

Chemical Deposition of Composite Copper - Diamond Coatings on Non-Metallic Substrate

I. Influence of the composition of trilonic electrolyte and of the regime of the deposition on the rate formation of copper matrix

MIHAELA GEORGIEVA^{1*}, MARIA PETROVA¹, DIMITAR DOBREV², ELENA VELKOVA³, DIMITAR STOYCHEV^{1*}

¹Institute of Physical Chemistry-Bulgarian Academy of Sciences, Acad.G.Bonchev Str., Bl.11, 1113 Sofia Bulgaria

²Institute of Mathematics and Informatics-Bulgarian Academy of Science, Acad.G.Bonchev Str., Bl.8, 1113 Sofia, Bulgaria

³Institute of Chemical Engineering-Bulgarian Academy of Science, Acad.G.Bonchev str., Bl.103, 1113 Sofia, Bulgaria

The options to deposit chemically a functional composite copper-diamond coating from trilonic electrolyte have been studied with respect to textile polyethylene terephthalate substrate. The optimal basic composition of the electrolyte for surface treatment and the optimal conditions of deposition has been found from the viewpoint of the deposition rate, respectively the thickness of qualitative layer of the copper matrix. A systematic study of the influence of different types and concentrations of surface active agents (SAA) and different temperatures of the electrolyte at continuous air flow stirring has been realized, aimed co-deposition of copper metal-matrix composite, containing diamond particles (sizes, varying within the range 3-70µm).

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It is known that in the case of composite copper coatings, obtained by electrochemical deposition, the amount of co-deposited dispersing agents is a small one [1]. The same study reports that the concentration of the synthetic diamond powder, included in the composite coatings, depends on the properties of the metallic matrix both in the case of electrochemical deposition and in the case of chemical deposition. It has been established that in order to obtain a high concentration of diamond particles in the coating, the size of the metal grains should be 5-10 times smaller than the size of the diamond particles, while the micro-hardness of the matrix should be not less than 1200-1500 MPa. Upon co-depositing of metals, such as Ni and Co, together with diamond particles, the smaller in size crystallites of the metal matrix, being deposited, are attached on the periphery of the diamond particle and they grow up around it and they hold it strongly in the growing coating. For this reason the concentration of the diamond in these coatings is quite high. The large crystallites of metals, such as copper, are commensurable with the dimensions of the diamond particle and in the process of electro-crystallization they somehow lift up the particle in the process of the coating growth. This hampers its incorporation into the matrix.

According to [2] the reason for the formation of composite coatings from acidic electrolytes, designed for coating copper electrochemically (in the presence of particles of Al_2O_3 , TiO_2 , $BaSO_4$ and SiO_2 in the electrolyte) with low content of the dispersion agent, included inside them, is the presence of chlorine ions.

A supposition is put forward about the inhibiting effect of the chlorine ions. It is considered that the chlorides (bromides), adsorbed on the cathode, represent a barrier layer for the adhesion of the dispersing agent, and for this reason it is not included in the coating.

In [3] it is reported the effect of changing some operations upon the characteristics of the composite coatings $Cu-Al_2O_3$ and $Cu-TiO_2$ prepared electrochemically.

The authors established that the effectiveness of electro-deposition of copper from the selected solution is comparatively high (98.5%) and it is growing up with the increase in current density and in the pH value of the solution. The content of inert particles in the coating reaches 1.7% for Al_2O_3 and 2.3% for TiO_2 . The investigations have shown that there exists a direct correlation between the concentration of inert dispersed particles in the electrolyte, their morphological form and the hardness of the dispersion coating.

In a series of publications [4-7] chemical methods for coating copper have been described in the form of nano-particles or micro-particles of different dispersion agents, used in case of preparing composite materials by some other methods. The metalized dispersed particles are most often pressed at high temperature and pressure and the obtained products, which are distinguished with very good physico-mechanical properties, good thermal conductivity and electrical conductivity, find wide application in the techniques. For example in [4] SiC_w is coated with copper and the so prepared particles are pressed at 600°C, 300MPa for 15 min in air medium.

On the basis of the literature survey one can state that the composite coatings based on a matrix of the so called "soft metals" (Cu, Zn and Cd) have not been studied extensively. At the same time, the copper composite coatings, especially those containing diamond powder, can be utilized for the finishing treatment of hard materials (corundum, hard alloys etc.), as in the soft copper matrix, in the course of operation of the instrument, the small particles of the processed material are being included and in this way they do not injure its surface [1]. Moreover, in micro-electronics and production of components for it, as well as in many other fields of contemporary techniques, composite materials are needed, deposited on a flexible support, which possess sufficiently high electrical conductivity and thermal conductivity. In this connection the current literature describes methods for chemical

* email: stoychev@ipc.bas.bg; mgeorgieva@ipc.bas.bg

deposition of copper coatings on different kinds of materials [8-10].

