ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 16, No. 1. 2010

The Impact of Carbon Nanomaterials on the Formation and Properties of Electrodeposited Copper Composite Coatings

Viktorija MEDELIENĖ[1*], **Remigijus JUŠKĖNAS**[1], **Marija KURTINAITIENĖ**[1], **Aušra SELSKIENĖ**[1], **Vojtech STANKEVIČ**[2]

[1]*Institute of Chemistry, A. Goštauto 9, LT-01107 Vilnius, Lithuania*
[2]*Semiconductor Physics Institute, A. Goštauto 11, LT-01107 Vilnius, Lithuania*

Received 16 September 2009; accepted 19 January 2010

A relation has been found between the crystalline parameters of the existing forms of carbon nanomaterials (CNMs), in steady state and transient conditions, structural morphology and crystallography of the electrodeposited copper composite coatings as well as its functional performance (hardness, roughness, resistivity).

It has been found that the surface formed in the presence of CNMs in electrolyte-suspension has a lower R_a parameter of the standard surface roughness: 84 ±33 for Cu-CNM1, 70 ±42 for Cu-CNM2, 190 ±137 for Cu-CNM3, while R_a of a pure copper coating is 254 ±39 nm and consequently it has a smoother profile than that of a pure copper coating. The CNMs have a hardening effect on the metal matrix and its hardness increases from 190 kgf·mm^{-2} to 340 kgf·mm^{-2}. The temperature coefficient of resistivity of composite coatings is close to that of pure copper.

Keywords: copper, carbon nanonmaterial, hardness, roughness, resistivity, temperature coefficient of resistivity.

INTRODUCTION

It is known that the inclusions of inert particles of micrometer-size affect fine structure parameters and can increase the concentration of packing defect deformations and twinning types in polycrystalline materials. The coatings having a dispersion-hardened heterogeneous metallic matrix with an evenly distributed solid phase of particles of oxides, carbides, etc traditionally are used in the automotive industry and in the aeronautics as wear, corrosion and high-temperature oxidation resistance coatings [1 – 4].

Relatively little information is available on the formation of metal matrix composite coatings in aqueuos electolyte-suspension with particles of nanometer-size and their impact on copper lattice parameters and properties of matrix [5, 6]. There is no question, that nanophases have recently generated considerable scientific interest because of the improvements in a variety of properties that are expected to result from grain-size reduction to the nanometer-scale. Nanostructured and nanocomposite materials possess unique structural and physical properties, and because of these characteristics they usually find applications in nano technology, especially for production of miniature devices [7 – 9].

Our purpose was to investigate the surface morphology and topography of the copper metal matrix composite coating formed in electrolyte-suspension with carbon nanomaterials (CNMs) and its functional performance (hardness, roughness, electric resistivity). Furthermore, in this work we explored the use of aqueous solution and electrochemical method to incorporate carbon nanomaterials (CNMs) into copper coating in a stable and controlled way as an alternative to other method. Thus, this research aims towards the actual realization of a new generation of advanced materials.

EXPERIMENTAL DETAILS

Electroplated 10 μm thick copper and copper composite coatings were studied. Copper coatings modified with carbon nanomaterials (CNMs) were electrodeposited in electrolytes containing (mol): $CuSO_4 \cdot 5\,H_2O$ – 0.25, H_2SO_4 – 0.5 at a cathodic current density (i_c) of 2 A·dm^{-2} at 18 °C ±1 °C. The agitation conditions of electrolyte were suited to a turbulent fluid flow. The motive force of turbulent fluid flow directed the particles of CNMs 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^{-3}·h^{-1}. Electrolytic copper (AnalaR, BDH Chemicals LTD, UK) was used as an anode. Analytical grade chemicals and bidistilled water were used to prepare electrolytes.

