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COMPOSITES THEORY AND PRACTICE

Anna Sałacińska[1]*, Jerzy Bieliński[2], Milena Zawadowska[1], Rafał Kozera[1]
Anna Boczkowska[1], Krzysztof J. Kurzydłowski[1]

[1] Warsaw University of Technology, Department of Materials Science and Engineering, ul. Wołoska 141, 02-507 Warsaw, Poland
[2] Warsaw University of Technology, Department of Chemistry, ul. Noakowskiego 3, 00-664 Warsaw, Poland
** Corresponding author. E-mail: anna.salacinska@o2.pl*

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ELECTROLESS DEPOSITION OF Ni-P/NANO-Al_2O_3 COMPOSITE COATINGS ON PET AND CARBON FIBRES SUBSTRATES

This paper presents the results of studies on the electroless deposition of Ni-P/nano-Al_2O_3 composite coatings on pretreated polymeric bases (PET polyester Mylar A type) and on carbon fibres (24k fibres with 7 µm Tenax rovings). The Ni-P matrix was deposited from a solution consisting of $NiSO_4$ 0.1 M; NaH_2PO_2 0.2 M; glycine 0.21 M, with a pH = 7.5÷8.5 and thiourea added as a stabilizer, as well as cetyltrimethylammonium bromide as a surfactant. Aluminium oxide C (DNC - Degussa, grains 13 nm) or A16 (Alcoa, grains 400 nm) were powders amounting to 10÷30 g/l, with ultrasonic homogenization of the suspension. Under the experimental conditions applied, partial sedimentation of the A16 powder occurred, thus a further study on carbon fibres metallization was performed with the use of the DNC nanopowder. Deposition was performed in the temperature range 60÷70°C, during 5÷60 minutes, while the bases rotated at 1 rpm and the suspension was agitated with a stirrer. The composition of the deposited layers was determined by chemical methods and their surface morphology was investigated using SEM. A procedure for the preparation of the PET substrates for the tests was set out to obtain good adhesion of the Ni-P layers. Under the applied conditions, Ni-P/Al_2O_3 layers of a thickness within 130÷720 nm, aluminium oxide content up to 25% by weight, and 2÷4% phosphorus by weight were obtained.

Keywords: **electroless composite deposition, Ni-P/Al_2O_3 composite, deposition rate and microstructure, PET and carbon fibres metallization**

BEZPRĄDOWE OSADZANIE WARSTW KOMPOZYTOWYCH Ni-P/NANO-Al_2O_3 NA FOLII PET I WŁÓKNACH WĘGLOWYCH

W pracy przedstawiono wyniki badań nad bezprądowym osadzaniem warstw kompozytowych Ni-P/Al_2O_3 na podłożach polimerowych typu Mylar (poliester PET) oraz na włóknach węglowych (wiązki 24k włókien 7 µm Tenax). Osnowa Ni-P osadzana była z roztworu $NiSO_4$ 0,1 M; NaH_2PO_2 0,2 M; glicyna 0,21 M, o pH = 7,5÷8,5 z dodatkiem tiomocznika jako stabilizatora oraz bromku cetylotrimetyloamoniowego jako surfaktanta. Dodawano proszków tlenku glinu Aluminiumoxide C (DNC - Degussa, ziarna 13 nm) lub A16 (Alcoa, ziarna 400 nm) w ilości 10÷30 g/l, z ultradźwiękową homogenizacją zawiesiny. W zastosowanych warunkach doświadczeń stwierdzono częściową sedymentację proszku A16, stąd dalsze badania nad metalizacją włókien węglowych prowadzono z nanoproszkiem DNC. Osadzanie prowadzono w zakresie temperatur 60÷70°C, w czasie od 5 do 60 minut, podłoża obracały się z szybkością 1 obr/min, a zawiesina mieszana była mieszadłem magnetycznym. Określano chemicznie skład osadzanych warstw oraz morfologię ich powierzchni za pomocą SEM. W próbach z podłożami PET ustalono procedurę przygotowania tego materiału dla uzyskania dobrej adhezji warstw Ni-P. W zastosowanych warunkach osadzone bezprądowo warstwy kompozytowe Ni-P/Al_2O_3 o grubości 130÷720 nm zawierały do 25% mas tlenku glinu oraz 2÷4%mas fosforu.

