

AMM0017

Enhancing hardness and tribological characteristics of amorphous Cr-C films deposited in the baths without and with addition of cations

Nguyen Van Tai¹, and Nguyen Van Cuong^{1,*}

¹ College of Engineering Technology - Can Tho University, Campus II - 3/2 Street, Can Tho City, VietNam

* Corresponding Author: E-mail: nvcuong@ctu.edu.vn, Telephone Number: +84 9 89909034, Fax Number: +84 710 3831151

Abstract

Effects of the addition of different cations (i.e., Na⁺, Mg²⁺) added in the Cr(III) bath at different ionic strengths on the structure, composition and hardness of Cr-C films were investigated in this work. Direct current cathodic polarization (CP) was used to understand the effect of the cations on the mechanism of Cr (III)-electrochemical deposition in the baths with and without the addition of abovementioned cations. Results showed that the amount of bubbles in the Cr-C coatings obtained in the baths with addition of Na⁺ and Mg²⁺ reduced significantly while the ionic strengths increased from 7.00 to 10.75. The coating structure was analyzed by X-ray diffractometer (XRD); the results indicated that the deposits belonged to amorphous structure in the presence of cations added in the baths such as Na⁺ and Mg²⁺. The examination by X-ray photoelectron spectrometer (XPS) showed that the deposits had a composition of metallic Cr, Cr-C, and Cr(III) oxides. The hardness and wear resistance of the deposits may be sufficiently enhanced in the baths added with Na⁺ or Mg²⁺ in comparison with those in the bath without addition of cations. The hardness of Cr-C films in the baths containing Na⁺ or Mg²⁺ ion reached the values of 1200 to 1300 HV; meanwhile, that value obtained in the free-bath was from 850 to 950 HV.

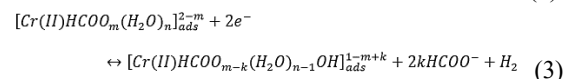
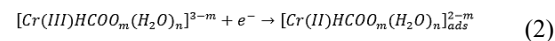
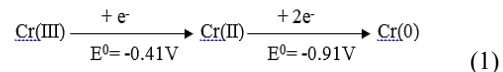
Keywords: cations; electrodeposition; hardness; trivalent chromium.

1. Introduction

Chromium electrodeposition is one of the most important electroplating technologies to deposit a thin film of metallic chromium for utilizing in various applications which will give a good appearance to the product, with greater hardness, more resistant to wear and corrosion and value added by metal fabrication parts [1]. Hard chromium coating offers a Cr-layer with the thickness greater than 0.8 μm on the purpose for industrial applications [2]. The life span of most parts would be much shorter without the physical properties offered by electroplated chromium deposits leading to the parts would have to be either repaired or replaced more frequently, or made from more expensive materials, thus wasting valuable resources. The hard Cr-coatings generally have a low surface energy, so they can be used on things like engines, pumps, compressors hydraulic and pneumatic rods for their high resistance to corrosion and good hardness (56 to 74 HRC), thus serving with longer self-life [3]. Recently, trivalent chromium electrodeposition has widely used to replace the hexavalent chromium electrodeposition thanks to their less toxic properties. The process involving Cr(III) baths is an eco-friendly alternative to the conventional hexavalent chromium baths. This has been considered as a very promising technology in modern Cr-electroplating.

The trivalent chromium electrodeposition process occurs via two steps as presented in Eqs. (1)-(3). The reduction of Cr(III) to Cr(II) was strongly affected by diffusion process, in which Cr³⁺ ions will move from bulk solution to the cathode surface via an adsorption layer called cathodic film (CF) that contains bivalent

chromium complexes. Intermediate complexes were formed in the inner portion of CFs due to partial reduction of electrochemical reduction [4]. At the formed CF, the competition happens sharply between ions such as Cr³⁺, Cr²⁺, H⁺, and etc. for adsorptive sites, in which hydrogen evolution depended directly on the amounts of H⁺ ion leading to the penetration of bubbles and pores into the Cr-C film, and the reduction of hardness and wear resistance. The adsorption layer was significantly controlled by cations [5-8]. Hence, we suggested mechanistic schemes related to the formation of intermediate complexes of chromium during the electrodeposition process. Further, we performed an intensive investigation to evaluate the stability and the role of cations following the proposed mechanism.



