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

II. Influence of the hydrodynamic regime on the number of co-deposited diamond layers

MIHAELA GEORGIEVA[1]*, MARIA PETROVA[1], DIMITAR DOBREV[2], ELENA VELKOVA[3], DIMITAR STOYCHEV[1]*

[1]Institute of Physical Chemistry-Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl.11, 1113 Sofia Bulgaria
[2]Institute of Mathematics and Informatics-Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl.8, 1113 Sofia, Bulgaria
[3]Institute of Chemical Engineering-Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl.103, 1113 Sofia, Bulgaria

The options to deposit chemically a functional composite copper-diamond coatings from trilonic electrolyte have been studied with respect to the influence of the air flow stiring conditions of deposition. They have been elucidated in regard to the structure of the copper metal-matrix and the number of the co-deposited diamond particles. Optimal composition has been established as well as the best hydrodynamic regime for chemical deposition of the functional composite copper-diamond coatings (with respect to the number of the co-deposited diamond particles observed by SEM and the thickness of the composite layer) upon the addition of an appropriate surfactant compound Na-laurylsulfonate (NaLS) to the electrolyte, which is preventing the agglomeration and precipitation of the diamond particles in the electrolyte.

Keywords: functional composites; coating; metal-matrix composites (MMCs); non-metallic substrate

Composite materials obtained on the base of diamond particles as synthetic powders are used for improving the physicomechanical properties of various materials and surfaces. Compared to other hard abrasive and wearresistant materials, diamond is characterized by one of the highest microhardness, which gives diamond dispersed composites (tools covered by these composites) considerable wear and abrasive resistance. A basic characteristic of these composites is that diamond particles are incorporate into the base deposition matrix metal, thus forming the second phase. Most often, electroless nickel and cobalt alloys are used as a matrix material for diamond composites [1-13].

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, Cd, Ag) have not been studied extensively [14-17]. 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 [18]. 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 supports [19-20].

The aim of the present work was to study the options for electroless co-deposition of copper coatings and diamond particles of different grit size, on flexible support of polyethylene terephthalate on the base of an electrolyte investigated in [21].

Experimental part

Samples (surface area of 8 cm² - 2 x 2 x 0.05 cm) of flexible textile polyethylene terephthalate (PETF) were used as a substrate. These were subject to preliminary treatment, in accordance with the following technological scheme: 1) Etching in alkaline solution; 2) Activation in colloidal solution of $PdCl_2$; 3) Acceleration in accordance with conditions described in [21].

The so treated samples-supports were immersed in a solution for depositing copper coating chemically, which has been reported in details in ref. [11, 21]. 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 concentrations 1 – 7.5 g/L. The dispersion coatings were obtained upon continuous and/or interrupted stirring by air stream at different concentrations of NaLS.

The relative thickness of the deposited copper coating was determined gravimetrically [21]. The morphology and the structure of the coatings, as well as the distribution of the diamond particles 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

Influence of the hydrodynamic regime on the kinetics of deposition of the composite coating (copper matrix – diamond particles) and the quantity of the co-deposited dispersed particles

It is known that the hydrodynamic regime exerts substantial influence on the thickness of the deposited composite coating, as well as on the quantity of co-deposited dispersoids. We estimated the influence of the hydrodynamic regime (stirring by air flow at a rate of 100mL/min in 250 mL of electrolyte) on the thickness (δ, μm) of the copper composite coating and the amount of co-deposited diamond particles (number (N)/cm²), in the course of our experimental runs based on the mass (Δm,

g) of the deposited coating and in view of the number of the diamond particles registered on the surface of the samples.

Regimes of deposition were investigated, in which the time intervals of rest and consecutive stirring by air bubbling through the electrolyte, from which the composite coating was being deposited, were varied as follows:

a) continuous air flow stirring;
b) 2 min of air flow stirring, 10 min of rest;
c) 2 min of air flow stirring, 5 min of rest;
d) 2 min of air flow stirring, 2 min of rest;
e) 2 min of air flow stirring, 1 min of rest;
f) 1 min of air flow stirring, 1 min of rest.

The measurements in the cases of regimes „a" [21] and "b" have been carried out with all sizes of the diamond particles (3/5, 7/10, 14/20, 20/28 or 70/60μm), studied by us, while in the cases of the other regimes - „c", „d", „e" and "f" – the measurements have been carried out only with diamond particles of size 14/20μm.