The concentration (c) of CNMs in the electrolyte-suspension was (g·dm^{-3}): $c_1 = 0.02$; $c_2 = 0.4$ and $c_3 = 1.0$. The size and shape of CNM was determined with TEM (MORGAGNI 268) an acceleration voltage of 71 kV. The average size of particles of CNMs powder of (50 – 100) nm was used to suspension preparation. The carbon nanomaterials (CNMs) synthesized at 800 °C ±10 °C by catalytic chemical precipitation and decomposition of CH_4 gas by Boudouard reaction using a $Fe(CO)_5$ catalyst precursor (CNM1), 5 % H_2S gas was injected into a separate stream of gaseous media (CNM2) and 5 % NH_3 gas was injected into a separate stream of gaseous media to synthesize (CNM3).

The surface topography of the coatings was examined in a nanometric scale using Atomic Force Microscopy (AFM). The AFM images were recorded in semi-contact (tapping) mode with a gold-coated Si_3N_4 tip to reveal the topography of the coatings by an Explorer (VEECO-Dimension 3100 Microscope), using Hybrid XYZ scanner and a scan rate of 0.5 Hz/line. All scans were acquired at room temperature under atmospheric pressure and

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[*] Corresponding author. Tel.: +370-5-2648890; fax: +370-5-2649774.
E-mail address: *viktorija.medeliene@gmail.com* (V. Medelienė)

characterized by measuring the arithmetic average of the absolute values of the surface roughness (R_a /or R_{av}) as well as topography parameters.

The crystalline state of carbon nanomaterials used both in copper composite coatings and in the powder form were identified by the XRD method. The XRD studies were carried out using an X-ray diffractometer D8 Advance with Cu K$_\alpha$ radiation ($U_a = 40$ kV, $I_a = 40$ mA) and parallel beam optics. XRD patterns of crystalline state of Cu, CuO; graphite and FeC_3 were measured in the 2θ range of 20°– 85° using step scan mode (Θ) with a step size of 0.04° and data acquisition time of 10 s.

The electrical resistivity (ρ) of materials was measured using a standard four-probe technique. For this purpose the deposited samples were separated from the titanium substrate and cut into narrow strips to which the contacts were brought. A 20 mA current was used for the measurements. For averaging the values of resistivity, measurements were made on the strips cut out in different regions of the deposited samples. All the measurements were performed in a temperature range of 170 K – 370 K in the air atmosphere. The temperature coefficient of resistivity (α) was calculated according to the equation:

$$\alpha = \frac{1}{\rho}\frac{d\rho}{dT} \tag{1}$$

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

$$HV_{20} = \frac{1857.4\,P}{d^2},\ \text{kgf·mm}^{-2} \tag{2}$$

where: P is the load, g; d is the diameter of diamond prism, mm. The average value was calculated from 5 measurements.

RESULTS AND DISCUSSION

The indentation hardness as a characteristic of a solid material, expressing its resistance to permanent deformation, increases due to the hardening and smoothing effect of optimal (0.4 g·dm^{-3}) concentration of CNMs on the metal matrix. The hardness of a pure copper coating reaches 190 kgf·mm^{-2}, while the hardness of the smoother copper nanocomposite coatings formed in electrolyte-suspension with the all investigated CNMs, increases up to 340 kgf·mm^{-2} (Fig. 1).

The electrical resistivity of copper composite coatings slowly increases, when the optimal concentration of both carbon nanoderivatives is exceeded in electrolyte-suspension, but the electrical properties of materials have not changed as the values of electrical resistivity and of temperature coefficient of electrical resistivity testify (Fig. 2 and Table 1).

The investigated carbon nanomaterials (CNMs No. 1 – 3) stimulated formation of nanostructured coatings with a smoother relief on the nanometre level as compared with that of pure copper coating (compare Figs. 3 and 4) and has lower R_a parameters of the standard surface roughness: 84.0 ±33 for Cu-CNM1, 69.3 ±42 for Cu-CNM2, 190.3 ±137 for Cu-CNM3, while R_a of a pure copper coating is 253.7 ±39 nm (Table 2).

