Electroless deposition of composite Co-P-diamond layers and their polishing properties

D. Stoychev[1*], E. Dobreva[2], N. Razkazov[2], M. Stoycheva[3], N. Koteva[2]

[1] Institute of Physical Chemistry "Acad. R.Kaischew", Bulgarian Academy of Sciences, Sofia 1113, Bulgaria

[2] Technical University, Bulgaria

[3] Institute of Electrochemistry and Energy Systems "Acad. E. Budewsky", Bulgarian Academy of Sciences, Sofia 1113, Bulgaria

The options for electroless deposition of Co-P-diamond composite layers on substrate of polyethylene terephthalate have been studied using alkaline chloride electrolytes and NaH_2PO_2 as reducing agent. The effects of the concentration (1-25 g/L) and the particle size (0,03 – 100 μm) of the dispersed phase (diamond powder), added to the working electrolyte have been studied, with the view to determine the amounts of diamond particles co-deposited in the cobalt matrix, as well as the mass and the average thickness of the composite layers being formed. Thereupon the ranges of sizes and concentrations of the diamond particles in the electrolyte have been defined, at which the quantities of the particles included in the cobalt matrix are satisfactory in regard to the formed composite layers, applicable to the production of flexible PETF/Co-P-D polishing discs. Preliminary testing of the polishing effect of the *PETF/*Co-P-D discs has been carried out under laboratory conditions (the discs contain diamond particles of sizes: 63-75; 38-45; 20-28; 14-20; 7-10; 3-7 and 0.03-0,5 μm) on limestone samples and on two kinds of marble samples. The obtained results for the values of the coefficients R_z and R_a are completely in accordance with the requirements for finishing surface polishing treatment of similar materials.

Keywords: Electroless deposition, composite Co-P-Diamond layers, Polishing properties

INTRODUCTION

The chemically deposited cobalt coatings are used in the technique mainly in view of their hardness, resistance to abrasion and magnetic properties. By chemical cobalt coating it is possible to obtain composite layers/materials possessing great hardness, on the basis of co-deposition and incorporation into the solid cobalt matrix of some very hard nano- or micro-particles such as ceramic materials, carbon nanotubes, diamond, SiC, boron nitrides and others.

One of the important advantages of the chemical method for deposition of metal coatings is the option to cover dielectrics with metal coatings. In this case the operation "activation" is determining a series of properties of the deposited composite coating on their surface. It exerts considerable influence on the quality and on the properties of the system coating-matrix, as it determines the nature and the character of the distribution of the active sites, on which the process of reduction of the metal ions is taking place, and thereupon it influences also the co-deposition of the solid dispersoid.

It is known that the alkaline electrolytes are the most suitable for the electroless deposition of cobalt coatings. The occurring of the process in acidic medium is unfavorable due to the low rate of deposition [1, 2].

The authors [3] compare the chemical (electroless) deposition of composite coatings on the basis of nickel or cobalt matrix and SiC particles. They established substantial differences in the process of deposition of the two metals-matrixes, although they have similar physical and chemical properties. Maleic acid is added to the electrolytes for depositing metal coatings in its function as a stabilizer. Its optimal concentration depends on the nature of the deposited metal. It has been ascertained that the inclusion of SiC in the coating is of greater quantity in the case of cobalt matrix compared to the nickel one. The observation of the morphology of the composite coatings Ni-P/SiC and Co-P/SiC also shows that the nickel coating is compact and it is shaped in regular sphere grains, while the cobalt coating is characterized by higher smoothness, needle-like

structure and in some cases by formation of pitting defects.

The presence of SiC in the solution reduces the rate of deposition of the metal matrix. This effect is most probably due to the fact that the solid-non-metal particles exert no catalytic effect on the oxidation of NaH_2PO_2. They are adsorbed on the substrate, upon which the coating is being deposited and this hinders the contact between the metallic surface and the electrolyte thus reducing the quantity of the deposited metal. The investigations show that OH^- groups are being adsorbed on the surface of SiC. In this connection it is supposed that the negative charge of the particles adsorbed on the substrate repels the anion of the reducing agent and therefore the rate of deposition is decreased.

The authors [4] consider the properties of the chemically deposited composite coating of Co-P/PTFE having a thickness of 5-10 μm, which is deposited on the steel surface. The reasons for choosing cobalt as a metal matrix of the composite coating are its good functional properties and strong adhesion to the surface of steel articles. The composite coating contains 9% PTFE, 5.1 % P and 85.9% cobalt. The properties and the structure of the coating have been studied by X-ray diffraction analysis, scanning electron microscopy and electron specroscopy for chemical analysis. The results show that it has a good adhesion to the substrate, hexagonal crystalline structure and great hardness. The investigations, carried out so far, have established a definite orientation of the particles of PTFE. The fluorine atoms are dominating on the surface of the coating, while the phosphorus and the cobalt are included uniformly in the form of elemental phosphorus and Co^{3+}. The Co-P/PTFE composite layers possess good tribological properties. Their hardness is increasing upon heating them.

Chemically deposited nano-composites on the basis of nickel and cobalt (Ni-P/diamond; Ni-W-P/SiC; Ni-W-B/SiC; Co-B/diamond; Co-P/diamond; Ni-P/diamond; Ni-P/SiC), which could be used as alternative to hard chromium coatings, have been reported in [5]. It is known that toxic chemicals are being used during the electrodeposition of chromium coatings – the salts of the six-valence chromium Cr^{6+}. Aiming at protection of the environment and improving the working conditions there is an ongoing search of alternatives to chromium coatings. Ref. [5] provides evidence that such alternatives could be the nano-composite cobalt coatings, characterized by improved properties with respect to hardness,

losses due to abrasion and corrosion stability. This search has ascertained that in analogy to coating nickel chemically, the deposition of cobalt coating, the properties of the composite coating appear to be function of the content of P or B, which depend on the concentration of reducing agent; the conditions of treatment at high temperature; the nature and the concentration of the dispersed phase and others. In the case of chemical coatings for example the incorporation of nanosized diamond particles improves their hardness, which in its turn promotes the stability of the performance of the so prepared abrasive material. Co-P coatings (4 to 6 wt.%), which have 500 nm size of the included diamond particles has identical or even better properties compared to the hard chromium coating. Therefore very often the composite coatings, containing nanoparticles of great hardness, are better than the conventional coatings deposited chemically or electrochemically.

