UDK 621.793/.795:621.357:669.058.7
Original scientific article/Izvirni znanstveni članek

ISSN 1580-2949
MTAEC9, 47(5)601(2013)

ELECTRO-CODEPOSITED Cr-SiC COMPOSITE COATINGS: EFFECT OF THE PULSE-CURRENT FREQUENCY ON MORPHOLOGY AND HARDNESS

KOMPOZITNA PREVLEKA IZ ELEKTRONANESENEGA Cr-SiC: VPLIV FREKVENCE PULZIRAJOČEGA TOKA NA MORFOLOGIJO IN TRDOTO

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Prejem rokopisa – received: 2012-12-18; sprejem za objavo – accepted for publication: 2013-01-31

In this research, submicrometer silicon-carbide (SiC) (*APS* = 200 nm) ceramic particles were co-deposited with chromium metal (Cr) via an electrodeposition system to fabricate Cr-SiC metal-matrix composite films. Phase identifications of the fabricated composite coatings were performed with an X-ray diffractometer (XRD) and surface morphologies were investigated using a scanning electron microscope (SEM) with an energy dispersive X-ray spectroscopy (EDS) system attachment. Mechanical properties of the coatings such as hardness were determined under an applied load of 980.7 mN using a micro-hardness tester. It was concluded that SiC ceramic particles were physically adsorbed on the cathode surface forming a composite film structure with Cr metal and that a co-deposition of the sub-micron-sized ceramic particles with metals via an electrodeposition system was successful. In addition, in comparison with the reference coatings, the hardness of the SiC-reinforced composite coatings was increased by up to 50 %. The frequency, being a parameter of pulse current, is determined as an effective parameter in a co-deposition of ceramic particles with metals.

Keywords: co-deposition technique, pulse current (PC), composite coatings, micro-hardness

V tej raziskavi so bili za izdelavo kompozitne tanke plasti Cr-SiC s kovinsko matrico sonaneseni mikrometrski keramični delci silicijevega karbida (SiC) (*APS* = 200 nm) z elektronanosom kovinskega kroma (Cr). Identifikacija faz v izdelani kompozitni prevleki je bila narejena z rentgenskim difraktometrom (XRD), morfologija površine pa je bila preiskana z vrstičnim elektronskim mikroskopom (SEM) z dodano energijsko disperzijsko spektroskopijo (EDS). Mehanske lastnosti prevleke, kot je trdota, so bile ugotovljene z merilnikom mikro-trdote z obtežbo 980,7 mN. Ugotovljeno je bilo, da so keramični delci SiC fizikalno adsorbirani na površini katode in da je z elektronanosom mogoč uspešen nastanek kompozitne plasti s strukturo iz kovinskega Cr in sonanosom keramičnih delcev, manjših od mikrometra. Glede na referenčno prevleko s SiC ojačena kompozitna prevleka izkazuje do 50-odstotno povečanje velikosti trdote. Ugotovljeno je, da je frekvenca kot parameter pulzirajočega toka učinkovit parameter pri sonanašanju keramičnih delcev in kovin.

Ključne besede: tehnika sonanašanja, pulzirajoč tok (PC), kompozitna prevleka, mikrotrdota

1 INTRODUCTION

Electrodeposition is a surface finishing technique that has been used to improve the properties such as hardness, wear and corrosion resistance compared to the parent (substrate) metals for decades. This technique involves only pure metal[1,2] or alloy[3–5] depositions on the substrates. However, a promising technique called the co-deposition (electrolytic co-deposition) involves a deposition of fine ceramic particles with metals on the metal substrates. There are not many alternatives to obtaining the materials with both improved corrosive and mechanical properties. It is known that "combining the best properties of two different materials to obtain one material with excellent properties" is the main idea of fabricating composites. Based on this idea, several research groups focused on the co-deposition of metal-ceramic pairs such as: Ni-SiC,[6–8] Zn-Al_2O_3,[9–11] Ni-Al_2O_3,[10,11] Cr-Al_2O_3[12,13] to improve the mechanical and/or corrosive properties of the coatings. Within this scope, a production of less studied Cr-SiC composite films[12,14] was performed, new systems were designed replacing the traditional electrodeposition cells, and coatings were fabricated within these systems using different electrodeposition parameters such as the pulse current (PC) and its sub-parameters (pulse-current frequency) that directly affect the co-deposition.