Słowa kluczowe: **bezprądowe osadzanie kompozytu Ni-P/Al_2O_3, szybkość osadzania i mikrostruktura, PET, metalizacja PET i włókien węglowych**

INTRODUCTION

Composite materials make an essential contribution to functional and engineering materials applied in crucial branches of modern industries. Carbon fibre composites are an important group of such materials, including metallic matrix composites (MMC) [1-4]. The poor wettability of carbon fibres by metal and the formation of adverse Al_4C_3 are problems affecting MMC technology based on an aluminium alloy matrix. In the current project, Ni-P alloy layers deposited by the electroless method have been applied as coatings to prevent reaction between carbon and aluminium [5-7]. However, previous studies showed the rapid dissolving of Ni-P coatings by liquid aluminium [8]. Since it is impermissible to increase the thickness of Ni-P coatings on carbon fibre (due to harmful excess nickel and phosphorus in the final composite), methods are sought to decrease the dissolving of the Ni-P coating during the infiltration process. The introduction of particles, such as e.g. Al, Si or Ti oxides, into Ni-P coatings are one of the ways to delay the dissolving process of the coating. Introduction of the particles into the the metallic matrix provided an increase in metal hardness, reduction of abrasive wear or friction factor, as well as an increase in the resistance to high temperature and corrosion [9-19]. The work in this area was begun from the tests on the electroless deposition of an Ni-P/Al_2O_3 composite coating [9-12], which turned out as a valuable testing object due to its availability and the low price of aluminium oxide powders.

A literature review which was required for this study shows that research on the electroless deposition of Ni-P/Al_2O_3 composites focused on obtaining relatively thick coatings (between at least 5 μm and more than 50 μm) featuring high aluminium oxide contents [20--36].

The current growth in the application of nanomaterials has enhanced interest in aluminium oxide nanopowders, also in the studies on Ni-P/Al_2O_3 composites [27-31, 35]. Unlike conventional micropowders, nanopowders undergo agglomeration in aqueous solutions, and also in solutions applied for the purpose of electroless metallization. This leads to an uneven distribution of particles in the composite and to the precipitation of sediments from the suspensions. The way to avert these phenomena is to use surfactants or functional polymers [30, 39]. The hydrodynamics of the suspension flow at the surface of the base being coated is also important - pumps, propeller and magnetic stirrers, sample rotation [9, 13] and ultrasonics [31] have been applied, however, no final conclusions could be found (only indications that too much intensive suspension agitation reduces the oxide content in the composite).

Summing up the studies in relation to the needs of the deposition process of Ni-P/Al_2O_3 layers on carbon fibres, it may be stated that they contain valuable data, however, referring mostly to the electroless deposition process of thick composite coatings on metallic substrates. The description of carbon fibre metallization from suspensions is unavailable, as are any broader descriptions of depositing relatively thin layers with a low phosphorus content (1÷3%), i.e. from alkaline solutions [5-7, 38].

The aim of this study was to determine the conditions for electroless deposition of a Ni-P/Al_2O_3 composite coating on a flat (PET) base, and then to verify these conditions on a carbon fibre substrate.

EXPERIMENTAL PROCEDURE

PET polymer substrates are more useful than carbon fibres to develop the conditions for the electroless deposition of Ni-P and Ni-P/Al_2O_3 layers, because of easier observation of the quality of the coatings and their adhesion. Thus, in the first part of this study, the conditions for the electroless deposition of Ni-P and Ni-P/Al_2O_3 coatings from alkaline glycine solutions onto polymer substrates were investigated. The second part included verification of the developed metallization conditions using carbon fibre.