Ref. [6] analyzes the influence of particles of diamond, B_4C, BN, WC on the properties of electrochemically deposited cobalt coatings, containing phosphorus. It has been reported that Co-P (2-5%) shows identical or even better properties than the hard chromium coating, and the stability of Co-P/B_4C (22%) to abrasion wearing away is greater.

Studies on the corrosion stability of electrochemically deposited cobalt coatings (nano-Co and nano-Co-P with a thickness of about 50 μm), carried out in the course of 1000 hours in a salty fog and compared to the hard chromium coating ($\sim$ 100 μm) prove that both kinds of cobalt coating are more durable. The content of P in the coating improves also its corrosion stability. According to these authors there are no published data on the corrosion resistance of composite cobalt coatings, which do not contain any phosphorus.

Other composite systems, containing nano- or micro-particles, have also been studied with the view to replace the chromium coatings [7]. Electrochemically prepared nano-crystalline cobalt with or without co-deposited WC has also been studied, as well as chemically deposited nickel (Ni-P) with diamond particles of various size (150, 1000, 2000 and 150÷1000 nm), Ni-P, Ni-Co-P, Co-P and Ni-B with or without incorporated diamond particles. Their adhesion, thickness, hardness and abrasion resistance have been studied. The results show that all the chemically deposited coatings (Ni-P, Co-P, Ni-Co-P having included diamond particles) possess the needed adhesion, hardness and tribological properties and they can eliminate

the necessity of using chromium coatings in the technique.

Based on the current literature survey a conclusion was drawn that the chemically deposited Co-P composite coatings (with included very hard particles) are characterized by better properties both in the aspect of improving the adhesion, as well as with respect to the hardness, resistance to abrasion and their corrosion protective ability in comparison to the electrochemically or chemically deposited composite coatings based on the Co-B matrix. There are, however, quite a few data on chemically deposited composite coatings on non-metal substrate (and in particular flexible ones), which could illustrate directly the inter-connection between the nature and the quantity of the co-deposited dispersoids on one hand, and their tribological properties on the other hand.

In this aspect the aim of the present study was to establish the options of chemical (electroless) deposition of Co-P matrix on flexible substrate of polyethylene terephthalate (PETF), with some diamond particles included in the matrix. The realization of such a system (PETF/Co-P-Diamond) represents special interest for the production technology for polishing and finishing flexible disks for surface treatment of different mineral and metal materials (rocky materials, non-ferrous metals, alloys and others).

EXPERIMENTAL SECTION

All the studies have been carried out using samples of dimensions 9 x 2 cm, cut out of gauffer (wafer-type) sheet of polyethylene terephthalate (non-woven textile of thickness 1,5 mm), placed horizontally in the working cell of volume 1 L. These were treated following the technological scheme:
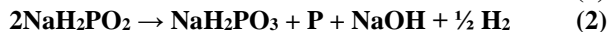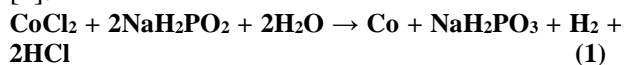
Preliminary treatment
- etching (15 min) in solution of 250 g/L NaOH at 60°C;
- treatment (5 min) in 3M HCI solution at room temperature;
- activation (5 min) in colloid solution of PdCl$_2$ (0.4 g/L) at room temperature;
- acceleration (5 min) in solution of NaOH (40 g/L) at room temperature.

The chemical coating of cobalt was done in an electrolyte with a composition, optimized (concerning: concentrations of CoCl$_2$, NaH$_2$PO$_2$, pH and co-deposited P, evaluating hydrogen and thickness of the cobalt coating, respectively) previously by us [8], which contains:

CoCl$_2$.6H$_2$O	30 g/L
NaH$_2$PO$_2$.H$_2$O	20 g/L

Sodium citrate	100 g/L
NH$_4$Cl	50 g/L

at pH 9 and temperature of the solution 90°C, in accordance with the following reaction mechanism [1]:

$$CoCl_2 + 2NaH_2PO_2 + 2H_2O \rightarrow Co + NaH_2PO_3 + H_2 + 2HCl \quad (1)$$
$$2NaH_2PO_2 \rightarrow NaH_2PO_3 + P + NaOH + \tfrac{1}{2} H_2 \quad (2)$$
$$NaH_2PO_2 + H_2O \rightarrow NaH_2PO_3 + H_2 \quad (3)$$

The options to deposit composite Co-P-diamond coatings were studied, whereupon different concentrations (1 - 25 g/L) of synthetically prepared diamond particles (diamond powder) were added to the basic electrolyte for coating cobalt chemically and their sizes varied: 0,03-0,5 μm, 3-5 μm, 7-10 μm, 14-20 μm, 20-28 μm and 60-70 μm. To improve the degree of wetting of the diamond particles they were subjected to preliminary treatment in a solution of sodium laurylsulfonate (0.1 g/L) for 15 min at room temperature. The composite coatings were prepared under continuous or interrupted (2 min of stirring/10 min of rest) stirring of the solution with magnetic stirrer (speed of 400 rpm).