The process of co-deposition of copper and diamond particles on PETF substrate for all regimes of stirring of the working electrolyte was accomplished in the course of 1 or 5 h (total time interval for deposition of the composite coating) at temperature 45±0.5°C. The quantity of the dispersed diamond phase was 5g/L – one and the same for all electrolytes and regimes.

Regime "a": Continuous air stream stirring (τ_{dep} – 1 h)
These results in detailed are presented and discussed in [21].

Regime "b": 2 min of air stream stirring, 10 min of rest (τ_{dep} – 1 h)
The inclusion of diamond particles, having dimensions 3/5μm, in the working electrolyte determines a high degree of inclusion of the dispersed diamond phase in the copper metal matrix (fig. 1), which is being deposited respectively at the bottom of the pressed groove concave sections and on the polyester fibers of the PETF substrate material. The number of the co-deposited diamond particles under the conditions of this regime is twice higher in comparison with the regime "a" [21].

The deposited copper matrix is built up of crystallites of dimensions ~1μm, forming spheroidal agglomerates of size ~2-5μm, which include the diamond particles (fig. 1c, 1d). Although the thickness of the copper coating, deposited in the course of one hour, is commensurable with the size of the diamond particles, there appear also some non-covered with copper diamond particles, which are clearly observable.

The results, obtained during co-deposition of copper with diamond particles of dimensions 14/20μm, are illustrated in figure 2. It follows from them, that the bigger size of the diamond particles, added to the working electrolyte, determines a relatively smaller number of included particles, both on the bottom of the gauffered blind aperture, as well as on the polyester fibers.

Both in the case of one-hour deposition, as well as five-hour deposition of copper coating, the diamond particles, due to their larger size, in comparison to the thickness and to the size of the crystallites of the copper coating, remain sticking out of the copper matrix (fig. 2c). The structure of the copper matrix both on the flexible substrate of PETF, as well as on the diamond grains, is homogeneous, whereupon the size of the copper crystallites, deposited on the PETF substrate and of the diamond particles is practically the same (fig. 2d).

The effect of the longer 5-h time interval of deposition of copper consists in depositing a thicker copper coating both on the flexible substrate, as well as on the diamond particles, which are covered with an uninterrupted copper crust.

Upon increasing the size of the diamond particles, added to the working electrolyte, up to 20/28μm, their number, deposited together with the copper matrix on the flexible polyester substrate, decreases even more. The structure of the copper layer and that of the copper coating deposited on the diamond crystallites is analogous to those, obtained in case of layers with inclusion of diamond particles having a size of 14/20μm.

The next increase in the size of the diamond particles, added to the working electrolyte, up to 70μm practically leads to a total absence of incorporated particles in the copper coating of the material. If there happen to be some attached diamond particles at all, their attachment is to the bottom of the grooves of the PETF material. There were
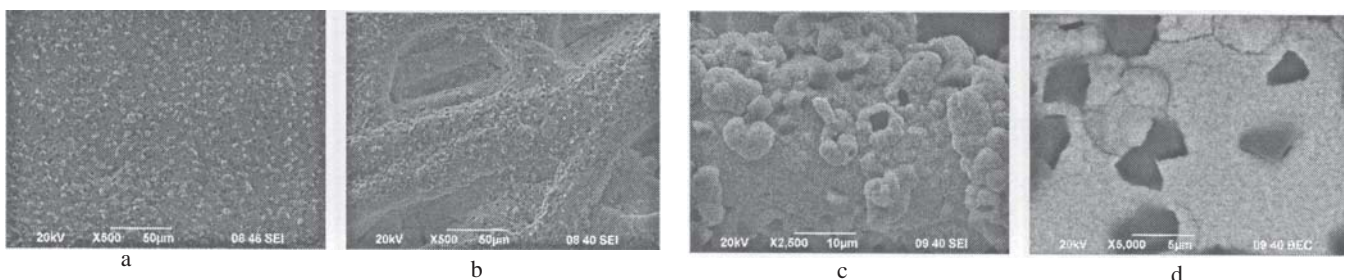

