conducted on the SMC-2 wear tester (produced in Russia) under unlubricated conditions. The 20  $\mu\text{m}$  Cr–C alloy films were deposited on a steel block with inner diameter of 50 mm. The counterpart was a tempered steel disk. The wear and friction tests were carried out at a rubbing speed of  $0.79 \text{ m s}^{-1}$  over a total sliding distance of 3140 m. The sample wear weight losses from four identical test conditions were measured gravimetrically.

The chemical composition of the coatings under study was determined by XPS investigations which were described in detail in Ref. [12]. In addition, chemical composition of electrodeposits was established by means of a usual spectrophotometric analysis. For this purpose, coatings obtained were dissolved in hot solution of hydrochloric acid. After formation of intensively colored complex of Cr(III) with EDTA, absorbance of solution was measured at  $\lambda = 540 \text{ nm}$  using standardized procedure [19]; and then chromium content in electrodeposit (Cr %) was calculated. The content of carbon in coatings was determined as the difference

$$\text{C}\% = 100\% - \text{Cr}\%$$

The results of Cr content determination by means of XPS study, on the one hand, and by spectrophotometric technique, on the other hand, coincide entirely.

### 3. Results and discussion

It was stated that the electrodeposits obtained from the bath under study contain about 9% of carbon. Varying off time duration from 0 to 2 s (at a constant pulse duration time of 1 s) does not practically affect the carbon content at current densities of 30, 35 and 40  $\text{A dm}^{-2}$ . Thus, one can assert that using pulsed electrodeposition virtually has no effect on the composition of Cr–C deposits obtained from the plating chromium bath under study.

The radius of gyration in nanocrystalline structure ( $R_0$ ) can be expressed from SAXS experiment results via Guinier function [20]:

$$I(s) \approx I(0) \exp\left(-\frac{s^2 R_0^2}{3}\right)$$

where  $I(s)$  is the scattered intensity,  $I(0)$  is the scattered intensity at zero scattering angle,  $2\theta$  is the angle between the incident X-ray beam and the detector measuring the scattered intensity,  $\lambda$  is the wavelength of the X-rays and  $S = \frac{4\pi \sin(\theta)}{\lambda}$  is the magnitude of the scattering vector.

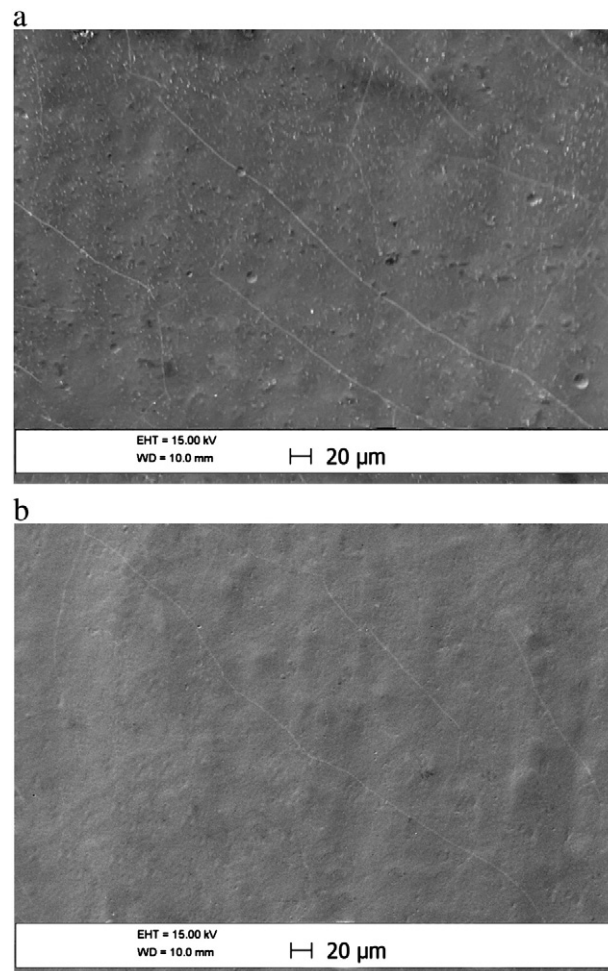
The size of the regions with atomic ordered arrangement in bulk material ( $R_0$ ) was calculated using Guinier equation by linearizing experimental dependences in coordinates  $\ln I$  vs.  $s^2$ .

