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Structural and Functional Properties of Electrodeposited Copper Metal Matrix Composite Coating with Inclusions of WC

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The matrix durability properties were improved when micrometer-sized tungsten carbide (WC) particles were incorporated into an electroplated copper matrix. The WC particles have a hardening effect on the metal matrix and its hardness increases from 160 kgf·mm^{-2} of pure copper coating to 185 kgf·mm^{-2}. The wear resistance of dispersion-hardened Cu-WC composite coating is slightly higher than that of pure copper. The inclusions of tungsten carbide particles promoted the formation of a smooth crystalline structure of copper matrix. The surface formed in the presence of WC micro particles has lower R_a parameters of the standard roughness and a smoother profile than those of a pure copper coating. It has been found that the wetting ability of Cu-WC composite coating surface is the same as that of pure copper.

Keywords: copper, tungsten carbide, hardness, roughness, wear resistance, wetting ability.

INTRODUCTION

Protective coatings play an important role in materials science owing to the possibility to obtain modern technical design, for example, obtaining functional wear resistant coatings. Often the machinery components are coated with pure ceramic materials or metal matrix composite coatings for applications range of wear resistant materials mainly formed with refractory and hard carbides [1 – 9].

It is clear, that cohesion as well as hardness of the material is a very important characteristic. In materials science, hardness is the characteristic of a solid material expressing its resistance to permanent deformation. Tungsten carbide (WC) is used as a hardening additive to various cutting tools and shearing scissors due to its great specific density. Copper has been chosen to obtain composite Cu-WC coating, because copper is a malleable and ductile metal with an excellent electrical conductivity and finds extensive use as an electrical and heat conductor, as a building material as well as a component of various alloys [10]. According to our previous work [9], the increase in temperature from 100 K to 370 K resulted in increase in electrical resistivity of materials from $1.2 \times 10^{-8}\ \Omega$ m to $2.8 \times 10^{-8}\ \Omega$ m for pure copper and from $1.14 \times 10^{-8}\ \Omega$ m to $2.7 \times 10^{-8}\ \Omega$ m for Cu-WC composite coating.

On the other hand, non-metallic inclusions incorporated in the metal can change its electron structure and the crystal lattice, which will result in changes in the physical and mechanical properties of the electrodeposits. The inclusions of inert particles affect fine structure parameters and can increase the concentration of packing defect deformations and twinning types, and lead to the increase in the dislocations density. The density of dislocation in a material can be also increased by various deformations [11, 12].

The relationship between the structure and morphology of a composite coating with inclusions of WC and its functional performance were investigated as a subject of materials science, which is an interdisciplinary field, studying the properties of material and its applications in various areas of science and technology. Our purpose was to investigated the structure, morphology, surface roughness as well as interfacial phenomena: wetting ability and wear, because this research aims towards the actual realization of advanced new materials with special functionality such as wear resistance displays.

EXPERIMENTAL

Electroplated 50 μm and 100 μm thick copper coatings and copper composite with tungsten carbide coatings were studied. Copper coatings modified with WC were electrodeposited in electrolytes containing (g·dm^{-3}): $CuSO_4 \cdot 5H_2O$ – 200, H_2SO_4 – 50 at a cathodic current density (i_c) of 5 A·dm^{-2} at 20 °C. The agitation conditions of electrolyte were suited to a turbulent fluid flow. The motive force of turbulent fluid flow directed the particles of WC to the cathode surface and prevented them from sedimentation in the bulk of electrolyte. The intensity of compressed air was estimated by using a rotameter and was maintained as high as 300 dm·h^{-1}. The concentration of WC in the electrolyte-suspension was 100 g·dm^{-3}. The size of particles of WC micro powder was 3 μm–5 μm. Analytical grade chemicals and bidistilled water were used to prepare electrolytes. Electrolytic copper (AnalaR, BDH Chemicals LTD, UK) was used as an anode.