According to the data presented in Table 3, carbon nanomaterials have a small impact on the crystalline parameters of the electrodeposited copper coatings. The nanomaterials have no influence on the values of interplanar distances (d) of copper, which testifies that carbon does not insert into the copper crystal lattice, but they affect the growth of crystals during electro crystallization and change the type of morphology (Fig. 3).

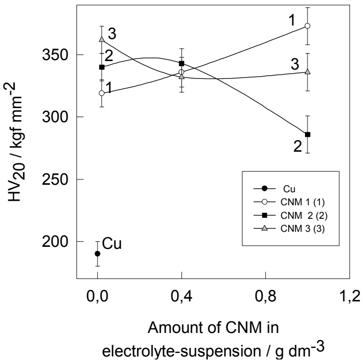


Fig. 1. Dependence of hardness of copper and composite Cu-CNMs coatings formed with CNMs No. 1 – 3 vs. concentration in electrolyte-suspension

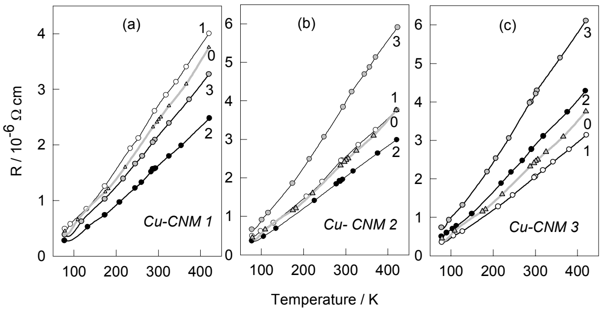
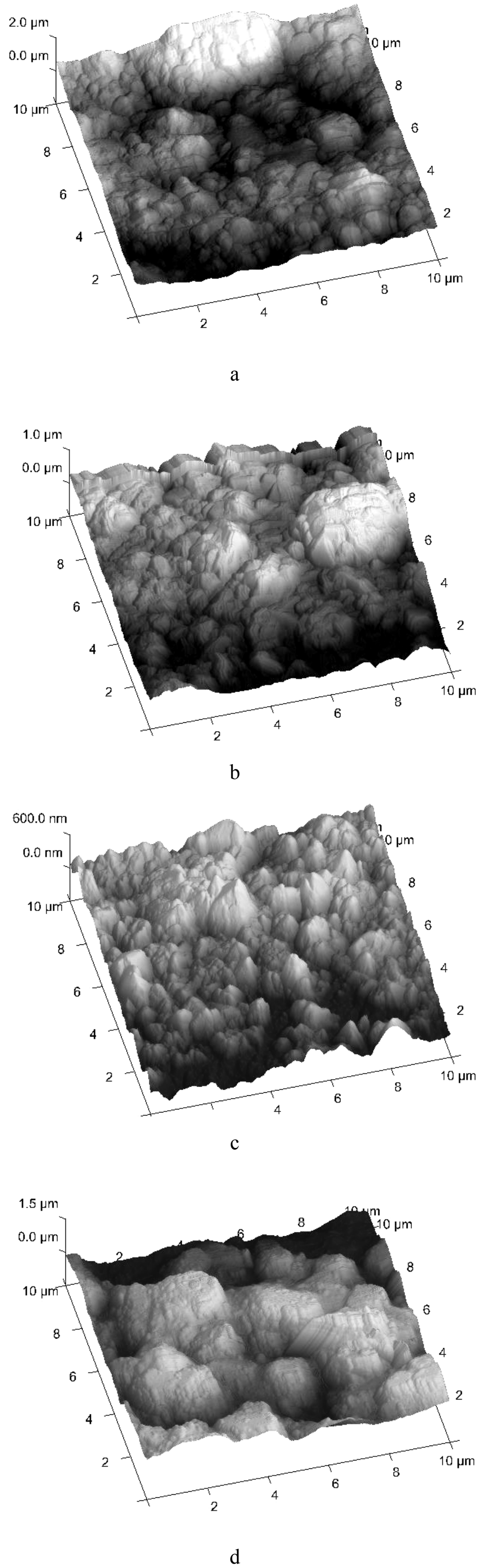