When testing the polymer substrate, 2.5 x 9 cm Mylar A 75 μm type polyester (PET) foil strips were utilized. The PET samples were initially degreased in acetone and then underwent swelling by a mixture of dimethylformamide and ethyl acetate. Etching to provide good adhesion between Ni-P and the polymer was performed in an H_2SO_4 solution of CrO_3, followed by neutralization in NaOH and HCl solutions [40]. Coating with a Pd catalyst was obtained in two steps, in $SnCl_2$ and $PdCl_2$ solutions [40], with additional re-activation of the catalyst in an NaH_2PO_2 solution before the metallization process [38]. The solution for Ni-P deposition was composed of: $NiSO_4$ - 0.1 M; NaH_2PO_2 - 0.2 M; glycine - 0.21 M, and NaOH as a pH-stabilising additive within the 7.5÷8.5 range. Thiourea $SC(NH_2)_2$ (TU 0.01÷0.02 mM) was added as the stabilizer, and cetyltrimethylammonium bromide CTAB (0.1 mM) - as the surfactant. When testing the deposition of the Ni-P/Al_2O_3 composite on the polymer substrate, aluminium oxide powders amounting to 10÷30g/l were introduced into this solution. The A16 ALCOA submicropowder (α-Al_2O_3, 400 nm average grain size) and the Degussa AG Aluminium Oxide C nanopowder (δ/γ-Al_2O_3, 13 nm nominal grain size) were employed. The powder suspension was subjected to homogenization by means of a mechanical stirrer or ultrasonic disintegrator (Sonics&Materials VCX 750). The metallization process was performed in thermostatic beakers (500 ml solution, 60÷70°C) on samples perpendicularly hung and rotated at 1 rpm. Both the solution and the suspension were additionally agitated with a magnetic stirrer. The coatings deposition time was varied from 30 to 60 minutes. The samples after deposition were carefully rinsed with distilled water, then dried and stored in an exsiccator for further tests. The composition of the coatings deposited was determined by the chemical method [38]. The aluminium oxide content was calculated from the difference in the sample masses and the PET foil remaining after removal of the coatings. The analytic results were then used for calculation of the coating thickness and the Ni reduction rate. The surface morphology and distribution of the aluminium particles were observed with both light (Nikon type ALPHAPHOT-2 YS2) and electron (HRSEM Hitachi S5500) microscopes at different magnifications: 10k, 50k and 100k.

Depositions of the Ni-P and the Ni-P/Al_2O_3 composite coatings were performed on Tenax HTA40 type carbon fibres in the form of 8÷11 cm long roving sections consisting of 12 or 24k fibres, 7 μm in diameter. The fibres surface preparation process for their further metallization was performed analogously likewise in the earlier described studies [6, 38] (sequentially: removal of epoxy resin sizing, sensitization in $SnCl_2$+HCl solution, activation in $PdCl_2$+HCl solution, re-activation in NaH_2PO_2+$NiSO_4$ solution, and metallization, including rinsing with distilled water after each individual step). In order to prevent spontaneous decomposition of the solution for metallization, the re-activation process was carried out in an ultrasonic washer. The final metallization process was performed with the ultrasonic action, and also without it. Observations of the coating surfaces were performed with use of SEM, analogously as for the samples deposited on the PET.

RESULTS AND DISCUSSION

Deposition of Ni-P and Ni-P/Al_2O_3 coatings on PET substrate

Experiments on the metallization of the PET polymer substrates were preceded by studies on the preparation of this type of material for electroless nickel plating from glycine solutions. The degreasing and etching procedures assumed according to study [40] were verified first for the deposition of thick Ni-P (5÷10 um) coatings, as required for further composite deposition and analysing its composition. The need to modify this procedure was encountered, since adhesion of the metal to PET was found insufficient, and consequently the Ni-P coatings underwent cracking and peeling (Fig. 1a). Both the insufficient substrate surface roughness and the inhibiting action from the Cr(VI) remnants in the polymer could be the reasons. Additional softening of the PET surfaces with a mixture of ethyl acetate and dimethylformamide, and also additional reduction of Cr(VI) with reducing agents solutions after etching [41] were conducted. The re-activation process of a palladium catalyst just before metallization, was also introduced. The tests performed show that it is sufficient to soften PET in an EtOAc + DMF solution jointly with further re-activation (Fig. 1b). Figures 2a and 2b show the polymer substrates before and after pre-treatment observed with a light microscope.

