E-ISSN: 2278-3229

IJGHC, December 2020 –February 2021 Sec.A; Vol.10, No.1, 053-059.
DOI: 10.24214/IJGHC/GC/10/1 /05359.

International Journal of Green and Herbal Chemistry

An International Peer Review E-3 Journal of Sciences

*Available online at* www.ijghc.com

Section A: Green Chemistry

Research Article

CODEN (USA): IJGHAY

# Copper composition electrochemical coatings with carbon material obtained from secondary raw materials

**Samkharadze Z.V., Marsagishvili T.A., Tatishvili G.D., Gachechiladze M.P., Metreveli J.A., Ananiashvili N.Sh., Matchavariani M.N., Tskhakaia E.T., Giorgadze N.V.**

Ivane Javakhishvili Tbilisi State University, R. Agladze Institute of Inorganic Chemistry and Electrochemistry. Mindeli str. 11, 0186, Tbilisi, Georgia,

**Received:** 22 January 2021; **Revised:** 03 February 2021; **Accepted:** 09 February 2021

**Abstract:** The purpose of this work is to study the possibility of obtaining composite electrochemical coatings (CEC) with a copper matrix containing nanocarbon from cheap secondary raw materials with improved running ability. The optimal carbon concentration providing high-quality coatings with improved properties was established. The process of stability of suspensions (containing carbon material obtained from the shell of hazelnuts) in time in water, aqueous solutions of surfactants, and in a nickel-plating electrolyte after dispersion has been investigated. It was found that dispersing has a positive effect on the stability of aqueous suspensions. The addition of an ionic surfactant does not affect the stability of the suspension. Non-ionic surfactants increase the stability of the medium and electrolyte solutions sharply reduce the stability. The wear resistance of carbon-containing composite coatings was investigated. The wear of the CEC copper-carbon material depends on the concentration of carbon material inclusions in the matrix. The maximum wear resistance is achieved at a concentration of the second phase in a suspension of 0.04 g/L, with a carbon content in composite coatings of 6.53-8.06% (mass). It is established that the wear of the CEC is 1.5 times less than the wear of “clean” copper coating.

**Key words:** carbon, secondary raw materials, surfactants, dispersion, suspension, stability.

## INTRODUCTION

Recently, are widely used (CEC), in which substances that change their physicochemical properties (wear resistance, hardness, corrosion resistance) are used as additives. The efficiency of using CEC is largely determined by the nature of the dispersed phase. A promising dispersed material is carbon, which has unique properties such as resistance to high temperatures, high electrical conductivity and chemical resistance to aggressive aqueous solutions. From the literature [1] it is known that due to these properties carbon is used in various industries, including as a solid lubricant in antifriction coatings, which significantly reduce wear and increase the working capacity and reliability of units and mechanisms. As the carbon material, graphene, carbon nanotubes, carbon black and fullerene are used [2- 4]. Currently, the cost price of most of these materials remains quite high.

Present work is devoted to the obtaining of copper-carbon composite coatings, by electrochemical deposition, at constant current, using carbon obtained from secondary raw materials (hazelnut shell), by the original method, which makes cheaper the whole process and final product. It was found that the content of carbon material in composite coatings does not correlate with its content in suspension.

## EXPERIMENTAL

**1.** The carbon material used in this work was obtained by the authors of the article, by an original method, from recycled cellulose-containing raw materials (hazelnut shells), milled in a nano-mill (50-100 nm) and is a dry free-flowing black powder. The physical characteristics of this product were measured using an ASAP 2020 Plus Physisorption Analyzer (specific surface, area and microspore volume), and the chemical composition was determined using a Scanning Electron Microscope (SEM). The ash content (ASTM D1506-15 USA) and the moisture of the product were also measured.

**2.** Further experiments were carried out without the addition of surfactants using only electrolyte dispersion.

For better wetting of particles of carbon material, their surface was treated with ethyl alcohol. The addition of ethyl alcohol does not stabilize the suspension, even with preliminary dispersion, but it can be used as a wetting agent for the dispersed phase, especially since the recipe for copper plating electrolyte includes ethyl alcohol [5].