Fig.1. SEM micrographs of the surface of the composite coating (in case the diamond particles have size 3/5μm in the working electrolyte), deposited under the conditions of regime "b": at the bottom of groove concave sections (a,c) and on the fibers (b-d) in the fibrous zone of PETF substrate
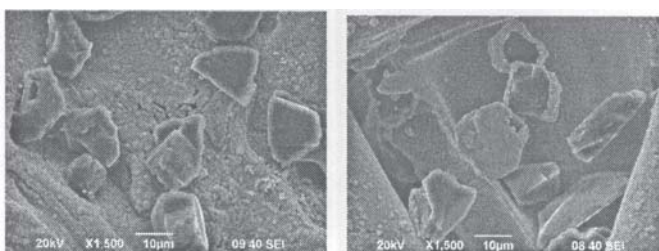

Fig.2. SEM micrographs of the surface of the composite coating (in case of diamond particles size in the working electrolyte 14/20μm), deposited under the conditions of regime "b": at the bottom of the groove concave sections (a) and on the fibers (b) in the fibrous zone of the PETF support
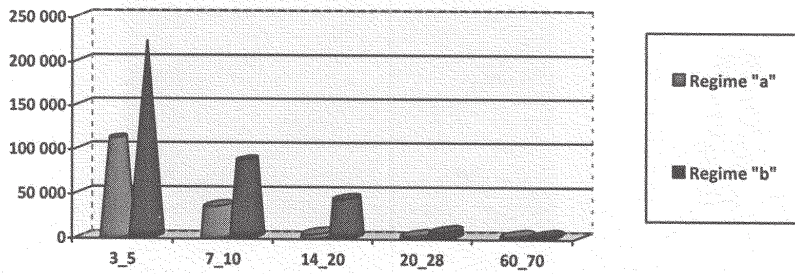
Fig.4. SEM micrographs of the surface of the composite coating (size of the diamond particles in the working electrolyte 14/20μm), deposited under the conditions of regime "c": at the bottom of the concave sections (a,c) and on the fibers (b,d) in the fibrous zone of the PETF substrate
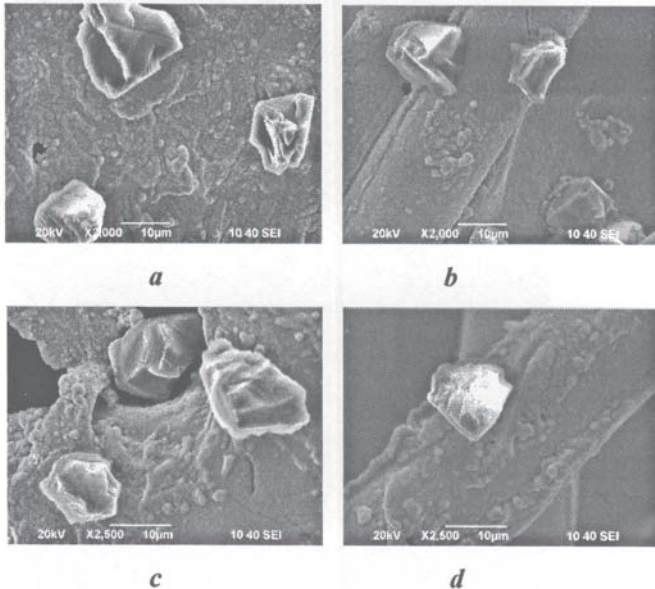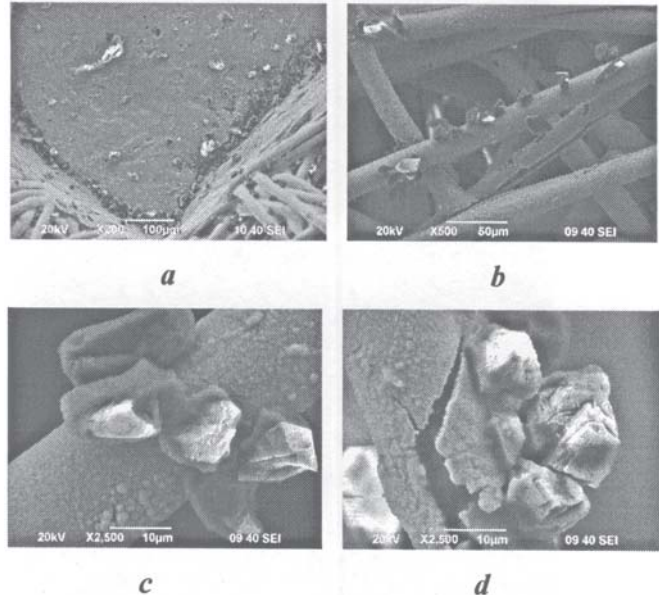
Fig.5. SEM micrographs of the surface of the composite coating (size of the diamond particles in the working electrolyte 14/20μm), deposited under the conditions of regime "f": at the bottom of the concave sections (a) and on the fibers (b-d) in the fibrous zone of the PETF substrate

practically no diamond particles, registered to be included on the fibers.

