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The effect of current density on microstructural homogeneity, hardness, fracture toughness and electrochemical behavior of electrodeposited Cu-0.5Co/WC nano-composite coating

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Hardness;
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Resistance.

Abstract. The Cu-0.5Co/WC nano-composite coating was synthesized on CP-copper substrate using Direct Current (DC) electrodeposition method. In this work, it was tried to increase the hardness of surface without considerable degradation of copper's particular physical properties such as electrical conductivity. The effect of current density on microstructural homogeneity, hardness, fracture toughness, and electrochemical behavior of coating was investigated. The copper plates with the purity of 99.99% were used as electrodes. The electrolyte consists of tungsten carbide particles (30 g/l), copper sulfate (200 g/l), sulfuric acid (50 g/l), cobalt sulfate (50 g/l), and Sodium Dodecyl Sulfate (SDS) (0.3 g/(g of WC)) as surfactant. The particle size of tungsten carbide powder was in the range of 40-70 nm. The distribution of tungsten carbide particles in coating was studied using FESEM. Micro-hardness measurement was performed in Vickers scale. The fracture toughness of coating was determined by Vickers indentation test. The corrosion resistance of the electrodeposited Cu-Co and Cu-Co/WC nano-composite coatings was evaluated by polarization studies. Referring to the results, the use of optimum current density value (60 mA/cm^2) during the electrodeposition process improves hardness and corrosion resistance of nano-composite coating. Additionally, Cu-Co/WC composite coating shows more corrosion resistance than the unreinforced one.

1. Introduction

Improving the performance and service life of a product by modifying its surface properties has remained a research topic for long. Nanostructured composites deposited by the method of electrochemical deposition (electrodeposition) have been extensively studied during the last decade due to their interesting electronic, magnetic, electrochemical and optical properties and potential use as catalytic and electrode materials in various devices [1]. Electrochemical deposition has a widespread use in nanotechnology since it can be used to fill three-dimensional features at room temperature with good control of thickness and morphology [1]. During the last few decades, researchers have attempted to improve the properties through electrocodeposition of hard particles such as WC, Al_2O_3, SiC, and Si_3N_4 [2-5] in various metal matrix materials such as Ni and Cu [2,3]. The copper electroplates are widely

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used in engineering applications due to their high electrical and thermal conductivity, proper ductility, and required corrosion resistance. Nevertheless, these specimens show low hardness and wear resistance. In order to improve or modify the properties of copper coatings, ceramic particles [3] were incorporated into copper. The properties of nano-composites are dependent on both uniform distribution and the amount of incorporated particles within the matrix. The incorporation of nano-sized particles is influenced by various process parameters, including particle concentration, shape, size, bath composition, additives, pH, and current density. Researchers suggested that the applied current density, particle type, particle concentration, and bath agitation are the main influencing factors in the co-deposition process [5,6]. The aim of the present work is the production of Cu-Co/WC nano-composite coating using copper sulfate bath and also specification of optimum processing condition. The influence of current density on the tungsten carbide particles distribution, some mechanical properties, and corrosion behavior of coating was analyzed. The present Cu-Co/WC nano-composite coatings showed a significant improvement in hardness, fracture toughness, and corrosion resistance as compared to the previous composite coatings [2-4]. These improvements mainly depended on the nature and content of the tungsten carbide co-deposited particles, as well as on their distribution in the metallic matrix.

2. Materials and method

Cu-0.5Co/WC nano-composite coating was co-electrodeposited using the electrolyte containing copper sulfate (200 g/l), sulfuric acid (50 g/l), cobalt sulfate (50 g/l), and Sodium Dodecyl Sulfate (SDS) (0.3 g/(g of WC)) and suspended nano-sized tungsten carbide particles (30 g/l) at temperature 50°C and pH of 1.25. The tungsten carbide powder of 40-70 nm size was maintained in suspension by magnetic stirring at 600 rpm. Direct current was used for electrodeposition. The current density varied in the range of 20-80 mA/cm^2. The copper plate with the thickness of 0.5 mm, and purity of 99.99% was selected as cathode (substrate). The cathode exposure surface area was considered as 1 cm^2. Prior to electrodeposition, the substrates were mechanically polished. The resultant coating thickness was equal to 60 μm after 30 min. The distribution of tungsten carbide particles in coating was studied using FE-SEM (Model of Mira 3-XMU). Vickers micro-hardness tests were performed using a Wolpert-MC110 instrument at three different areas at load of 30 g for a duration of 15 s. The coating toughness was determined by Vickers indentations test. The applied load was in the range of 30-50 kg, and the following equation [7] was used for the calculation:

$$K_c = 0.0889 \left(\frac{H_\nu . P}{\sum_{i=1}^{4} c_i} \right)^{1/2}, \tag{1}$$

where K_C, H_V, P, and c are fracture toughness, hardness, indentation load, and crack length from the centre of indentation impression, respectively. The corrosion resistance of Cu-Co and Cu-Co/WC nano-composite coatings was evaluated by electrochemical measurements in 3.5% NaCl solutions at scan rate of 0.5 V. The Auto Lab PG STAT 302 N instrument was used for plotting the polarization curves. Consequent results were analyzed by Eco Chemie Nova 1.6 software.

3. Results and discussion

Figure 1(a)-(d) reveals the distribution of tungsten carbide particles on the surface of Cu-Co/WC nano-composite coating prepared by applying various current densities. In Figure 1(c), approximate homogenous distribution of tungsten carbide on the coating surface at optimum current density (60 mA/cm^2) can be seen. Figure 2 shows the Energy dispersive X-Ray spectroscopy) (EDS) (spectra of electrodeposited Cu-Co/WC nano-composite coatings at different current densities, confirming the presence of copper, tungsten, and cobalt elementals in the composites. The difference in intensity of W peaks is noticeable. The effect of current density on co-deposited tungsten carbide particles content is shown in Figure 3 using results of EDS analysis. It is clear that the content of the co-deposited tungsten carbide nano-particles is enhanced initially with the current density increase and is reached to a maximum value at 60 mA/cm^2. Beyond this current density value, the amount of co-deposited tungsten carbide particles decreases. Before reaching the maximum, the increment can be attributed to the increased tendency for absorbed particles to be attached to the cathode surface, which is consistent with Guglielmi's model [8]. When current density is higher than 60 mA/cm^2, the decreasing trend can be explained by the fact that an increase in current density results in more rapid deposition of the metal matrix and fewer ceramic particles could be embedded in the coating. A typical XRD pattern of the as-synthesized Cu-Co/WC nano-composite coating at optimum current density is shown in Figure 4. The XRD pattern shows diffraction peaks of Cu, Co, and WC. The appearance of the intense diffraction peak corresponding to Cu in coating pattern is due to the usage of copper as a substrate in the present study.

The micro-hardness values of Cu-Co/WC nano-composite coatings produced in different conditions are shown in Table 1. It reveals that the hardness enhances by increasing the current density from 20

