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ELECTROLESS DEPOSITION OF Ni-P/nano-SiO₂ COMPOSITE COATINGS ON PET AND CARBON FIBER SUBSTRATES

This paper presents the results of studies on the electroless deposition of Ni-P/nano-SiO₂ composite layers on pre-treated polymeric bases (PET polyester Mylar A type) and on carbon fibers (24k fibers with 7 μm Tenax rovings). The Ni-P matrix was deposited from a bath consisting of NiSO₄ 0.1 M; NaH₂PO₂ 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. Silica powders (Sigma, grains 7 and 14 nm) were added in amounts of 10÷30 g/l, with ultrasonic homogenization of the suspension or by using a homogenizer. Under the applied experimental conditions, the deposition of composites with two types of silica on two types of substrate was carried out. The deposition was performed in the temperature range of 60÷70°C, during 5÷60 minutes, while the samples 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/SiO₂ layers of a thickness within 120÷710 nm, an aluminium oxide content up to 17.3 wt.%, and 2÷3 wt.% phosphorus were obtained.

Keywords: electroless composite deposition, Ni-P/SiO₂ composite layer, deposition rate and microstructure, PET and carbon fibers metallization

BEZPRĄDOWE OSADZANIE WARSTW KOMPOZYTOWYCH Ni-P/nano-SiO₂ NA FOLII PET I WŁÓKNACH WĘGLOWYCH

Przedstawiono wyniki badań nad bezprądowym osadzaniem warstw kompozytowych Ni-P/SiO₂ na podłożach polimerowych typu Mylar (poliester PET) oraz na włóknach węglowych (wiązki 24k włókien o średnicy 7 μm Tenax). Osnowa Ni-P osadzana była z roztworu NiSO₄ 0,1 M; NaH₂PO₂ 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 krzemu (Sigma, ziarna 7 i 14 nm) w ilości 10÷30 g/l z ultradźwiękową homogenizacją zawiesiny oraz z zastosowaniem homogenizatora. W zastosowanych warunkach doświadczeń prowadzono osadzanie na dwóch rozmiarach ziaren o nanometrycznej wielkości ziaren na dwóch rodzajach podłoża. 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 zastosowanych warunkach osadzone bezprądowo warstwy kompozytowe Ni-P/SiO₂ o grubości 120÷710 nm zawierały do 17,3% mas tlenku krzemu oraz 2÷3% mas fosforu.

Słowa kluczowe: bezprądowe osadzanie kompozytu Ni-P/SiO₂, szybkość osadzania i mikrostruktura, PET, metalizacja PET i włókien węglowych

INTRODUCTION

The preparation of carbon fiber composites with a metallic aluminium matrix allows one to obtain material with high strength combined with low weight. However, on the interface between the carbon and aluminium, brittle Al₄C₃ material is formed by chemical reaction. The solution is a barrier coating which does not impair the mechanical properties of the final composite and at the same time ensures good adhesion to the fiber and aluminium alloy [1, 2]. In studies performed in the framework of the German-Polish project [3, 4], electroless deposition was used for a barrier layer

such as Ni-P [4-7]. However, further experiments showed that with a longer time of infiltration, there is local contact of molten aluminium with the surface of the infiltrated carbon fibers. Increasing the thickness of the Ni-P coating was disadvantageous due to the introduction of a large amount of Ni and P to the aluminium alloy. However, it is possible to inhibit the dissolution of the barrier coating by co-depositing Ni-P along with more inert oxide particles. Previous experiments have shown that Ni-P/Al₂O₃ coatings contain only up to 8 wt.% oxide [7], whereas the metallization bath for the

electroless deposition of an Ni-P/TiO₂ layer is highly unstable [8]. It was assumed that another oxide which could be applied in a barrier composite layer in an Ni-P matrix may be nano-SiO₂ [3].