A representative set of data in figure 3, extracted for the sake of comparison from the results obtained for regime "a" and "b". One can observe in it that:

- with the increase in the size of the diamond particles in the electrolyte for depositing a composite coating, the number of the particles, co-deposited in the copper matrix, becomes lower;

- under the conditions of the regime of continuous stirring of the electrolyte, at all sizes of the diamond particles, the number of those co-deposited in the copper matrix is smaller;

- the studied trilonic electrolyte for chemical deposition of copper composite coatings (copper-diamond) enables the deposition of a sufficiently large number of diamond particles, representing practical and technological interest, in the cases when the diamond particle size is lower than 20μm;

- obviously in the case, studied by us, the concept is valid that the number of the co-deposited particles of the dispersion agent depends directly on the ratio between the size of the crystallites, building up the metal matrix, and that of the dispersed phase (in our case the diamond phase) particles.

Regime "c": 2 min of air stream stirring, 5 min of deposition without stirring (τ_{dep} – 1 h)

Figure 4 illustrates the results, obtained in the case of deposition of the composite coating under the conditions of the regime of stirring "c", from an electrolyte that contains 5 g/L diamond particles of dimensions 14/20μm.

It is seen in figure 4a, 4b, characterizing the concave groove sections and the fibrous zones at higher magnifications, that the attachment of the diamond particles to the copper matrix is accomplished by the copper film, which grow up on them. Obviously the copper bridges between the copper films covered diamond particles and the copper coating itself, which grew up on the PETF substrate, determine the strength of the bonding between the separate components/phases of the composite, which pre-conditions the much greater sticking force of attachment between them in comparison to the purely adhesion forces.The studies, carried out at much larger magnifications, show that the composite copper coating, deposited on groove concave zones and on polyester fibers of the substrate, is growing up layer by layer (fig. 4c, d).

Regime "d": 2 min of air stream stirring, 2 min of deposition without stirring (τ_{dep} – 1 h)

The results, obtained in the course of investigating the copper composite coating, deposited under the conditions of regime "d", from an electrolyte, containing 5 g/L diamond particles of size 14/20μm, showed (the SEM micrographs are not shown) that in comparison to regime "c" the number of the diamond particles co-deposited in copper matrix is even smaller (fig. 6) and they are partial covering with a copper film.
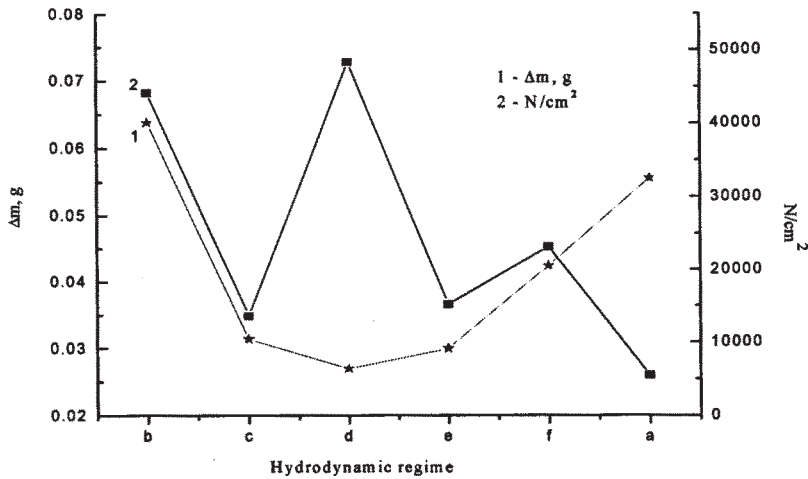
Fig.6. Dependence of the mass of the deposited dispersion copper coating ("m) and the number of diamond particles (N/cm²) co-deposited in it under regime "stirring-rest" (a-f) of the electrolyte
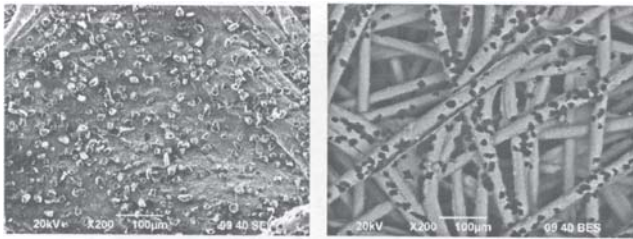