Composite coatings containing copper with carbon inclusions were deposited on steel (cathode area 3 $cm^2$) from an electrolyte of the following composition g/L: $CuSO_4 \cdot 5H_2O$ –250, $H_2SO_4$– 50, ethyl alcohol - 8. Copper plates served as the anode (the anode area is 10 times the area of the cathode). To determine the optimal conditions for obtaining the CEC, the cathodic current efficiency was studied as a function of the current density. The results showed that 1 A / $dm^2$ is optimal, at which coatings are uniform in color, smooth, without dendrites. Electrolysis temperature: t = 25-30°C. The concentration of particles of the dispersed phase was (g/L): 0.04; 0.06; 0.08; 0.1; 0.4; 1.2.

To better moistening of the carbon particles, it was treated with ethanol and then mixed with electrolyte. The coating thickness was ~ 40µm.

For uniform distribution and reduction of agglomerates, after adding carbon material to the electrolyte, it was exposed by ultrasonic treatment each time (processing frequency 40 kHz, power 60 W).

The morphology and composition of the obtained composite coatings were studied using a TESCAN VEGA 3, LMU scanning electron microscope and Oxford Instruments, AZtec One energy-dispersive spectrometer integrated to it.

A study of the wear resistance of a CEC with copper matrix containing carbon-base material (obtained from hazelnut shells) on a grinding and polishing facility, under constant load and at a fixed speed, by the weight method was made.

## RESULTS AND DISCUSSION

The composition and the physicochemical characteristics of the carbon material obtained from hazelnut shells were studied. The results are given in **Tables 1, 2**. For comparison, the characteristics of factory-made birch activated carbon (BAC-A) are given.

**Table 1:** Physical characteristics of carbon material obtained from cellulose-containing secondary raw material

| Sample | Specific surface, ($m^2/g$) | Micropore area, ($m^2/g$) | Micropore volume, ($cm^3/g$) | Ash content, (%) | Moisture, (%) |
|---|---|---|---|---|---|
| Hazelnut shell | 637.33 | 427.65 | 0.20 | 2.95 | 8.4 |
| Factory-made activated carbon (BAC-A) | 708.70 | 473.78 | 0.21 | 8.95 | 3.55 |

**Table2:** The composition of the carbon material obtained from the hazel nutshells (wt %)

| Sample | C | O | Ca | K | Si | S | Fe | Ni | Cu | Zn | Al | F |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Hazelnut shells | 86.7 | 10.1 | 0.64 | 0.56 | 0.05 | 0.37 | 0.49 | 0.37 | 0.20 | 0.43 | 0.11 | - |
| Factory-made activated carbon (BAC-A) | 89.6 | 8.69 | 0.70 | 0.36 | 0.01 | - | 0.09 | - | 0.38 | 0.01 | 0.04 | 0.17 |

**1.** As can be seen from the table, the physical characteristics of the carbon material obtained from the secondary raw material (hazelnut shell), is not very different from the parameters of activated carbon obtained by the factory method. It should be noted also that the product we received is cheap, because feedstock - cellulose-containing renewable waste, is thermochemically processed with a cheap reagent, without additional activation.

To obtain composite coatings with the required microstructure and mechanical characteristics, the simplest and most effective method is electrochemical deposition. The problem with obtaining composite coatings is the agglomeration of carbon in suspension and the instability of solutions over time. In the literature are listed the ionic [6] and nonionic [7] surfactants, the introduction of which into the initial electrolyte leads to an increase in the stability of suspensions containing carbon nanotubes, fullerene, and graphene as a second phase.

We have identified and tested surfactants that stabilize an aqueous suspension containing a carbon material [8], but do not contribute to the production of CEC with the required characteristics.

However, these substances do not contribute to the obtaining of CEC with the required characteristics. This can be explained by the fact that the structure of the material obtained by us differs from the structure of carbon nanotubes, fullerene, and graphene.

**2.** Composite coatings from electrolyte suspensions with various concentrations of carbon-based material from secondary raw materials were obtained.

**Figure 1** shows photographs of the CEC obtained at constant current at different concentrations of the dispersed phase in the suspension.