The aim of the present work was to study the options for electroless deposition of composite copper coatings, containing diamond particles of different dimensions, on flexible support of polyethylene terephthalate.

Experimental part

Samples of textile polyethylene terephthalate (PETF) were used in their function as substrate, upon which the copper coatings were deposited chemically, having a surface area of 8 cm² (2 x 2 x 0.05cm). These were subject to preliminary treatment, in accordance with the following technological scheme:

- etching in alkaline solution (200 g/l NaOH for 15 min, at 60°C);
- activation in colloidal solution of PdCl₂ (0.8 g/L PdCl₂, 20 g/L SnCl₂ and 3M HCl) for 5 min at room temperature;
- acceleration (treatment in alkaline solution of NaOH for 5 min, at room temperature).

The so treated samples-supports were immersed in a solution for depositing copper coating chemically, which has been reported in details in [11]. The main component of the solution for chemical copper coating is copper sulfate (10 g/L), while the reducing agent is formaldehyde (10 g/L). Na₂-EDTA was used as complexing agent (40 g/L), as well as various stabilizers, buffering compounds and surfactant. As a surface active agent we investigated the influence of three types of organic compounds: nonylphenol-polyglycoether (Veronal), Na-laurylsulfonate (NaLS) and polyethylene glycol with molecular mass 4000 (PEG-4000).

To this basic solution we added diamond powder with different sizes of the particles – varying from 3 up to 70 μm, which were studied at concentration 5 g/L. The pH of the solution for coating copper chemically was 12.8÷13, while the studied temperature interval was varied from 20 to 60°C. The time interval of the immersion treatment was varied from 1 to 5 h.

The relative thickness of the deposited copper coating was determined gravimetrically – based on the difference in the weights of the samples made of PETF prior to and after the deposition of the studied coating i.e. $\Delta m = M - M_0$, where Δm is the mass of the deposited dispersion coating, M is the mass of the sample after its coating with the composite film, and M₀ is the initial mass of the samples-supports.

The morphology and the structure of the coatings, as well as the distribution of the particles over their surface were studied by means of scanning electron microscopy (SEM) using a JSM 6390 electron microscope (Japan). The average amount of co-deposited diamond particles per square centimeter was determined based on the number of diamond particles, counted on the surface of the composite coating by SEM (the counting was done in three arbitrarily chosen zones).

Results and discussions

Kinetics of deposition of copper coating on PETF substrate

The results, obtained in the course of observing the rate of deposition of pure copper coating (not containing any diamond dispersed particles) from the electrolyte studied by us for coating copper chemically, are represented in table 1. One can see in the table that up to about the 60th minute of deposition the quantity of deposited copper is practically proportional to the time interval of deposition and thereafter – until the 300th min the rate of deposition of

Table 1

DEPENDENCE OF THE MASS – Δm , g (RELATIVE THICKNESS – δ , μm) OF THE COPPER COATING ON THE TIME INTERVAL OF DEPOSITION AT ELECTROLYTE TEMPERATURE 45°C.

	10 min	30 min	60 min	300 min
Δm , g	0,0119	0,0255	0,0653	0,1026
δ , μm	1,52	3,26	8,34	13,10

copper starts to decrease gradually. This effect could be attributed to the possible occurrence of the reaction of Cannizzaro whereupon as a consequence of the interaction of formaldehyde with sodium hydroxide its effective concentration in the working solution is decreasing. The obtained results were used as initial database in the course of our further investigations on the influence of the added surfactants and dispersing agent, respectively with the aim to optimize the electrolyte composition and the regime of preparing the copper matrix, into which the diamond particles were included.

Study of the influence of the surfactants, added to the electrolyte, on the kinetics of the copper coating deposition

The surface tension of most electrolytes, intended for coating metals chemically, although comparatively low, does not aid sufficiently well the wetting of the larger share of the dispersing agents added to them. For this reason, which is leading to their agglomeration, they are not distributed homogeneously in the bulk of the solution, when they are being added to the electrolytes for chemical deposition of metal composites. The surface tension between the electrolyte solution and the dispersed particles can be reduced by adding a suitable surfactant compound. Thus for example in [12] it is proposed to treat the diamond powder with 50% solution of HCl, and thereafter to neutralize it and to treat it with a solution of surfactant.