The morphology and the structure of the composite coating, as well as the distribution of the included particles, were studied by means of scanning electron microscopy (electron microscope model YSM C390 - Japan), while their mass and the conditional thickness were determined gravimetrically. The content of co-deposited phosphorus was determined by X-ray fluorescent analysis.

The polishing effect and the tribological behavior of the composite layers, deposited on model disks of PETF (with diameter of 70 mm and thickness of 2 mm), was tested on the home-made apparatus specially designed by us. It enabled realizing the experiments at various velocities of rotation of the studied disk (100 up to 3000 rpm) and at pressure upon the tested samples (limestone, two kinds of marble and granite) 0.2-2 kg/cm^2. The changes in the surface roughness (average deviation, R$_a$ and attitude roughnesses, R$_z$) were determined by means of profile-recorder-profile gauge Perthen.

EXPERIMENTAL RESULTS AND DISCUSSION

3.1. Influence of the size and the concentration of the diamond particles in the working solution on the thickness and quantity of co-deposited diamond particles in the chemically deposited composite layers.

Table 1. Dependence of the thickness of the chemically deposited composite Co-P-D coatings on PETF substrate on the concentration (1 to 25 g/L) of the diamond particles, dispersed in the working solution, with particle size 0.03 – 0.5 μm. Deposition time interval 30 min.

Diamond particle size, μm	Concentration of dispersed diamond, g/L	Thickness of the deposited composite coating, μm	Weight of the deposited composite coating, g
0,03 - 0,5	1,0	0,61	0,0097
0,03 - 0,5	3,0	0,68	0,0108
0,03 - 0,5	5,0	0,74	0,0117
0,03 - 0,5	7,0	0,93	0,0150
0,03 - 0,5	10,0	1,60	0,0257
0,03 - 0,5	15,0	1,78	0,0285
0,03 - 0,5	25,0	3,77	0,0597

During the first cycle of the investigations carried out the effect of the diamond particle size was studied as well as their concentration in the solution for chemical cobalt deposition on the mass, respectively on the thickness of the deposited composite coating of Co-P(5%)-Diamond denoted as (Co-P-D). The obtained results are represented in Tables 1-3.

Table 1 comprises the results, obtained in the course of the formation process of the composite coating from solutions containing 1 to 25 g/L diamond powder, which is characterized by particle size 0.03 – 0.5 μm. It is seen from the table that with the increase in the concentration of the particles in the electrolyte the mass is growing up, respectively the thickness, of the deposited composite layer. A similar effect has also been observed by other investigators in the chemical deposition of nickel composites coatings, including polycrystalline diamond particles in them [9]. The explanation put forward in this case is connected with the presence of catalytically active sites, catalyzing the oxidation reaction of $H_2PO_2^-$, determined by the specific morphological peculiarities of the diamond particles and/or by residual transition metals used (and included) in its synthesis [10,11].

SEM observations of the same samples confirm this supposition. It is seen from the represented micrographs that the reduction of the cobalt ions is accomplished both on the growing cobalt matrix as well as on the diamond particles. This leads to a substantial increase in the number of the diamond particles co-deposited in the cobalt matrix (Fig.1b-e) and as a result of their coalescence there is a substantial growth in the thickness of the composite layer with the increase in the concentration of the particles in the electrolyte. While in the case of diamond particles concentration in the working solution 1 g/L, the number of the particles in the Co matrix co-deposited upon the fibers (Fig.1a) is very low (Fig.1b), at the other concentrations (Fig.1c – 3 g/L, Fig. 1d – 7 g/L and Fig.1e – 10 g/l) it is growing up considerably, following a proportional dependence.

Thereupon an increase in the number of grains is observed, respectively in the roughness of the composite Co-P-D coating. This result is in accordance with the above made supposition about the role of the specific morphological peculiarities of the diamond particles and/or the presence of catalytically active transition metals included in them during the synthesis. In support of such a hypothesis comes the registering of increased frequency of appearance of spheroid agglomerates of diamond particles with the increase in particles concentration in the electrolyte (Fig.1d, 1e), being formed as a consequence of the chemical deposition of Co on the diamond particles. Their "self-cobalting" process, occurring in parallel to the process of formation of the cobalt matrix on the PETF substrate, is leading (as a consequence of superficial forces of interaction) to formation of such agglomerates and their growing up. Obviously, their addition to the cobalt matrix is accomplished via "bridges" of metallic cobalt (Fig.1d, 1e). The further increase in the concentration of the diamond powder in the working solution does not change substantially the number of the particles co-deposited in the Co matrix, but it is only increasing the amount of spheroid agglomerates grown on the surface of the composite coating. For this reason it can be accepted that the optimal working concentration for this size of the diamond particles lies within the interval 3-5 g/L.

