NANOCARBON PRODUCTS OBTAINED FROM SECONDARY RAW MATERIALS FOR MODIFICATION OF COMPOSITION COATINGS

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We obtained carbon composite materials with desired mechanical characteristics, electrical conductivity, magnetic properties, which are widely used in the production of rubbers, cables, sorption materials from various secondary raw materials like wastes of agricultural production (sawdust, fruit bones, coal industry wastes, etc.) with using a new thermochemical method. The composition of the obtained materials was carried out with scanning electron microscopy (SEM); Surface and porosity of the obtained materials were measured by use of instrument Gemini VII. Electrochemical Cu–C coatings were obtained with the use of carbon nanomaterials and tribological properties of the obtained coatings were investigated. The nanocarbon particles with large specific surface area and high porosity could also be used in composition electrocoating (CEC). The optimal concentration of carbon nanomaterials when CECs have best tribological properties has been determined.

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INTRODUCTION

The advanced level of fundamental research of condensed systems has led to a unique opportunity to create new devices and equipment. Today, small devices that consume low energy and at the same time perform the functions of a complex of devices are becoming increasingly popular. To create such devices, new often nano-sized particles play a significant role. The interaction of nanoscale particles with a solid matrix into which these particles are introduced depends on the properties, size and distribution of nanoparticles. Using these materials, we can obtain composite materials with desired mechanical characteristics, electrical conductivity, magnetic properties and likes.

At the same time, the utilization of devices, equipment and materials that are unsuitable for further operation becomes urgent. The ability to extract components useful for further use from them often makes it possible to reduce using and production of new materials significantly.

One of the tasks of the present work is to obtain nanocarbon materials, which are very widely used in the production of rubbers, cables, sorption materials, etc. Appropriately, the waste of the agricultural output containing carbon is also of interest.

In this connection, nanocarbon particles, because of their large specific surface area and high porosity, as subminiature structures may be used in composition electrocoating (CEC). In order to modify the surface of metal products and impart them new properties, composition electrocoatings are the most suitable materials.

The process of CEC (electric composition coatings) formation is influenced by many factors,[1, 2] one among them is the nature of the material used for the modification. It is possible to create modified, composite metal coatings of multifunctional purpose with unique properties by using this type of nanocarbon materials.[3] In conventional coarse-grained coatings these properties cannot be achieved.

The other task of the present work is the creation of CEC on the basis of copper plus nanocarbon, with improved tribological properties and study of the kinetics of the electrodeposition process in the presence of the carbon phase.

EXPERIMENTAL

The measurements were carried out on devices: Hitachi TM 3030 Plus – Scanning electron microscope (SEM) for determination of the composition of the materials (K-series), (Figures 1 and 2; Tables 1, 2, 3) and Gemini VII for determination of surface area and porosity (Table 4).

The coating studies were carried out using the standard copper coating electrolyte of the following composition, g L^{-1}: $CuSO_4 \cdot 5H_2O$ – 200 and H_2SO_4 – 50 at pH = 0.35, with constant stirring with a magnetic stirrer. The concentration of carbon nanoparticles in the electrolyte was from 1.0 to 25.0 g L^{-1}. For better wetting and uniform distribution of the dispersed nanomaterial, the carbon particles were treated with ethyl alcohol, filtered, and thoroughly mixed with the electrolyte. Coatings were applied to the steel plates and the ends of the bushings with an area of 3 cm^2. The copper plate served as the anode. The thickness of the coatings was approximately ~ 25–40 µm. The morphology of the surface of copper coatings was studied using a Euromex microscope.

Tribotechnical tests were carried out on an inertial friction test machine by a particular method at a load of 0.1 MPa, sliding speed 0.25 m s^{-1} and at ambient temperature. The material of the counter body was steel 40×, hardness 60HRC. Running-in was carried out at this same load until the complete contact was established over the entire friction surface. The coefficient of friction was determined for the steady-state friction regime without lubrication.