Fig.7. SEM micrographs of the surface of the composite coating (size of the diamond particles in the working electrolyte 14/20μm), deposited under the conditions of copper deposition regime "a": at the bottom of the concave sections (a) and on the fibers (b) in the fibrous zone of the PETF substrate

Regime "e": 2min of air stream stirring, 1min of deposition without any stirring (τ_{dep} – 1 h)

The data, obtained under this regime of deposition, have showed that under these conditions of co-deposition of diamond particles on the copper matrix the number of these particles is also the smallest, compared to that under regimes a-d (fig. 6). What are making impression are practically the absence of copper coating on the diamond particles, as well as the appearance of some defects in the copper coating in the zones of contact between the fibers.

Regime "f": 1 min of air stream stirring, 1 min of deposition without any stirring (τ_{dep} – 1 h)

Under the conditions of regime "f" the co-deposition of the diamond particles is occurring mainly on the periphery of the grooves, pressed in the material (fig. 5a). Beyond these sections, on the fibers (fig. 5b), the diamond particles are being co-deposited in quantities, commensurable with those under regimes "c"-"e".

In comparison with the concave sections of the material, the quantity of the included diamond particles on the fibers of the material is less and at the same time the structure of the deposited copper coating (the matrix) is large-granular (fig. 5c, d). Under the conditions of this regime of deposition the diamond particles are covered thickly with a copper film, which is formed of spheroid macro-crystals. Although it is seldom observed, in the case of piling up of many diamond particles, co-deposited closely to one another, one observes cracking and separation of the copper matrix from the PETF fibers (fig. 5d).

Figure 6 represents the summarized results, characterizing the influence of the hydrodynamic conditions upon the variation in the mass/the thickness of the deposited copper coatings and the number of the co-deposited diamond particles (which should be accepted as a relative quantity, as it is determined by the average number of the diamond particles, counted on the surface per one square centimeter of the composite coating). It follows from here that: The greatest number of co-deposited diamond particles is observed under regime "b" – time interval of stirring 2 min, time interval of rest – 10

min; The greatest thickness of the copper coating is observed under regime "d" – time interval of stirring 2 min, time interval of rest – 2 min; The conditions of regime "b" can be accepted as optimal.

On the basis of these results, in the course of our further investigations we used always the conditions of the regime "b".

Influence of the NaLS under the conditions of the hydrodynamic regime of deposition "b"

In the light of the above represented results, [21] and figure 6 – we carried out the next cycle of investigations, in which we applied the trilonic electrolyte for coating copper film, containing various concentrations of the NaLS, under the optimal conditions of the hydrodynamic regime "b" of deposition of the composite copper coating.

The effect of NaLS on the inclusion of the dispersion phase on the surface of the fibers and at the bottom of the pressed concave zones was studied under the following conditions of depositing a copper coating:

- preparation of composite coating with diamond particles, which have been treated in advance for 15 min in solutions, containing 0.01g/L, 0.05g/L or 0.1g/L NaLS. After their preliminary treatment, without any washing, the particles were added (5 g/L) to the electrolyte for coating copper film and the deposition of the composite coating was carried out at an electrolyte temperature of 45⁰C in the course of 1 hour;

- preparation of composite coating with diamond particles, which have not been treated in advance in solution, containing NaLS. The depositing of the composite coating on PETF substrate was carried out from an electrolyte, intended for coating copper film chemically, to which 0.1 g/L NaLS and 5 g/L diamond particles have been added directly. The temperature of the electrolyte and the time interval for depositing a copper coating are identical as those in item 1).