It should be pointed out as an important feature of the process of formation of the composite Co-P-D coatings on gauffer (wafer) type of substrate of PETF the considerable differences in the numbers of co-deposited diamond particles on the fibers and
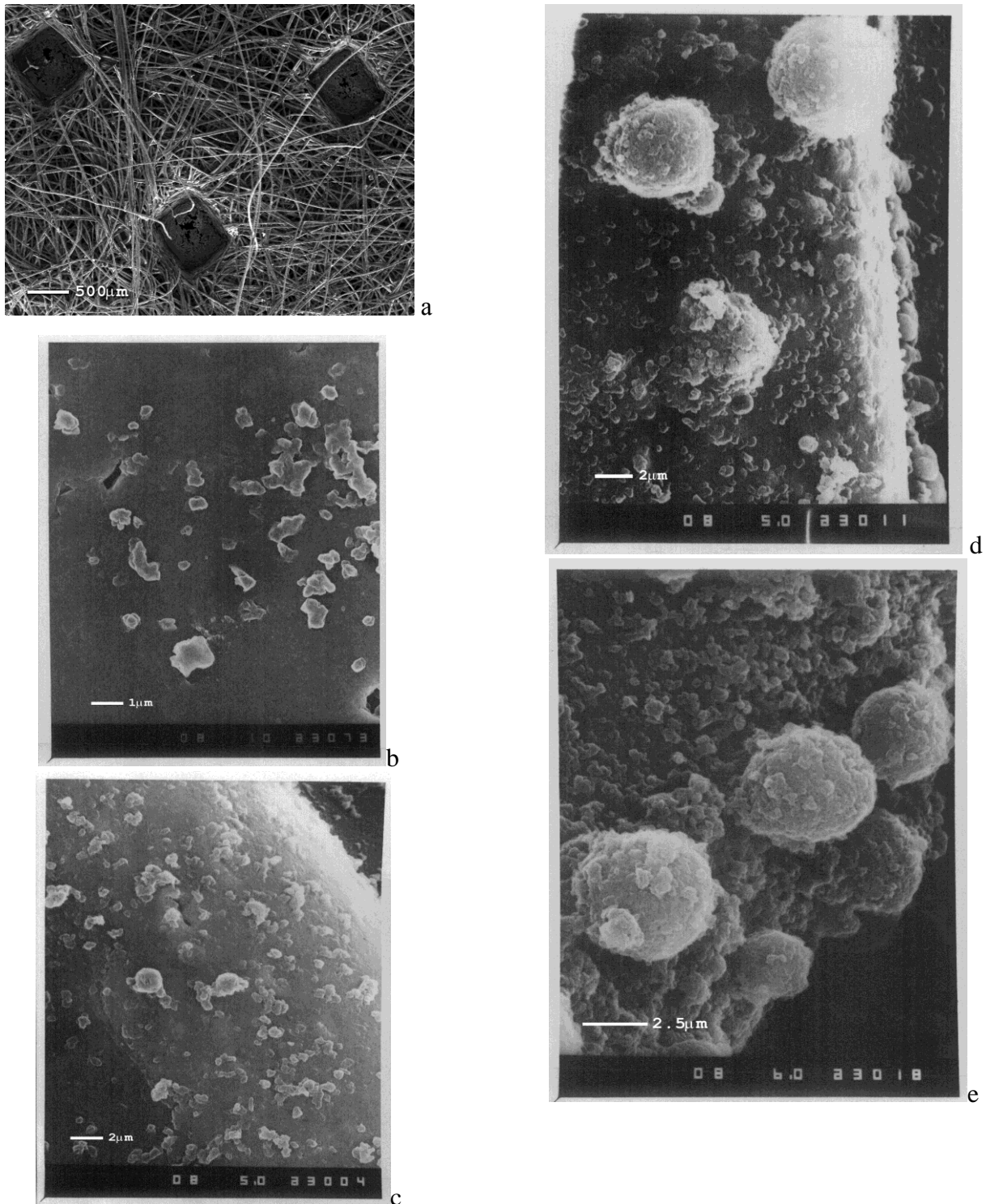
Fig.1. SEM micrographs of the PETF substrate surface (a), after electroless deposition of cobalt-diamond composite coating on the fibrous of the substrate in electrolytes containing different concentrations (b- 1 g/L; c – 3 g/L; d – 7 g/L; e – 10 g/L) of diamond particles with sizes 0,03-0,5 μm.

on the bottom rhomboid zones (Fig. 1a) of the substrate. As a consequence of sedimentation and convection effects, the number of the particles on the bottom of the pressed sections for all the studied sizes and concentrations of the studied particles was considerably greater (and sufficient from technological point of view) than the number of co-

deposited on fibrous zones of the substrate. For this reason in Fig. 1, as well as in the next figures, the illustrative photographs of the concave sections are not given here.

Part of the results from analogous investigations, carried out with diamond particles of sizes 3 -7 μm and 7 – 10 μm, are shown in Table 2 and in Fig. 2.

It is seen from the table that in this case upon increasing the concentration of the diamond particles in the working electrolyte, the thickness of the deposited composite coating is growing up. Thereupon the conditional thickness of the coatings is higher than that, obtained in the case of the composite coatings, in which particles of sizes 0,03 – 0,5 μm are included (Table1). At the same time aiming at obtaining a desired number of particles, included in cobalt matrix, the particles on the fibers sections, it is necessary to increase the concentration of the diamond powder in the working electrolyte in the interval 5 – 10 g/L (Fig. 2b and 2d). When the size of the particles is 7 – 10 μm, the effect of decreasing the number of co-deposited diamond particles with the growth in their size is better expressed (Fig 2c, 2d). It is obviously connected both with the higher rate of sedimentation of the larger dispersed particles, as well as with the fact that having such size of the particles at several times smaller thickness of the layer of the cobalt matrix, their direct addition and incorporation inside the cobalt matrix becomes already impossible. It becomes quite clear from Fig. 2d that these large particles are sticking out above the formed Co matrix and their connection with it is accomplished by means of co-bonding of the cobalt coating being formed simultaneously on the PETF substrate and on the diamond particles. In this connection it can be also noted that in the case of particle sizes 3 -7 μm the number of spheroid agglomerates being formed is still substantial (Fig. 2b), while at sizes 7 – 10 μm their number is abruptly decreased – the cobalt matrix comprises practically only separate diamond particles (Fig. 2d). At the next increase in the diamond particle size (20-28 μm; 38-45 μm; 63-75 μm; 80-100 μm), added in the form of diamond powder to the working electrolyte, the number of the co-deposited

particles continues to drop down. At sizes above 80 μm the deposited composite coating are already unable to answer the requirements for number of included particles, necessary for the production of composite layers, which are applicable to the manufacturing of polishing and finishing instruments/disks. For this range of sizes, the diamond particles are included in the cobalt matrix mainly in the pressed sections of the PETF (Fig. 3a), as well as in the zones, in which the fibers of PETF are overlapped and/or form sections advantageous for attachment to the growing cobalt matrix (Fig. 3b). In this case also the inclusion of the diamond particles is accomplished by means of binding bridges (Fig.3c), which are leading to the effect of "co-bonding" (Fig. 3d) as a consequence of the simultaneous deposition of the metallic cobalt both on the PETF and on the diamond particles.