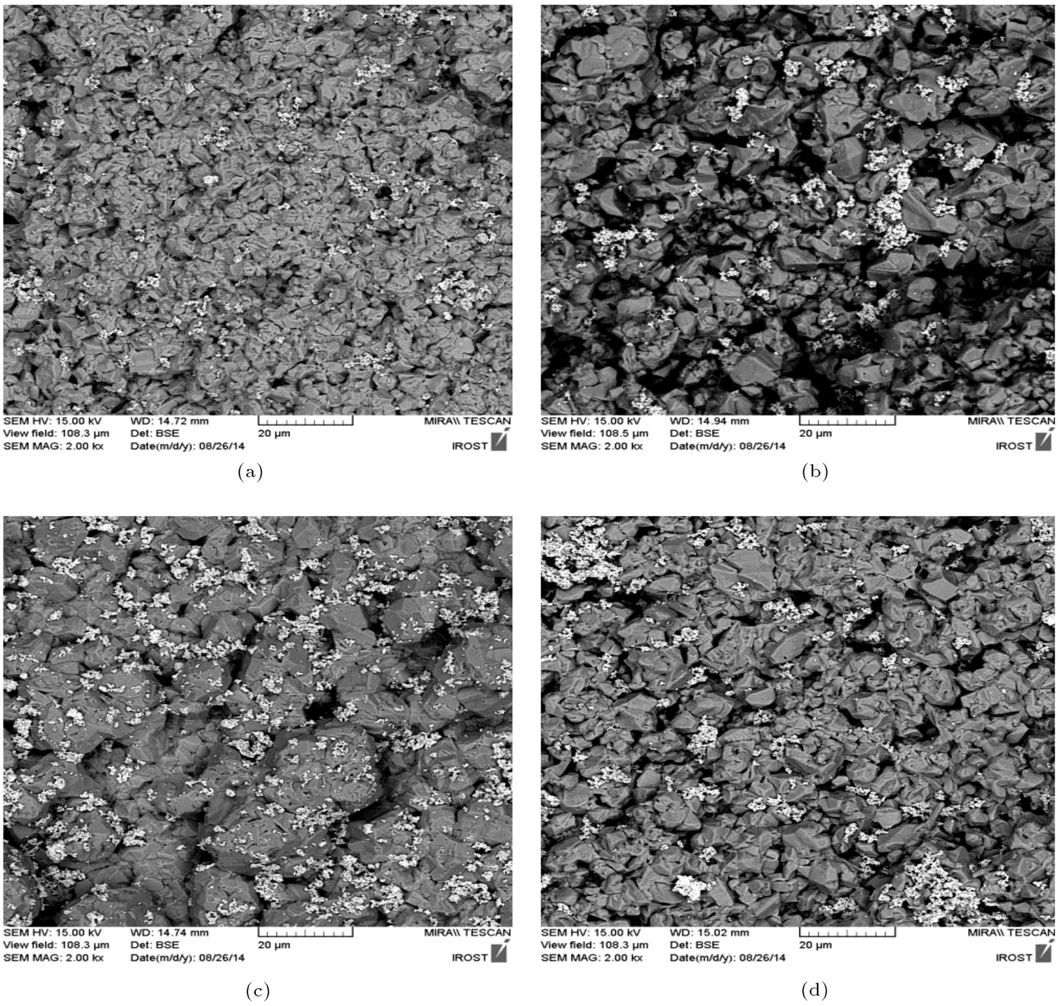

Figure 1. FESEM images showing the distribution of tungsten carbide particles on the surface of Cu-Co/WC nano-composite coating produced using a current density of: (a) 20 (b) 40 (c) 60 and (d) 80 mA/cm^2 (white and gray regions showing tungsten carbide particles and Cu-Co matrix, respectively.)

Table 1. The effect of current densities on micro-hardness of the Cu-Cu-Co/WC nano-composite coatings.

Coating	Cathodic applied current density (mA/cm^2)	Micro-hardness (HV)
Cu-Co/WC	20	415 ± 50
Cu-Co/WC	40	422 ± 26
Cu-Co/WC	60	530 ± 28
Cu-Co/WC	80	512 ± 27

to 60 mA/cm^2 and decreases by further increase of the current density to 80 mA/cm^2. This is due to maximum incorporation of hard tungsten carbide nano particles at current density of 60 mA/cm^2. The hardness improvement from 110 HV (pure Cu) to 530 HV (Cu-Co/WC)) is comparable with the results reported by Tsyntsaru et al. [8]. It is also observed that Cu-Co/WC nano-composite coating has a much higher micro-hardness value (530 HV) than that of the Cu/WC nano-composite coating [9].