In this work, the commonly used electrolytes including sulfate salts containing different cations with various valences (Na⁺ and Mg²⁺) are considered to adjust their concentration for control the magnitude of ionic strength (from 7.00 to 10.75) in the bath of Cr (III)-electrochemical deposition process. The structure and composition of Cr-C films with the baths added by different cations affect to the mechanical hardness and tribological property are also investigated.

AMM0017

2. Experimental Methods

The trivalent chromium electrodeposition process is conducted in the aqueous baths containing trivalent chromium chloride salt (CrCl_3) as source of Cr^{3+} ion, formic acid (HCOOH) as complexing agent, boric acid as pH- buffering agent, sodium dodecyl sulfate as surfactant and sulfate salts with various cations (Na^+ ; Mg^{2+}) as conducting salt. The bath compositions are also summarized in table 1 that include: 0.5 M $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, 0.5 M HCOOH , 0.5 M H_3BO_3 and 0.0035 M sodium dodecyl sulfate and Na_2SO_4 or MgSO_4 at different concentration to control the ionic strength from 7.00 to 10.75.

Table.1 Composition of baths without and with addition of cations at different ionic strength for Cr(III) electrodeposition

Notation	Additives	Concentration of additives (M)	Ionic strength
S_f	-	-	7.00
S_{Na_1}	Na_2SO_4	0.25	7.75
S_{Na_2}	Na_2SO_4	0.75	9.25
S_{Na_3}	Na_2SO_4	1.25	10.75
S_{Mg_1}	MgSO_4	0.19	7.75
S_{Mg_2}	MgSO_4	0.38	9.25
S_{Mg_3}	MgSO_4	0.94	10.75

After mixing the components, the prepared electrolytes were heated and stirred for 2 hours at temperature of 70 ± 2 °C. Then, they were cooled to room temperature and stored for 15 days to ensure that formation of Cr(III) complex, $[\text{Cr}(\text{H}_2\text{O})_{6-n}(\text{HCOO})_n]^{3-n}$, would be completely formed and reached the final thermodynamic equilibrium state before the commencement of deposition process [9-10]. The pH of electroplating baths had been adjusted by the addition of NaOH or HCl to achieve 1.7.

Prior to each experiment, copper sheets, platinized titanium electrode and an SCE electrode were used as substrate (cathode), anode in order to prevent anodic oxidation of Cr(III) ions and as reference, respectively. The substrates were mechanically polished by abrasive SiC papers down to 2000-grit silicon carbide abrasive paper and picked in a 1 M hydrochloric acid solution for 1 minute prior to electrochemical deposition.

The cathodic polarization curves were slowly scanned from $E = -0.2$ V to $E = -2.5$ V vs. SCE at scan rate 1 mVs^{-1} to understand the mechanism of Cr(III) electrodeposition in Cr(III) - baths containing different kind of cations using Potentiostat/Galvanostat Model 273A, without any separation of anodic and cathodic compartments. Then, the electrodeposition was carried out by using direct current chronoamperometry with current density of 5 A/dm^2 , temperature of 30 °C in 60 minutes to assess the effect of cations on trivalent chromium electrodeposition process.

Before examination the characteristics of the Cr-C deposits, distinctive samples were washed by deionized water, and then dried by N_2 gas after being cut into 1 x 1 cm (electrodeposited area). The

morphology of the surface were examined by SEM observation. While the structure and chemical state of the Cr - C coatings were characterized using an X-ray diffractometer (XRD) and determined by X-ray Photoelectron Spectroscopy (XPS) analysis, respectively.