The comparative Table 3 lists the averaged values of the thickness and the mass of the cobalt composite coatings (prepared under the same conditions – concentration of the particles in the solution – 5 g/L and time interval of deposition – 30 min), depending on the size of the diamond particles added to the working solution, respectively incorporated into the cobalt matrix.

It is seen from the above given results that upon increasing of the particle size from 0.03 to 10 μm both the average thickness of the composite Co-P-D coatings and the mass of the incorporated composite are growing up. Within a range of particle sizes 14 to 28 μm it is observed that the thickness (respectively the mass) of the deposited composite layers is decreasing. This is connected with the significantly lower number of particles of the separate particles, the average weight of the coating is diminishing.

Table 2. Dependence of the thickness of the chemically deposited composite Co-P-D coatings on PETF substrate on the concentration (1 - 5 g/L) of the diamond particles dispersed in the working solution at particle sizes 3 – 7 μm and 7 – 10 μm. Time interval of deposition 30 min.

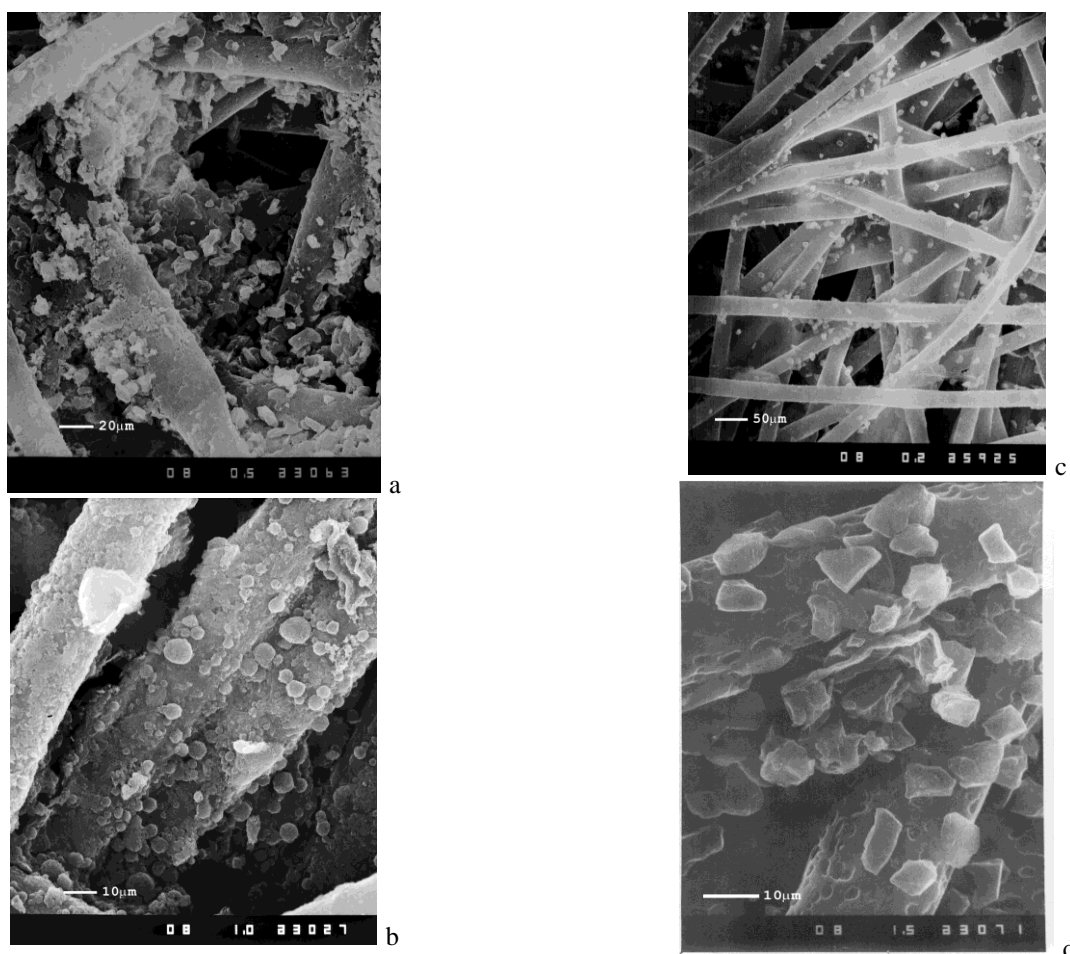| Size of the diamond particles, μm	Concentration of the diamond particles, g/L	Thickness of the composite coating, μm
3-7	1	1,07
3-7	3	2,10
3-7	5	2,00
7-10	1	0,70
7-10	3	2,90
7-10	5	3,10

Fig.2. SEM micrographs of the cobalt-diamond composite coating on the fibrous of the substrate in electrolytes containing different concentrations - a- 1 g/L and b – 5 g/L - of diamond particles with sizes 3-7 µm, and - c- 1 g/L and d – 10 g/L - of diamond particles with sizes 7-10 µm.

included in a unit of volume of the composite coating (as a result of the increased rate of sedimentation of the particles but also as a result of considerable misbalance of the ratio "thickness of the incorporating metal matrix/size of the co-deposited particles") and in spite of the larger mass.

