

Investigation of Tribological Behavior of Electrodeposited Cr, Co-Cr and Co-Cr/TiO₂ Nano-Composite Coatings

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Abstract—Electrodeposition is a simple and economic technique for precision coating of different shaped substrates with pure metal, alloy or composite films. Dc electrodeposition was used to produce Cr, Co-Cr and Co-Cr/TiO₂ nano-composite coatings from Cr(III) based electrolytes onto 316L SS substrates. The effects of TiO₂ nanoparticles concentration on co-deposition of these particles along with Cr content and microhardness of the coatings were investigated. Morphology of the Cr, Co-Cr and Co-Cr/TiO₂ coatings besides their tribological behavior were studied. The results showed that increment of TiO₂ nanoparticles concentration from 0 to 30 g L⁻¹ in the bath increased their co-deposition and Cr content of the coatings from 0 to 3.5 wt.% and from 23.7 to 31.2 wt.%, respectively. Microhardness of Cr coating was about 920 Hv which was higher than Co-Cr and even Co-Cr/TiO₂ films. Microhardness of Co-Cr and Co-Cr/TiO₂ coatings were improved by increasing their Cr and TiO₂ content. All the coatings had nodular morphology and contained microcracks. Nodules sizes and the number of microcracks in the alloy and composite coatings were lower than the Cr film. Wear results revealed that the Co-Cr/TiO₂ coating had the lowest wear loss between all the samples, while the Cr film had the worst wear resistance.

Keywords—Co-Cr alloy, electrodeposition, nano-composite, tribological behavior, trivalent chromium.

I. INTRODUCTION

ELECTRODEPOSITION of chromium is widely used in aerospace, automotive, and other engineering industries to produce wear and corrosion resistant coatings with high hardness and good appearance [1]-[4]. Conventional chromium coatings were deposited from hexavalent chromic acid solutions for many years [4]-[7]. However, Cr (VI) plating should be replaced by alternative processes, because hexavalent chromium is carcinogenic and toxic [2]-[7]. Unfortunately, a few coatings could be an alternative for the conventional hard chromium films [4], [6]. In recent years; electrodeposition of Cr from trivalent chromium electrolytes is considered to be a convenient and low cost method to replace conventional Cr (VI) plating [3]-[8]. However, Cr (III) based coatings have lower corrosion and wear resistance than those obtained from Cr (VI) electrolytes [8], [9]. Properties of these coatings can be improved by adding iron family metal ions

(i.e. iron, nickel, and Co) to the Cr (III) bath and electrodeposition of M-Cr alloys [1], [4]-[10].

Co-Cr alloys are used for medical prosthetic implant devices, components in the power generation, marine, aerospace, and oil and gas industries due to their good wear, corrosion and fatigue resistance along with biocompatibility [1], [10], [11]. Optimum mechanical properties and corrosion resistance of these alloys are usually obtained in the presence of 10-30% chromium [10]. Although some research on electrodeposition of Co-Cr alloys from Cr(III) baths as well as characterization and investigation of their magnetic and corrosion properties have been conducted, there are limited studies about electrodeposition of Co-Cr alloys from chromium sulfate based electrolytes and examination of their tribological behavior. Moreover, most of the previous research has been focused on production of unreinforced Co-Cr alloys, while co-deposition of fine particles into metallic electrodeposits as the second phase results in enhanced hardness, corrosion and wear resistance of the metallic coatings [1], [8], [12], [13]. In the present study, DC electrodeposition technique was used to produce Co-Cr and Co-Cr/TiO₂ nano-composite coatings. The aim of this study is to investigate the morphology, microstructure, hardness, and wear behavior of these coatings and compare the results with electrodeposited Cr film and the substrate.

II. EXPERIMENTAL

Cr, Co-Cr and Co-Cr/TiO₂ coatings with average thickness of about 25 µm were produced by DC electrodeposition from chromium sulfate based electrolytes. The bath compositions and plating conditions are presented in Table I. Analytical grade chemicals and double distilled water were used for preparation of the electrolytes. The pH value of the bath was adjusted by adding either 4 M H₂SO₄ or 1 M NaOH solution. Prior to composite plating, 24 h stirring along with 45 min ultrasonic treatment were used for better dispersion of the nanoparticles within the electroplating bath.