The identification of the heterogeneous disperse phase in the metallic coating surface area (F_{dp}) was determined by preparing cross-section metallographic specimens of coating. The metallographic specimens were investigated using an optical microscope Neophot 2. The surface percentage F_{dp} was calculated according to equation (1):

$$F_{dp} = \frac{Z_{dp}}{Z}, \% \qquad (1)$$

where: Z is the total amount of marks on a special mask coinciding under the microscope with the investigated

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area; Z_{dp} is the part of the marks coinciding with the dispersed particles at the investigated area. The volume percentage of co-deposited particles was calculated from statistical equivalency between the surface (F_{dp}) and volume (V_{dp}) concentrations of disperse phase in the material with the proportionality constant equal to 0.80 [13]. The mass percentage (G_{dp}) of disperse phase was calculated from the value of (V_{dp}) by the equation:

$$G_{dp} = \frac{\rho_{dp} V_{dp} \, 100}{\rho_{dp} V_{dp} + \rho_{Cu} V_{Cu}}, \% \tag{2}$$

where: ρ_{dp} and ρ_{Cu} are the specific densities of WC and Cu equal to 15.8 g·cm^{-3} and 8.94 g·cm^{-3}, respectively.

The morphology of Cu coatings was studied and micro graphed with a Hitachi Tabletop Microscope TM-1000 (Japan). The image of worn specimens surface was investigated using a Stereo Metric Microscope MBS-9 (SMM) (Russia).

Vickers hardness (HV) was measured using an indenter PMT-3 on a 50 μm thick surface by a 20 g indentation of load for 10 s and was calculated by the formula:

$$HV_{20} = \frac{18574\, P}{d^2}, \text{ kgf·mm}^{-2}, \tag{3}$$

where: P is the load, g; d is the diameter of diamond prism, mm. The average value was calculated from 10 measurements.

The surface topography of the coatings was examined on a nano-metric scale using Atomic Force Microscopy (AFM). The AFM images were recorded in contact mode with a Si_3N_4 cantilever with the constant force of 0.032 N·m^{-1} to reveal the surface topography of the coatings by an Explorer (VEECO-Thermo Microscope SPM), using a 10-μm scanner and a scan rate of 1 Hz/line. All scans were acquired at room temperature under atmospheric pressure and characterized by measuring the arithmetic average of the absolute values of the surface roughness (R_a /or R_{av}) as well as other parameters.

The wear tests of 100 μm thick copper and copper composite coatings were performed according to GOST 20811 Standard (Russia) at room temperature with a relative humidity of 45 %–55 % under dry sliding conditions on flat surfaces of system: coating-abrasive paper [14]. An abrasive micro grits paper (FEPA P 500 grade with the average size of SiC particles 30.2 μm ±1.5 μm (ISO 634) was used as the counter body. All tests were performed under a load of 2.3 N on coating and abrasive paper with a velocity of sliding – 7.10^{-2} m·s^{-1}. The overall sliding distance of 4000 series cycles – 160 m.

The initial mass as well as the mass loss after wear tests of specimens was measured using a micro balance (VLA 200 g ±0.00005 g). The gradient of the linear section of a plot of cumulative coating mass loss (Δm) on a sliding distance (L_m) under a load (F_N) was calculated as the rate of linear wear (W_l):

$$W_l = \frac{\Delta m}{F_N L}, \text{ g·N}^{-1}\text{·m}^{-1}, \tag{4}$$

where: (Δm) is the mass loss of specimens, g; (F_N) is the normal load applied to the specimen during sliding, N; L_m is the sliding distance, m.

The specific wear rate (W_s) / or wear factor (k_i) was calculated by the following equation [15]:

$$W_s = k_i = \frac{\Delta m}{\rho F_N L}, \text{ cm}^{-3}\text{·N}^{-1}\text{·m}^{-1}, \tag{5}$$

where: Δm is the mass loss of specimens, g. The volume loss of materials at wear (V_i) was calculated by equations (6) of (7):

$$V_i = k_i \, F_N \, L, \ 10^6\text{·cm}^3, \tag{6}$$

$$V_i = \Delta m / \rho, \ 10^6\text{·cm}^3. \tag{7}$$

In the case of Cu-WC composite coating Δm to take count of ρ_{dp} of disperse phase of WC particles; F_N is the normal load applied on the specimen during sliding, N; L_m – the total sliding distance, m.