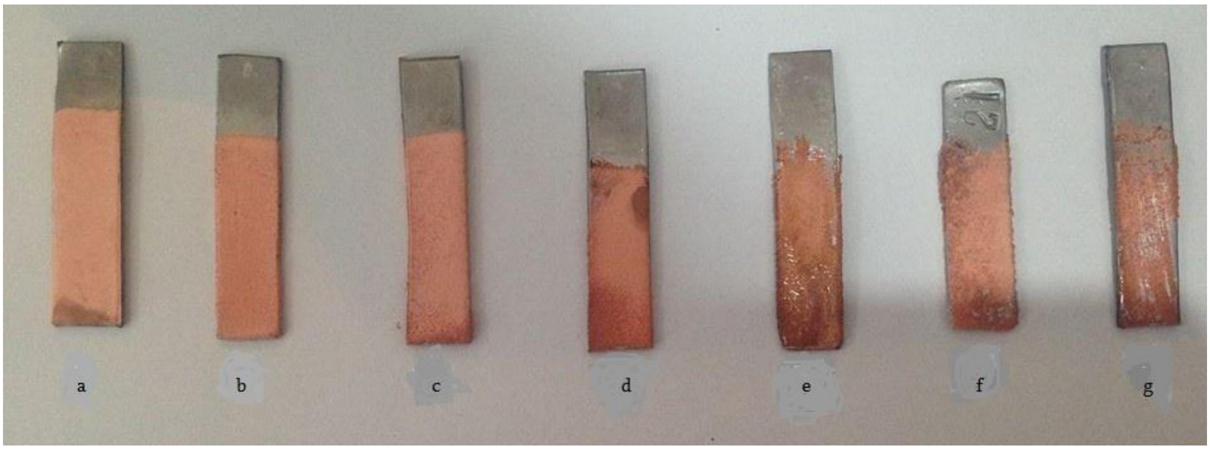


**Figure 1:** Photographs of copper-carbon coating sat concentration of second phase, g/L:
a – 0; b – 0,04; c – 0.06; d – 0.08; e– 0.1; f – 0,4; g – 1,2.

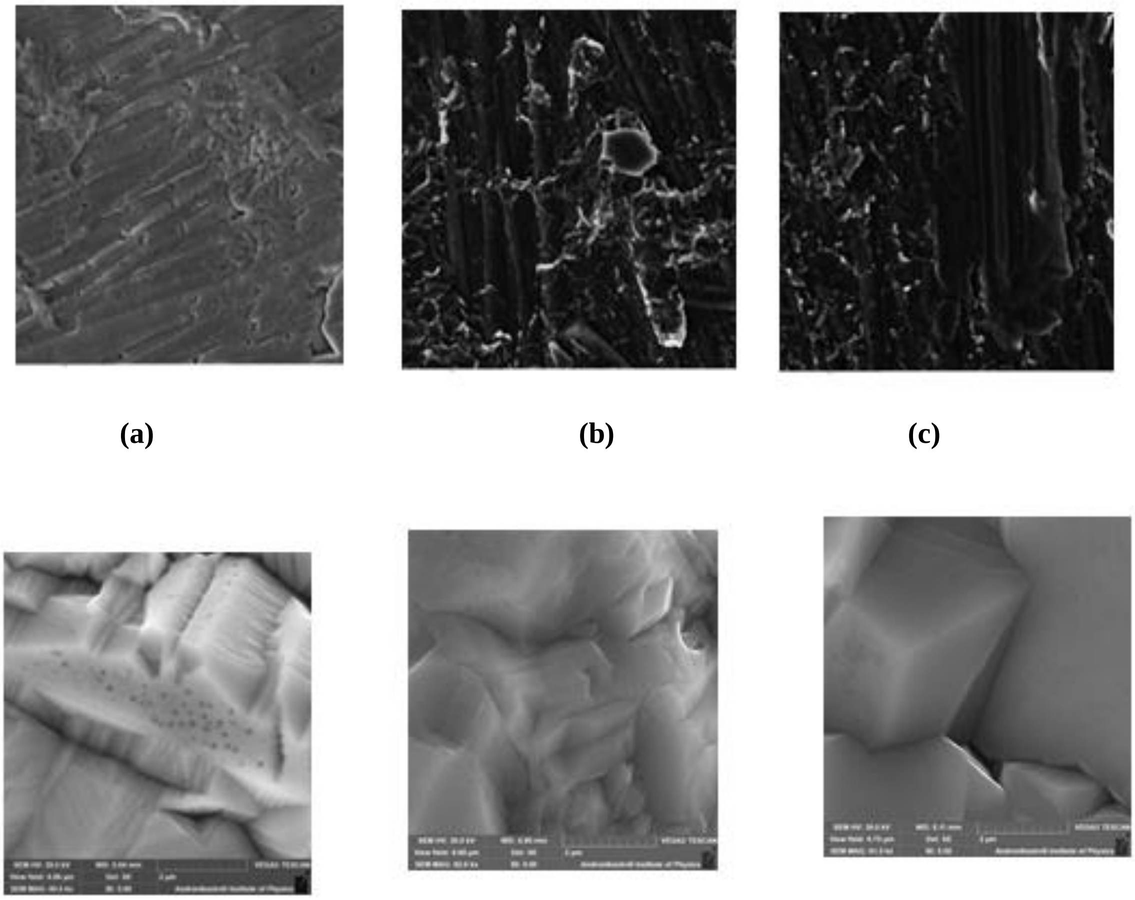
**Figure 1** shows the quality of the coatings. As can be seen from the figure, with an increase in the concentration of the dispersed phase (0.1 g/L or more), the coatings become inhomogeneous. **Table 3** shows the values for the presence of carbon in the composite coatings, from the substrate side and from the electrolyte side, determined using a scanning electron microscope.