A double electrode cell was used for electroplating experiments. 316L stainless steel plates with a thickness of 2.5 mm and exposed area of 9 cm² (3×3 cm) were used as the substrate. A similar dimension of a Ti/IrO₂ dimensionally stable anode was used as the anode that was vertically maintained at 3 cm from the cathode. Prior to electrodeposition, the substrates were abraded with different grades of emery papers from 120 to 2000 grit which were then ultrasonically cleaned in acetone for 10 min at room

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temperature, washed in distilled water and degreased in an alkaline solution (NaOH , Na_2CO_3 , $\text{Na}_2\text{PO}_4 \cdot 12\text{H}_2\text{O}$) at 70°C for 15 min. Activation of the 316L SS cathodes was done in a solution containing combination of HCl and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ at room temperature, according to ASTM B254. With this technique, the oxide layer on the surface of 316L SS is removed, and a thin cobalt layer is deposited onto the surface. According to previous researches, this layer can improve adhesion and properties of chromium contained electrodeposits on steel substrates [7]. The substrates were transferred to the electroplating bath after activation, immediately.

TABLE I
BATH COMPOSITIONS AND PLATING CONDITIONS

Bath composition	Cr coating	Co-Cr and Co-Cr/ TiO_2 coatings
$\text{Cr}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$	0.3 M	0.35 M
$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	-	0.1 M
H_3BO_3	0.9 M	0.9 M
Na_2SO_4	0.6 M	0.6 M
$\text{C}_3\text{H}_4\text{O}_4$	0.5 M	0.6 M
$\text{C}_6\text{H}_8\text{O}_7$	-	0.4 M
$\text{NaC}_{12}\text{H}_{25}\text{SO}_4$	0.2 g L^{-1}	0.2 g L^{-1}
TiO_2 particles	-	$0\text{--}30 \text{ g L}^{-1}$
Deposition condition		
Current density	140 mA cm^{-2}	$140, 150 \text{ mA cm}^{-2}$
Temperature	$30 \pm 1^\circ\text{C}$	$30 \pm 1^\circ\text{C}$
pH	1.5	1
Stirring speed	250 rpm	250 rpm
Deposition time	45 min	30 min

Hardness measurements were carried out on an AMSLER D-6700 Vicker's microhardness testing machine, using an applied load of 1 N for 15 s. The mean values of at least five measurements conducted at various locations on each sample were considered.

Dry sliding ball-on-disc wear tests on the substrate and coated samples were carried out in a laboratory atmosphere with 30–40% relative humidity and at room temperature. An alumina ball with a diameter of 6 mm was used as the counterface. Wear tests were performed under the applied load of 8 N, with the sliding distance of 300 m, at a sliding speed of 0.1 m s^{-1} and a wear track diameter of 1.6 mm. Both ball and disc samples were cleaned in an ultrasonic acetone bath for 2 min and dried with compressed air before and after testing.

The electrodeposited and worn surface morphologies of the coated samples, along with the amount of co-deposited TiO_2 nano-particles within the Co-Cr matrix and worn surface composition were examined using a scanning electron microscope equipped with energy dispersive X-ray spectrometer (EDS).

III. RESULTS AND DISCUSSIONS

A. TiO_2 Effects

The effect of TiO_2 nano-particles in the bath on the TiO_2 and chromium content of the deposits is shown in Fig. 1. Volume fraction of incorporated TiO_2 nano-particles promotes

from 0 to 3.5 wt.% (0 to 6.6 vol.%) with an increase of the bath TiO_2 concentration from 0 to 30 g L^{-1} , tending to attain a steady value at high TiO_2 concentrations. The curve is similar to the Langmuir adsorption isotherm, which is consistent with previous investigations and Guglielmi's model of adsorption [12], [14]. According to this model; the first step is adsorption of metal ions onto the ceramic particles and loose physical adsorption of the particles onto the cathode. The second step is the strong adsorption and entrapment of the particles within the metal matrix. Increasing the concentration of TiO_2 particles in the solution can in turn raise the amount of loosely adsorbed particles on the cathode surface. Hence, higher volume fractions of the nano-particles can be strongly adsorbed at the next step.