Experimental results with diamond particles of size 14/20μm

The preliminary treatment of the diamond particles in solution, containing NaLS, leads to a substantial increase

		$C_{NaLS} = 0$ g/l, continuous stirring (regime "a")	$C_{NaLS} = 0$ g/l, periodical stirring (regime "b")	$C_{NaLS} = 0.01$ g/l (regime "b")	$C_{NaLS} = 0.03$ g/l (regime "b")	$C_{NaLS} = 0.05$ g/l (regime "b")	$C_{NaLS} = 0.1$ g/l (regime "b")
1 g/l diamond powder	Δm,g	0.0284	-	0.0497	-	-	0.032
	(δ, μm)	(3.63)		(6.35)			(4.09)
	N/см^2	6067	-	51605	-	-	14549
2.5 g/l diamond powder	Δm,g	0.0466	-	0.0679	0,0401	0,0527	0.0383
	(δ, μm)	(5.95)		(8.67)	(5,12)	(6,73)	(4.98)
	N/см^2	4648		51670	36534	522246	20147
5 g/l diamond powder	Δm,g	0.0555	0,0638	0.0471	0,0361	0,0458	0.0703
	(δ, μm)	(7.09)	(8.14)	(6.01)	(4,61)	(5,63)	(8.98)
	N/см^2	5478	44200	58000	22214	51605	118982
7.5 g/l diamond powder	Δm,g	0.0261		0.0386	-	-	0.0346
	(δ, μm)	(3.33)		(4.93)			(4.42)
	N/см^2	6415		68067	-	-	120345

Table 1
INFLUENCE OF THE CONCENTRATIONS OF NALS AND OF THE DIAMOND PARTICLES (SIZES 14/20 μm) IN THE ELECTROLYTE ON THE THICKNESS OF THE DEPOSITED COPPER COATING AND THE NUMBER OF THE DIAMOND PARTICLES, INCLUDED IN IT AFTER TIME INTERVAL OF DEPOSITION
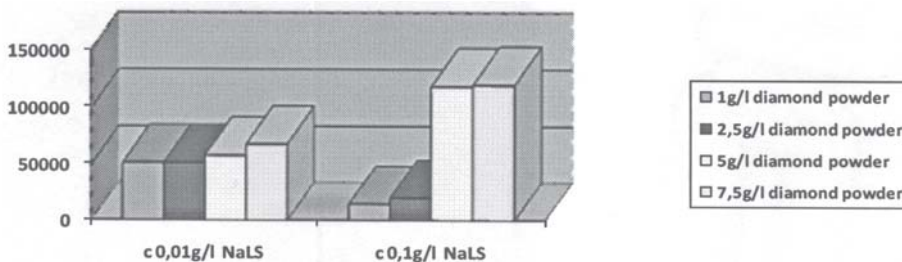

Fig.8. Dependence of the number of the diamond particles, included in the chemically deposited copper coating, on the concentrations of NaLS and of the diamond particles in the electrolyte

in their number both on the fibers of the polyester material, as well as on the concave zones of the PETF substrate. Figure 7 represents the typical SEM micrograph of the surface of the composite copper-diamond coating, obtained in the electrolyte, studied by us, intended for coating a copper film, to which diamond particles have been added, which have been treated in advance in a solution, containing 0.1g/L NaLS.

The juxtaposition of these results, with those represented in figure 2 shows that the preliminary treatment of the diamond particles with a surfactant leads to a multiple increase in the number of co-deposited particles in the copper matrix. In this aspect the effect of NaLS is even more strongly expressed, when it has been added as a component of the electrolyte intended for chemical deposition of composite copper-diamond coating. The summarized information about the influence of the concentrations of: the diamond particles and that of the NaLS, added to the electrolyte for composite copper coating deposition, on the thickness of the composite coating and on the number of the diamond particles, included in it, is given in table 1.

An excerpt has been taken for comparison from the results in table 1 for the number of the co-deposited diamond particles as a function of the concentrations of

NaLS and the diamond particles in the electrolyte and it is given in the histogram (fig. 8).

It is seen from the obtained results (table 1 and fig. 8) that: in the absence of NaLS and upon continuous stirring of the electrolyte (regime "a") the number of the diamond particles, co-deposited in the copper matrix, is practically only slightly dependent on their concentration in the electrolyte; in the absence of NaLS and periodical stirring of the electrolyte the number of the co-deposited diamond particles can grow up several times (regime "b"); the low concentrations of NaLS influence effectively the number of the co-deposited diamond particles at low concentrations of the diamond particles in the working electrolyte (up to 2.5 g/L), while at high concentrations (5-7 g/L) the effectiveness of the action of NaLS is expressed to a maximum degree at NaLS concentration of 0.1 g/L.