The presence of tungsten carbide nano particles in electrodeposited coating reduces the fracture toughness of copper. It seems that the indentation fracture toughness of coatings has been affected by current density and tungsten carbide content of coating (Figure 5). The fracture toughness of Cu-Co/WC nano-composite coating is more than that in WC-Co cemented carbide [10]. However, the applicability of the indentation models for nano-composite coatings with low amounts of reinforcing particles should be further investigated. The corrosion potential (E_{corr}) and current (i_{corr}) of Cu-Co and Cu-Co/WC nanocomposite coatings were determined from the Tafel polarization curves (Figure 6). The related values are given in Table 2. It can be concluded that the corrosion currents (i_{corr}) of all Cu-Co/WC nanocomposite coatings decrease compared to that of electrodeposited Cu-Co. In corrosion potential of Cu-Co/WC nano-composites,

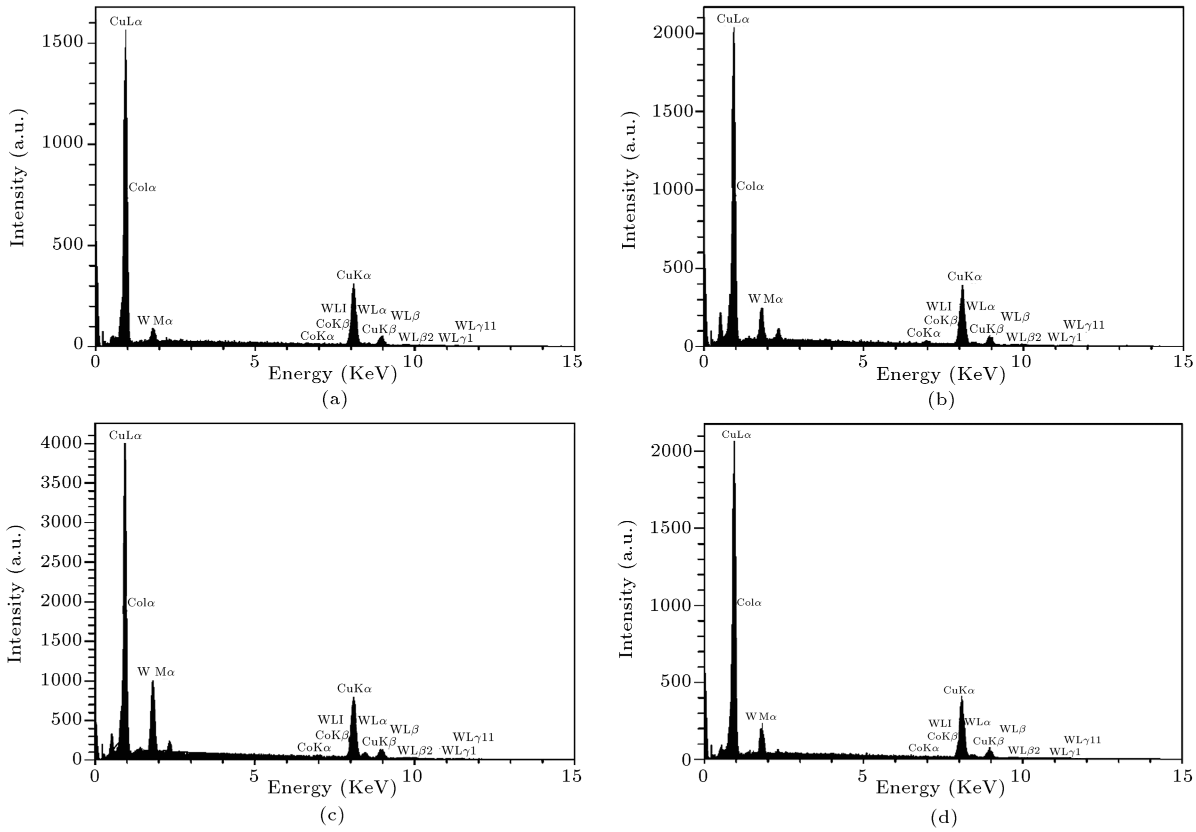

Figure 2. EDS spectra of Cu-Co/WC nano-composite coatings at different current densities: (a) 20, (b) 40, (c) 60, and (d) 80 mA/cm^2.