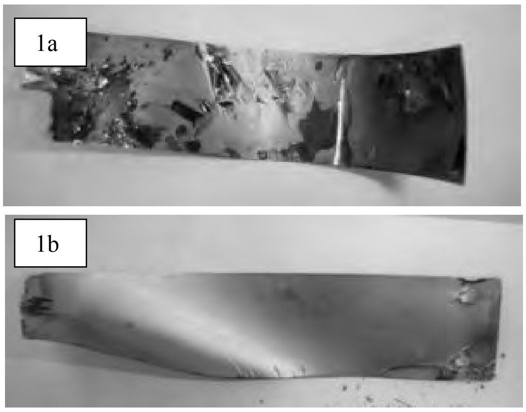

Fig 1. Examples of Ni-P layer obtained on PET substrates: a) example of cracked layer with insufficient adhesion; b) example of uniform layer with good adhesion

Rys 1. Przykłady warstw Ni-P otrzymanych na folii PET: a) przykład warstwy popękanej o złej adhezji, b) przykład wartwy jednolitej

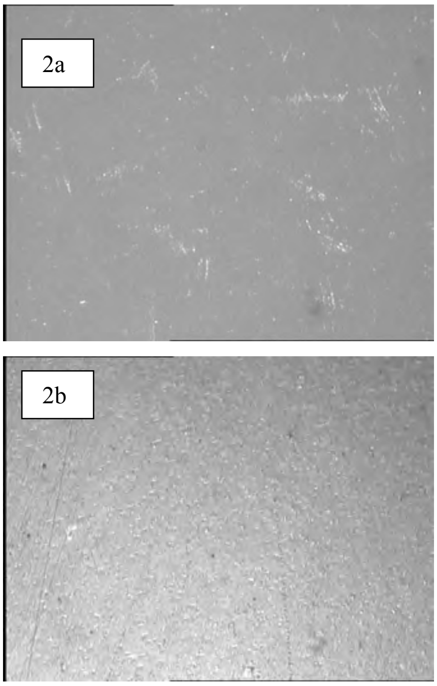

Fig. 2. PET surface: a) without pre-treatment; b) surface after softening in EtOAc + DMF solution for 30 sec and etching in solution of CrO_3 for 1min

Rys. 2. Powierzchnia PET: a) stan początkowy powierzchni; b) powierzchnia po zmiękczeniu w roztworze EtOAc + DMF w czasie 30 s i trawieniu w roztworze CrO_3 w czasie 1 min

The tests to deposit Ni-P from a solution without the surfactant (CTAB) and stabilizer (TU) additives proved that these conditions provide long-lasting PET metallization (Table 1).

TABLE 1. **Influence of electroless deposition parameters on quality and thickness of Ni-P coatings on PET substrates**

TABELA 1. **Wpływ parametrów procesu bezprądowego osadzania warstw Ni-P na podłożu PET na jakość i grubość powłok**

Concentration of CTAB [mM]	Concentration of TU [mM]	pH	Temp time	VNi [µm/h]	P [% mas]	Thickness Layer quality
$0^{a)}$	0	8,5	70°C 60 min	4,1	3,3	4,1 µm uniform
$0^{a)}$	0	8,5	70°C 60 min	4,6	3,6	4,6 µm non-uniform
CTAB $^{a)}$ 0,1	-	8,5	70°C 60 min	4,0	4,0	4,0 µm uniform
CTAB $^{a)}$ 0,1	TU 0,02	8,5	70°C 60 min	13,4	2,3	13,4 µm cracked
CTAB $^{a)}$ 0,1	TU 0,01	7,5	70°C 60 min	11,4	1,8	11,4 µm cracked
CTAB $^{a)}$ 0,1	TU 0,01	8,5	60°C 60 min	8,9	2,8	8,9 µm cracked
CTAB $^{a)}$ 0,1	TU 0,01	8,5	70°C 30 min	13,6	1,7	11,4 µm non-uniform

a)$NiSO_4$ 0,1M; NaH_2PO_2 0,2M; glicyna 0,21M
a) $NiSO_4$ 0,1M; NaH_2PO_2 0,2M; glycine 0,21M