2 EXPERIMENTAL DETAILS

In the present study, we draw attention to the microstructural and mechanical properties of the composite coatings formed on steel substrates with an electrocodeposition process. Low-carbon steel cylinders with 13 mm diameters were used as the cathode and a Pb-7 % Sn alloy was used as the anode. Prior to electroplating, the substrates were mechanically ground with SiC abrasive paper to achieve the final surface quality of

2400 grit and then ultrasonically cleaned in trichloroethylene for 10 min to remove the contamination. After that, etching at 20–30 A/dm^2 in a volume fraction 60 % H_2SO_4 solution was performed for 1–2 min.

For the experimental studies two different electrolytes (baths) were prepared: a bath without SiC and a bath with a 4g/(100 ml) SiC (*APS* = 200 nm) addition defined as Bath-Ref and Bath-S, respectively. The composition of Bath-Ref and electrodeposition conditions for all the processes are listed in **Table 1**. The bath codes relating to their ceramic contents and the sample codes derived for different deposition parameters are given in **Table 2**. To avoid a precipitation of the ceramic content in the electrolyte, the baths were circulated with both a magnetic stirrer and air ventilators during the process.

Table 1: Composition of the electrolytes and electrodeposition conditions

Tabela 1: Sestava elektrolita in parametri elektrononanašanja

Bath composition:	
Chromium oxide (CrO_3)	300 g/L
Catalyst*	30 g/L
Sulfuric acid (H_2SO_4)	2.18 ml/L
Gas-reducer additive**	6.5 ml/L
Bath conditions:	
Temperature	40–50 °C
Current density	60 A/dm^2
Agitation type	Magnetic stirring & air ventilation

Catalyst* (AK 3651 D AKROM) and gas-reducer additive** (AK 3301 FS) are the registered trademarks of ATILIM CHEMICALS COMPANY, ISTANBUL

Table 2: Bath codes and sample codes (R, S1, S2, and S3) according to their ceramic contents and pulse-frequency conditions

Tabela 2: Oznaka kopeli in vzorcev (R, S1, S2 in S3) glede na vsebnost keramike in frekvenco pulza

Bath codes (Electrolyte codes)	Ceramic-particle content and type (g/(100 ml))	Pulse-frequency conditions of the samples (Hz)		
		10	25	50
Bath-Ref.	–	–	R	-
Bath-S	4-SiC	S1	S2	S3

Table 3: Pulse-current parameters for the electrodeposition

Tabela 3: Parametri pulza toka pri elektrononanašanju

Frequency (Hz)	Pulse-base time (ms) Work time (%)			Current density (A/dm^2)	
	T_{on}	T_{off}		Peak (I_p)	Average ($I_{avr.}$)
10	80	20	0.80	75	60
25	20	20	0.50	120	60
50	15	5	0.75	80	60

Using some of the optimization sets reported in our previous study,[14] the optimum parameters were found to be 60 A/dm^2, simultaneous air ventilation and magnetic stirring, and PC (pulse current) for the current density, agitation type and current type, respectively. In addition to this, a set of samples was fabricated for three different frequency conditions in the pulse current to compare the current type and pulse-frequency effect on the properties. These parameters applied to all the sets are given in **Table 3**.