The results from our investigations, carried out after the addition of three kinds of surfactants to the electrolyte for chemical copper coating Veranol, NaLS and PEG-4000, show that NaLS is the most suitable one from the viewpoint of the rate of deposition of the copper coating (table 2).

Obtaining composite copper-diamond particles coatings at continuous air flow stirring

The results, obtained under this regime of deposition, are represented in figure 1. Here figure 1a illustrates an average statistical segment of the surface of not covered by composite coating flexible PETF support at low microscope magnifications. The fibrous structure of the polyethylene terephthalate material is seen in it and some sections with grooves (obtained during the pressing), which are distributed uniformly having a rhomboid form. Figure 1b-1g shows at greater microscopic magnifications the respective groove sections (fig. 1b, 1d, 1f) and a fibrous zone (fig. 1c, 1e, 1g) for samples, upon which a composite coating is deposited from an electrolyte, containing 5 g/L diamond particles of sizes respectively: b, c – 3/5 μm; d, e – 7/10 μm and f, g – 14/20 μm. It is seen in the so represented figures that the diamond particles are distributed uniformly, whereupon with the increase in their size the number of the co-deposited particles is decreasing. This number is decreased drastically for sizes larger than 7/10 μm, while in the case of sizes above 20 μm it does not represent practical interest.

VERANOL					
	0.1 g/l	0.3 g/l	0.5 g/l	-	-
Δm	0,0216	0,0224	0,0206	-	-
δ	(2.76)	(2.86)	(2.63)	-	-
NaLS					
	0.1 g/l	0.3 g/l	0.5 g/l	0,01 g/l	0,05 g/l
Δm	0,0816	0,0724	0,0514	0,0387	0,0399
δ	(10.42)	(9.25)	(6.56)	(4.94)	(5.10)
PEG-4000					
	0.01 g/l	0.03 g/l	0.060 g/l	0.60 g/l	-
Δm	0,0214	0,0229	0,0261	0,02	-
δ	(2.73)	(2.93)	(3.33)	(2.55)	-

Table 2
Dependence of the mass - Δm , g (relative thickness - δ , μm) of the deposited copper coating on the kind and on the quantity of the used surfactant (electrolyte temperature 45°C, τ_{dep} - 1h)

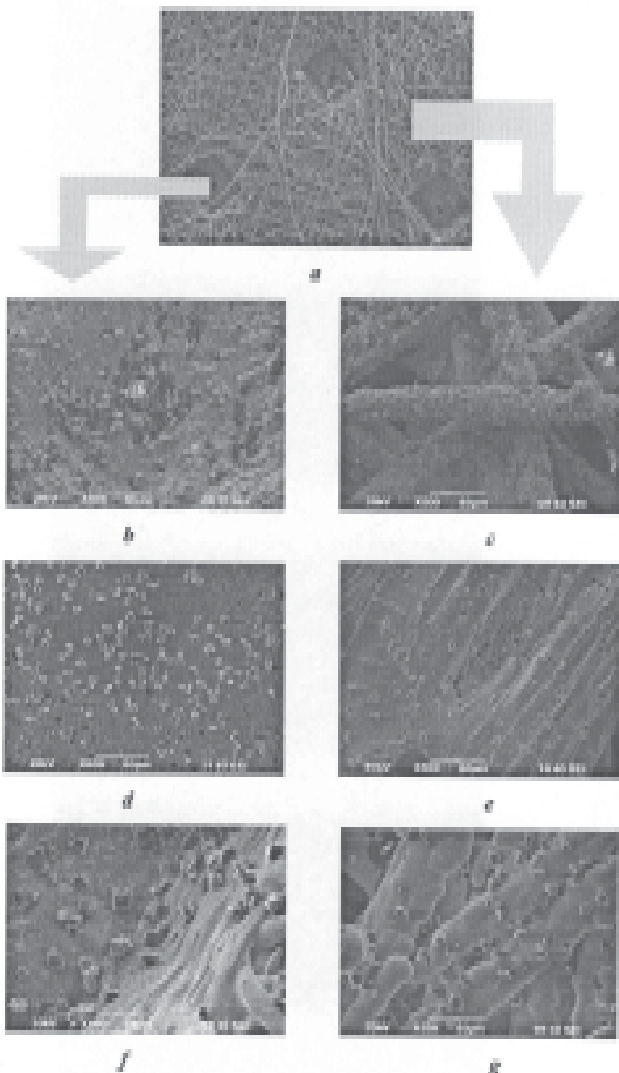


Fig.1. SEM micrographs of the surface of PETF substrate non-covered with copper composite coating (a-200x) and of the composite coating, deposited under regime "a": at the bottom of the groove sections (b,d,f-500x) and on the fibers in the fibrous zone of PETF substrate (c,e,g-500x). Sizes of the diamond particles: b,c - 3/5 μm ; d,e - 7/10 μm ; f,g- 14/20 μm . τ_{dep} - 1h

