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ELECTROLESS DEPOSITION OF COMPOSITE NICKEL-PHOSPHOROUS COATINGS WITH DIAMOND DISPERSOID

The composite Ni-P coating with diamond particles (D) deposited on the flexible substrates of pressed polyethylene terephthalate material (PET) was obtained, to be used in the development of efficient, flexible grinding and polishing tools. The optimal conditions of the hydrodynamic regime, deposition time and temperature were found. The influence of the concentration and size of the D particles (3/7 ÷ 225/300 μm) on the coating thickness and number of co-deposited particles were studied. By Scanning Electron Microscopy (SEM) images were defined the morphology of dispersion coatings and number of co-deposited particles in them, and Energy Dispersive Spectroscopy (EDS/INCA) was used to determine the elemental chemical composition of the composite coatings.

Keywords: functional composites; electroless coatings; metal-matrix composites; non-metallic substrate

1. Introduction

The diamond (D) and cubic boron nitride (cBN) are some of the hardest abrasive materials with high potential in the manufacture of cutting tools. Most of them are obtained by hot pressing technique at a high pressure and high temperature [1].

Another method for the preparation of such cutting tools is the electroless plating, which is introduced by Brenner and Riddell in 1946 [2-3] and is based on the autocatalytic reduction of metal ions to the metal on the catalytically active surface, by the action of a reducing agent added to the working electrolyte [4].

The composite coatings deposited on different substrates are used to improve the surface properties of metal parts. A basic characteristic of these coatings is that solid particles (dispersoids) are included into the chemical deposited metal or alloy (called matrix), thus forming a second phase. Most often, chemical nickel-phosphorous coatings are used as the matrix. In the last few years, diamond particles, mostly natural and/or synthetic in the form of powder, have been used as dispersoid. The authors in [5] were studied the electroless plating of nickel-phosphorous and cobalt matrix on a flexible substrate including particles of cBN as dispersoid.

In the recent years, for the preparation of coatings with good physical and mechanical properties, and greater wear resistance are used diamond particles as a dispersoid co-deposited in the metal matrix.

Natural diamond is polycrystalline. It is a natural polymorphic allotrope of carbon and is practically non-wearable. It is the hardest substance of natural origin. Synthetic diamonds can be either monocrystalline or polycrystalline. The latter are produced by a method of chemical deposition and reaction between gases through evaporation, which results in the formation of synthetic diamonds. Synthetic monocrystalline diamonds exist as single crystals comprising face-centered cubic array of carbon atoms, these are characterized by sharp edges and peaks. Shock-synthesized diamonds are polycrystalline.

Composite coatings with incorporated diamond particles into the metal matrix have the aim to improve the hardness, corrosion and wear-resistance, as well as other properties of the coatings [6-8]. Even small amounts of dispersoid in the composite coating may improve the latter's wear resistance and they are less expensive as compared to solid chromium at that and adequate tribological properties. Shortcomings to the production of these coatings include reduced electrolyte stability and increased costs [8-13].

The aim of the present study is to obtaining of Ni-P composite coatings with diamond particles with different size, on a flexible substrate of polyethylene terephthalate (PET). The optimum electrolyte deposition conditions and influence of the concentration and size of the diamond particles on the relative thickness of the coating and the number of incorporated particles on it were investigated.

2. Experimental Studies

Polyethylene terephthalate (PET) samples with a surface area of 8 cm^2 were used for these investigations. The samples were pre-treated employing the following technological scheme [14-15]: Etching in alkaline solution OA-84-2 (a commercial product of Technical University-Sofia) at T = 65 ˚C and τ = 15 min; Pre-activation in 3M HCl at T = 25 ˚C and τ = 5 min; Activation in colloidal solution of PdCl$_2$ A-75-12 (a commercial product of Technical University-Sofia) at T = 25 ˚C and τ = 5 min, and Acceleration in alkaline solution

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X-75-4 Accelerator (a commercial product of Technical University-Sofia) at T = 25 ˚C and τ = 5 min.

After the above pre-treatment, the samples were immersed in the solution for chemical nickel plating [16] with solution composition presented in Table 1.