In order to determine the acidic and basic characteristics of electrolytes, the pH values of the prepared solutions were measured using a standard pH meter with a Mettler Tolede electrode. X-ray diffraction (XRD) patterns of the electrodeposited composite coatings were determined by means of a multipurpose RIGAKU-D/Max-2200/PC model diffractometer with a Cu-K_α radiation using a multipurpose thin-film attachment. The surface morphologies of the coatings were examined with a scanning electron microscope (JEOL-JSM 6060 SEM) with an energy-dispersive x-ray spectroscopy (IXRF System EDS) system attachment. An accelerating voltage of 20 kV was used for SEM imaging and SEM/EDX analyses. Weight percentage distributions and an elemental mapping of the elements were determined with EDS. A SHIMADZU-HMV-2 model micro-hardness tester was used for the hardness tests. In this study, all the hardness tests were handled under an applied load of 980.7 mN ($HV_{0.1}$).

3 RESULTS AND DISCUSSION

The anti-corrosion coatings fabricated with the electrodeposition have been widely investigated in the literature.[15,16] With the development of nanoceramic particles, the nanocomposite electrodeposition has attracted more attention due to its potential applications in improving the corrosion resistance.[17–19] Benea et al.[17] reported that SiC nanoparticles in a Ni-SiC composite coating decreased both the electrochemical corrosion and the wear corrosion, compared with the pure-nickel coating. Zn-Ni alloys have been widely applied as highly corrosion-resistant coatings, especially in the automobile industry.[20,21] Al_2O_3/SiC/WC possesses an excellent

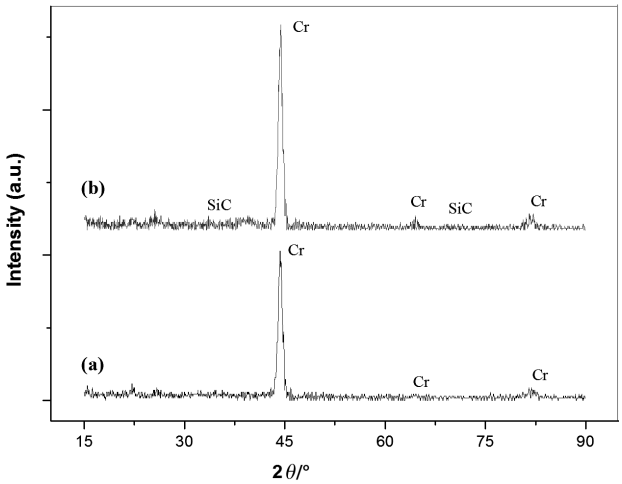

Figure 1: XRD patterns of: a) pure-Cr and b) SiC-reinforced composite coatings produced with the electrodeposition system

Slika 1: Rentgenska posnetka: a) čisti Cr in b) s SiC ojačana kompozitna prevleka, izdelana z elektrononanosom

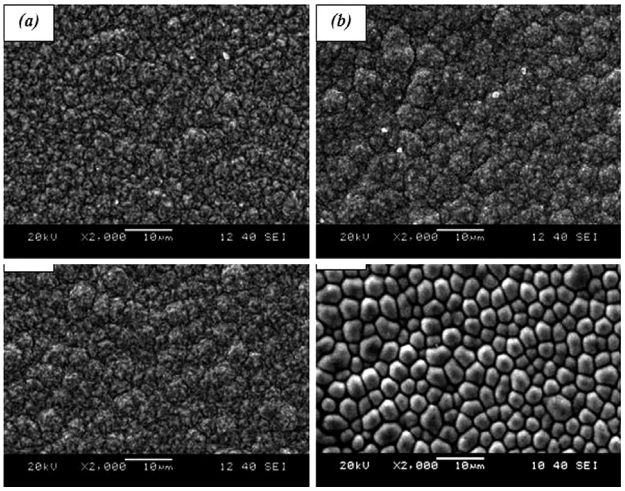

Figure 2: SEM images of: a) R1, b) S1, c) S2 and d) S3 samples (embedded and metal-coated agglomerates of the ceramic particles at 2000x magnification)

Slika 2: SEM-posnetki, ki pripadajo vzorcem z oznakami: a) R1, b) S1, c) S2 in d) S3 (vloženi keramični delci in aglomerat prevleke pri 2000-kratni povečavi)

chemical stability and good mechanical properties, such as high microhardness and wear resistance. It has been used extensively in the metal-matrix composite coatings.[22–25] In our present work, the method of fabricating hard, wear-resistant Cr-SiC coatings has been determined. The objective of the present study is to reveal the coating process, analyze the co-deposited products and investigate the mechanical behavior.