Fig. 2. Dependence of electrical resistivity vs. temperature of copper (curve 0) and copper composites: Cu-CNM1 (a), Cu-CNM2 (b) and Cu-CNM3 (c). The concentration (c) of CNMs in electrolyte-suspension (g dm^{-3}): curves 1 – 0.02, 2 – 0.4 and 3 – 1.0 (a – c)

Table 1. The values of electrical resistivity (ρ) measured at – 273 K (0 °C) and its temperature coefficient of resistivity (α) of copper and copper composite coatings electrodeposited in electrolyte-suspension with CNMs additives of various concentration

Coating	ρ, 10^{-6} Ω cm	α, 10^{-3} deg^{-1}
Cu	2.1	4.8
Cu-CNM1 c_1	2.4	4.7
Cu-CNM1 c_2	1.4	5.0
Cu-CNM1 c_3	1.9	4.8
Cu-CNM2 c_1	2.3	4.7
Cu-CNM2 c_2	1.8	4.5
Cu-CNM2 c_3	3.5	4.9
Cu-CNM3 c_1	1.8	4.9
Cu-CNM3 c_2	2.5	4.7
Cu-CNM3 c_3	3.7	4.7



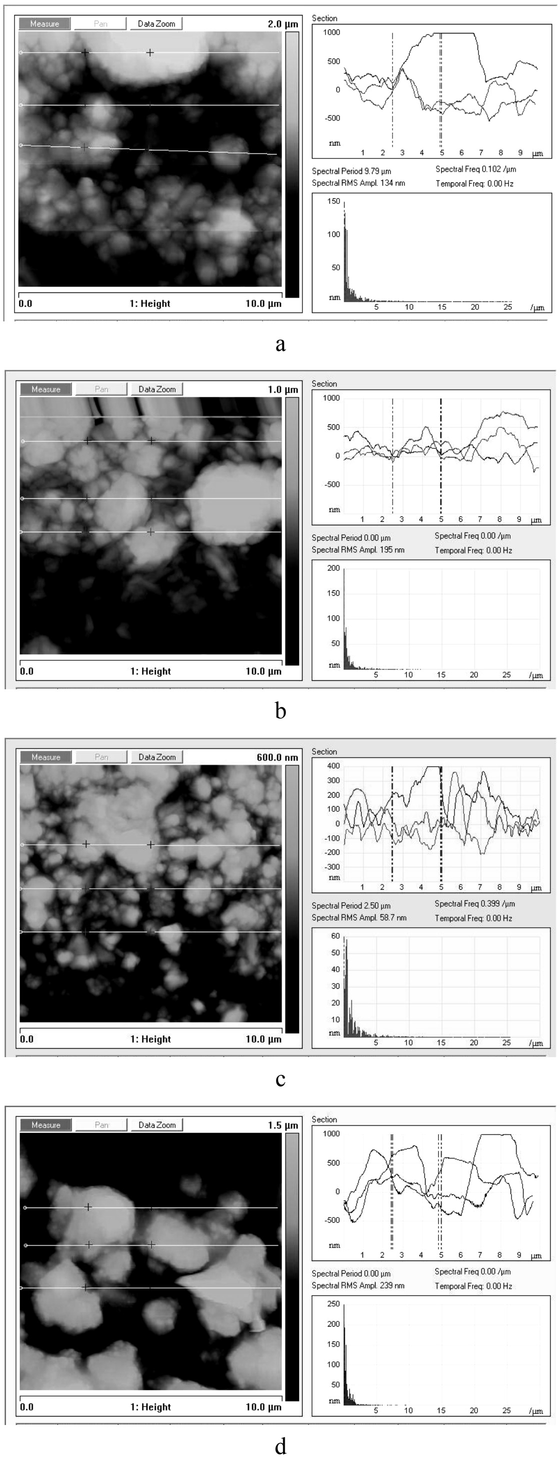
a

b

c

d

Fig. 3. AFM 3D image of surfaces topography of Cu (a) and composite Cu-CNM coatings formed with CNM No. 1 – 3 (b – d)