The hardness of Cr-C films was measured by using WOLPERT 401 MVD Micro-hardness Tester, with a 0.2 N load and 10 s indentation time. The indentation was only performed when the deposit thickness was sufficiently high.

3. Results and discussion

The effect of cations (Na^+ and Mg^{2+}) on the hardness of deposits obtained in the different electrolytes where without and with addition of cations is showed in Fig.1. This results were obtained with the ionic strength (M) from 7.00 to 10.75, at pH 1.7, temperature at 30 °C, and a constant current density for 60 minutes. The hardness of deposit electroplated in the bath S_f was very low (44.4 HRC) in comparison with that coming from the baths containing Na^+ and Mg^{2+} to change the ionic strength (M) from 7.75 to 10.75 (68.3 HRC and 67.8 HRC for the deposits come from the S_{Na_3} bath and the S_{Mg_3} bath at ionic strength 10.75, respectively). In the rise of ionic strength from 7.75 to 10.75, the hardness of coatings also increases lightly from 63.2 HRC to 68.3 HRC for the baths added with Na^+ ion, and from 61.8 HRC to 67.8 HRC for the baths containing Mg^{2+} ion. It can be attributed to reduction of bubbles and pinholes on the coatings.

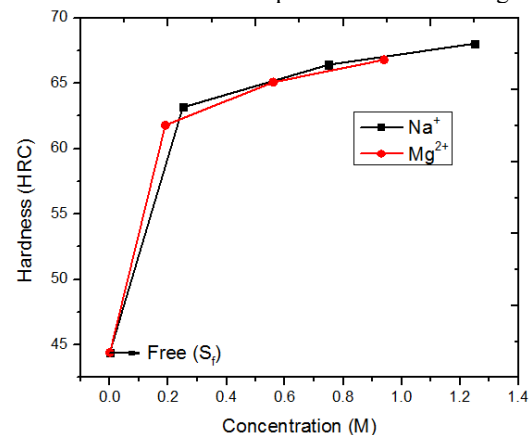


Fig. 1 Hardness of the deposits come from the baths of addition-free, and addition of sodium sulfate and magnesium sulfate under different concentrations.

The trivalent chromium electrochemical deposition occurred via 3 regions A, B and C was proved in Fig.2; in which hydrogen evolution occurred firstly at cathode when potential is more negative than -0.30 V (vs. SHE) in region A. Fig. 2 also pointed out that the highest current density (with $\beta_c(S_f) < \beta_c(S_{\text{Mg}_3}) < \beta_c(S_{\text{Na}_3})$) at a constant potential can be obtained in the addition-free bath in comparison with the baths added with Na^+ or Mg^{2+} . This has led to the hydrogen evolution in the bath of S_f that

AMM0017

was sharply promoted in region A via Eq. (4); resulting many bubbles penetrated into coating and made a worse deposit.

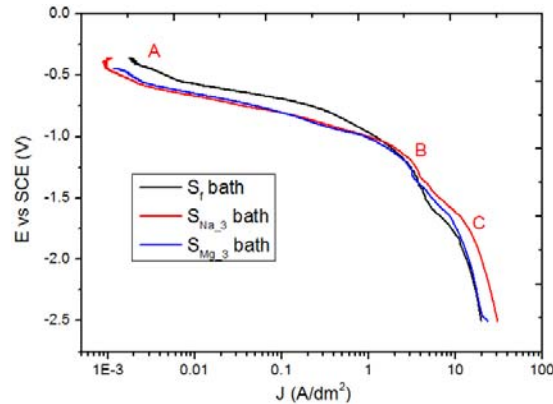


Fig. 2 Potentiodynamic polarization curves (Tafel curve) for electrolytes containing different cations (conditions: pH = 1.7, T = 30 °C).