The phase identifications of the coatings were performed with the XRD technique for all the Cr-matrix composite coatings. **Figure 1** denotes the XRD patterns of the pure Cr coating and the samples chosen from the SiC-reinforced composite coatings.

As it is seen in **Figure 1a**, the coating fabricated in the reference chromium bath contains only the metallic Cr-phase structure. On the other hand, from the patterns belonging to the coatings fabricated in the SiC (containing) bath, it is clear that the co-deposition process was successful having no chemical interaction (alloying, intermetallic-phase formation, etc.) between the electrolyte and the particles (**Figure 1b** for details).

SEM images are part of a systematic study being interpreted on the basis of the particle addition and pulse-frequency effect on the coating structures. **Figure 2** presents the SEM images according to the increased frequency values (10, 25 and 50) Hz. Once the images are compared with each other, a small decrease in the grain size with an increased frequency is observed. As known theoretically, a decrease in the grain size gives the material advanced mechanical properties such as high hardness.

The X-ray mapping results in **Figure 3** indicate that the sub-micron-sized SiC ceramic particles were successfully co-deposited with chromium metal. Even though it was thought that the surface morphologies were homogenous, when all the coated surfaces were inspected, it became clear from the mapping results that there are also non-homogenous local parts on the surfaces.

Micro-Vickers hardness tests were performed for the Cr-matrix composite coatings. But as seen from the figures, the ceramic-reinforced composite coatings,

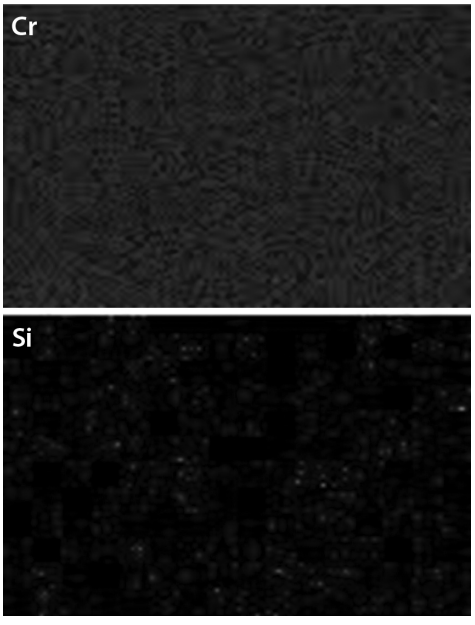

Figure 3: X-ray mapping results for the SiC-reinforced Cr-composite coatings

Slika 3: Rentgenski posnetek razporeditve elementov v kompozitni Cr-prevleki, ojačeni s SiC