a

Spectral Period 9.79 µm
Spectral RMS Ampl. 134 nm
Spectral Freq 0.102 /µm
Temporal Freq: 0.00 Hz

b

Spectral Period 0.00 µm
Spectral RMS Ampl. 195 nm
Spectral Freq 0.00 /µm
Temporal Freq: 0.00 Hz

c

Spectral Period 2.50 µm
Spectral RMS Ampl. 58.7 nm
Spectral Freq 0.399 /µm
Temporal Freq: 0.00 Hz

d

Spectral Period 0.00 µm
Spectral RMS Ampl. 239 nm
Spectral Freq 0.00 /µm
Temporal Freq: 0.00 Hz

Fig. 4. AFM analysis data of the standard roughness (R_a) of copper (a) and Cu-CNMs No. 1 – 3 (b – d) coatings of various line profile

Table 2. The value of of average roughness ($\overline{R}_{MS}$) of copper and copper composite Cu-CNMs coatings

Coating	$\overline{R}_{MS}$, nm	± dispersion
Cu	253.7	±39
Cu-CNM1	84.0	±33
Cu-CNM2	69.3	±42
Cu-CNM3	190.3	±137

Table 3. The values of XRD parameters: *d* (Obs. Max) – the interplanar distance between two neighbouring crystalographic planes with the same Muller indexes (hkl), estimated from the peak maximum; Net Height – peak intensity without background (Cps – counts per second); I/I_{max} – relative intensity; FWHM – full width at half maximum; I. Breadth – integral breadth; Net Area – the peak area without background of copper crystals size electrocrystallized in electrolyte-suspension with carbon nanomaterials (CNMs) No. 1 – 3

XRD peak	Samples	*d* (Obs. Max), Å	Net Height, Cps	I/I_{max}	FWHM $2\theta°$	I. Breadth, $2\theta°$	Gravity C, $2\theta°$	Net Area, Cps x $2\theta°$
Cu (111)	Cu-CNM1 c_2	2.08846	2749	100	0.139	0.171	43.287	470.9
Cu (111)	Cu-CNM1 c_2	1.80844	626	22.8	0.157	0.210	50.428	131.6
Cu (200)	Cu-CNM1 c_2	1.27849	286	10.4	0.151	0.190	74.098	54.36
Cu (111)	Cu-CNM2 c_2	2.08821	3516	100	0.146	0.181	43.296	638.2
Cu (111)	Cu-CNM2 c_2	1.80845	971	27.6	0.156	0.205	50.422	199.5
Cu (200)	Cu-CNM2 c_2	1.27855	182	5.2	0.171	0.311	74.096	41.7
Cu (111)	Cu-CNM3 c_2	2.08858	3341	100	0.159	0.193	43.289	644.5
Cu (111)	Cu-CNM3 c_2	1.80829	487	14.6	0.215	0.277	50.418	134.9
Cu (200)	Cu-CNM3 c_2	1.27849	504	15.1	0.261	0.326	74.115	164.6
Cu (111)	Cu	2.08837	2940	100	0.141	0.182	43.308	536.0
Cu (200)	Cu	1.27851	254	8.6	0.190	0.271	74.129	68.7

The analysis of XRD parameters shows that crystallographic orientation of copper crystallites is changed slowly, when copper composite coatings are formed in electrolyte-suspension with carbon nanomaterials (Table 3). The presence of carbon nanomaterials in electrolyte slightly affects the preferred orientation of crystallites: in all the cases, most of them are oriented in the direction <111>, however, in the presence of CNM2 in the coating there is the lowest number of crystallites oriented in the direction <110>. This is seen from the data presented in column I/I_{max}. The highest distortion of the lattice of copper is typical for the coating electrodeposited in the electrolyte with CNM3 and the lowest one in that with CNM1 (see columns FWHM and I. Breadth) and thus has a strong impact on the morphology of coatings (Fig. 3).