TABLE 1

Solution composition and working conditions for chemical deposition of composite coatings

Electrolyte's compositions	
NiSO$_4$.7H$_2$O, g/l	25.0
NaH$_2$PO$_2$.2H$_2$O, g/l	20.0
CH$_3$COONa, g/l	20.0
Lactic acid (80 %), g/l	20.0
Stabilizer 2, mg/l	1.0
pH	4.6 – 4.8

The deposition time and temperature were varied within the range from 15 to 300 min and from 50 ºC to 87 ºC, respectively. Diamond particles (D) of various sizes were added to the solution for chemical deposition: from 3/7 μm (corresponding to a mixture of diamond particles sized from 3 μm to 7 μm) to 225/300 μm (corresponding to a mixture of diamond particles sized from 225 μm to 300 μm). The diamond particles were added in concentrations from 1.0 to 10.0 g/l. For their better wetted was investigated the effect of two surfactants: sodium laurylsulfonate (SLS) and polyethylene glycol with molecular weight 4000 (PEG-4000) at a concentration of 0.01 g/l. The air flow agitation of the electrolyte was employed (100 ml/min for 250 ml electrolyte) under different hydrodynamic conditions as descried in the Experimental Results section.

The deposition rate, expressed by the amount of deposited nickel, resp. the relative thickness of the obtained coating (δ, μm) is determined gravimetrically as the difference in sample mass before and after deposition of the composite coating:

$$\Delta m = M – Mo, [g]$$

where: **Δm** is the mass of the deposited coating, Mo and M - the sample's mass before and after the deposition.

The morphology and structure of the obtained coating, as well as the distribution of the dispersoid particles on its surface, were examined by Scanning Electron Microscopy (SEM) using a JEOL JSM 733 (Japan) microscope. The average number of co-deposited dispersoid particles per square centimeter of coating surface (**N/cm²**) was determined from the SEM images, counting the number of particles in three randomly selected zones at x200 magnification. The Energy Dispersive Spectroscopy (EDS/INCA) was used to determine the elemental chemical composition of the composite coatings.

3. Results and discussion

3.1. Influence of the surface active substances (SAS)

Independently the intense agitation of the plating solution some dispersoids wetted difficult and hence cannot be uniformly distributed in the suspension. They agglomerate and, though of a higher density than the working solution, float partially to the surface [10]. Therefore, it is necessary to use SAS.

The experiments were carried out with 1.0 g/l D 3/7 μm, using two types of surfactants: sodium lauryl sulfate (SLS) and polyethylene glycol with molecular weight 4000 (PEG-4000), added in concentration of 0.01 g/l.

The results of the tests without SLS and with two types of SAS (Table 2) indicate that the addition of a surface active substance to the plating electrolyte has a significant effect not only on the thickness of the obtained composite coating, but also on the number of co-deposited particles in it. When composite coatings are deposited, with or without dispersoids, wherein the addition of SLS to the working electrolyte, the thickness of Ni-P coatings is greater than the results obtained in the presence of PEG 4000, which is also confirmed by the EDS analysis and by SEM pictures in Figure 1.
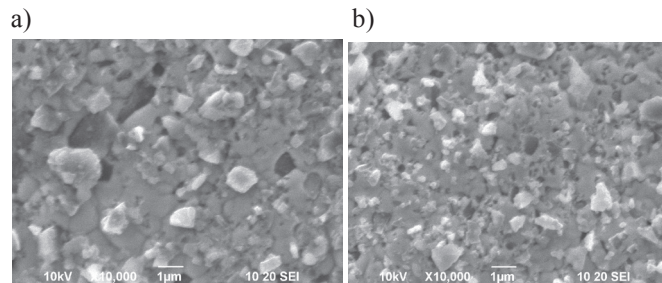
a)   b)

Fig. 1: SEM images of the surface of Ni-P composite coatings with: a) SLS, b) PEG-4000 (T = 82 ºC; τ = 60 min; continuous stirring)

These conclusions are also supported by the fact that SLS is most often used in practice, which provided one more argument to conduct all further investigations with this surface active substance.