**Table 3:** The carbon content in composite coatings Cu-C (weight %)

| # | **Concentration of carbon in suspension, (g/L)** | **Carbon content in composition coatings Cu-C (weight %)** | |
|---|---|---|---|
| | | **Substrate** | **surface** |
| 1 | 0.04 | 2.96-3.69 | 6.53-8.06 |
| 2 | 0.06 | 3.14-3.60 | 4.29-12.18 |
| 3 | 0.08 | 1.32-1.66 | 2.09-2.95 |

The table shows that the content of carbon material in composite coatings does not correlate with its content in suspension. When increasing the concentration of the dispersed phase in the electrolyte (0.04-0.06 g/L), the content of the second phase in the CEC increases. The largest number of carbon inclusions in CEC is observed at a concentration of carbon material in suspension of 0.06 g/L. At the concentration of the second phase in the electrolyte 0.08 g/L, in the suspension the content of carbon material in the CEC decreases, in this case the system probably loses stability and deposition occurs. In addition, the greatest amount of the dispersed phase is contained in the surface layers of composite coatings, for all concentrations of the carbon material in suspensions.

A study of the morphology of coatings on the substrate side **(Fig. 2a to c)** showed that it repeats the morphology of the steel substrate and its study is less interesting. The analysis of the obtained data showed that the formation of copper layers is carried out in large blocks with a crystalline structure **(Fig. 2.d to f).** The totality of some of these blocks rises above the surface by tens of micrometres. The main difference between the samples is that when the content of the carbon phase in the suspension is 0.04 g/L, nanopores with a diameter of up to 150 nm perpendicular to the crystal growth are observed.



**(a)** **(b)** **(c)**

**(d)** **(e)** **(f)**

**Fig.2:** Morphology of CEC coating copper-carbon at various concentrations of carbon in suspension, g/L:

From the side of the substrate a – 0.04; b – 0, 06; c – 0, 08;
From the side of the electrolyte d – 0.04; e – 0, 06; f – 0, 08.

A study was made of the wear resistance of copper-matrix CEC containing carbon material. **Figure 3** shows the experimental dependence of the wear of the copper CEC on the concentrations of the carbon material in the suspension.

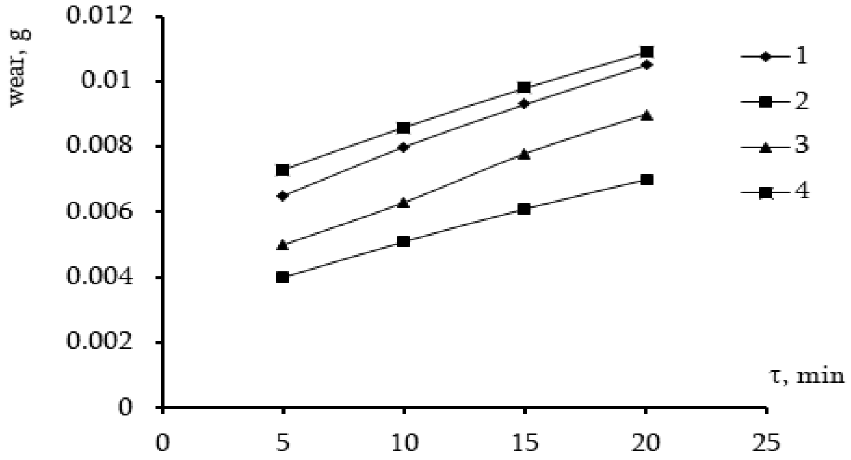


**Fig.3:** Dependence of the wear of the copper CEC on the concentration of the carbon Material in the suspension g/L: 1 - 0; 2 - 0.04; 3 - 0.06; 4 - 0.08.