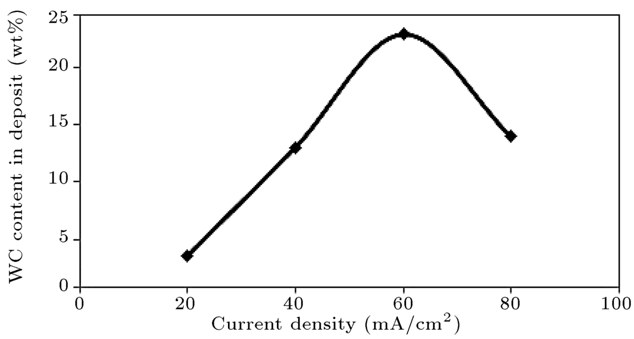

Figure 3. The weight percentage of co-deposited WC particles versus applied current density during processing of Cu-C0/WC nano-composite coating, according to the results of EDS analysis.

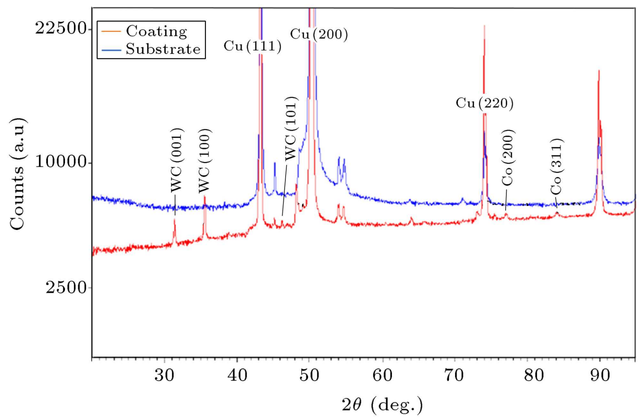

Figure 4. The XRD patterns of copper substrate and Cu-Co/WC nano-composite coating.

a negative shift can be seen, confirming the cathodic protective nature of the coatings. This observation is opposed to the corrosion investigation results of pulse electrodeposited Ni-W-SiC coating [4], but similar to those reported for Ni-W/ZrO_2 nano-composite coatings [11] and WC-Co/Fe nano-composite coatings [12].

In Table 3, the results of some reported studies on copper and cobalt matrices are summarized concisely. In spite of differences in processing routes and parameters such as particle size and content, there is a convergence in the properties of the produced composites.

Table 2. The Corrosion potential and current of Cu-Co, Cu-Co/WC nano-composite coatings.

Coating	**Cathodic current density (mA/cm^2)**	**Corrosion current density ($\times 10^{-5}$ A)**	**Corrosion potential (V)**
Cu-0.5Co	60	1.18	−0.10856
Cu-Co/WC	20	2.1909	−0.2623
Cu-Co/WC	40	1.1124	−0.2823
Cu-Co/WC	60	0.052	−0.38115
Cu-Co/WC	80	0.31	−0.3483

Table 3. A summary of some reported works' results for copper- and cobalt-matrix reinforced with tungsten carbide particles.