The contact angle measurement was carried out using a fully computer-controlled contact angle meter KSV's CAM 200 (Denmark). The static contact angle (SCA) method in measuring range from 0° to 180° with inaccuracy ±0.1° at 20 °C in an environmental chamber was used. The double distilled water of micro volume of 1 μdm^{-3} as the polar liquid was laid onto the solid surfaces by a micro-syringe. The contact angle / or wetting angle is the angle between the tangent plane to the surface of the liquid and the tangent plane to the surface of the solid, at any point along their line of contact. The different degrees of wetting ability of hydrophobic / or hydrophilic materials explain the fact that near a hydrophobic surface, dipoles of water are found to be mainly oriented parallel to the surface and near a hydrophilic surface the ones oriented normal to it. A wettable surface may also be considered as a hydrophilic one while a not-wettable surface as a hydrophobic [16].

RESULTS AND DISCUSSION

The tungsten carbide particles have a hardening effect on the metal matrix and its hardness increases from 160 kgf·mm^{-2} of pure copper coating to 185 kgf·mm^{-2} (Fig. 1). The indentation hardness after the wear process of a dispersion-hardened Cu-WC composite coating is higher than that of pure copper. The hardness of worn surface of Cu-WC composite coating increases to 300 kgf·mm^{-2} (Fig. 1, curve 2). Thus, the matrix durability properties were improved when micro meter-sized WC particles were incorporated into an electroplated copper matrix.

Electro conductive WC micro particles activated the copper cathode during electro co-deposition with copper, which resulted in formation of copper crystals. The pure copper has a crystallite structure (Fig. 2). It is evident that crystalline materials contain uniform planes of atoms organized in a long-range order. Planes may slip past each other along their close-packed directions. The presence of non-metallic inclusions decreases the likelihood of planes slipping and stabilizes the copper matrix.

A Cu-WC composite coating with incorporated WC micro metre sized particles shows a slightly higher wear resistance as compared with those of crystallite surface and the matrix of pure copper.

At dry friction during intensive abrasive wear the wear mass loss after overall sliding cycles of pure copper was 47 mg and 45 mg – of Cu-WC coatings (Fig. 3). The specific micro wear rate (*W*s) of Cu-WC coating decreased fifteenfold: from 2.0×10^{-6} cm^3·N^{-1}·m^{-1} to 1.3×10^{-7} cm^3·N^{-1}·m^{-1} and that of pure copper decreased tenfold: from 1.4×10^{-6} cm^3·N^{-1}·m^{-1} to 1.4×10^{-7} cm^3 N^{-1} m^{-1}. It may be emphasized, that in the initial stage of dry friction the metal mass loss and the specific wear rate of Cu-WC composite coating increases more as that of pure copper. Other authors also noticed the some dependence, when they used composites with inclusions of micro metre sized particles.