TABLE 2

Influence of the type of SAS on the mass and number of co-deposited particles in composite coatings (T = 82 °C; τ = 60 min; continuous stirring)

	Without SAS		With SAS (PEG-4000)		With SAS (SLS)	
	Ni-P	Ni-P/ D 3/7 μm	Ni-P	Ni-P/ D 3/7 μm	Ni-P	Ni-P/ D 3/7 μm
Δm, g	0.2839	0.3396	0.3502	0.4699	0.3568	0.526
(δ, μm)	(36.25)	(43.37)	(44.72)	(60.00)	(45.56)	(67.16)
N/cm²	No incorporation	200 000	No incorporation	>350 000	No incorporation	>350 000
Ni, wt.%	87.76	38.68	84.30	33.77	85.92	29.42
C, wt.%	6.17	60.30	8.32	65.60	7.14	69.00
P, wt.%	6.07	1.02	7.38	0.63	6.94	1.58

3.2. Influence of deposition time

The deposition time and its influence on the rate of deposition are very important in the process of electroless deposition of composite Ni-P coatings. In this context, the experiments were conducted with 5.0 g/l D 14/20 µm for various deposition times: from 15 to 300 min (Table 3).

TABLE 3

Influence of the deposition time on the mass and number of co-deposited particles in composite coatings (0.01 g/l SLS; T = 82 °C; continuous stirring)

τ, min	15	30	45	60	300
Δm, g	0.1396	0.2897	0.3781	0.4704	0.7528
(δ, µm)	(17.82)	(36.99)	(48.28)	(60.07)	(96.13)
N/cm²	152 300	164 700	184 600	314 000	315 000

The obtained data show that with increasing the deposition time, the mass of the composite coating and the numbers of incorporated dispersoid particles therein were increased. It is seen, that the long deposition process (60 and 300 min) do not lead to exponential increase in coating mass, which is also confirmed by the small difference in the number of incorporated particles in the coatings deposited for the two deposition times. This is probably due to deficiency of the basic electrolyte components which have been used up during the process and hence the working electrolyte should be refreshed every 30 min.

3.3. Influence of the electrolyte temperature

The rate of Ni^{2+} reduction depends on the composition and pH of the solution, but also on the temperature. H. Petrov [17] has found that the rate of the deposition process at T = 60-90 °C may reach up to 20-30 µm/h, which corresponds to the rate of electrochemical nickel plating. That is why in the present experiments for deposition of composite coatings with 5 g/l D 14/20 µm we have studied the influence of the temperature within the range 50 °C - 85 °C.

TABLE 4

Influence of the working electrolyte's temperature on the mass and number of co-deposited particles in composite coatings (0.01 g/l SLS; τ = 60 min; continuous stirring)

Temperature, °C	50 ÷ 55	60 ÷ 65	70 ÷ 75	80 ÷ 85	Over 85
Δm, g (δ, µm)	0.0988 (12.61)	0.1486 (18.98)	0.237 (30.26)	0.4704 (60.07)	Decomposition of the working electrolyte
N/cm²	144 600	168 500	163 400	314 000	-

The experimental results in Table 4 show that the temperature increase leads to an increase in deposition rate and in the number of co-deposited particles. At temperatures above 85 °C, decomposition of the working electrolytes was observed and hence further investigations were conducted at temperatures within the range from 80 to 85 °C.

3.4. Influence of the dispersoid concentration in the electrolyte

The incorporation of disperse particles in the composite coating depends greatly on their concentration in the electrolyte. G. Gavrilov and collaborators have established that the solid phase concentration should be between 5 and 200 g/l, which results in dispersoid particle's inclusion in the coating from 1-5 vol.% to no more than 20 vol.%. The higher the dispersoid concentration in the electrolyte, the higher is the amount of incorporated particles in the coating. However, this increase has, most probably, an upper limit above which further increase in dispersoid concentration may not lead to significant improvements [6].

