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COMPOSITES THEORY AND PRACTICE

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ELECTROLESS DEPOSITION OF Ni-P/NANO-TiO_2 COMPOSITE COATINGS ON PET AND CARBON FIBRES SUBSTRATES

This paper presents the results of studies on the electroless deposition of Ni-P/nano-TiO_2 composite coatings on pretreated polymeric substrates (PET polyester Mylar A type) and on carbon fibres (24k fibres with 7 μm Tenax rovings). The Ni-P layer 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. Titanium(IV) oxide (Aldrich, grains 25 nm) in powder form was added, amounting to 10÷30 g/l, with ultrasonic homogenization of the suspension. Under the experimental conditions applied, partial sedimentation of the powder occurred. Deposition was performed at the temperature of 70°C, during 5÷15 minutes for the carbon fibers and 60 minutes for PET. The substrates were 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. Under the applied conditions, Ni-P/TiO_2 layers of a thickness within 0.3÷1 μm, titanium oxide content up to 17% by weight, and 2÷3% phosphorus by weight, were obtained.

Keywords: **electroless composite deposition, Ni-P/TiO_2 composite, deposition rate and microstructure, PET and carbon fibers metallization**

BEZPRĄDOWE OSADZANIE WARSTW KOMPOZYTOWYCH Ni-P/NANO-TiO_2 NA FOLII PET I WŁÓKNACH WĘGLOWYCH

W pracy przedstawiono wyniki badań nad bezprądowym osadzaniem warstw kompozytowych Ni-P/ TiO_2 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 proszku tlenku tytanu (IV) (Aldrich, ziarna 25 nm) w ilości 10÷30 g/l, z ultradźwiękową homogenizacją zawiesiny. Stwierdzono częściową sedymentację tlenku. Osadzanie prowadzono w temperaturze 70°C, w czasie od 5 do 15 min dla podłoża węglowego i 60 min dla PET. 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 zastosowanych warunkach osadzone bezprądowo na włóknach węglowych warstwy kompozytowe Ni-P/TiO_2 o grubości 0,3÷1 μm zawierały do 17% mas. tlenku tytanu oraz 2÷3% mas. fosforu.

Słowa kluczowe: **bezprądowe osadzanie kompozytu Ni-P/TiO_2, szybkość osadzania i mikrostruktura, PET, metalizacja PET i włókien węglowych**

INTRODUCTION

The manufacturing technology of metal matrix composites (MMC) reinforced with carbon fibres requires that during the infiltration process, undesirable products of reactions between carbon and metal, in particular Al_4C_3 in the case of an aluminium matrix do not form. This can be prevented by the application of suitable barrier coatings on the carbon fibres, which give at the same time changeless mechanical properties in the fibres-matrix system. One of the solutions may be to apply Ni-P alloy layers on the carbon fibres (rovings, fabrics), deposited by the electroless method [1]. However, even for such barrier layers when the infiltration process is too long, local dissolution of Ni-P was observed. The introduction of inert particles, such as oxides: Al_2O_3, TiO_2, SiO_2 into the Ni-P layers is one of the ways which delays the dissolving process. The work on the electroless deposition of Ni-P/Al_2O_3 nanocomposites shows [2] that they can be repeatedly deposited on carbon fibres, however, the content of the oxide phase was relatively low (5÷8 wt.%). This paper presents the results of research on the electroless deposition of the Ni-P/TiO_2 nano-composite. According to literature data, this composite can contain much more TiO_2 particles in coatings than 8%.

Composite Ni-P/TiO_2 coatings were obtained by the electroless method mainly as anticorrosive materials with enhanced wear resistance and high hardness. The electroless process is particularly useful for covering parts of complex shapes. The substrates were mostly steel [3-16], rarely Al and Mg alloys [17-23], copper, its alloys and other metals [19, 24-28], or sometimes polymers [29]. A separate group constituted Ni-P/TiO_2 layers with electro-catalytic properties (hydrogen evolution, photodegradation of pollutants) [30-32] and layers in electronics, such as barrier coatings in circuit boards [25, 26]. Only in paper [33] was the deposition of Ni-P/ZrO_2 composites on carbon fibres, destined for MMC, described. The analysis of literature data for carbon fibres metallization showed that it is difficult to find direct and useful information because of the variety of metallization purposes, the huge variety of applied conditions and also significant incompleteness of data, as well as some contradictions in the presented conclusions.