Composite coatings consisting of a nickel matrix with an addition of SiO₂ were one of the first electro-composites and at the beginning were used in a decorative coatings system [9]. Then, it was used as functional coatings on steel [9-11]. Electroless metallization was applied in the deposition of an Ni-P/SiO₂ composite layer on different types of substrates [10-12]. The objective was to improve the corrosion resistance [10, 13-19], to increase their hardness and wear resistance [12, 15, 16, 18, 20-25], and to obtain other functional properties [20, 22, 25]. It was found that the deposited composites exhibit better anti-corrosion or tribological properties than Ni-P coatings. Finally, a few works presented a more detailed study of the composite deposition process [15, 20, 24, 26]. Ni-P/SiO₂ coatings were deposited mostly on steel, less on copper or other metals and rarely on polymer [20, 22]. There is no information about the electroless metallization of the mentioned composite on carbon fibers or other samples with high surface area substrates. Conventional baths were used for Ni-P electroless deposition. The basic composition contained an Ni(II) salt, a hypophosphite as a reducing agent, buffering and complexing agent (hydroxyacid salts-citrates, hydroxyacetates and hydroxypropionate with the addition of acetate or propionate, sometimes some borate or ammonium salts). They were mostly acidic solutions (pH = 4.5÷5.0), less alkaline (pH = 9÷9.5 [20, 21, 26]. There is no information about other functional additives such as stabilizers (only in [13, 27] was a Pb(II) salt added) or a bath with commercial additives was used [17, 19, 24]. Additionally, there are no particular studies on the influence of the components in the solution on the deposition rate or the composition of the deposited coatings, except [20].

Ni-P/SiO₂ composite layer deposition takes place after the introducing SiO₂ powder to the Ni-P bath, usually in the form of nano-particles [13, 15-25] in amounts of 0.1 to 30 g/l. Micro-powders were used in previous studies or in selected experiments [10, 12, 26, 27]. The need for adequate mixing of the powder with the electroless bath before deposition was emphasized. Sometimes ultrasound was used as a mixing factor [13, 17, 18, 23]. The deposition was carried out with mixing the resulting suspension and the temperature range was relatively narrow (from 82 to 95°C). The basic characteristics of the deposition process of the composite coating is the relation of the content of second phase particles in the composite layers with respect to the concentration of particles in the suspension for the metallization [10, 28, 29]. Unfortunately, only a few works [20, 24, 25] contained data about the observed maximum of the SiO₂ content in the layer for the applied changes of powder concentrations in the bath. The huge variety of applied bath compositions and of electroless

deposition conditions does not allow one to predict how this relationship for the deposition of Ni-P/SiO₂ from the glycine bath used in our studies might look like [7, 8, 30]. The objective of the present work was to determine the proper parameters for the electroless deposition of composite Ni-P/nano-SiO₂ layers for their use as barrier coatings in a carbon fiber-aluminum alloy system.

EXPERIMENTAL PROCEDURE

The parameters of the electroless deposition of Ni-P and Ni-P/SiO₂ layers from an alkaline glycine-buffered bath were similar to studies described earlier on the deposition of Ni-P/Al₂O₃ and of Ni-P/TiO₂ composite layers [7, 8]. They were proved initially on flat polymer foil then applied to carbon fibers roving metallization.

As the reference specimen, strips of PET foil (2.5 x 9 cm Mylar A 75 μm) were used. The way of preparing the specimen surface was precisely described in [7]. Activation of the surface with a Pd catalyst was accomplished in two steps: by immersion in SnCl₂ and PdCl₂ solutions. Immediately before metallization, the re-activation process of the catalyst was applied, involving immersion of the specimen in a reducer solution (NaH₂PO₂). The bath for Ni-P deposition was composed of 0.1 M nickel(II) sulfate, 0.2 M sodium hypophosphite (phosphate(I) sodium) and 0.21 M glycine. As a pH-regulating additive, H₂SO₄ and NaOH were used. Thiourea SC(NH₂)₂ was added as the stabilizer (TU, 0.02 mM), and cetyltrimethylammonium bromide - as the surfactant (CTAB, 0.1 mM).

Metallization proceeded within the 7.5÷8.5 pH range. Additionally, silicon dioxide SiO₂ powder with a 7 and 14 nm grain size (Sigma) was added as the composite nanofiller. Silicon dioxide powders in the amounts of 10 and 30 g/l were introduced at ambient temperature into the Ni-P bath. In order to obtain a stable suspension, a laboratory homogenizor and an ultrasonic disintegrator (Sonics&Materials VCX 750) were used. The main plating conditions for the electroless coatings were as follows: time - 60 minutes, temperature - 70°C and bath volume - 500 ml. The double mixing method was used; the suspension was agitated with a magnetic stirrer and the samples were rotated at 1 rpm with a mechanical stirrer. After deposition, the samples were carefully rinsed with distilled water, then dried, weighed and stored in a desiccator for further tests. Deposit composition analysis, performed just like in [7], allowed for calculation of the deposition rate and the content of Ni, P and SiO₂.