The surface morphology of deposits come from the addition-free bath and the baths added with Na⁺ or Mg²⁺ ion are depicted in Fig. 3 and Fig. 4. There are many bubbles and pores observed on the surface of coatings are obtained in the bath without addition. It can be attributed to the hydrogen evolution reaction via Eq. (4), competes strongly to the reduction of Cr³⁺ leading to the bubbles and pores formed on the surface. Further, the deposits come from the baths, which are added with Mg²⁺ ion to control the ionic strength from 7.75 to 10.75, showed the less much free-carbs surface in comparison to the deposits obtained from the baths containing Na⁺ ion shown in Fig. 3 because of the percent of C in the coatings [11-13].

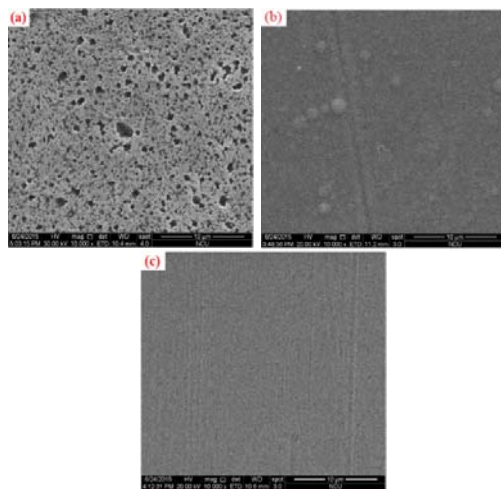


Fig. 3 The surface morphology of Cr-C coatings deposited from the baths without and with addition of cations: (a) S_f; (b) S_{Na_3}; (c) S_{Mg_3}. (experimental conditions: current density = 5 A/dm², deposition time = 15 min; pH = 1.7)

The increase of mechanical hardness of Cr-C films obtained in the baths with addition of cations (Na⁺ or Mg²⁺) in comparison to the free-bath can be explained that the content of C doped into the deposits makes change the order of deposited structure from nano-crystalline to amorphous structures, which controls and affects directly to the hardness of deposits.

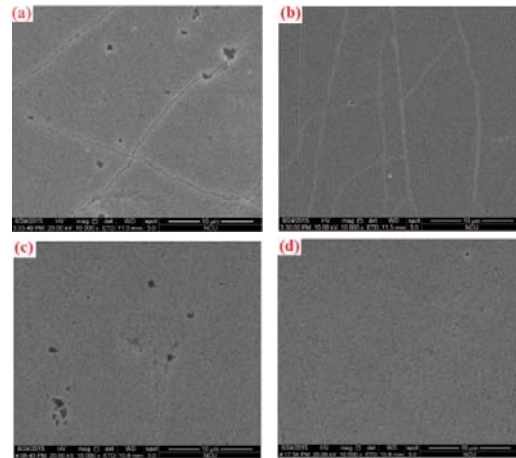


Fig. 4 The surface morphology of Cr-C coatings obtained from different baths: (a) S_{Na_1}; (b) S_{Na_2}; (c) S_{Mg_1}; (d) S_{Mg_2}. (experimental conditions: current density = 5 A/dm², deposition time = 15 min; pH = 1.7).

Results of XPS analysis is presented in Fig. 5. The content of C in deposits electroplated from the baths with Mg²⁺ ion was lower than in the deposits came from the baths with Na⁺ ion. The analysis results also shown that the hardness of the coating deposited in the bath with Mg²⁺ ion decreased lightly in comparison with the deposit came from the bath with Na⁺ ion. The approximate binding energies of C1s band were detected around 283.2 eV and 284.8 eV. In which, the first binding energy (~ 283.2 eV) characterized the chromium – carbide bond (Cr₃C₂), and the another intensive peak contributed to C-O bonding. However, Fig. 5a only showed the peak of C-O bonding that was mainly ascribed to the low hardness of the deposit obtained from the S_f bath. When the ionic strength increased from 9.25 to 10.75, the components of the deposits also represented with the Cr₃C₂ and C-O bonding in the C1s band.