The effect of the off time duration on the radii of gyration (as a rough approximation, the sizes of nanocrystals [12]) is given in Table 1. As seen, an increase in the off time duration leads to a decrease in the  $R_0$  value. It seems probable that the pulsed electrolysis during off time results in the partial passivation of a freshly formed chromium surface in plating electrolyte, since metallic chromium is well known to tend to self-passivation in aqueous solutions. A

**Table 1**  
Influence of off time duration on the radius of gyration.

Electrodeposition mode	$R_0$ (nm)
$t_{\text{off}} = 0 \text{ s}$ (direct current)	3.5
$t_{\text{off}} = 0.5 \text{ s}$ (pulsed current)	3.2
$t_{\text{off}} = 1.0 \text{ s}$ (pulsed current)	3.0

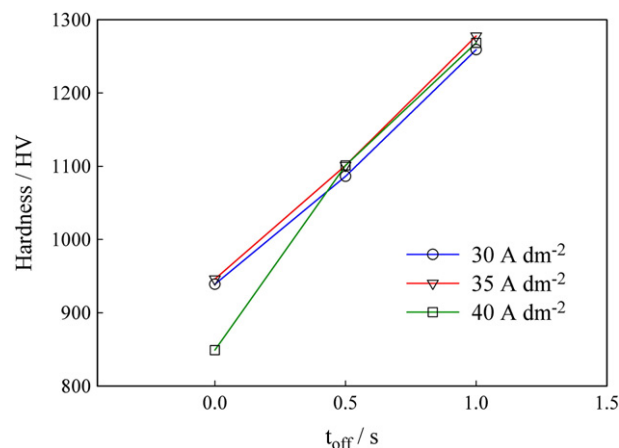
Pulse duration time 1 s; current density 35  $\text{A dm}^{-2}$ ; bath temperature 35  $^\circ\text{C}$ .



**Fig. 1.** SEM images of Cr–C electrodeposits obtained (a) under steady-state electrolysis and (b) under pulsed electrolysis ( $t_{\text{on}} = t_{\text{off}} = 1 \text{ s}$ ). Current density 40  $\text{A dm}^{-2}$ .

consequence of passivation may be formation of a large number of nanosize nuclei with smaller radius in the following current pulse.

Fig. 1 is the surface morphology of Cr–C deposits observed by SEM. As can be seen, the surface of coatings obtained under pulsed current condition becomes smoother and more uniform in comparison with coatings deposited under steady-state electrolysis. Additionally, utilizing pulsed electrodeposition reduces the number of cracks per



**Fig. 2.** Dependence of hardness of Cr–C deposits on off time duration (pulse duration time 1 s).

**Table 2**  
Influence of pulsed current on friction coefficient of Cr–C deposits (at a load of 1 MPa).

Current density, A dm <sup>−2</sup>	Friction coefficient	
	Direct current	Pulsed current
30	0.14	0.12
35	0.14	0.11
40	0.14	0.13

unit area. Improving surface morphology under pulsed electrodeposition was also detected earlier in case of Cr electroplating from another trivalent chromium bath when the carbon content in coatings was rather low [21].

Fig. 2 shows the effect of the off time duration on the hardness of coatings. The hardness is considerably enhanced at an increase in the off time duration in the range from 0 to 1 s at any value of current density. The observed values of coatings hardness come up to 1200–1300 HV; generally speaking, they are rather large. It should be noted that such high values of the hardness for Cr–C electrodeposits were earlier reported only after their annealing [14].

For tribological tests, we used Cr–C deposits obtained at  $t_{\text{on}} = t_{\text{off}} = 1$  s as these conditions correspond to the largest values of HV. Using pulsed electrodeposition proved to improve the wear characteristics (Tables 2 and 3) — both weight losses and friction coefficient decrease in comparison with the deposition at direct current.

The hardness of the chromium deposits is known to be significantly dependent upon grain size [17]. It is reasonable to assume that the above-mentioned decrease in the size of the nanocrystals when utilizing pulsed current results in the observed enhancement of the hardness of deposits [21]. Simultaneously, wear parameters of coatings improve. Indeed, hardness, coefficient of friction and wear resistance are the properties which exhibit strong grain size dependence [22]. Relatively little changes in the grain size may lead to significant changes in such properties.

#### 4. Conclusions

Thus, the application of pulsed electrolysis leads to the decrease in the nanocrystals size when Cr–C coatings are deposited from the trivalent chromium bath. The hardness and tribological parameters of the electrodeposits under consideration may be sufficiently improved when using pulsed current.

#### References

- [1] Kwon SC, Kim M, Park SU, Kim DY, Kim D, Nam KS, et al. Characterization of intermediate Cr–C layer fabricated by electrodeposition in hexavalent and trivalent chromium baths. *Surf Coat Technol* 2004;183:151–6.
- [2] Survilene S, Nivinskiene O, Cesuniene A, Selskis A. Effect of Cr(III) solution chemistry on electrodeposition of chromium. *J Appl Electrochem* 2006;36:649–54.
- [3] Survilene S, Jasulaitiene V, Nivinskiene O, Cesuniene A. Effect of hydrazine and hydroxylaminophosphate on chrome plating from trivalent electrolytes. *Appl Surf Sci* 2007;253:6738–43.