However, reproducible homogeneity of the samples surfaces was unattainable. Initial tests with the CTAB solutions, but without any stabilizer additives showed that their spontaneous decomposition occurs sporadically with longer Ni-P deposition times. Hence, the addition of the stabilizer - thiourea (TU). The choice of the nickel plating conditions with that stabilizer was already the subject of earlier studies on the metallization of ceramics and carbon fibres [42]. The introduction of TU and CTAB into the PET metallization solution resulted in approximately a three-fold increase in the Ni-P deposition rate (Table 1) when compared to the deposition from solutions without stabilizer and surfactant. The layers deposited featured a high thickness that caused their partial cracking. Reduction in the Ni-P layers thickness through a reduction in the deposition time and abatement of the solution temperature, or its pH, led to a reduction in the metallization rate, however, slight crackings were still visible on the coatings surfaces. The changes implemented in the parameters of the Ni-P deposition process also resulted in a changed phosphorus content in the layers deposited (1.7÷4.0% P, by weight).

The electroless deposition of the composite coatings began with testing the homogenization of the powder in the solution for metallization. It was found that only ultrasonic homogenization provides an absence of rapid sedimentation of aluminium oxide powder on the bottom of the metallization reactor during further agitation with the magnetic stirrer. Aluminium oxide powders amounting to 5, 10 and 15 g per 500 ml of nickel plating solution (Table 2) were introduced. The Alcoa A-16 oxide featured a higher differentiation of particle size and that could account for its better matching the PET surface and the Ni-P coating structures during co-deposition. In turn, the Degussa C oxide (DNC) is a nanopowder which may account for its more intense penetration in between the carbon fibres of the rovings. A fault of this nanopowder is its tendency to form agglomerates which reduce the quantity of oxide in the Ni-P matrix [30]. For the research conditions applied currently, composites featuring the highest oxide content were obtained by using the Alcoa powder in a stabilizer-free solution, however, such solutions were not stable.In the comparative series with the addition of both oxides, there is greater incorporation of the Alcao oxide in the Ni-P layer (Table 2). Nevertheless, sedimentation of the larger particles was observed as the deposition time prolonged. Hence, further tests were performed just with the Degussa nanopowder. Deposition with the DNC powder produced Ni-P/Al_2O_3 composite coatings containing up to 8÷10% oxide, by weight. Reduction of the solution temperature and pH, and of the deposition time, led to a decrease in nano-oxide contents in the deposited coatings. The introduction of oxide powders into the metallization solution slightly increased the deposition rate. The phosphorus content in the deposited composites was a bit lower when compared to the composition of the Ni-P matrix. The SEM images of the composite surface coatings with the DNC oxide shown in Figures 3a, b, indicate that the particles agglomeration effect occurs, despite the ultrasonic process and the application of CTAB.

TABLE 2. **Influence of electroless deposition parameters on quality and thickness of Ni-P coatings on PET substrates**

TABELA 2. **Wpływ parametrów procesu bezprądowego osadzania warstw Ni-P/Al_2O_3 na podłożu PET na jakość i grubość powłok**

Concentration of additives a)	Al_2O_3 [g/l]	Temp. Time	VNi [μm/h]	P [%mas]	Al_2O_3 [%mas]	Thickness Layer quality
CTAB 0,1	A-16 10	70°C 60 min	16.6 R d)	1.4	18.3	16.6 μm non-uniform
CTAB 0,1	DNC 10	70°C 18 min	4.7 R d)	2.1	0.1	4.7 μm non-uniform
CTAB b) TM	A-16 10	70°C 60 min	16.5	1.8	12.4	16.5 μm cracked
CTAB b) TU	DNC 10	70°C 60 min	15.6	1.4	8.2	15.6 μm non-uniform
CTAB b) TU	A-16 20	70°C 60 min	16.8	1.7	6.6	16.8 μm uniform
CTAB b) TU	DNC 20	70°C 60 min	14.1	1.8	3.3	14.0 μm uniform
CTAB b) TU	A-16 30	70°C 60 min	15.6	1.8	7.1	15.7 μm uniform
CTAB b) TM	DNC 30	70°C 60 min	13.8 R d)	1.7	9.8	13.8 μm uniform
CTAB b) TU	DNC 10	60°C 60 min	7.9	2.7	2.3	7.9 μm uniform
CTAB b) TM	DNC 10	70°C 60 min	13.2	1.6	5.5	13.2 μm uniform
CTAB c), TU	DNC 10	70°C 45 min	13.6	1.6	5.4	10.2 μm non-uniform

a) $NiSO_4$ 0.1 M; NaH_2PO_2 0.2 M; glycine 0.21 M pH = 8.5; b) CTAB 0.1 mM+TU 0.01 mM c) pH = 7.5; d) R- solution decomposition

a) $NiSO_4$ 0,1 M; NaH_2PO_2 0,2 M; glicyna 0,21 M pH = 8,5; b) CTAB 0,1 mM+TU 0,01 mM; c) pH = 7,5; d) R - samorozkład