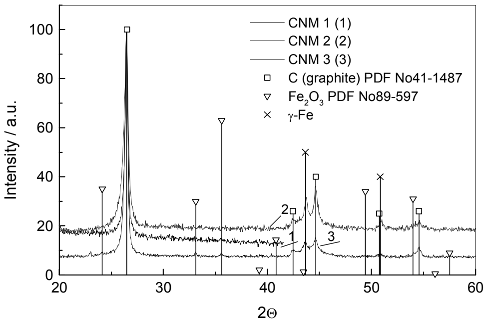


Fig. 5. XRD analysis data of powder of CNMs No. 1-3

Crystalline forms of carbon nanoderivatives in a pure form both in powder and in coatings were identified by XRD analysis with crystals lattices of graphite and a quasi-stable solid FeC_3 solution of angstrom-size (Figs. 5 and 6). It should be noted that the XRD analysis data for other Cu-CNM1 and Cu-CNM2 were similar to the data in Fig. 6 (they are not presented in the paper). The behaviour of graphite in acidic copper electrolyte has a following peculiarity. Hence, graphite oxidizes in the aerated strongly acidic copper electrolyte to graphite oxide, which is soluble in the aqueous electrolyte. It is then that graphene layers can be disengaged and separated. The bonds between the graphene planes are very weak [10 – 12].

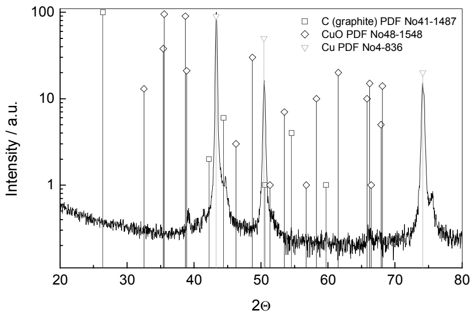


Fig. 6. The XRD analysis data of copper composite coating formed with an additve CNM3

According to [13], positive charged graphene layers in graphite play the same role as positive ions do in crystalline lattice of metals. Similarly to graphite, electrically conductive and positively charged graphene can interact with the cathode and co-deposit with copper. Thus, incorporated into the copper matrix graphite and/or graphene oxides of angstrom size produced changes in copper coating properties and material durability. A new generation of copper nanocomposite coatings has been obtained. The coexistence of these mobile graphene planes improved the characteristics of a new class of graphene-based materials and widened their perspective use in a variety of applications. It is known that graphene has been used as reinforcement in polymer composites as a less expensive substitute for carbon nanotubes [11, 12]. One possible route to put these properties to practical use would be to incorporate graphene sheets in a composite material. Graphite, inexpensive and available in large quantities, unfortunately does not readily exfoliate to yield individual graphene sheets without mechanical or chemical treatment.

CONCLUSIONS

The matrix durability properties were improved when CNMs were incorporated into an electroplated copper matrix. They have a hardening effect on the metal matrix and its hardness increases from 190 kgf·mm^{-2} for a pure copper coating to 340 kgf·mm^{-2} for composites. The investigated carbon nanomaterials stimulated formation of nanostructured coatings with a smoother relief on the nanometer level as compared to that of a pure copper coating. Their electrical properties do not change and have the same cofficient of electric resistivity. The graphite /or graphene oxides incorporated into the copper matrix promoted formation of copper nanocomposites of a new generation.

Acknowledgments

The authors wish to express their gratitude to prof. J. Barkauskas and dr. A. Rukšėnas for the synthesis of the CNMs (Vilnius University, Department of Chemistry, Vilnius, Lithuania)

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Presented at the National Conference "Materials Engineering'2009" (Kaunas, Lithuania, November 20, 2009)