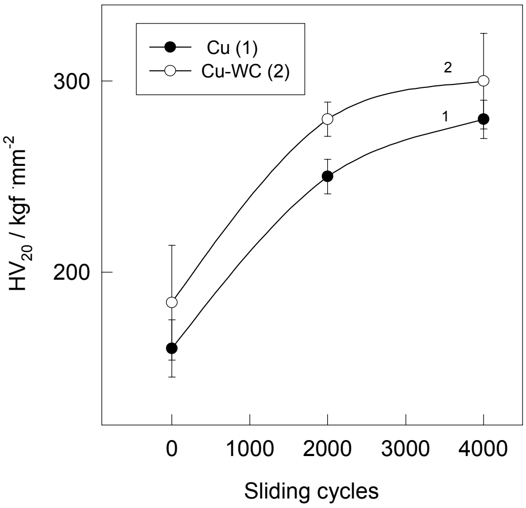
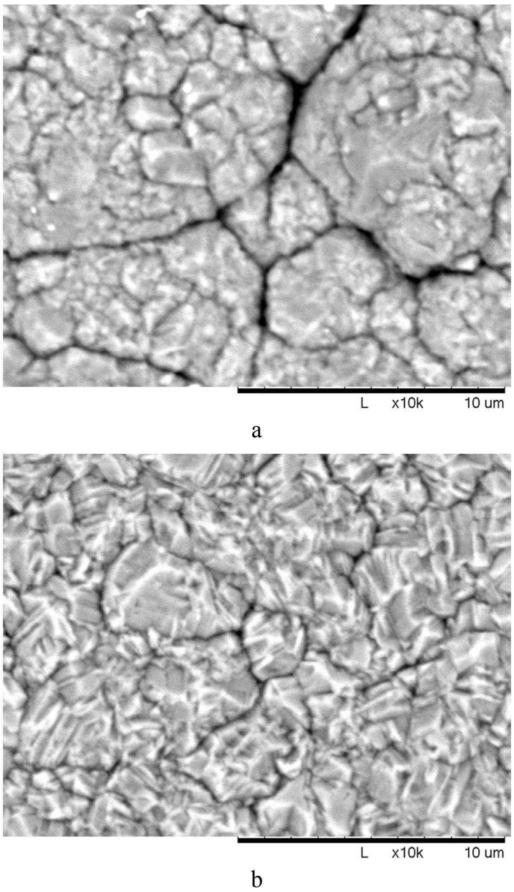


Fig. 1. Dependence of indentation hardness of copper and Cu-WC composite coatings *vs.* sliding cycles



a

b

Fig. 2. TTM image of surfaces of Cu (a) and Cu-WC composite (b) coatings

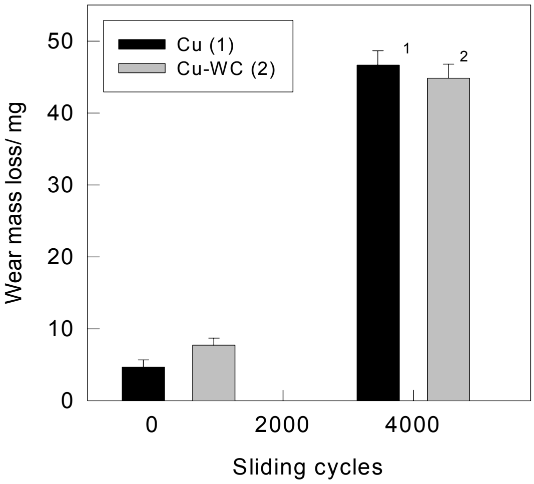


Fig. 3. Wear mass loss of pure copper (1) and Cu-WC (2) coatings after initial 400 and total sliding cycles in air without a lubricant on flat surfaces of abrasive paper and coating

The image of SMM observations of the worn surfaces after overall sliding cycles of the Cu-WC composite coating are presented in Fig. 4. Many continuous and wide parallel grooves are observed as abrasion tracks on a pure copper coating but not shown here. A formed twist network on the surface of investigated Cu-WC coating indicates the resistance to sliding against abrasive paper, which is a reflex of the resistance to permanent deformation during friction of compact Cu-WC composite coating against abrasive paper and perfect cohesion of metallic copper matrix and non-metallic inclusions of WC particles and results in a higher durability as compared with that of pure copper coating (Figs. 2 and 4).