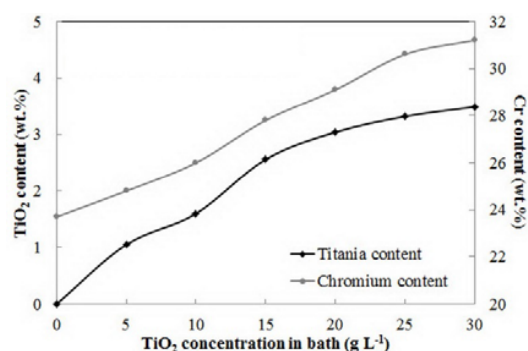


Fig. 1 Effect of bath TiO_2 nano-particles concentration on weight percent of co-deposited particles and Cr content of the coatings, electrodepositing at 140 mA cm^{-2}

Fig. 1 also shows that chromium content of the coatings is enhanced by increasing the bath TiO_2 concentration. According to the previous studies, alloy coatings with higher chromium contents are obtained by increasing cathodic current density [15], [16]. Our results also show that, the chromium percentage of the Co-Cr alloy coatings rises from 23.7 to 29.3 wt.% with increasing the current density from 140 to 150 mA cm^{-2} . Co-deposition of inert particles can cause surface blockage and reduce electroactive electrode area, resulting in an increment of current density on the cathode surface [17]. Therefore, higher chromium content of the composite coatings as compared to the alloy film can be attributed to the reduced active electrode area and increased cathodic current densities.

The microhardness of the produced coatings is shown in Fig. 2. Hardness value of the substrate is also presented for the purpose of comparison. It is clear that all the coatings have higher microhardness as compared to the substrate. These hardness values are also higher than that of the bulk and sprayed Co-Cr-Mo alloys [11], [18]. The hardness of Cr is greater than that of Co, thus harder coatings accompanied by higher Cr content. A similar trend has also been observed by other researchers for Co-Cr and Ni-Cr coatings [15], [16], [19].

The hardness of the coatings elevates with increasing their nano-particles content to a certain value at 3 wt.%, after which remains almost constant. Hardness improvement by

incorporation of TiO_2 nano-particles is related to dispersion strengthening effect, which inhibits plastic deformation of the metal matrix by preventing free motion of the dislocations [19]. However, agglomeration of the nano-particles in the presence of high concentrations of them in the bath may weaken dispersion strengthening effect of the nano-particles and decrease coatings hardness [20].

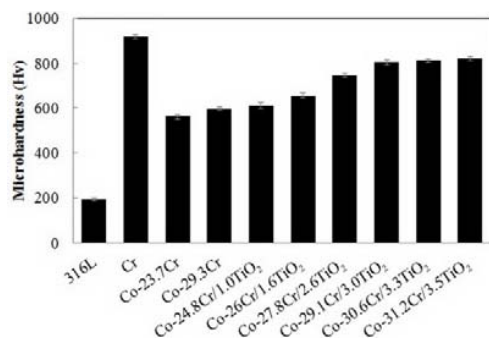


Fig. 2 Microhardness values of different samples

Considering the obtained results, the Co-29.1Cr/3.0TiO₂ coating is selected as the most appropriate composite film for further investigations. Morphology and tribological behavior of Cr and Co-29.3Cr coatings are also examined, and the results are compared to the composite film. From now on, the selected alloy and composite coatings are briefly called Co-Cr and Co-Cr/TiO₂.

B. Morphological and Microstructural Investigation

SEM micrographs from the surface of the Cr, Co-Cr and Co-Cr/TiO₂ coatings are presented in Fig. 3. Deposits show nodular surface morphology with microcracks. Nodules size along with the number and size of microcracks in Cr coating are greater than the alloy and the composite films. Similar results have also been obtained by [6]. Formation of cracks is characteristic of electrodeposited Cr coatings. Cracks are formed due to hydrogen inclusion and incorporation of basic chromium compounds, which develop internal stresses in the deposited films and deteriorate the mechanical properties. Co-deposition of Co with Cr can decrease both hydrogenation and the incorporation of basic chromium compounds. Thus, internal stresses are reduced [4], [15], resulting in lower cracks density of Co-Cr alloy coating.

Lower cracks number in the Co-Cr/TiO₂ nanocomposite coating as compared to the Co-Cr film can be attributed to the increased toughness of the composite coating by incorporation of particles, as also reported by other researchers [13], [21].

XRD patterns of the coatings are presented in Fig. 4. These patterns reveal that the as-deposited Cr film has an amorphous structure, whereas Co-Cr and Co-Cr/TiO₂ coatings have a crystalline structure. The structure of the alloy and composite coatings is a solid solution of Cr in Co with hexagonal close-packed (hcp) lattice. Broad peaks are a result of ultra-fine crystallite sizes of these samples. The structure of Co-Cr alloy coating is not changed by co-deposition of TiO₂ particles.