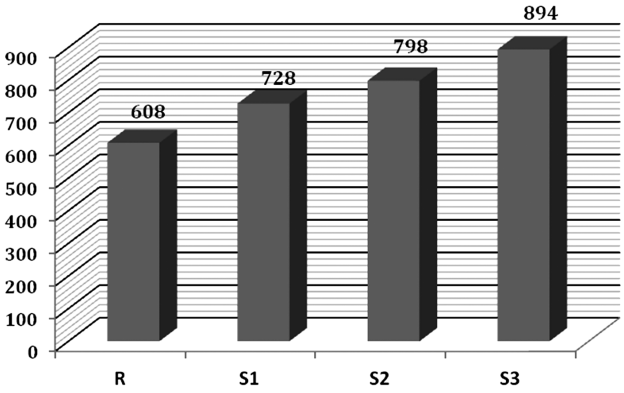

Figure 4: Comparable hardness results for the R- and S-coded samples

Slika 4: Primerjava trdote vzorcev z oznako R in S

Table 4: Hardness ($HV_{0.1}$); results of the R- and S-coded samples

Tabela 4: Trdota ($HV_{0,1}$); rezultati za vzorce z oznako R in S

	R1	S1	S2	S3
1. indentation	561	680	739	785
2. indentation	592	693	745	937
3. indentation	672	811	910	961
Average value	608	728	798	894

whose grains were coarser than those of the reference sample, showed better performances during the micro-Vickers tests. The main reason for this result is thought to be the effect of the ceramic particles with high hardness values embedded into the metal matrix. In other words, it was proven that the SiC-addition characteristics dominated over the grain-size effect. The obtained hardness results given in **Table 4** and **Figure 4** schematically show an increase in the hardness values for the composite coatings with the ceramic additions depending on an increase in the pulse frequency.

4 CONCLUSIONS

In summary, a co-deposition of the sub-micron-sized SiC ceramic particles with Cr metal via an electrodeposition system was successfully carried out. The general results obtained during this process are as follows:

It was seen that the pulse current is an alternative and optimum method for co-depositing the metals with ceramic particles such as Cr-SiC pairs. The obtained phase results proved that the SiC particles were physically adsorbed on the cathode surface and made a composite structure with Cr metal. For the sets containing the sub-micron-sized ceramic particles, the obtained mapping results show particle-dense regions; however, they generally show homogenous behavior. The extreme hardness results obtained for these sets are thought to be the hardness results for these dense regions. However, the mapping results support the XRD analysis. When the coatings were compared (the coatings with no reinforcement and the SiC-reinforced ones), it was seen that the hardness values for the ceramic-particle-reinforced composite coatings were increased. With respect to the reference coatings, the performance of the SiC-composite coatings is increased by up to 50 %. Frequency, being a parameter of the pulse current, is determined as a parameter affecting the co-deposition of the ceramic particles with metals, and when the frequency increases the co-deposition performance increases as well.

Acknowledgement

The present study was supported by The Turkish Ministry of Science, Industry and Technology under the project code 0099-STZ-2007-1.

5 REFERENCES

[1] R. C. M. Salles, G. C. G. de Oliveira, S. L. Díaz, O. E. Barcia, O. R. Mattos, Electrodeposition of Zn in acid sulphate solutions: pH effects, Electrochimica Acta, 56 (**2011**), 7931–7939

[2] R. Inguanta, S. Piazza, C. Sunseri, Influence of electrodeposition techniques on Ni nanostructures, Electrochimica Acta, 53 (**2008**), 5766–5773

[3] V. D. Jovi, B. M. Jovi, M. G. Pavlovi, Electrodeposition of Ni, Co and Ni–Co alloy powders, Electrochimica Acta, 51 (**2006**), 5468–5477

[4] F. Hu, K. C. Chan, Equivalent circuit modelling of Ni–SiC electrodeposition under ramp-up and ramp-down waveforms, Materials Chemistry and Physics, 99 (**2006**), 424–430

[5] V. C. Kieling, Parameters influencing the electrodeposition of Ni-Fe alloys, Surface and Coatings Technology, 96 (**1997**), 135–139

[6] Z. Wu, L. Liu, B. Shen, C. Zhong, W. Hu, Effect of a-Al_2O_3 coatings on the mechanical properties of Ni/SiC composites prepared by electrodeposition, Materials Science & Engineering, 556 (**2012**), 767–774

[7] Y. Yao, S. Yao, L. Zhang, H. Wang, Electrodeposition and mechanical and corrosion resistance properties of Ni–W/SiC nanocomposite coatings, Materials Letters, 61 (**2007**), 67–70