After the preliminary experiments, deposition was carried out on samples of Tenax HTA40 carbon fiber in the form of 11 cm long roving consisting of 24k fibers (7 μm in diameter). The fiber surface preparation process for their further metallization was performed in the same manner as in earlier described studies [6, 7] (in sequence: removal of epoxy resin, sizing, activation in two steps in SnCl₂ solution and next in a PdCl₂ solution,

re-activation in an $\text{NaH}_2\text{PO}_2 + \text{NiSO}_4$ bath, rinsing with distilled water after each individual step). The deposition time was shortened from 60 to 5–15 minutes. The metallization process was performed in a thermostatic reactor and thermostatic ultrasonic washer (IS-20-Intersonic, 1200 W power). The deposit composition analysis was performed in the same manner as for the PET specimens. Observations of the composite coating surfaces were performed with the use of SEM (HRSEM Hitachi S5500, magnifications: 20k and 100k).

RESULTS AND DISCUSSION

Deposition of Ni-P/SiO₂ on PET substrate

The main problem in the electroless deposition of composite layers with nanofillers is to obtain a homogeneous bath with uniform dispersion of particles. Previous studies showed [7, 8] that ultrasonic deagglomeration ensures a homogenous suspension and prevents rapid sedimentation of the aluminium and titanium oxides powder in the reactor. The SiO₂ powders with a grain diameter of 7 and 14 nm had a tendency to form a colloidal solution when the disintegrator or homogenizer was used in the preparation of the powder and then ultrasonic vibration and mechanical agitation at the deposition step.

The experiment of metallization of the PET substrate (Table 1) allowed for initial visual control of the quality of the deposited coating and its adhesion to the polymer.

TABLE 1. Ni-P/SiO₂ deposition on PET substrates from glycine buffered bath pH 8.5 - changes in process parameters

TABELA 1. Osadzanie powłok Ni-P/SiO₂ na folii PET z roztworu glicynowego o pH 8,5 - zmiany parametrów procesu

SiO ₂	Deposition time [min]	Deposition rate [mg/m ² *s]	P content [% mas]	SiO ₂ content [% mas]	Grain size SiO ₂ [nm]/dispersion
10 g/l	60	15.8	1.9	3.6	7/hom
20 g/l	60	14.7	1.9	1.4	7/hom
30 g/l	60	15.6	2.1	4.9	7/hom
10 g/l	60	20.4	1.9	1.4	7/UD
20 g/l	60	20.4	2.1	4.3	7/UD
30 g/l	60	15.9	2.3	17.3	7/UD
10 g/l	60	21.9	1.8	2.2	14/UD
20 g/l	60	15.4	0.9	2.7	14/UD
30 g/l	60	14.7	1.0	2.9	14/UD

The deposition conditions (time 60 min; pH 7.5–8.5; temp. 70°C) allowed us to obtain good quality coatings with a thickness within the 6–10 μm range. Suspensions with three concentrations of SiO₂ powder - 10 g/l, 20 g/l and 30 g/l were applied. The content of nanopowder in the coatings depends mainly on the concentration of powder in the bath. The content of SiO₂ in the compo-

site coating was 14 wt.% (7 nm grain size) and 2.2 wt.% (14 nm grain size) for 10 g/l of powder in the bath. A change to 30 g/l in the bath allowed for 17.3 wt.% (7 nm grain size) and 2.9 wt.% (14 nm grain size) content of SiO₂ in the coatings correspondingly.

Increasing the content of powder in the bath resulted in a distinct increase in the content of 7 nm grain size SiO₂ powder in the composite coating. A decrease in the rate of metallization with an increasing concentration of SiO₂ in the bath was observed. It is likely a result of covering the active Ni surface by grains of powder.

Deposition of Ni-P/SiO₂ on carbon fiber substrate

Coating of the carbon fiber substrate samples was conducted at three relatively reduced times of deposition 5, 10 and 15 minutes (Tables 2, 3).

These parameters were used because of the high load factor of the bath and rapid exhaustion of its components. That deposition time allowed us to obtain composite coatings with thicknesses up to 0.3 μm, which is demanded for the subsequent step of the aluminium infiltration process in the manufacture of an MMC [3, 4]. The other metallization parameters were the same as for the PET substrates. The glycine-buffered bath having a pH of 8.5 allowed us to obtain a coating with a phosphorus content of about 2–3 wt.%. Increasing the content of the powder in the bath resulted in a decrease in the powder content in the composite coating. An increase in grain size did not have a significant influence on the content of the SiO₂ powder in the composite layer. The nanofiller content varied from 4 to 7 wt.%. Increasing the acidity of the solution from 8.5 to 7.5 resulted in an increase in the content of SiO₂ in the composite coating to a maximum of 13 wt.% (for smaller grain size 7 nm).