Ni-P barrier layers and composite layers should have a small thickness (under 500 nm when fibre diameter is 7 μm) and possibly the lowest phosphorus content (2÷4 wt.%), which prevent the introduction of large amounts of Ni and P into the final aluminium matrix. The oxide grain size should not exceed 50÷100 nm in order to be effectively embedded in the Ni-P layer. However, the vast majority of papers refer mostly to the production of relatively thick anticorrosive Ni-P/TiO_2 coatings (5÷40 μm), which were deposited by the electroless method from acidic solutions. The usage of acidic baths led to obtaining a phosphorus content from 6% to even 15 wt.% [24]. The solutions for the deposition of Ni-P contain mostly nickel sulfate (II), sodium hypophosphite and buffering agents, which are usually simple organic acids and their salts. There is still insufficient information about the applied stabilizers, which are indispensable especially in the deposition of composite layers. Pd(II) salt [3, 6, 12, 24, 28] or thiourea [22] usually play the role of stabilizers. It is known that surfactants are an important component of the solution for the electrodeposition of composite coatings [34, 35], and they determine the amount of embedded oxide powder and also the homogeneity of the composite. Paper [36] indicates that the role of surfactants is very important in the electroless deposition of Ni-P layers with the addition of ceramic particles, but there are still very few details about such additives in solutions for the deposition of Ni-P/TiO_2 [15, 18, 28].

Despite the average grain size, the characteristics of the added TiO_2 powder were often incomplete in terms of information about the producer, oxide purity and particle distribution. Previous work has almost exclusively concerned a micro or sub-micro powder with a particle size more than 200 nm, rose to 10 μm [4-6, 11, 18, 24]. The development of nanopowder manufacturing technology and the manufacture of homogeneous dispersion during the deposition of Ni-P/TiO_2 have led to more common usage of nanopowders nowadays (15÷60 nm) TiO_2 [13-16, 19-22, 26-30, 32]. The nanopowder of anatase (Degussa, Merck) was the most frequently used. It seems that the nanopowders were not always used properly, usually there is no information on the initial deglomeration of the powder in the solution for deposition and the only way to make the suspension homogeneous was the usage of a magnetic stirrer or gas barbotage. Suspension conditioning before layer deposition should be preceded by mixing the powder with the solution for many hours [7, 15]. The use of ultrasound to obtain good nanopowder deaglomeration in the suspension is only mentioned in [27, 32].

The content of the powder in the coating of its concentration in the suspension is essential when obtaining galvanic composite layers (metal-ceramic powder type) [8, 34-38]. This kind of dependences has also been obtained for the electroless deposition of Ni-P/TiO_2 [3, 12, 14, 16, 17, 20, 21, 24, 26, 27, 29]. All of the described dependences are characterized by an increase in TiO_2 content in the layer with an increase in the amount of powder in the suspension at the first stage of the process. Only for the highest concentration is the stability of the composition of the coatings noticeable or even a decrease in the TiO_2 amount in the layer [3, 16, 17, 24, 29]. It is worth noticing that the introduction of TiO_2 to the solution for Ni-P deposition causes an increase in the metallization rate at the beginning. However, at high concentrations of powder the deposition rate decreases. A reduction in catalytically active nickel surface deposition also leads to a slight decrease in P in the resulting Ni-P/TiO_2 coatings. However, the course of the individual dependences is very diverse because of the large differences in the conditions used in the experiments (1 to 40 g/l TiO_2). For instance, for the range of 5÷40 g/l, 7÷17 wt.% in [3] and for 1÷10 g/l just 2÷4% [26] or 3÷8% [16] amount of TiO_2 have been obtained in the layer. The TiO_2 content has not reached 20÷30 wt.%, which can be obtained in the electrodeposition of layers [38]. Nevertheless, in comparison experiments with Al_2O_3 and TiO_2, it has been found that a higher amount of oxides in the Ni-P layer was obtained for TiO_2 [6, 20, 37, 38]. Numerous studies have been performed on the physicochemical properties of Ni-P/TiO_2 composite layers. It has been found that adding TiO_2 does not change the structure or morphology of the basic Ni-P coating significantly. However, the wear resistance, corrosion resistance, microhardness also sometimes cracking resistance and adhesion to the specimen rose.