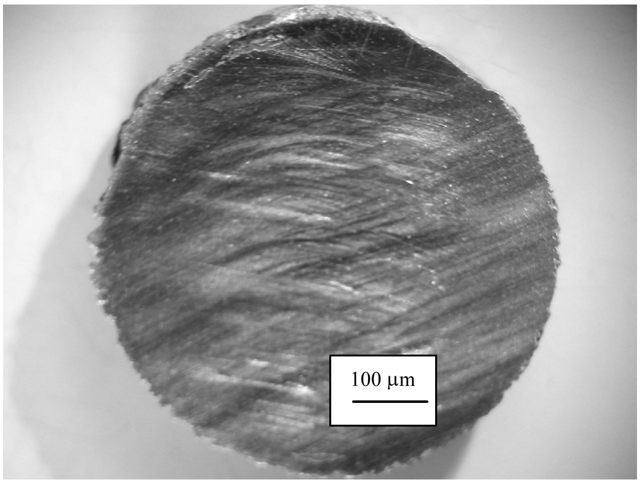
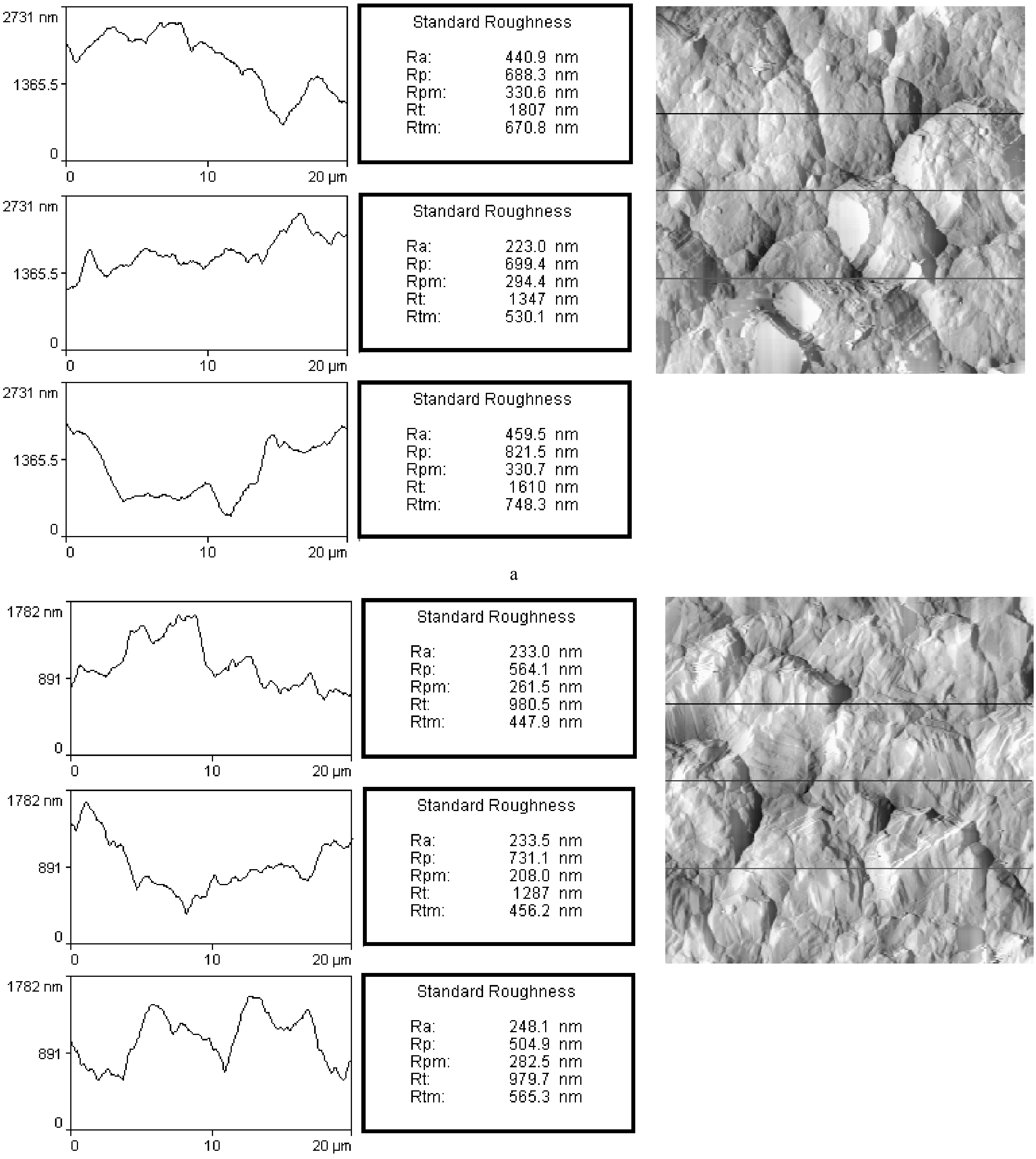