The information, supplied by this regime of deposition for all sizes of the studied particles, for time of deposition 1 hour, is listed in table 3. On the basis of the obtained data it follows that in the case of continuous stirring of the electrolyte, with the increase in the size of the diamond particles, the thickness of the copper matrix becomes lower. The number of the co-deposited diamond particles in the composite coating is also considerably decreased.

The main conclusion that one can draw about this regime of deposition of the copper composite coating is that in this case the quantity of co-deposited diamond particles satisfies completely only for the sizes up to 3/5 μm . For diamond particle sizes of 7/10 μm the result is acceptable, while at the greater sizes of the added to the working electrolyte particles the number of the co-deposited ones is not satisfactory.

As far as data are available in the literature that the temperature of the electrolyte can influence the quantity of the co-deposited dispersion agent in a metal matrix-host, it was of some interest to study the temperature effect in the case of trilonic electrolyte at this regime. The obtained results (for sizes of the diamond particles 14/20 μm and 20/28 μm) are included in table 4. On their basis it is possible to draw the following conclusion.

Increasing the temperature of the electrolyte in the cases of the systems studied by us the number of the co-deposited diamond particles is growing up considerably. This means that the temperature of the electrolyte for preparing a

	3/5 μm	7/10 μm	14/20 μm	20/28 μm	60/70 μm
$\Delta\text{m, g}$	0,2359	0,0653	0,0555	0,0282	0,0362
$\delta, \mu\text{m}$	30,12	8,34	7,09	3,60	4,65
N/cm^2	111534	35900	5478	3262	3023

	14/20 μm		20/28 μm	
	$\Delta\text{m,g}$ ($\delta, \mu\text{m}$)	N/cm^2	$\Delta\text{m,g}$ ($\delta, \mu\text{m}$)	N/cm^2
30°C	0,0069 (0,88)	No inclusion	0,0054 (0,69)	No inclusion
45°C	0,0555 (7,09)	5478	0,0282 (3,60)	3262
60°C	0,0424 (5,41)	11395	0,0458 (5,63)	5545
80°C	0,0455 (6,32)	24395	0,0496 (6,33)	22214

copper composite coating with diamond particles incorporated in it can be a favorable factor for increasing the number of the particles.

Conclusions

The present investigation reveals the possibilities of utilizing trilonic electrolytes for coating a copper film chemically with the aim to obtain composite copper-diamond coating. Optimal conditions have been established from the viewpoint of rate of deposition, respectively thickness of the copper coating – this includes the composition of the electrolyte and the regime of deposition. Having once the optimal composition then further the options have been studied for co-deposition of diamond particles in the copper matrix at continuous air flow stirring regime. It is found that this composition and regime for chemical co-deposited copper-diamonds composite layer are appropriate for the size of the diamond particles down to 10 μm . To obtain composite layers satisfying co-deposited number of diamond particles with sizes higher than 10 μm , it is necessary to optimize the hydrodynamic regime of deposition described in the second part of this study [13].

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Table 3

DEPENDENCE OF THE MASS - $\Delta\text{m, g}$ (RELATIVE THICKNESS - $\delta, \mu\text{m}$) OF THE COPPER COATING, DEPOSITED FROM TRILONIC ELECTROLYTE AND THE NUMBER OF THE DIAMOND PARTICLES (N) REGISTERED ON ITS SURFACE ON THEIR SIZE (FROM 3/5 TO 60/70 μm) IN CASE OF CONTINUOUS AIR STREAM STIRRING (THE REGIME "a"), $\tau_{\text{dep}} - 1\text{h}$

Table 4

DEPENDENCE OF THE THICKNESS OF THE COATING AND THE NUMBER OF CO-DEPOSITED DIAMOND PARTICLES ON THE TEMPERATURE OF THE ELECTROLYTE AT CONSTANT AIR STREAM STIRRING OF THE ELECTROLYTE. THE SIZE OF THE ADDED TO THE ELECTROLYTE DIAMOND PARTICLES WAS 14/20 μm AND 20/28 μm , $\tau_{\text{dep}} - 1\text{h}$

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