To sum up, it is possible to affirm that the above literature review has provided a number of valuable suggestions about the obtained dependencies and properties of the layers. Nonetheless, it leads to the conclusion that detailed studies are needed to work out the authors' own condition of layer deposition, especially since in the literature there is a lack of publications about Ni-P/TiO_2 deposition on carbon fibers.

EXPERIMENTAL PROCEDURE

The conditions of electroless deposition of Ni-P and Ni-P/TiO_2 layers from an alkaline glycine solution on a flat polymer surface were defined in the first part of the publication, which is similar to studies on the deposition of Ni-P/Al_2O_3 [2]. In the second part, the developed metallization conditions were checked on the carbon fibre surfaces.

As the reference specimen, PET foil strips (2.5 x x 9 cm Mylar A 75 μm) were utilized. The way of preparing the specimen was precisely described in the previous publication [2]. Application of the catalyst was carried out in two steps (in $SnCl_2$ and $PdCl_2$ solutions). Re-activation of the catalyst involving immersing the specimen in an NaH_2PO_2 solution was done just before metallization. The bath for electroless deposition consisted of 0.1 M nickel(II) sulfate, 0.2 M sodium hypophosphite (phosphate(I) sodium) and 0.21 M glycine. As a pH-stabilising additive, H_2SO_4 and NaOH were used. Metallization proceeded within the 7.5÷8.5 range. Thiourea $SC(NH_2)_2$ (TU 0.02 mM) was added as the stabilizer, and cetyltrimethylammonium bromide CTAB (0.1 mM) - as the surfactant. Additionally, titanium dioxide TiO_2 anatase with a < 25 nm grain size (Aldrich) was added. Titanium dioxide powders in the amounts of 10 and 30 g/l were introduced into the electroless metallization solution. In order to obtain a stable suspension, an ultrasonic disintegrator (Sonics&Materials VCX 750) and a magnetic stirrer were used. The conditions of electroless deposition were as follows: time - 60 minutes, temperature - 70°C and volume - 500 ml. The suspension was agitated with a magnetic stirrer and the samples were rotated at 1 rpm with a mechanical stirrer. The samples after metallization were carefully rinsed with distilled water, then dried, weighed and stored in an exsiccator. Layer composition analysis, just like in [2], allowed the authors to define the content of Ni, P and TiO_2. The developed electroless deposition method on a flat specimen allowed us to adjust the experiment conditions on carbon fibre Tenax HTA40 in the form of 11 cm sections consisting of 24k fibres (7 μm in diameter). The fibres surface preparation process for their further metallization was performed in the same manner as in earlier described studies [1, 2, 39] (sequentially: removal of epoxy resin sizing, sensitization in $SnCl_2$ solution, activation in $PdCl_2$ solution, re-activation in NaH_2PO_2+$NiSO_4$ solution, including rinsing with distilled water after each individual step). The metallization time was shortened to 5÷15 minutes. The metallization process was performed in a thermostatic reactor and thermostatic ultrasonic washer (IS-20-Intersonic, 1200 W power). The layers composition analysis was performed the same as for the PET specimen. Observations of the coating surfaces were performed with the use of SEM (HRSEM Hitachi S5500, magnifications: 20k and 100k).

RESULTS AND DISCUSSION

Deposition of Ni-P/TiO_2 on PET substrate

The major problem in the electroless deposition of composite layers is to obtain a homogeneous bath with a uniform dispersion of particles. The tests on carbon fibres metallization with the Ni-P/Al_2O_3 layer described in [2] had shown that previous ultrasonic deglomeration ensures homogenous suspensions and prevents rapid sedimentation of aluminium oxide powder on the bottom of the metallization reactor. The TiO_2 powder with a grain diameter of 25 nm had a high tendency to agglomeration and sedimentation, and therefore in order to ensure good dispersion during deposition, ultrasonic vibration and mechanical agitation (magnetic and propeller stirrer) were used.