Fig. 4. SMM images of top view of worn surface of Cu-WC coating with a visible twist network of wear tracks at tenfold magnified of real surface

It has been found that the surface formed in the presence of WC micro particles has a smoother profile than that of a pure copper coating and lower parameters of the standard roughness: the average roughness (R_a), maximum height of the profile above the mean line (R_p), maximum peak-to-valey height in the profile (R_t) and mean values more representative of the entire profile (R_{pm} and R_{tm}) (Fig. 5). The calculated average mean of roughness ($\overline{R}_a$)



Standard Roughness	
Ra:	440.9 nm
Rp:	688.3 nm
Rpm:	330.6 nm
Rt:	1807 nm
Rtm:	670.8 nm

Standard Roughness	
Ra:	223.0 nm
Rp:	699.4 nm
Rpm:	294.4 nm
Rt:	1347 nm
Rtm:	530.1 nm

Standard Roughness	
Ra:	459.5 nm
Rp:	821.5 nm
Rpm:	330.7 nm
Rt:	1610 nm
Rtm:	748.3 nm

a

Standard Roughness	
Ra:	233.0 nm
Rp:	564.1 nm
Rpm:	261.5 nm
Rt:	980.5 nm
Rtm:	447.9 nm

Standard Roughness	
Ra:	233.5 nm
Rp:	731.1 nm
Rpm:	208.0 nm
Rt:	1287 nm
Rtm:	456.2 nm

Standard Roughness	
Ra:	248.1 nm
Rp:	504.9 nm
Rpm:	282.5 nm
Rt:	979.7 nm
Rtm:	565.3 nm

b

Fig. 5. Analysis data of standard roughness of copper (a) and Cu-WC (b) coatings of various line profile measured by AFM

based on the R_a of three profile lines presented in Fig. 5 is equal: for Cu-WC composite coating $\overline{R}_a = 238$ nm ±9 nm, while for the copper coating surface $-\overline{R}_a = 375\,\text{nm} \pm 132$ nm. Thus, the smooth-faced Cu-WC composite coating has lower dispersion ($\pm\sigma$) of roughness measurement in a nano metre scale as compared with the different dispersion of uneven surface of pure copper coating.

Table 1. The average values of the apparent static contact angle (θ) on the worn surfaces of copper and Cu-WC composite coatings

Coating	θ_{left}	θ_{right}	Average of θ_{left} and θ_{right}
1. Cu	114.4	119.4	116.9
2. Cu-WC	112.2	112.9	112.6

Contact angle measurements have shown that both before and after the wear process the surfaces of investigated copper coatings have a hydrophobic character (Table 1). Liquids condensed on such a coated surface form droplets because of a high contact angle and fall down easily. All investigated copper coatings after the wear process are metallic coatings of a good quality.

CONCLUSIONS

The matrix durability properties were improved when micrometer-sized WC particles were incorporated into an electroplated copper matrix. The tungsten carbide particles have a hardening effect on the metal matrix and its hardness increases from 160 kgf·mm^{-2} of pure copper coating to 185 kgf·mm^{-2}. The wear resistance of a dispersion-hardened Cu-WC composite coating is slightly higher than that of pure copper. The inclusions of tungsten carbide particles promoted formation of a smooth crystalline structure of copper matrix. The surface formed in the presence of WC micro particles has lower R_a parameters of the standard roughness and a smoother profile than that of pure copper coating. All surfaces of the investigated copper coatings after the wear process are metallic coatings of a good quality. The wetting ability with water of Cu-WC composite coating surface both before and after the wear process has the same hydrophobic character as that of pure copper. They can be used when the materials need to have both a good resistance against wear, a high heat and electrical conductivity.

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