In the case of sizes of the co-deposited diamond particles within the interval 38-75 µm, the mass of the considerably greater diamond particles is obviously compensating the smaller number of included particles, as a consequence of which the

measured average thickness and mass of the composite coatings is again increased. At particle size above 80 µm, however, the number of the co-deposited diamond particles is decreased even more drastically, and therefore the thickness (respectively the mass) of the deposited Co-P-D coating become much lower. The composite layers, obtained at such sizes of the diamond particles, are practically inapplicable for the production of polishing PETF disks.

Table 3. Average value of the thickness and of the mass of cobalt composite coatings depending on the size of the diamond grains used as dispersed phase.

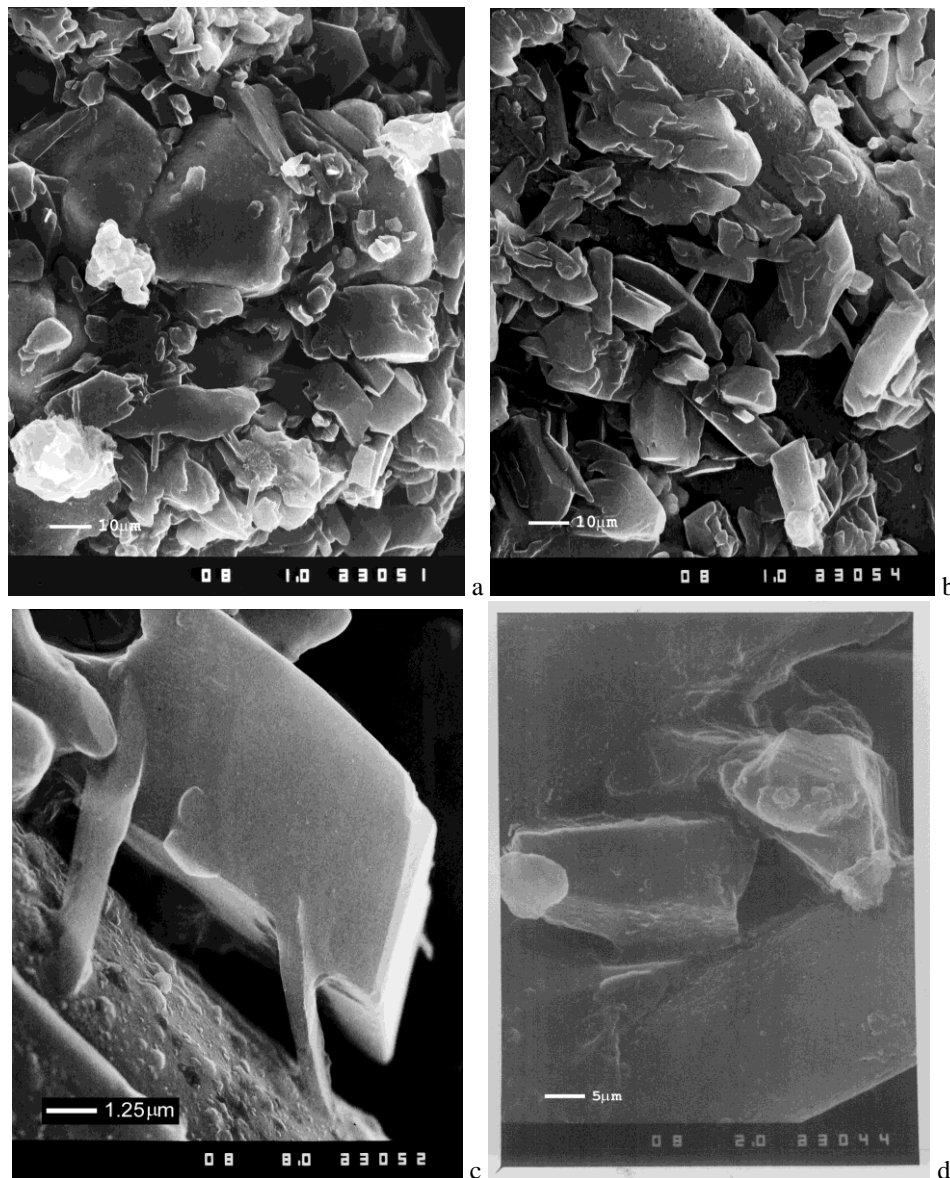| Size of the diamond particles, µm	Thickness of the coating, µm	Mass of the coating, g
0,05- 0,5	0,74	0,0117
3 - 7	2,0	0,0317
7 - 10	3,1	0,0490
14 - 20	2,4	0,0379
20 - 28	2,50	0,0395
38 - 45	3,35	0,0540
63 - 75	5,49	0,0857
80 -100	1,0	0,0158

Fig.3. SEM micrographs of the cobalt-diamond composite coating at the bottom of the rhomboidal press-hole (a) and at the fibrous (b-d) of the PETF substrate obtained in electrolyte containing 10 g/L diamond particles with sizes 20-28 µm.

3.2 Characterization of the polishing effect of the composite layers, containing diamond particles of various sizes.

In this cycle of experimental runs the influence of the size of the co-deposited inside the cobalt matrix diamond particles was studied with respect to the polishing effect of the deposited on the flexible PETF substrate composite Co-P-D coating during the processing of different rocky materials – limestone and two kinds of marble. The studies were carried out at various loading/pressure and rate of rotation of the polishing PETF/Co-P-D disc. We estimated the polishing effect based on the changes in the surface roughness (R_a and R_z) of the

studied samples. The obtained results are represented in Table 4.