RESULTS AND DISCUSSION

Tables 1–3 contain data obtained by the SEM measurements for the composition of the samples of sawdust, nectarine kernel and activated coal (particle size 40 µm). The surface and spectra of a sawdust sample studied by SEM, with magnification 40× can be seen on Fig.1 and 2 respectively.

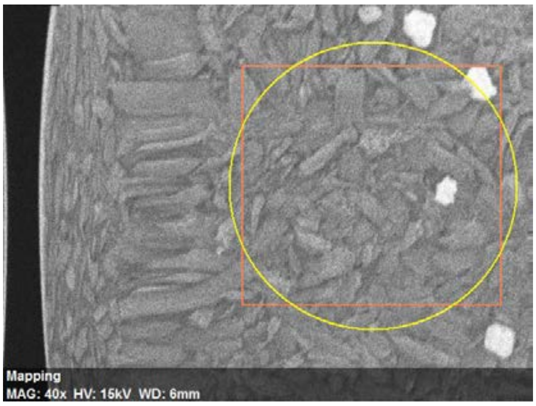


Figure 1. Micrograph of the surface of sawdust sample studied on SEM, with magnification 40×.

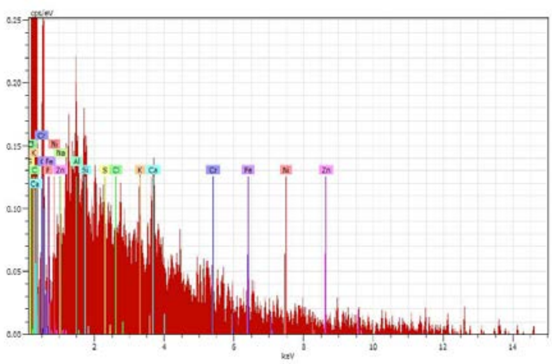


Figure 2. Spectra of sawdust sample studied on SEM.

The amount of zinc, sulfur, and chlorine in the sawdust based product, the amount of zinc, silicon, copper, nitrogen and chromium in the nectarine kernel based product, and the amount of chromium, lead and nitrogen in the activated carbon samples, while the amount of sodium and nickel in all, three products were below the detection limit.

To study the effect of carbon nanomaterial on copper electrodeposition, optimal conditions for obtaining CEP Cu–C were determined.

Table 1. EDAX composition of sawdust sample.

Element	Atomic number	Carbon content, %	
		weight	atom
Carbon	6	91.27	93.74
Oxygen	8	7.65	5.90
Calcium	20	0.41	0.13
Potassium	19	0.21	0.07
Iron	26	0.15	0.03
Chromium	24	0.10	0.02
Aluminum	13	0.08	0.04
Silicon	14	0.07	0.03
Fluorine	9	0.06	0.04

Table 2. EDAX composition of nectarine kernel sample.

Element	Atomic number	Carbon content, %	
		weight	atom
Carbon	6	92.36	94.53
Oxygen	8	6.71	5.15
Iron	26	0.28	0.06
Aluminum	13	0.23	0.10
Potassium	19	0.16	0.05
Chromium	24	0.10	0.02
Calcium	20	0.15	0.04
Sulfur	16	0.07	0.03
Fluorine	9	0.03	0.02

Table 3. EDAX composition of activated carbon sample.

Element	Atomic number	Carbon content, %	
		weight	atom
Carbon	6	89.05	92.26
Oxygen	8	9.10	7.08
Calcium	20	0.77	0.24
Zinc	30	0.30	0.06
Fluorine	9	0.06	0.04
Potassium	19	0.21	0.07
Aluminum	13	0.15	0.07
Silicon	14	0.08	0.03
Sulfur	16	0.07	0.03
Iron	26	0.03	0.01

Table 4. BET surface area, *t*-plot micropores area and *t*-plot external surface area of samples, m^2 g^{-1}

Starting material	BET	Micropores	Outer surface
Sawdust	470.6377	369.8977	100.7400
Nectarine kernel	520.948	434.6722	86.2759
Activated carbon	828.6867	528.3176	300.3691

The current yield (*W*) of copper was studied and was established for the following values of cathode current densities i_c: 0.5, 1.0, 1.5, 2.0, and 3.0 mA cm^{-2}. The experimental data are presented in Figure 3.