**Table 3**  
Influence of pulsed current on weight losses of Cr–C deposits.

Load, MPa	Weight losses, g km <sup>−1</sup>	
	Direct current	Pulsed current
1	0.00270	0.00230
2	0.00495	0.00445
3	0.00662	0.00615
4	0.00762	0.00708

Current density 35 A dm<sup>−2</sup>.

- [4] Edigaryan AA, Safonov VA, Lubnin EN, Vykhodtseva LN, Chusova GE, Polukarov YuM. Properties and preparation of amorphous chromium carbide electroplates. *Electrochim Acta* 2002;47:2775–86.
- [5] Huang CA, Liu YW, Yu C, Yang CC. Role of carbon in the chromium deposit electrodeplated from a trivalent chromium-based bath. *Surf Coat Technol* 2011;205:3461–6.
- [6] Ghaziof S, Golozar MA, Raeissi K. Characterization of as-deposited and annealed Cr–C alloy coatings produced from a trivalent chromium bath. *J Alloys Compd* 2010;496:164–8.
- [7] Ghaziof S, Raeissi K, Golozar MA. Improving the corrosion performance of Cr–C amorphous coatings on steel substrate by modifying the steel surface preparation. *Surf Coat Technol* 2010;205:2174–83.
- [8] Zeng Z, Wang L, Liang A, Zhang J. Tribological and electrochemical behavior of thick Cr–C alloy coatings electrodeposited in trivalent chromium bath as an alternative to conventional Cr coatings. *Electrochim Acta* 2006;52:1366–73.
- [9] Huang CA, Liu YW, Chuang CH. The hardening mechanism of a chromium–carbon deposit electrodeplated from a trivalent chromium-based bath. *Thin Solid Films* 2009;517:4902–4.
- [10] Huang CA, Lieu UW, Chuang CH. Role of nickel undercoat and reduction-flame heating on the mechanical properties of Cr–C deposit electrodeplated from a trivalent chromium based bath. *Surf Coat Technol* 2009;203:2921–6.
- [11] Zeng Z, Liang A, Zhang J. Electrochemical corrosion behavior of chromium–phosphorus coatings electrodeposited from trivalent chromium baths. *Electrochim Acta* 2008;53:7344–9.
- [12] Danilov FI, Protsenko VS, Gordienko VO, Kwon SC, Lee JY, Kim M. Nanocrystalline hard chromium electrodeposition from trivalent chromium bath containing carbamide and formic acid: Structure, composition, electrochemical corrosion behavior, hardness and wear characteristics of deposits. *Appl Surf Sci* 2011;257:8048–53.
- [13] Protsenko VS, Danilov FI, Gordienko VO, Kwon SC, Kim M, Lee JY. Electrodeposition of hard nanocrystalline chrome from aqueous sulfate trivalent chromium bath. *Thin Solid Films* 2011;520:380–3.
- [14] Zeng Z, Wang L, Liang A, Chen L, Zhang J. Fabrication of a nanocrystalline Cr–C layer with excellent anti-wear performance. *Mater Lett* 2007;61:4107–9.
- [15] Saravanan G, Mohan S. Pulsed electrodeposition of microcrystalline chromium from trivalent Cr–DMF bath. *J Appl Electrochem* 2009;39:1393–7.
- [16] Mohan S, Vijayakumar J, Saravanan G. Influence of CH<sub>3</sub>SO<sub>3</sub>H and AlCl<sub>3</sub> in direct and pulse current electrodeposition of trivalent chromium. *Surf Eng* 2009;25:570–6.
- [17] Choi Y, Kim M, Kwon SC. Characterization of chrome layer formed by pulse plating. *Surf Coat Technol* 2003;169–170:81–4.
- [18] Song YB, Chin DT. Pulse plating of hard chromium from trivalent baths. *Plat Surf Finish* 2000;87(9):80–7.
- [19] Lavrukhina AK, Yukina LV. Analytical Chemistry of Chromium. Moscow: Nauka; 1979 (in Russian).
- [20] Glatter O, Kratky O. Small Angle X-ray Scattering. Academic Press; 1982.
- [21] Danilov FI, Protsenko VS, Butyrina TE, Krasinskii VA, Baskevich AS, Kwon SC, et al. Electrodeposition of nanocrystalline chromium coatings from Cr(III)-based electrolyte using pulsed current. *Prot Met Phys Chem Surf* 2011;47:598–605.
- [22] Erb U. Size effects in electroformed nanomaterials. *Key Eng Mater* 2010;444:163–88.