The samples for the testing were cut out in the form of cylindrical cores of diameter 20 mm and length of 20-30 mm from rocky materials, the deposits of which are located in Mezdra quarry – west part of Balkan mountains (for the limestone); in Ilinden stone-pit – south part of Pirin mountain (for "Ilinden" marble) and in Chernomorets stone-pit – nord-east part of Strandzha mountain (for "Strandzha" marble). Each one of the samples, after its being cut out of the rock, was subjected consecutively to preliminary (rough) polishing with commercially available discs Bulcat-100, IDT-800 and IDT-1800, with the aim to achieve a certain

degree of roughness, requiring thereafter finer polishing and finishing using the PETF discs, developed by us. This treatment was carried out in the following order of using the discs: PETF/Co-P-$D_{63-70\mu m} \rightarrow$ PETF/Co-P-$D_{40-28\mu m} \rightarrow$ PETF/Co-P-$D_{28-20\mu m} \rightarrow$ PETF/Co-P-$D_{3-5\mu m} \rightarrow$ PETF/Co-P-$D_{0,05-0,5\mu m}$. The obtained results have been summarized in Table 4.

The data in Table 4 show that after the preliminary rough polishing of the samples of limestone they were characterized by a coefficient of roughness R_z=12 and R_a - 1,94. In the next cycles I-IV of processing with the discs, which contain diamond particles of size 63-70 μm, the achieved coefficients were R_z=7,44-4,95 μm and R_a - 1,70-0,61 μm; upon using the discs, which contain diamond particles of size 40-28 μm; respectively - R_z = 4,35-3,58 μm and R_a = 0,58-0,47; R_z = 3,54-3,50 μm and R_a = 0,45-0,37 μm with the discs, containing diamond particles of size 28-20 μm; R_z = 3,40-3,26 μm and R_a = 0,44-0,34 μm with the disks containing diamond particles of size 3-5 μm; R_z = 3.10-3.00 μm and R_a = 0.32-0.31 μm with discs, containing diamond particles of size 0.05 – 0.5 μm.

The surface treatment with the same discs, in analogous order and the same duration, of the marble samples "Ilinden", for which after their preliminary rough polishing the following coefficients of roughness were achieved R_z=10,82 and R_a - 1,84, leading later to their values of R_z = 6,98 μm and R_a = 1,03 μm up to R_z = 2,32 μm and R_a = 0,35 μm. In the case of marble "Strandzha" samples, for which after their preliminary rough polishing the following coefficients of roughness were achieved R_z=11,54 μm and R_a – 2,10 μm, this treatment enables achieving values of R_z and R_a respectively 7,19 μm and 1,35 μm until the final values were obtained 2,65 μm and 0,29 μm (Table 4).

The final values of the coefficients R_z and R_a for the three kinds of materials, represented in Table 4, were compared with the values, measured for them on samples, taken after analogous treatment in the case of serial production/treatment with polishing discs, which are commercially available products, imported from foreign companies. The results from this comparison are illustrated in Table 5.

Table 4. Measured values of R_a and R_z on the consecutively treated with polishing discs (PETF/Co-P-$D_{70-0,05\mu m}$) samples (Limestone"Mezdra", Marble "Ilinden" and Marble "Strandzha" of dimensions Φ-20 mm and L-25 mm), obtained at pressure on the polishing disc 0.35 кг/cm² and rate of rotation of the disc 1000 rpm. Number of cycles of polishing for each disc – 4. Duration of one cycle – 2 min.

Size of the diamond particles [μm], included in *PETF*/Co-P-D polishing disc; No of the cycle	Limestone "Mezdra"		Marble "Ilinden"		Marble "Strandzha"	
	R_z, μm (value before polishing 12,00)	R_a, μm (value before polishing 1,94)	R_z, μm (value before polishing 10,82)	R_a, μm (value before polishin 1,84)	R_z, μm (value before polishing 11,54)	R_a, μm (value before polishing 2,10)
63/70						
I	7,44	1,70	6,98	1,03	7,19	1,35
II	7,02	1,51	5,86	0,73	6,01	0,92
III	5,70	0,74	5,08	0,72	4,92	0,71
IV	4,95	0,61	4,23	0,64	4,68	0,69
40/28						
I	4,35	0,58	3,91	0,81	4,43	0,53
II	3,92	0,55	3,74	0,51	4,10	0,43
III	3.66	0,47	3,62	0,50	3,66	0,38
IV	3,58	0,47	3,56	0,45	3,48	0,37
28/20						
I	3,54	0,45	3,74	0,51	3,62	0,37
II	3,50	0,46	3,34	0.50	3,48	0,37
III	3,50	0,35	3,11	0,43	3,42	0,36
IV	3,50	0,37	2,98	0,42	3,23	0,35
3/5						
I	3,40	0,44	3,10	0,39	3,43	0,37
II	3,36	0,44	2,82	0,33	3,29	0,35
III	3,36	0,36	2,80	0,34	3,10	0,31
IV	3,26	0,34	2,54	0,35	2,96	0,31
0,05/0,5						
I	3,10	0,32	2,88	0,40	3,10	0.30
II	3,00	0,33	2,80	0,35	2,84	0,29
III	3,00	0,31	2,50	0,34	2,74	0,29
IV	3,00	0,31	2,32	0,35	2,65	0,29

Table 5. Measured final values of R_a and R_z on samples of "Limestone", Marble "Ilinden" and Marble "Strandzha", treated consecutively using the polishing discs, made by us (PETF/Co-P-D$_{70-0,05\mu m}$) and on samples of the same materials, taken after analogous treatment using commercially available serially production discs.

Type of the treated material	R_z, µm, obtained using the discs made by us	R_a, µm, obtained using our discs	R_z, µm, obtained using commercial discs	R_a, µm, obtained using commercial discs
Limestone	3,00	0,31	5,90	0,97
Marble "Ilinden"	2,32	0,35	1,32	0,19
Marble "Strandzha"	2,65	0,29	2,76	0,37

It is seen from the results represented in Table 5 that the polishing effect when using the discs, prepared by chemical deposition under laboratory conditions, is comparable to the effect, obtained with the imported discs, generally accepted for industrial practice. It is even slightly better in the case of limestone and marble "Strandzha", while in the case of samples of "Ilinden" marble there is insignificant advantage in favor of the imported discs.