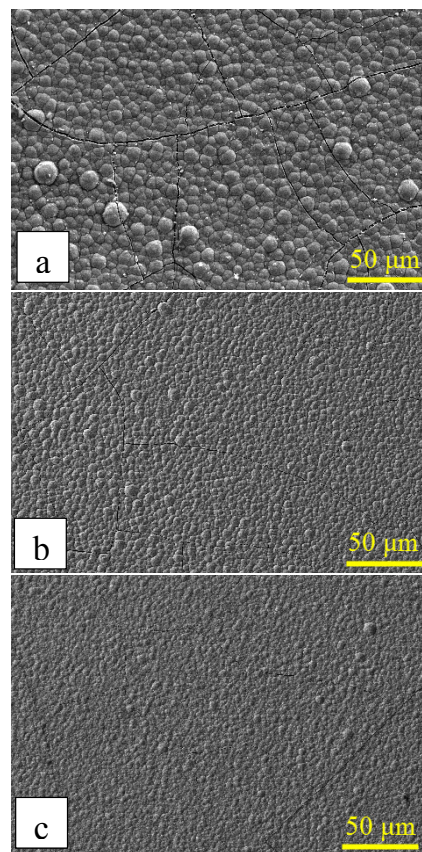


Fig. 3 SEM micrographs from the surface of the as-deposited (a) Cr, (b) Co-Cr and (c) Co-Cr/TiO₂ coatings

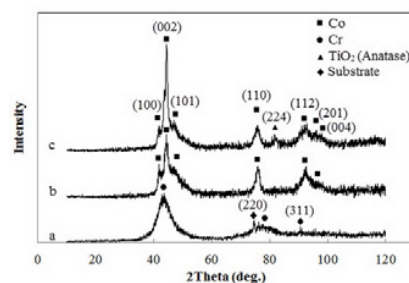


Fig. 4 XRD patterns of (a) Cr, (b) Co-Cr and (c) Co-Cr/TiO₂ coatings

C. Tribological Behavior

Wear volume losses of 316L SS substrate, Cr, Co-Cr and Co-Cr/TiO₂ coatings are 1.03, 1.18, 0.34 and 0.14 mm³, respectively. According to the Archard theory, wear resistance is proportional to the hardness of the material [22], [23]. Given hardness values of the samples (Fig. 2), better wear resistance of the Co-Cr and Co-Cr/TiO₂ coatings is due to their higher hardness as compared to the 316L SS substrate.

The wear behavior of Co-Cr alloy coating is improved by incorporation of TiO₂ nanoparticles, which is consistent with the results of other investigators [19], [23]. Enhanced wear resistance of nanocomposite coating as compared to the alloy film can be a result of its higher hardness along with the dispersion strengthening effect of TiO₂ nanoparticles, which

prevents grains movement and grain boundaries migration during the wear test [23].

The wear volume loss of the Cr film is about 13% higher than the substrate, although Cr coating is significantly harder than the 316L SS (Fig. 2). This discrepancy can be explained by considering this fact that the Archard's theory is limited to idealized sliding conditions. In this theory, the processes of crack nucleation and subsequent growth are disregarded [24]. Toughness also plays an important role in cracking and wear resistance [11]. The wear behavior of the chromium electrodeposits is a combined result of hard, brittle characteristics and cracked morphology of these coatings [2]. Therefore, low wear resistance of this coating can be due to high residual stresses and brittle nature of the electrodeposited Cr. The presence of a great number of microcracks in this film results in easier growth of cracks during wear and higher wear losses [20].

Typical SEM micrographs of worn surfaces of the 316L SS substrate, Cr, Co-Cr, and Co-Cr/TiO₂ are shown in Fig. 5. Wear track of the substrate is wider than the other samples. Narrowest wear track is observed in the case of Co-Cr/TiO₂ coating. These results are in agreement with the volume loss values. However, in spite of relatively narrow wear path of Cr coating, detachment of chromium in some areas increases volume losses, as shown in Fig. 5 (b).