Experimental results with diamond particles of size 20/28 and 60/70µm

Tables 2 and 3 represent the results, obtained in an analogous study (NaLS was added as component of the electrolyte) on the number of the co-deposited diamond particles, when their size is bigger – 20/28µm and 60/70µm.

It can be seen from the obtained results that at the larger sizes of the diamond particles, contained in the electrolyte, the number of the co-deposited such particles in the copper

		$C_{NaLS} = 0$ g/l, continuous stirring (regime "a")	$C_{NaLS} = 0$ g/l, periodical stirring (regime "b")	$C_{NaLS} = 0.01$ g/l (regime "b")
1h	Δm, g (δ, μm)	0.0282 (3.60)	0.0334 (4.27)	0.0619 (7.90)
	N/см^2	3262	8046	97208
5h	Δm, g (δ, μm)	0.0432 (5.51)	0.049 (6.82)	0.1157 (14.77)
	N/см^2	7395	8134	20131

Table 2
INFLUENCE OF THE REGIME OF DEPOSITION AND THE PRESENCE OF NaLS IN THE ELECTROLYTE ON THE THICKNESS OF THE DEPOSITED COMPOSITE COATING AND THE NUMBER OF THE DIAMOND PARTICLES INCLUDED IN IT HAVING SIZE 20/28 μm, AT CONCENTRATION OF THE DIAMOND PARTICLES IN THE ELECTROLYTE 5 g/L

		$C_{NaLS} = 0$ g/l, continuous stirring (regime "a")	$C_{NaLS} = 0$ g/l, periodical stirring (regime "b")	$C_{NaLS} = 0.01$ g/l (regime "b")	$C_{NaLS} = 0.1$ g/l (regime "b")
1h	Δm, g (δ, μm)	0.0362 (4.65)	0.041 (5.24)	0.0695 (8.87)	0.0824 (10.52)
	No. of part./cm^2	3023	3262	4886	9721
5h	Δm, g (δ, μm)	0.0471 (6.01)	0.0529 (7.79)	0.0799 (10.20)	0.0989 (12.63)
	No. of part./cm^2	7503	4567	5980	8046

Table 3
INFLUENCE OF THE REGIME OF DEPOSITION AND THE PRESENCE OF NaLS IN THE ELECTROLYTE ON THE THICKNESS OF THE DEPOSITED COMPOSITE COATING AND ON THE NUMBER OF DIAMOND PARTICLES OF SIZE 60/70 μm INCLUDED IN IT, AT CONCENTRATION OF THE DIAMOND PARTICLES IN THE ELECTROLYTE 5 g/L

matrix becomes lower. Thereupon one can state that: under the conditions of the regime of continuous stirring of the electrolyte (regime "a") the increase in the time interval of deposition leads to increase both in the thickness of the composite coating, as well as in the number of the co-deposited diamond particles; the above-mentioned effect of increase both in the thickness of the composite coating, as well as in the number of the co-deposited diamond particles under the conditions of the hydrodynamic regime "b" is observed also in the case of larger particle sizes; the addition of NaLS determines a considerable increase in the number of the co-deposited diamond particles in the composite coating. This effect becomes lower with the increase in the time interval of deposition of the composite coating (at τ = 5 h), which is most probably due to a decrease in the effective concentration of the diamond particles in the electrolyte, as a consequence of their depletion in the course of longer duration of the operation with one and the same electrolyte. The increase in the concentration of NaLS leads to a significant increase in the number of the co-deposited diamond particles also in the cases of sizes 20/28 and 60/70μm.

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 varying their dimensions in a wide range. On the basis of a systematic study carried out with respect to the influence of hydrodynamic regime of deposition on the structure of the copper matrix and on the number of co-deposited diamond particles the optimal hydrodynamic conditions have been selected, corresponding to a regime of 2 min stirring and 10 min of rest of the working electrolyte, which is carried out in consecutive cycles in the course of 1 to 5 h, depending on the desired thickness of the composite layer. The investigated composition and the regime for chemical deposition of composite copper-diamond coating have been optimized with respect to the number of the co-deposited diamond particles and the thickness of the composite coating upon the addition of a suitable

surfactant to the electrolyte – sodium lauryl sulfonate (NaLS), which prevents the agglomeration and the precipitation of diamond particles in the solution.

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