In order to determine the coating structure (crystalline or amorphous structure), XRD pattern had been used to analyze and to compare with PDF Card No.00-006-0649 and 00-004-0836 [14]. It revealed that the peaks located approximately at 2θ = 43.2; 2θ = 44; 2θ = 50.4 and 2θ = 74.1 reflecting to Cr(111) plane, Cr(110) plane, Cu(200) plane and Cu(220) plane, respectively (Fig. 6).

AMM0017

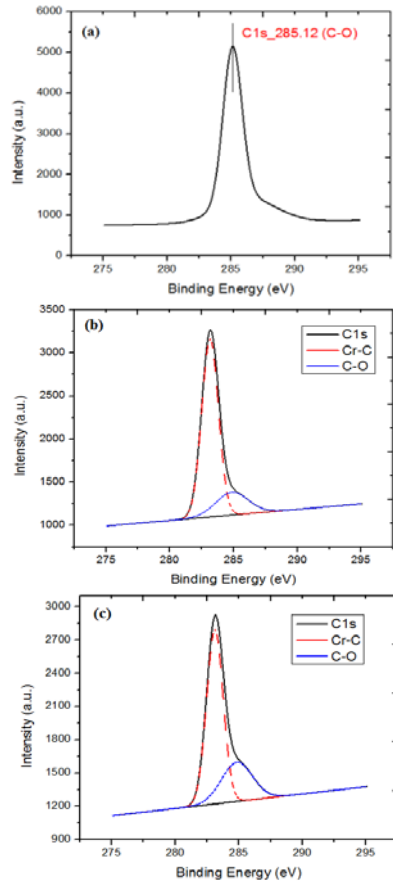


Fig. 5 XPS spectrum of C1s for the deposits come from the different baths: (a) S_f ; (b) S_{Na_1} ; (c) S_{Mg_1} . (experimental conditions: the ionic strength = 7.75, current density = 5 A/dm², deposition time = 15 min, pH = 1.7)

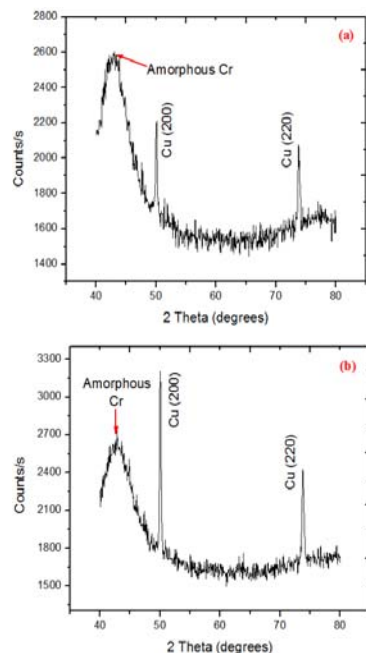


Fig. 6 XRD patterns of Cr – C coatings deposited from S_{Na_3} and S_{Mg_3} baths at ionic strength 10.75.

The structure of deposits electroplated in the bath with addition of Na⁺ or Mg²⁺ ion is displayed in Fig. 6. This figure showed that the very broad peak was clearly found at around $2\theta = 44$. This revealed the deposits had the characteristic of amorphous structure, reflecting the property of Cr–C coating [14, 15]. It can be attributed the action of carbon alloying elements into the chromium crystal lattice that changed the order of Cr atoms and formed the Cr – C film.

4. Conclusions

The harness test pointed out that the mechanical harness of the deposits were significantly improved in the baths added with Na⁺ or Mg²⁺ ions. The baths added Na⁺ ion gave the deposits with the higher content of C in comparison with that came from other baths. There was the strong hardness improvement of the coatings. The XRD patterns revealed that the coatings showed the amorphous structure.