TABLE 5

Influence of the D's concentration on the mass and number of co-deposited particles in composite coatings (0.01 g/l SLS; T = 82 °C; τ = 60 min; continuous stirring)

D's concentration, g/l		Size of diamond particles	
		D 3/7µm	D 14/20µm
1.0	Δm, g (δ, µm)	0.5259 (67.16)	0.4511 (57.60)
	N/cm²	>350 000	224 800
2.5	Δm, g (δ, µm)	0.4919 (62.82)	0.4659 (59.50)
	N/cm²	>350 000	287 600
5.0	Δm, g (δ, µm)	0.3937 (50.28)	0.4704 (60.07)
	N/cm²	>350 000	314 000
10.0	Δm, g (δ, µm)	0.4089 (52.22)	0.461 (58.87)
	N/cm²	>350 000	300 600

The obtained experimental results in Table 5 indicate that with increase of the concentration of particles sized 3/7 µm the mass of the deposited coating, respectively its relative thickness, decrease. This finding can be explained by the fact that the increased dispersoid mass leads to substantial increase in surface area. As a result, the active centres on the surface subject to nickel plating are blocked by the neutral particles and the rate of the deposition process decreases at high dispersoid concentrations. Nevertheless, a great number of incorporated particles can be observed in the coating, above 350 000. While the experiments with bigger dispersoid particles (D 14/20 µm) show that the highest deposition rate and number of incorporated particles are achieved at 5.0 g/l. At the higher dispersoid concentration of 10.0 g/l, both the mass of the obtained coatings and the number of included particles decrease as a result of the particles' surplus in the electrolyte. This results are confirmed by SEM images in Fig. 2
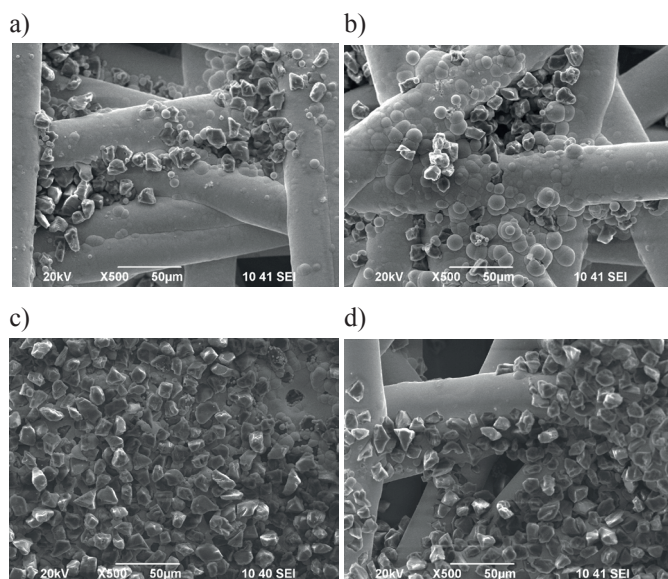
a)   b)

c)   d)

Fig. 2: SEM images of the surface of composite Ni-P composite coatings obtained at different concentrations of D 14/20 μm: a) 1.0 g/l; b) 2.5 g/l; c) 5.0 g/l; d) 10.0 g/l (0.01 g/l SLS; T = 82 °C; τ = 60 min; continuous stirring)

3.5. Influence of the hydrodynamics

According to H. Petrov [17], the hydrodynamic regime exerts significant influence on the thickness of chemically deposited composite coatings. In this connection, solutions with 5.0 g/l D 14/20 μm have been studied in the following deposition regimes:

Regime „a" – continuous air flow agitation;
Regime „b" - 1 min air flow agitation, 1 min rest;
Regime „c" - 2 min air flow agitation, 1 min rest;
Regime „d" - 2 min air flow agitation, 2 min rest;
Regime „e" - 2 min air flow agitation, 5 min rest;
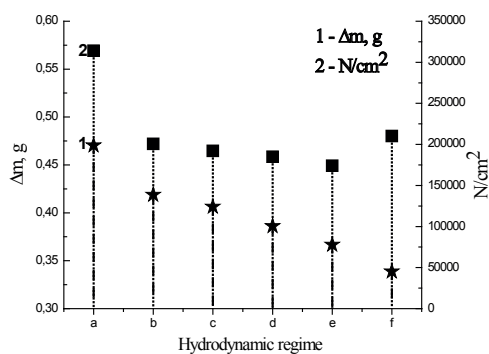Regime „f" - 2 min air flow agitation, 10 min rest.