As can be seen from **Figure 3**, the wear of the CEC depends on a certain concentration of inclusions of carbon material in the matrix. The maximum wear resistance is achieved when the concentration of the second phase in the suspension is 0.04 g/L (curve 2), the carbon content in the CEC is 6.53-8.06 weight %. With an increase in the concentration of carbon material in the suspension (0.06 g/L) when its content in the CECis 4.29-12.18 (weight %), wear also increases, but to a lesser extent than in the previous case (curve 3). Such a relative decrease in wear, with an increase in the concentration of the second phase in the copper matrix, may be due to the combination of individual particles into agglomerates. Such agglomerates in a metal matrix crumble when an abrasive load is applied. With a further increase of the content of the second phase in the suspension (0.08 g/L), the carbon content in the coating decreases (2.09-2.95) and the wear of such a sample is practically equal to the wear of a "clean" sample.

Thus, the CEC with a matrix of copper with inclusions of carbon nanoparticles (obtained from the shell of hazelnuts) of a certain concentration surpasses "clean" coatings in terms of operational characteristics. This is due to the fact that the structure and morphology of composite coatings varies with the number of particles embedded in the metal matrix. Particles of carbon material change the nature of copper electro crystallization and contribute to the formation of such a structure, which leads to an improvement in the characteristics of the CEC. The results obtained in the work lead to the following conclusions:

## CONCLUSION

1. It has been established that carbon material obtained from secondary raw materials (hazelnut shells) can be successfully applied to obtain copper-carbon composite coatings.
2. The introduction of carbon material affects the mechanical properties of copper-carbon CECs.

3. The content of carbon material in composite coatings does not correlate with its content in suspension.
4. The wear of the CEC (Cu-C) depends on the defined concentration of carbon material inclusions in the matrix. Maximum wear resistance is achieved at a concentration of the second phase in a suspension of 0.04 g/L, with carbon content in composite coatings of 6.53-8.06% (weight %).
5. The wear resistance of a CEC obtained from an electrolyte with a carbon material content of 0.04 g /L in the suspension is 1.5 times higher than that of a "pure" coating.

## ACKNOWLEDGEMENT

We are grateful to Scientific Council of the Institute for support.

## REFERENCES

1. Tarasevich M.R. Electrochemistry of Carbon-based materials. “Nauka”, Moscow, Nauka, 1984
2. V.N. Tselyikin, Electrochemical precipitation of composite coatings on the basis of nickel and copper. Published dissertation summary. Saratov, 2009.
3. O.D. Kozenkov, T.V. Ptashina, A.T. Kosilov, D.G. Zhiliakov. Bulletin of Voronezh State Technical University; 2015, 11 (5), 135.
4. R.U. Fomina, G.G. Mingazova, S.V. Vodopianova, V.Sh. Khaibieva, R.S. Saifulin. J. Bulletin of Kazan Technical University, 2013, 21, 306.
5. A.R. Gagatulin, V.S. Frantsuzova, S.A. Bogdanova, Y.G. Galiametdinov. J. Bulletin of Kazan Technical University, 2011, 10, 54.
6. V.G. Konakov, O.Y. Kurapova, N.N. Novik, S.N. Golubev. Materials Physics and mechanics, 2015, 24, 382.
7. Z. Samkharadze, T. Marsagishvili, G. Tatishvili, M. Gachechiladze, J. Metreveli, E. Tskhakaia, 6th International Caucasian Symposium on Polymers and Advanced Materials. Batumi, Georgia, 2019, 92
8. J.V. Vainer, M.A. Dasoyan. Technology of electrochemical coatings. Mashgiz. Moscow, Leningrad, 1962.

***Corresponding Author: Marsagishvili T.A,**

Ivane Javakhishvili Tbilisi State University, R. Agladze Institute of Inorganic Chemistry and Electrochemistry. Mindeli str. 11, 0186, Tbilisi, Georgia,