5. Acknowledgement

The authors acknowledge Ministry of Science and Technology of Taiwan for the fellowship to realize this work.

7. References

- [1] Nenad V. Mandich and Donald L. Snyder (2010). Electrodeposition of chromium, Modern Electroplating, John Wiley & Sons, New York.
- [2] E. Svenson (2006). Durachrome hard chromium plating, Plating Resources Inc. Cocoa, Florida, USA, vol.2.
- [3] N. Van Phuong, S.-C. Kwon, J.-Y. Lee, J. Shin, B. T. Huy, and Y.-I. Lee (2011). Mechanistic study on the effect of PEG molecules in a trivalent chromium electrodeposition process, *Microchemical Journal*, vol. 99, pp. 7-14.
- [4] X.-j. Hu, Y.-g. Liu, G.-m. Zeng, S.-h. You, H. Wang, X. Hu, et al. (2014). Effects of background electrolytes and ionic strength on enrichment of Cd (II) ions with magnetic graphene oxide-supported sulfanilic acid, *Journal of Colloid and Interface Science*, vol. 435, pp. 138-144.
- [5] T. Wang, W. Liu, L. Xiong, N. Xu, and J. Ni (2013). Influence of pH, ionic strength and humic acid on competitive adsorption of Pb (II), Cd (II) and Cr (III) onto titanate nanotubes, *Chemical Engineering Journal*, vol. 215, pp. 366-374.
- [6] J.-K. Yang and A. P. Davis (1999). Competitive adsorption of Cu (II)-EDTA and Cd (II)-EDTA onto TiO₂, *Journal of Colloid and Interface Science*, vol. 216, pp. 77-85.
- [7] J.-K. Yang, S.-M. Lee, and A. P. Davis (2006). Effect of background electrolytes and pH on the adsorption of Cu (II)/EDTA onto TiO₂, *Journal of Colloid and Interface Science*, vol. 295, pp. 14-20.
- [8] V. Protsenko, F. Danilov, V. Gordiienko, S. Kwon, M. Kim, and J. Lee (2011). Electrodeposition of hard nanocrystalline chrome from aqueous sulfate trivalent

AMM0017

chromium bath, *Thin Solid Films*, vol. 520, pp. 380-383.

[9] Z. Zeng, Y. Zhang, W. Zhao, and J. Zhang (2011). Role of complexing ligands in trivalent chromium electrodeposition, *Surface and Coatings Technology*, vol. 205, pp. 4771-4775.

[10] S. Ghaziof, M. Golozar, and K. Raeissi (2010). Characterization of as-deposited and annealed Cr-C alloy coatings produced from a trivalent chromium bath, *Journal of Alloys and Compounds*, vol. 496, pp. 164-168.

[11] C. Fontanesi, R. Giovanardi, M. Cannio, and E. Soragni (2008). Chromium electrodeposition from Cr (VI) low concentration solutions, *Journal of Applied Electrochemistry*, vol. 38, pp. 425-436.

[12] H.-H. Sheu, C.-E. Lu, K.-H. Hou, M.-L. Kuo, and M.-D. Ger (2015). Effects of alumina addition and heat treatment on the behavior of Cr coatings electroplated from a trivalent chromium bath, *Journal of the Taiwan Institute of Chemical Engineers*, vol. 48, pp. 73-80.

[13] H. Ramezani-Varzaneh, S. Allahkaram, and M. Isakhani-Zakaria (2014). Effects of phosphorus content on corrosion behavior of trivalent chromium coatings in 3.5 wt.% NaCl solution, *Surface and Coatings Technology*, vol. 244, pp. 158-165.

[14] S. Survilienė, A. Češūnienė, V. Jasulaitienė, and I. Jurevičiūtė (2012). The use of XPS for study of the surface layers of CrNi alloys electrodeposited from the Cr (III)+ Ni (II) bath, *Applied Surface Science*, vol. 258, pp. 9902-9906.