Fig. 3: Influence of the hydrodynamic regimes on the mass and number of co-deposited particles in composite coatings (0.01 g/l SLS; T = 82 °C; τ = 60 min)

It can be seen from the data in Fig. 3 that the optimum coating thickness and the number of incorporation particles are achieved under continuous air flow agitation, which leads to the conclusion that the optimum deposition regime for D 14/20 μm is regime „a".

The SEM images in Figure 4 show the morphology of the composite Ni-P coatings in two hydrodynamic regimes "a" and "f", where, also confirmed that it is appropriate in this size of D to operate at regime "a".
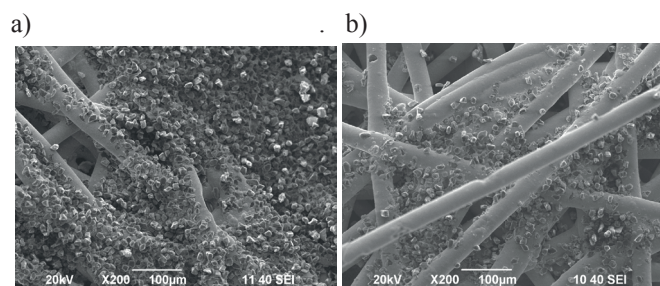
a)   . b)

Fig. 4: SEM images of the surface of Ni-P composite coatings with D 14/20 μm deposited under: a) regime "a"; b) regime "f" (0.01 g/l SLS; T = 82 °C; τ = 60 min)

In order to select an appropriate regime depending on particle size (14/20 μm - 225/300 μm) in Figure 5 is shown the effect on the mass and the number of incorporation particles in the composite coating at 5 h deposition time. On Figure 5a are shown the research conducted in regime "a" for D size (14/20 - 150/180 μm), and Figure 5b - regime "f" for D size (14/20 - 225/300 μm). From the graph in the hydrodynamic regime "a" is evident that with increasing the size of the dispersoid particles, the mass of the deposited coatings and number of incorporation particles in the composite coating decreased. From the obtained results for D 14/20 μm in Figures 5a and 5b, there was no large difference in the mass, but the number of incorporation particles in the composite coating is smaller in the regime "f", which is confirmed by the results of Figires 3 and 4b. In hydrodynamic regime "a" for the larger size diamond particles (over D 63/75 μm) the mass of the deposited coatings, the number of incorporated particles in it, and the fact that the attachment of the particles is less, gives us a reason to be concluded that, for deposition of composite coatings with dispersoid particle size above D 63/75 μm, it is more appropriate to use the hydrodynamic regime "f".
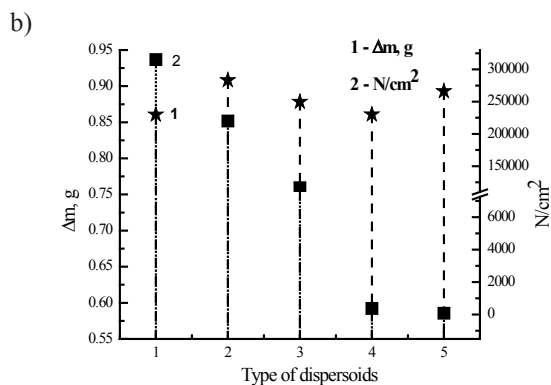
a)