The experiment of metallization of the PET substrate allowed initial visual assessment of the quality of the deposited coating, and its adhesion to the polymer. The deposition conditions (time 60 min, pH 8.5, temp. 70°C) allowed us to obtain homogenous coatings with a thickness within the 7÷11 μm range (Table 1). When testing the deposition on PET, titanium oxide powders amounting to 10÷30 g/l were introduced into the solution. The content of nanopowder in the coatings obtained from these suspensions did not differ significantly and amounted, for example, to 8.3% (for a suspension of 10 g/l TiO_2 concentration) and 7.1% (from a suspension of 30 g/l), which indicate the possibility of mechanical abrasion of the suspension particles on the layer surface in a solution with a higher concentration of TiO_2. An increase in the rate of metallization with an increasing concentration of TiO_2 in the suspension was observed. It may stem from increasing the real metallization surface (deposition of nickel also on the surface of TiO_2 powder).

TABLE 1. **Ni-P/TiO_2 deposition on PET substrates from glycine solution pH 8.5 - changes in process parameters**

TABELA 1. **Osadzanie powłok Ni-P/TiO_2 na folii PET z roztworu glicynowego o pH 8,5 - zmiany parametrów procesu**

TiO_2	Deposition time [min]	Deposition rate [mg/m^2·s]	P content [% mas.]	TiO_2 content [% mas.]	Thickness [μm]/ layer quality
10 g/l	60	14.7	2.1	8.3	7 uniform
30 g/l	60	23.0	2.3	7.1	11 uniform

Deposition of Ni-P/TiO_2 on carbon fibres substrate

Carbon fiber is a substrate with high surface development (the surface area of one bundle 24k length of 11 cm is about 2,9 dm^{-1}), so because of the high load factor[1] of the solution and the rapid exhaustion of its components, it was decided to carry out the plating in a reduced time ranging from 5 to 15 minutes. The other metallization parameters were the same as for the PET substrates. A shorter metallization time allowed us to obtain composite coatings with thicknesses from 0.30 to 0.95 μm (Table 2), which is enough for the subsequent step of the infiltration process in the manufacture of a MMC with carbon fibres reinforcement [1]. The coatings received from the glycine solution with pH 8.5 containing up to 2.5% phosphorus by weight and the content of TiO_2 was varied. A higher concentration of nanopowders in the suspension (30 g/l) gave lower contents in the deposited layer. From the bath containing 30 g/l nanopowder, coatings of 14÷17% TiO_2 by weight were obtained.

TABLE 2. **Ni-P/TiO_2 deposition on carbon fibers from glycine solution pH 8.5 - changes in process parameters**

TABELA 2. **Osadzanie powłok Ni-P/TiO_2 na włóknach węglowych z roztworu glicynowego o pH 8,5 - zmiany parametrów procesu**

TiO_2	Deposition time [min]	Deposition rate [mg/cm·min]	P content [% mas]	TiO_2 content [% mas]	Thickness [μm]
10 g/l	5	3.0	2.3	17.5	0.30
	10	2.0	2.3	17.3	0.36
	15	2.1	2.5	14.0	0.58
30 g/l	5	3.9	2.8	8.6	0.43
	10	2.7	2.5	11.8	0.60
	15	3.3	2.5	11.4	0.95

SEM observations show good penetration of the solution ingredients in between the fibres of the rovings - in all the trials continuous layers with TiO_2 grains were received (Fig. 1). Unfortunately, the agglomeration of nanopowder particles in the suspension was still a problem, which did not allow for maximum distribution of TiO_2 in the composite coating (Fig. 1). This effect has not been eliminated even in the solutions containing the surfactant (CTAB), which had been applied in previous work related to the metallization of carbon fibers with Ni-P layers [2, 39].

In the course of the study, instability of the suspension with TiO_2 was observed. Self-decomposition of the suspension occurred, which eliminated the possibility of reusing the bath in further processes. To prevent this, an additional portion of stabilizer was added to the bath. However, it did not resolve the problem, that is why it was decided to reduce the pH to 7.5 (Table 3). Lowering the pH of the glycine bath by one unit did not result in a significant decrease in the metallization rate or phosphorus content in the coating. There were also no differences in the morphology of the surface and agglomeration of the particles, and under these conditions coatings containing from 10 to 14% TiO_2 by weight were received. Solutions with a lower pH with the addition of a stabilizer can be stored for a few months and reused.