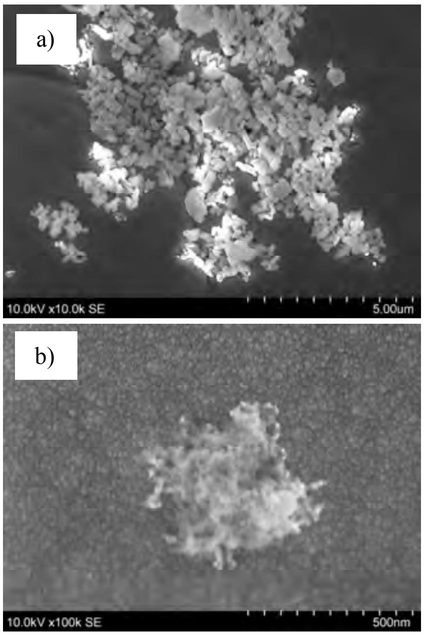

Fig. 3. Composite coating of Ni-P/Al_2O_3 on PET substrate obtained after 60 min of deposition at 70°C from solution containing: $NiSO_4$ 0.1 M; NaH_2PO_2 0.2 M; glicine 0.21 M, CTAB 0.1 mM, TU 0.01 mM, pH = 8.5 ; a) agglomeration of particles; b) separate particles

Rys. 3. Powłoka kompozytowa Ni-P/Al_2O_3 na folii PET otrzymana po 60 min osadzania w temperaturze 70°C z roztworu o składzie: $NiSO_4$ 0,1 M; NaH_2PO_2 0,2 M; glicyna 0,21 M, CTAB 0,1 mM, TU 0,01mM, pH = 8,5; a) aglomeracja cząstek, b) pojedyncza cząstka

Deposition of Ni-P and Ni-P/Al_2O_3 coatings on carbon fibre substrate

A series of experiments was carried out in which a sample consisting of 24k carbon fibre roving was placed perpendicularly into a suspension-filled container, subsequently in 500 and 200 ml suspension portions. Apart from the material differences, a major process change appeared as an expanded substrate surface for metallization, from about 0.5 dm^2 PET to 4.2 dm^2 and 5.8 dm^2 for carbon rovings (sequence of samples 1-3 and 4-6 in Table 3).

TABLE 3. **Influence of electroless deposition parameters on quality and thickness of Ni-P/Al_2O_3 coatings on carbon fibres**

TABELA 3. **Wpływ parametrów procesu bezprądowego osadzania warstw Ni-P/Al_2O_3 na włóknach węglowych na jakość i grubość powłok**

Additives.[a] mM	Al_2O_3 [g/l]	Temp Time	VNi [mg/cm* min]	P [% mas]	Al_2O_3 [% mas]	Thickness [µm]
CTAB[b] TU	DNC 10	70°C 5m	3.3	3.5	4.7	0.13
CTAB[b] T		DNC 10	70°C 10m	3.4	3.4	6.8
CTAB[b] 0.43 TU	DNC 10	70°C 25m	2.6 R[d]	3.0	5.8	0.21
CTAB[c] TU	DNC 30	70°C 5m	1.4	2.3	24.7	0.39
CTAB[c] TU	DNC 30	70°C 10m	2.4	4.2	6.7	0.64
CTAB[c] TU	DNC 30	70°C 45m	2.5 R	2.6	1.9	0.72
CTAB[c] TU	brak	70°C 15m	3.9	3.2	0	0.87

a) $NiSO_4$ 0.1 M; NaH_2PO_2 0.2 M; glicyna 0.21 M pH = 8.5; b) CTAB 0.1 mM+TU 0.01 mM; c) CTAB 0.1 mM + TM 0.02 mM;d) R- rozkład roztworu;

a) $NiSO_4$ 0,1 M; NaH_2PO_2 0,2 M; glycine 0,21 M pH = 8,5; b) CTAB 0,1 mM+TU 0,01 mM; c) CTAB 0,1 mM + TM 0,02 mM; d) R- solution decomposition