b)
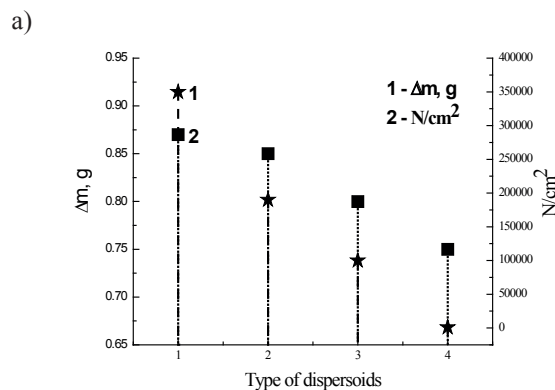
Fig. 5: Influence of size of the D on the mass and number of co-deposited particles in composite coatings (5.0 g/l D, 0.01 g/l SLS; T = 82 ℃; τ = 300 min) under: a) regime "a" and b) regime "f"
1) 14/20 μm; 2) 20/28 μm; 3) 63/75 μm; 4) 150/180 μm; 5) 225/300 μm

The conclusions are confirmed by SEM images (Figure 6) of the obtained Ni-P coatings including different size of diamonds.

a)

b)

c)

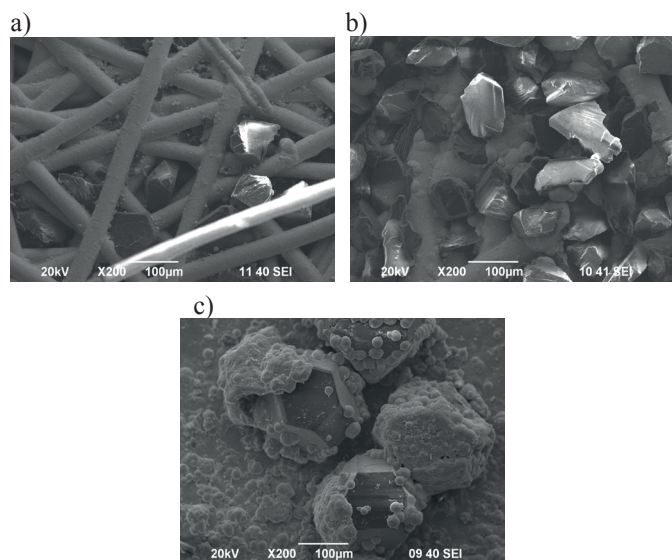Fig. 6: SEM images of the surface of Ni-P composite coatings with different size of the D (5.0 g/l D, 0.01 g/l SLS; T = 82 ℃; τ = 300 min) under regime "a": (a) 63/75 μm; and regime "f": (b) 63/75 μm; (c) 150/180 μm

4. Conclusion

The composite Ni-P coatings with diamond (3/7 - 225/300 μm) as dispersoid are deposited on a flexible substrate of polyethylene terephthalate (PET).

The influence of two types of surface active substances was investigated with the aim to improve wetting and prevent sedimentation of the dispersoid in the working electrolyte. It has been established that the composite coatings obtained in the presence of sodium lauryl sulfonate (SLS) are thicker and have a greater number of co-deposited particles as compared to the composite coatings deposited in solutions with addition of polyethylene glycol (PEG-4000).

It has been found that the longer deposition process is required to refresh the electrolyte every 30 min due to the exhaustion of the quantity of the basic components (a nickel salt and sodium hypophosphite).

The obtained experimental data carried out on the effects of temperature showed that the optimal temperature of the electrolyte for the preparation of composite coatings is 80 ÷ 85 ℃ because at higher temperatures is observed decomposition of the electrolyte.

From the studies conducted on the influence of dispersoid concentration is found that at the small size D 3/7 μm maximum thickness of the coating is observed at 1.0 g/l, while at the larger size D than 14/20 μm the best results are achieved at 5.0 g/l dispersoid concentration in the electrolyte.

Based on the conducted systematic studies on the influence of the hydrodynamic regime is found that at particles' size D 14/20 μm optimum regime corresponds to the continuous air flow agitation - regime "a" For dispersoids with particles' size above 63/75 μm, the most appropriate deposition regime includes 2 min air flow agitation, 10 min rest (regime "f") and the deposition time should be 5 h. Fine-grain dispersoid particles have been found to incorporate 100 % in the composite coating, whereas the larger particles are almost not included in the coating, because of their sedimentation in the electrolyte.

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