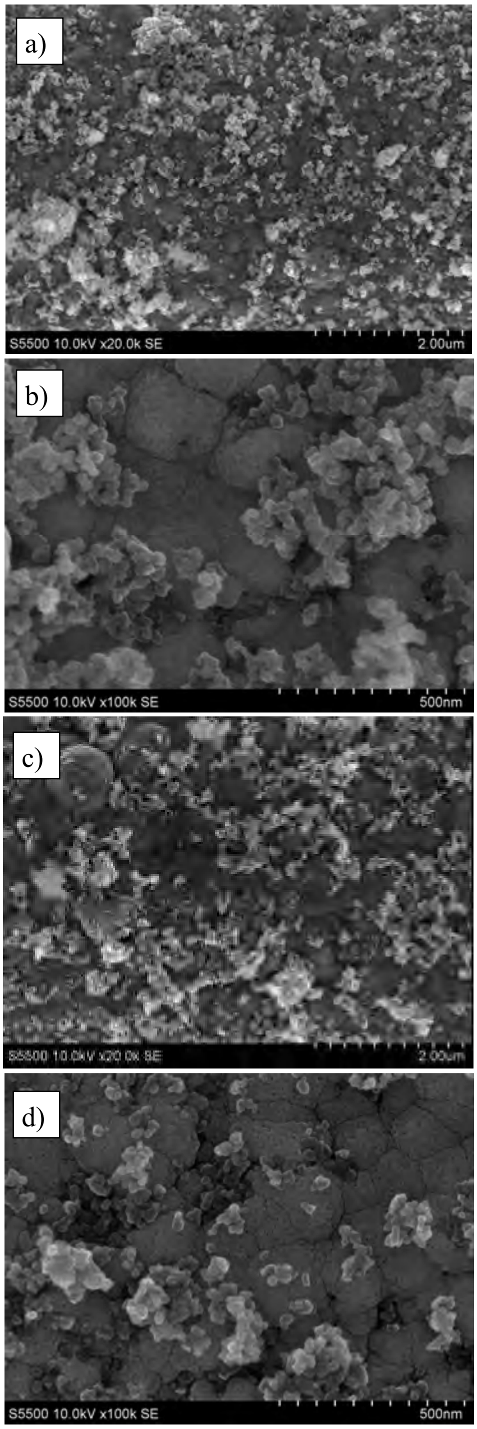

Fig. 1. Composite layer of Ni-P/TiO_2 on carbon fiber substrate obtained from glycine solution with pH 8.5, deposition time 5 min: a,b) TiO_2 concentration 10 g/l; c,d) 30 g/l TiO

Rys. 1. Powłoka kompozytowa Ni-P/TiO_2 na włóknie węglowym otrzymana z roztworu glicynowego, pH 8,5, czas metalizacji 5 min: a,b) 10 g/l TiO_2; c,d) 30 g/l TiO_2

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[1] In electroplating, the load factor is defined as the ratio of substrate surface to the solution volume. Electroless metallization usually requires loads of less than 5 dm^{-1}.

TABLE 3. **Ni-P/TiO_2 deposition on carbon fibers from glycine solution pH 7.5 - changes in process parameters**

TABELA 3. **Osadzanie powłok Ni-P/TiO_2 na włóknach węglowych z roztworu glicynowego o pH 7,5 - zmiany parametrów procesu**

TiO_2	Deposition time [min]	Deposition rate [mg/cm*min]	P content [% mas]	TiO_2 content [% mas]	Thickness [μm]
10 g/l	5	3.3	2.5	14.3	0.37
	10	1.9	2.1	12.1	0.28
	15	3.4	1.8	13.5	0.95
30 g/l	5	2.6	2.9	10.4	0.32
	10	1.9	2.4	12.9	0.42
	15	2.9	2.0	14.9	0.69

CONCLUSIONS

The research performed enabled the authors to draw the following conclusions:

- in the electroless process from the alkaline glycine solution, homogenous Ni-P/TiO_2 coatings with 17 wt.% TiO_2 and 2.5 wt.% phosphorus could be obtained;
- carbon fiber metallization can be carried out under conditions established for PET film, by reducing the processing time due to the higher load factor in the case of the carbon fibre. Reducing the metallization time to 5 minutes allows for obtaining continuous layers with thicknesses of about 0.3 μm, which is sufficient for the further application of fibers as reinforcement in MMC;
- for sufficient homogenization of the suspension, intensive ultrasound vibration is required, both before and during metallization;
- the introduction of stabilizer is necessary. The addition of thiourea to the solution prolongs its storage time and makes it possible to be reused;
- despite the ultrasonic process and application of surfactant, TiO_2 agglomeration was not fully eliminated.

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