IV. CONCLUSIONS

In the present study, Cr, Co-Cr and Co-Cr/TiO₂ nanocomposite coatings were produced from Cr(III) based electrolytes, and their composition, hardness, morphology and microstructure, together with tribological behavior were examined and compared to the 316L SS substrate. The outcome of the results can be summarized as follows:

- 1) An increase in the concentration of TiO₂ nanoparticles concentration from 0 to 30 g L⁻¹ in the bath could result in the increased amounts of their co-deposition and Cr content of the coatings from 0 to 3.5 wt.% and from 23.7 to 31.2 wt.%, respectively.
- 2) All the coatings indicated higher microhardness values as compared to that of the 316L SS substrate. Microhardness of Cr coating was about 920 Hv which was higher than that of Co-Cr and even Co-Cr/TiO₂ films. Microhardness of Co-29.3Cr alloy coating was about 6.0% higher than Co-23.7Cr sample. Microhardness of the alloy coatings improved with co-deposition of up to 3 wt.% TiO₂ nanoparticles to a value of 805 Hv and from then on remained almost constant.
- 3) All the coatings exhibited nodular morphology. Nodules size and micro-cracks densities of Co-Cr and Co-Cr/TiO₂ coatings were lower than those of Cr film. Electrodeposited Cr coating had an amorphous structure while alloy and composite films contained solid solutions of Cr in the hcp lattice of Co structure.
- 4) The wear resistance of the 316L SS substrate was improved by about 3 and 7.5 times after electrodeposition of Co-29.3Cr and Co-29.1Cr/3.0TiO₂ coatings, respectively. The wear volume loss of Cr coating was

about 13% higher than that of the substrate.

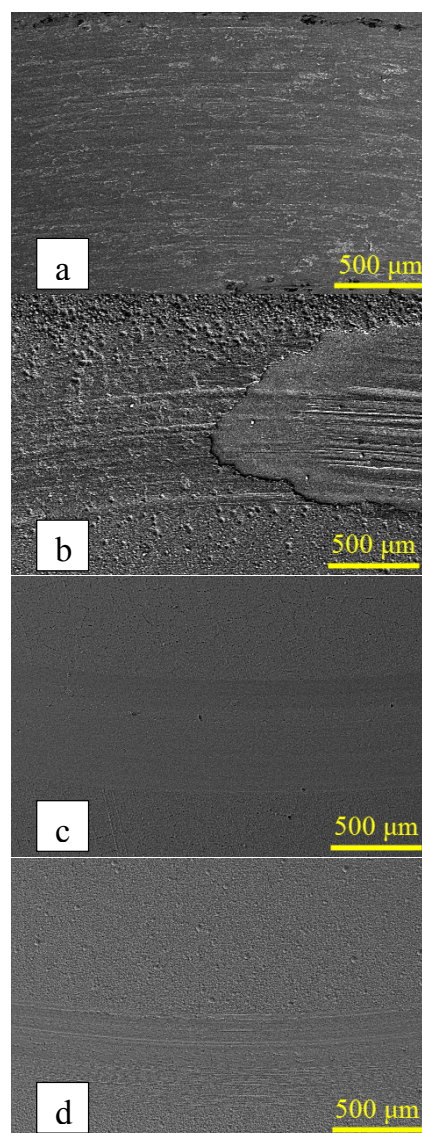


Fig. 5 Wear track morphology of (a) 316L SS substrate, (b) Cr, (c) Co-Cr and (d) Co-Cr/TiO₂ coatings

REFERENCES

- [1] C.U. Chisholm, Cobalt-chromium coatings by electrodeposition: Review and initial experimental studies, *Electrodepos. Surf. Treat.* 3 (1975) 321–333.
- [2] D.P. Weston, P.H. Shipway, S.J. Harris, M.K. Cheng, Friction and sliding wear behaviour of electrodeposited cobalt and cobalt–tungsten alloy coatings for replacement of electrodeposited chromium, *Wear* 267 (2009) 934–943.
- [3] V.S. Protsenko, F.I. Danilov, Chromium electroplating from trivalent chromium baths as an environmentally friendly alternative to hazardous hexavalent chromium baths: comparative study on advantages and disadvantages, *Clean Technol. Environ. Policy* 16 (2014) 1201–1206.
- [4] C.A. Huang, C.K. Lin, C.Y. Chen, Hardness variation and corrosion behavior of as-plated and annealed Cr–Ni alloy deposits electroplated in a trivalent chromium-based bath, *Surf. Coat. Technol.* 203 (2009) 3686–3691.