In the next cycle of studies the weight losses of the composite layers will be evaluated also on non-treated mineral materials samples and on this basis their tribological behavior will be characterized, respectively the "productivity" of the polishing discs PETF/Co-P-D. There follows, on the basis of the obtained results, to carry out on a larger scale some semi-industrial testing experiments, aiming at the optimization of the procedure of chemical deposition of Co-P-D composite layers, respectively to achieve the polishing effect on larger scale.

CONCLUSIONS

It follows from the above presented results that upon increasing the concentration of the diamond micro-particles in the working electrolyte, used for the chemical deposition of Co-P-D composite layers on a flexible support of polyethylene terephthalate, quantitative and qualitative changes are being observed in their structure and layer thickness. Thereupon it has been ascertained that the process of chemical deposition of cobalt is occurring simultaneously both on the PETF substrate, as well as on the diamond particles. As a result of this the incorporation of the particles is accomplished through joining of the fronts of the growing layers of cobalt on the surface of both phases – PETF and diamond. This mechanism of incorporation of the diamond particles determines their regular distribution/inclusion in the cobalt matrix up to sizes of 3-5 µm, which are juxtaposable with the thickness of the cobalt coating/matrix, being formed upon the PETF substrate. Upon increasing the size of the diamond particles, the number of the particles included in the cobalt matrix becomes lower as a result of their lower resistance to sedimentation (i.e. smaller number in the volume of the working electrolyte) and the longer time intervals needed for their binding (i.e. co-binding) via the growing cobalt layers on both phases. In this aspect with the aim to co-deposit the desired number of diamond particles in the composite layer, it becomes necessary to increase their concentration in the electrolyte when their size is increased – from 3 - 5 g/L for particles with a size up to 5 µm, further at 5 – 15 g/L for particles of size 7-10 µm. The positive effect achieved upon increasing their concentration, however, is valid only up to size 63-70 µm. At larger sizes of the diamond particles, their deposition number in the cobalt matrix does not satisfy the requirements for the formation of a composite layer, applicable in the production of polishing discs.

The preliminary testing of the polishing effect of discs *PETF/*Co-P-D, prepared under laboratory conditions upon limestone samples and two kinds of marble showed that values were reached for the coefficients R_z and R_a, which completely answer the requirements of the industrial practice for finishing surface treatment of such materials.

REFERENCES

1. K.M. Gorbunova, A.A. Nikiforova, G.A. Sadakov, V.P. Moiseev, M.I. Ivanov, Physico-chemical basis of the chemical deposition of cobalt coatings (in Russian), Nauka Publ.H., Moscow (1974).
2. M. Shalkauskas, A. Vashkjalis, Chemical metallization of plastics (in Pussian), Khimia Publ.H., Leningrad (1985).
3. E. Rudnik, K. Kokoszka, J. Lapsa, *Surface & Coating Technol.*, **202**, 2584 (2008).
4. J. Tang, S. Zhou, Y. Xie, *Plating&Metal Finishing*, **84**, 241(1998).
5. E.W. Brooman, *J. Appl. Surface Finishing*, **I,** 38 (2006).
6. E.W. Brooman, *Galvanotechnik,* **104,** 58 (2006).
7. M.L. Klingenberg, E.W. Brooman, *Plating&Metal Finishing*, 92, 42 (2005).

8. D. Stoychev, N. Koteva, M. Stoycheva, E. Velkova, D. Dobrev, *Materiale Plastice*, **49**, 20 (2012).

9. N. Feldstein, T. Lancsek, J. Electrochem. Soc., **131**, 3026 (1984).

10. M. Seal, Industrial Diamond Review, p.104, March (1968).

11. R. Komanduri, Proceeding, Diamond Partner in Productivity, p.174 (1974)].

БЕЗЕЛЕКТРОЛИЗНО ОТЛАГАНЕ НА КОМПОЗИТНИ СЛОЕВЕ ОТ КОБАЛТ, ФОРСФОР И ДИАМАНТИ И ТЕХНИТЕ ПОЛИРАЩИ СВОЙСТВА

Д. Стойчев[1*], Е. Добрева[2], Н. Разказов[2], М. Стойчева[3], Н. Котева[2]

[1] Институт по физикохимия "Акад. Р. Каишев", Българска академия на науките, София 1113
[2] Технически университет, София
[3] Институт по електрохимия и енергийни системи "Акад. Ев. Будевски", Българска академия на науките, София 1113

(Резюме)

Изследвани са възможностите за безелектролизно отлагане на композитни слоеве от кобалт, фосфор и диаманти върху носител от полиетилен терефталат (PETF). Използвани са електролити от алкалени хлориди и NaH_2PO_2 като редуктор. Изследвани са ефектите на концентрацията (1-25 g/L) и размера на частиците (0,03 – 100 µm) на дисперсната фаза (диамантов прах), добавени към работния електролит, с оглед определянето на количеството диаментени частици, съутаени с кобалтовата матрица, както и средната дебелина на формираните композитни слоеве. В резултат на това са определени размерите и концентрациите на диамантените частици, при които се формират композитни слоеве за Co-P-D-покрития при гъвкави полиращи дискове върху PETF.

Предварителните изпитания за полиращия ефект на PETF/Co-P-D-дисковете са извършени в лабораторни условия (при диамантени частици с размери: 63-75; 38-45; 20-28; 14-20; 7-10 и 0.03-0,5 µm) върху образци от варовик и върху два вида мраморни образци. Получените резултати за коефициентите R_z и R_a са изцяло в съгласие с изискванията за повърхностно полиране на тези материали.