Matrix	Particles	Processing route	Purpose of work	Remarks	Ref.
Cu, Co	WC	Co-electro-deposition of nano-sized tungsten carbide particles and copper-cobalt matrix.	To evaluate the influence of current density on the tungsten carbide particles distribution as well as hardness, indentation fracture toughness & electrochemical behavior of coating.	The use of proper surfactant and current density stabilizes WC nano-particles suspension, promotes the nanoparticles incorporation in the matrix, and consequently improves the microstructural homogeneity, hardness and corrosion resistance of Cu-0.5Co/WC nano-composite coating. The Cu-Co/WC nano-composite coating shows higher hardness, but lower indentation fracture toughness compared with the tungsten carbide free coating.	Present work
Cu	WC	Co-electrodeposition of micrometer-sized tungsten carbide (WC) particles and copper matrix.	To investigated the structure, morphology, surface roughness as well as interfacial phenomena (wetting ability and wear)	The tungsten carbide particles have a hardening effect on the metal matrix. The wear resistance of a dispersion hardened Cu-WC composite coating is slightly higher than that of pure copper.	[9]
Co	WC	High pressure melt infiltration	To realize the optimal distribution with WC & Co liquid to obtain better properties and performances.	The results of Vickers hardness tests, fracture toughness tests and cutting performance tests show that well-sintered WC-Co composites exhibit a prominent combination of high hardness & large fracture toughness value.	[10]
Cu	WC, Co	Hot pressing	To evaluate the effects of WC and Co particles content and size on the wear and corrosion properties of the copper composites.	The results show that the hardness, wear resistance and static corrosion weight loss of Cu/WC composites increase with a decrease of WC size or with an increase of WC content. The Cu/WC/Co composites show a much lower E_{corr} and significantly more passivity than Cu/WC composites. The Cu/WC/Co composites exhibit excellent wear corrosion resistance.	[13]
Cu	WC, Co	Hot pressing	To examine the influence of particulate WC & Co particles on wear, corrosion, and their synergistic effect on the properties of Cu/WC/Co MMCs.	It was observed that the average electrical resistivity of the composites increases about 1.6% at 8 wt.% WC particles. The hardness of the composites was found to increase with increased reinforcement content.	[14]

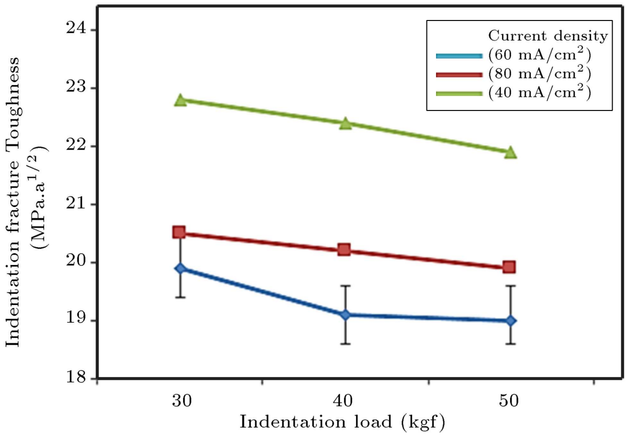

Figure 5. The indentation fracture toughness of Cu-Co/WC as a function of applied indentation loads.

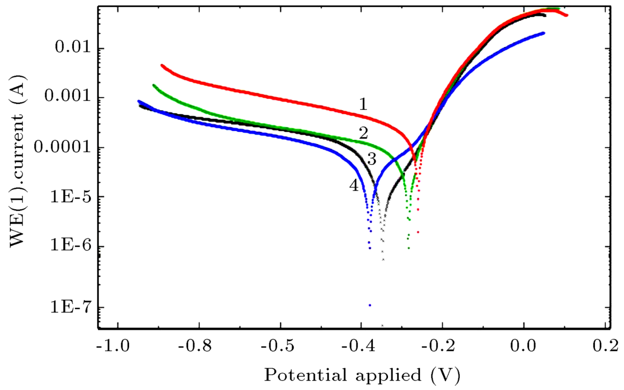

Figure 6. Polarization curves of Cu-Co/WC coating electrodeposited at current density of 20, 40, 80, and 60 mA/cm^2 designated as 1, 2, 3, and 4, correspondingly.

The effects of other micro- and nano-sized particles incorporation on mechanical, physical, and chemical properties of electrodeposited copper matrix are to some extent similar to those given in Table 3 [15,16]. Since the reinforcement type, bath and deposition variables, and characteristics of resulted composites are not alike, the findings are not completely compatible.

4. Conclusions

The effect of current density on microstructural homogeneity, hardness, fracture toughness, and corrosion resistance of Cu-0.5Co/WC nano-composite coating was successfully investigated. The use of optimum current density value (60 mA/cm^2) during the electrodeposition process improves hardness and corrosion resistance of nano-composite coating. Nevertheless, the indentation fracture toughness degrades by the incorporation of tungsten carbides particles, especially as the particles' content increases at current density of 60 mA/cm^2.

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