TABLE 2. Ni-P/SiO₂ deposition on carbon fibers from glycine buffered bath pH 8.5 - changes in process parameters

TABELA 2. Osadzanie powłok Ni-P/SiO₂ na włóknach węglowych z roztworu glicynowego o pH 8,5 - zmiany parametrów procesu

SiO ₂	Deposition time [min]	Deposition rate [mg/cm ² *min]	P content [% mas]	SiO ₂ content [% mas]	Grain size SiO ₂ [nm]
10 g/l	5	3.8	2.7	6.3	7
	10	2.4	2.2	6.0	7
	15	2.9	2.7	4.7	7
30 g/l	5	1.5	2.9	4.8	7
	10	1.2	2.9	4.8	7
	15	0.9	2.9	7.3	7
10 g/l	5	1.3	2.3	5.9	14
	10	1.1	2.3	5.0	14
	15	1.1	2.4	7.1	14
30 g/l	5	0.5	2.4	4.2	14
	10	0.8	2.8	4.6	14
	15	0.4	2.8	3.7	14

TABLE 3. Ni-P/SiO₂ deposition on carbon fibers from glycine buffered bath pH 7.5 - changes in process parametersTABELA 3. Osadzanie powłok Ni-P/SiO₂ na włóknach węglowych z roztworu glicynowego o pH 7,5 - zmiany parametrów procesu

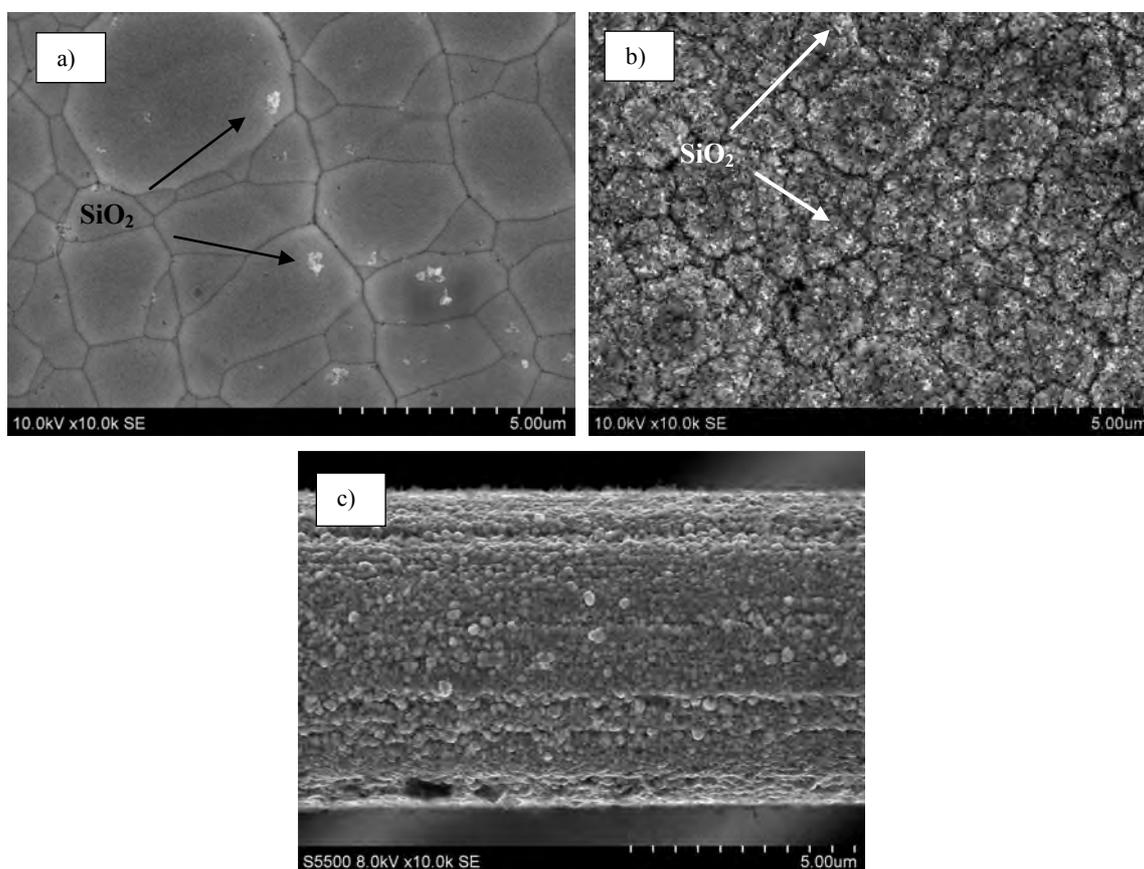
SiO ₂	Deposition time [min]	Deposition rate [mg/cm ² min]	P content [% mas]	SiO ₂ content [% mas]	Grain size SiO ₂ [nm]
30 g/l	5	1.8	2.5	13.8	7
	10	2.9	2.6	11.1	7
	15	2.7	2.3	11.0	7
10 g/l	5	1.6	2.3	5.0	14
	10	1.6	2.4	5.8	14
	15	1.6	2.3	5.5	14
30 g/l	5	0.6	2.4	13.0	14
	10	0.9	2.3	12.1	14
	15	0.2	2.3	9.3	14