- [5] Y.I. Choi, T. Eguchi, T. Asao, K. Kuroda, M. Okido, Mechanism for the formation of black Cr-Co electrodeposits from Cr^{3+} solution containing oxalic acid, *J. Electrochem. Soc.* 161 (2014) 713–718.
- [6] S. Survilienė, V. Jasulaitienė, A. Češūnienė, A. Lisowska-Oleksiak, The use of XPS for study of the surface layers of Cr-Co alloy electrodeposited from Cr(III) formate-urea baths, *Solid State Ionics* 179 (2008) 222–227.
- [7] C.A. Huang, U.W. Lieu, C.H. Chuang, Role of nickel undercoat and reduction-flame heating on the mechanical properties of Cr-C deposit electroplated from a trivalent chromium based bath, *Surf. Coat. Technol.* 203 (2009) 2921–2926.
- [8] Z. Zeng, J. Zhang, Electrodeposition and tribological behavior of amorphous chromium-alumina composite coatings, *Surf. Coat. Technol.* 202 (2008) 2725–2730.
- [9] M.S. Marwah, V. Srinivas, A. K. Pandey, S.R. Kumar, K. Biswas, J. Maity, Morphological changes during annealing of electrodeposited Ni-Cr coating on steel and their effect on corrosion in 3% of NaCl solution, *J. Iron. Steel Res. Int.* 18 (2011) 72–78.
- [10] G. Saravanan, S. Mohan, Structure, composition and corrosion resistance studies of Co-Cr alloy electrodeposited from deep eutectic solvent (DES), *J. Alloys Compd.* 522 (2012) 162–166.
- [11] R. Ahmed, H.L. de Villiers Lovelock, S. Davies, N.H. Faisal, Influence of Re-HIPing on the structure-property relationships of cobalt-based alloys, *Tribol. Int.* 57 (2013) 8–21.
- [12] M. Li, Z. Ke-chao, L. Zhi-you, W. Qiu-ping, Electrodeposition of Ni-Co- Fe_2O_3 composite coatings, *J. Cent. South Univ. Technol.* 17 (2010) 708–714.
- [13] J. Gao, J. Suo, Preparation and characterization of the electrodeposited Cr- Al_2O_3 /SiC composite coating, *Appl. Surf. Sci.* 257 (2011) 9643–9648.
- [14] N. Guglielmi, Kinetics of the deposition of inert particles from electrolytic baths, *J. Electrochem. Soc.* 119 (1972) 1009–1012.
- [15] B.A. Spiridonov, Electrodeposition of chromium-cobalt alloy coatings from sulfate electrolytes, *Russ. J. Appl. Chem.* 76 (2003) 65–70.
- [16] Y. Yu-fang, G. Zhu-qing, D. Li-yuan, L. Bei-ping, M. Yu-tian, Y. Zhen-hui, Electrodeposition of Ni-Cr alloy on aluminum substrate, *J. Cent. South Univ. Technol.* 13 (2006) 219–224.
- [17] M. Adabi, A.A. Amadeh, Electrodeposition mechanism of Ni-Al composite coating, *Trans. Nonferrous Met. Soc. China* 24(2014) 3189–3195.
- [18] A. Neville, V. Kollia-Rafailidi, A comparison of boundary wear film formation on steel and a thermal sprayed Co/Cr/Mo coating under sliding conditions, *Wear* 252 (2002) 227–239.
- [19] M. Masoudi, M. Hashim, H. Mohamed Kamari, M. Sapuan Salit, Fabrication and characterization of Ni-SiC-Cr nanocomposite coatings, *Appl. Nanosci.* 3 (2013) 357–362.
- [20] M. Rezaei-Sameti, S. Nadali, J. Rajabi, M. Rakhshi, The effects of pulse electrodeposition parameters on morphology, hardness and wear behavior of nano-structure Cr-WC composite coatings, *J. Mol. Struct.* 1020 (2012) 23–27.
- [21] S. Surviliene, V. Jasulaitiene, A. Lisowska-oleksiak, V.A. Safonov, Effect of WC on electrodeposition and corrosion behaviour of chromium coatings, *J. Appl. Electrochem.* 35 (2005) 9–15.
- [22] J.F. Archard, Contact and rubbing of flat surfaces, *J. Appl. Phys.* 24 (1953) 981–988.
- [23] S. Mahdavi, S.R. Allahkaram, Characteristics of electrodeposited cobalt and titania nano-reinforced cobalt composite coatings, *Surf. Coat. Technol.* 232 (2013) 198–203.
- [24] S. Mahdavi, F. Akhlaghi, Effect of the SiC particle size on the dry sliding wear behavior of SiC and SiC-Gr-reinforced Al6061 composites, *J. Mater. Sci.* (2011) 46:7883–7894.