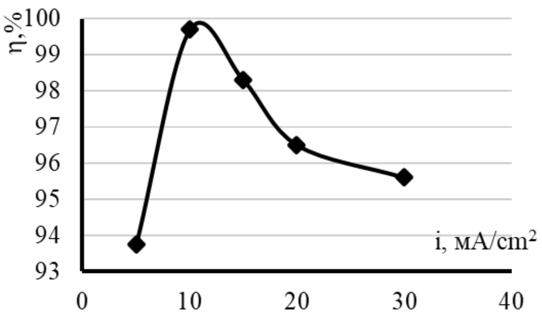
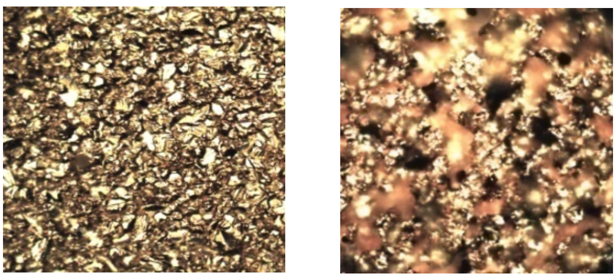


Figure 3. Dependence of copper current output on current density at the content in the electrolyte of carbon nanomaterial 1g L^{-1}.

Figure 3 shows that with a current density of 10.0 mA cm^{-2} the current output is maximal (~100.0 %). Qualitative coatings, uniform in color and without dendrites are formed. At current densities below and above 10.0 mA cm^{-2}, the current output of copper goes down. Further studies of the formation of CEC from this electrolyte were carried out at a current density of 10.0 mA cm^{-2}.

The surface of a copper coating (Figure 4a) comparing to a CEC Cu–C (Figure 4b) changes and the surface of the composite coating became more grained due to the insertion of carbon nanoparticles into CEC.



a **b**

Figure 4. The microstructure of the surface of electrolytic copper (a) and CEC Cu–C (b). Current density i = 10.0 mA cm^{-2}.

The inclusion of carbon nanomaterial into the coating leads to structural changes in the metal matrix, which affects the exploitation properties of the electrolytic deposit. The best tribological properties characterized by a coefficient of sliding friction (f) was available at 15 g L^{-1} carbon concentration. (Table 4). As can be seen from Table 4, the values of the friction coefficient f for Cu-C deposits are three times lower compared to the copper deposit, and a 12-fold decrease in the wear. This is the consequence of the lubrication effect of the dispersed carbon nanomaterial in the copper coatings.

Table 4. Tribological properties of copper coatings at the concentration of dispersed phase of 15.0g/l.

Material	**Friction**			**Wear, mg h^{-1}**
	Rate *v*, m/s	**Temp., °C**	**Sliding coefficient**	
Copper	0.125	55	1.0	102
Cu-C (steel 45 substrate)	0.125	32	0.32	8
Cu-C (stainless steel substrate)	0.125	28	0.29	6

CONCLUSIONS

Nanocarbon materials from various secondary raw materials (sawdust, fruit bones, coal industry wastes, etc.) were obtained by the thermochemical method. The tribological properties of the Cu-C electrochemical coatings obtained with the use of carbon nanomaterials were investigated. The best tribological properties of Cu–C CEC were obtained at 15 g L^{-1} carbon content used during the electrolysis. The values of the friction coefficient f decreased by three times in comparison to copper deposit, with a 12-fold decrease in wear. This is due to the lubricating effect of carbon nanomaterial, which is included in the structure of copper coatings and performs as dry solid lubricants.

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