A high surface development causes very rapid exhaustion of the components in the Ni-P deposition solution and leads to hampering of the metallization process. Hence, the deposition time was considerably reduced to 5÷10 minutes (Table 3). In the first series, the deposition process of the composite from the suspension featured a lower oxide concentration (10 g/l), whereas in the second series, the DNC concentration was increased to 30 g/l, however, it required an increased stabilizing agent content. The longer metallization time (25÷45 minutes) led to spontaneous decomposition of the suspensions.

The short metallization time applied in both series was sufficient enough to obtain composite layers of a thickness within the 300÷500 nm range. The first series produced Ni-P/Al_2O_3 composite layers containing up to 5÷6% by weight of aluminium oxide and 3÷3.5 wt.% of phosphorus. For the second series, even up to about 25 wt.% of aluminium oxide in the composite was obtained, with 2.3÷4.2 wt.% of phosphorus content. The SEM microscope observations of the composite-coated carbon fibre samples showed that the oxide particles penetrate in between individual fibres of the roving, as followed by their further building into the Ni-P layer. However, agglomeration of the DNC nanoparticles into larger agglomerates still poses a problem (Fig. 4).

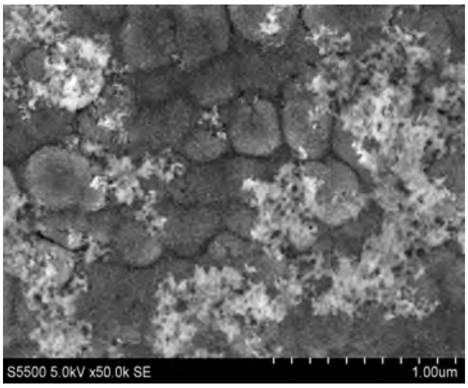

Fig. 4. Composite coating of Ni-P/Al_2O_3 on carbon fiber obtained after 15min of deposition at temperature of 70°C from solution containing: $NiSO_4$ 0.1M; NaH_2PO_2 0.2 M; glicine 0.21M, CTAB 0.1 mM, TU 0.02 mM, pH = 8,5

Rys. 4. Powłoka kompozytowa Ni-P/Al_2O_3 na włóknie węglowym otrzymana po 15 min osadzania w temperaturze 70°C z roztworu o składzie $NiSO_4$ 0,1 M; NaH_2PO_2 0,2 M; glicyna 0,21 M, CTAB 0,1 mM, TU 0,02 mM, pH = 8,5

CONCLUSIONS

The studies performed have led to the following conclusions:

- the deposition of Ni-P on PET substrates from a solution without surfactants and stabilizer did not provide reproducible homogeneity or a constant composition of the Ni-P/Al_2O_3 layer,
- the addition of surfactant (CTAB) enhanced the homogeneity of the Ni-P coating on the PET substrates, however, a slight reduction in the deposition rate was observed,
- the addition of stabilizer (TU) prevented spontaneous decomposition of the suspensions, moreover the presence of both CTAB and TU in the solution resulted in an increase in the deposition rate on the PET substrates,
- the electroless deposition of the Ni-P/Al_2O_3 layers on PET showed that the DNC nanopowder secures better conditions for stable (i.e. without any powder sedimentation and spontaneous decomposition of suspension) and reproducible deposition of both thin and thick composite coatings,
- transfer of the conditions for the deposition of composite layers developed for the PET bases is also possible to carbon fibre bases, after slight modification,
- to obtain an Ni-P/Al_2O_3 layer on carbon fibres, the deposition time was reduced to 5÷10 min, which

allowed us to produce a thin (300÷500 nm) layer with a low phosphorus content (2÷4%),
- despite the ultrasonic process and the application of surfactant, particles agglomeration still was observed.

Acknowledgments

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