Generally, the SiO₂ powder content in the coatings on the carbon fiber was lower than on the PET foil samples. It is mainly connected with the less preferable hydrodynamic conditions of suspension flow between the fibers in the roving sample. Another cause of that relation is the considerably lower coating thickness (0.2÷0.5 μm) on the carbon fibers in comparison to over

10 μm for the PET samples. It is interesting that the codeposition of SiO₂ powder with Ni-P causes a distinct decrease in P content in the coatings (from 2÷3 wt.% to 1.5÷2 wt.%). It could decrease the amount of undesirable phosphorus introduced to the final Al/carbon fiber composite.

SEM micrographs (Fig. 1a,b,c) demonstrated that the observed surface morphology of the composite coatings are very similar to the Ni-P coatings. The micrographs proved good penetration of the bath ingredients into the substrate surface. The main problem of the deposition of the composite coating was the agglomeration of nanopowder particles in the solution and then in the coatings. The consequences of this is uneven distribution of the SiO₂ powder particles, visible on the Ni-P/SiO₂ layer (Fig. 1a,b). This effect has not been eliminated yet even in the bath containing the surfactant - CTAB. Further investigations on the inner structure of Ni-P/SiO₂ composites (cross sections and TEM microscopy), depending on the deposition process parameters are planned.

Control of the temperature at the step of preparation of the suspension and an additional dose of stabilizer introduced immediately after the start of deposition ensured the stability of the bath. Therefore, the bath could be used again after proper correction of its component concentrations and pH.

Fig. 1. Composite layer of Ni-P/SiO₂ on PET substrate obtained from glycine buffered bath with pH 8.5, deposition time 60 min: a) SiO₂ concentration 10 g/l; b) 30 g/l SiO₂; c) Ni-P/SiO₂ on carbon fibreRys. 1. Powłoka kompozytowa Ni-P/SiO₂ na PET otrzymana z roztworu glicynowego, pH 8,5, czas metalizacji 60 minut: a) 10 g/l SiO₂; b) 30 g/l SiO₂; c) powłoka Ni-P/SiO₂ na włóknie węglowym

CONCLUSIONS

The performed studies have led to the following conclusions:

- the addition of a stabilizer (TU) prevented spontaneous decomposition of the suspensions and an additional portion of stabilizer after deposition provides bath stability during storage,
- the results presented in Table 1 pointed out that a change in diameter of nano-SiO₂ (7 and 14 nm) additive caused an increase in the SiO₂ content in the composite up to approximately 17 wt.% (for 7 nm),
- transfer of the conditions for the deposition of composite layers developed for the PET bases is also possible for carbon fiber bases, after slight modification,
- to obtain an Ni-P/SiO₂ layer on carbon fibers, the deposition time has to be reduced to 5÷10 min, which allowed us to produce a thin average 500 nm composite layer (which is sufficient for the application as reinforcement in MMC), with a low phosphorus content (1.5÷3 wt.%),
- despite the usage of ultrasound and a homogenizer and the application of a surfactant, particle agglomeration was still observed.

Further investigations are planned to increase the stability of the metallization bath and content of nanopowder in the composite layer, as well as additional works on more effective degglomeration of silica particles in the applied bath.

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