[8] M. R. Vaezi, S. K. Sadrnezhaad, L. Nikzad, Electrodeposition of Ni-SiC nano-composite coatings and evaluation of wear and corrosion resistance and electroplating characteristics, Colloids and Surfaces A: Physicochem. Eng. Aspects, 315 (**2008**), 176–182

[9] O. Sancakoglu, O. Culha, M. Toparli, B. Agaday, E. Celik, Co-deposited Zn-submicron sized Al_2O_3 composite coatings: Production, characterization and micromechanical properties, Materials and Design, 32 (**2011**), 4054–4061

[10] H. Zheng, M. An, Electrodeposition of Zn–Ni–Al2O3 nanocomposite coatings under ultrasound conditions, Journal of Alloys and Compounds, 459 (**2008**), 548–552

[11] H. Zheng, M. An, J. Feng, Surface characterization of the Zn–Ni–Al_2O_3 nanocomposite coating fabricated under ultrasound condition, Applied Surface Science, 254 (**2008**), 1644–1650

[12] J. Gao, J. Suo, Preparation and characterization of the electrodeposited Cr–Al_2O_3/SiC composite coating, Applied Surface Science, 257 (**2011**), 9643–9648

[13] Y. Zhou, H. Chen, H. Zhang, Y. Wang, Oxidation of Al_2O_3-dispersion chromizing coating by pack-cementation at 800 °C, Trans. Nonferrous Met. Soc. China, 18 (**2008**), 598–602

[14] O. Sancakoğlu, Co-deposition of metal films with ceramic nanoparticles on metallic substrates by electrodeposition system, MSc thesis, University of Dokuz Eylul, 2009

[15] O. Hammami, L. Dhouibi, E. Triki, Influence of Zn–Ni alloy electrodeposition techniques on the coating corrosion behaviour in chloride solution, Surface & Coatings Technology, 203 (**2009**), 2863–2870

[16] A. Vaskevich, F. Sinapi, Z. Mekhalif, Underpotential deposition of nickel on {1111}-textured gold electrodes in dimethyl sulfoxide, J. Electrochem. Soc., 152 (**2005**), 744

[17] L. Benea, Composite Electrodeposition-Theory and Practice, Porto-Franco, 1998

[18] Y. Yao, S. Yao, L. Zhang, H. Wang, Electrodeposition and mechanical and corrosion resistance properties of Ni–W/SiC nanocomposite coatings, Materials Letters, 61 (**2007**), 67–70

[19] X. Zhu, C. Cai, G. Zheng, Z. Zhang, J. Li, Electrodeposition and corrosion behavior of nanostructured Ni-TiN composite films, Trans. of Nonferrous Met. Soc. of China, 21 (**2011**), 2216–2224

[20] M. Gavrila, J. P. Millet, H. Mazille, Corrosion behaviour of zinc-nickel coatings electrodeposited on steel, Surf. Coat. Technol., 123 (**2000**), 2–3

[21] E. B. Lehman, P. Ozga, Z. Swiatek, Electrodeposition of Zn-Ni protective coatings from sulfate-acetate baths, Surf. Coat. Technol., 1 (**2002**), 151–152

[22] G. Wu, N. Li, D. Zhou, Electrodeposited Co-Ni-Al_2O_3 composite coatings, Surf. Coat. Technol., 176 (**2004**), 157

[23] S. Alirezaei, S. M. Monirvaghefi, M. Salehi, Effect of alumina content on surface morphology and hardness of Ni-P-Al_2O_3 electroless composite coatings, Surf. Coat. Technol.,184 (**2004**), 170

[24] C. Lee, C. Wan, A study of the composite electrodeposition of copper with alumina powder, Electrochem. Soc., 135 (**1988**), 1930

[25] N. K. Shrestha, D. B. Hamal, T. Saji, Composite plating of Ni-P-Al_20_3 in two steps and its anti-wear performance, Surf. Coat. Technol., 183 (**2004**), 247–253