Obtaining of electroless Ni-P/ZrO₂ composite coatings on flexible substrates of polyethylene terephtalate

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The incorporation of dispersed particles into metal matrices, achieved by the electroless codeposition process, has led to the obtaining of new generation of composite materials with definite chemical and physical properties.

The aim of these studies is to obtain Ni-P/ZrO₂ composite coatings by electroless plating process on flexible substrates from polyethylene terephthalate (PET). These coatings would ensure better mechanical properties in comparison with only electroless nickel plated samples.

In connection with the obtaining of these composite coatings, preliminary optimization of the electrolyte for electroless nickel plating is performed. For this purpose, the influence of its main parameters – i.e. $NiSO_4$, NaH_2PO_2, surface active agents (SAA, known also as surfactants) and pH has been studied.

1. INTRODUCTION

The electroless nickel plating represents autocatalytic reduction of nickel ions on the interface of heterogeneous system. The most widely used electrolytes for electroless nickel plating contain two main components: nickel salt and reducing agent, such as sodium hypophosphite, borohydride, bor-nitrogen compounds, hydrazine, etc. Most widely used in the practice are the solutions with sodium hypophosphite as reducing agent. They also contain ligands of the nickel ion, buffer substances, stabilizers, accelerators, surface active substances (SAS), brighteners, etc.

The electroless nickel plating process with hypophosphite as reducing agent possesses the following characteristics:

- the reduction of the nickel ions is conducted only on several metals, which are capable of catalyzing the process, or on catalyzed dielectric surfaces;

- the obtained product does not represent pure nickel and always contain phosphorous, which is included in the coating in the form of intermetal compound. The quantity of phosphorous in the coating is changing depending on the conditions for the process implementation. The phosphorous content increases with the increase of the solution acidity; the process speed strongly depends on the temperature [1].

Stabilizers are added to increase the stability of the electroless nickel plating solutions. J. Cheong et al. in [2] have established that the adding of thiourea to the electroless nickel plating solution increases its stability. With the thiourea concentration increase the phosphorous content decreases. Upon the adding of 180 - 300 ml/l Maleic acid the coating becomes bright.

The optimization of the electroless nickel plating process of textile fabrics is very important for the industry. The process parameters such as - time, temperature, pH - are crucial for the obtained electroless coatings. They have been discussed by S.Q. Jiang et al. in [3].

S. Armyanov et al. in [4, 5] have studied in detail electroless deposition and some properties of Ni-Cu-P and Ni-Sn-P coatings. The introduction of Cu or Sn as a third component improves considerably the corrosion resistance of Ni-P alloys.

Most frequently metalized among the flexible polymer substrates is the polyethylene terephthalate (PET), since the textile industry needs material with average molecular mass of approx. 15 000. It is a linear homopolymer and a dominating composition of polyester fibres [6]. At room temperature they are acid-resistant. Long boiling in hydrochloric acid destroys the polyester, and the action of 96 % sulphuric acid causes destruction of the polymer.

C.W.M. Yuen et al. in [7, 8] have studied the properties of electroless nickel plated polyester after treatment with low-temperature plasma. It contains oxygen and argon and is used to obtain

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hydrophilic properties of the polyester specimen and to facilitate the absorption of the palladium catalyst, which catalyzes the surface prior to the electroless nickel plating.

R.H. Guo, S.Q. Jiang et al. in [9] have also studied the properties of the electroless nickel plated polyester fabric, depending on the electrolyte composition and the metalizing conditions. It has been found out that with the increase of $NiSO_4$ concentration the deposition speed increases linearly, while the phosphorous contents decreases from 11 to 7 %. SEM-micrographs show nodular (knotty) type of coating structure, which is indicative of the presence of amorphous structure. The efficiency of the shielding of the nickel plated polyester fabric against the electromagnetic interferences depending on the concentration of Ni^{2+} in the electrolyte is studied and it varies from 20 to 40 dB within a frequency interval from 10 to 18 GHz.

The preliminary processing of polymer (polypropylene and polycarbonate) substrates, aiming at increasing the adhesion of the chemically deposited metal coating is studied in [10]. M. Charbonuier and M. Romand replace the classical roughening of the polymers using a mixture of CrO_3 and H_2SO_4 with preliminary treatment using plasma or UV laser in O_2, H_2 / NH_3 atmosphere.

Obtaining chemical dispersion Ni-P/ZrO₂ coatings is poorly studied. Ye Yuzhong et al. in [11] have been shown that coating containing 5.6 % ZrO₂ possesses higher high temperature oxidation resistance than the nickel coating itself.

K. Zielińska et al. [12] and P.A. Gay et al. [13] describe the deposition of the composite Ni-P/ZrO₂ coatings by electroless process, and the characterization of their mechanical and tribological properties.

From the literature review it has been concluded that the electroless nickel plating of the polyester fabric is of high importance for the practice.

The aim of this work is the development of appropriate in terms of composition and operation mode electrolytes for obtaining of disperse nickel-phosphorous coating with ZrO₂ particles on polyethylene terephthalate, as well as study of the properties of the obtained coatings.

2. EXPERIMENTAL

The experiments have been made using substrates of flexible non-woven fabric from polyethylene terephthalate (PET), subject to reinforcement through additional compaction (pressing). The surface of the PET substrate is 8 cm². The preliminary treatment of the substrates is accomplished according to the following technological scheme:

- Degreasing in alkaline solution at 60 ˚C for 15 min;
- Activation in $PdCl_2$ colloidal solution at room temperature for 5 min;
- Acceleration in alkaline solution at room temperature for 5 min;

The electroless nickel plating has been accomplished in a solution, containing the following components, described in Table 1.

Table 1. Chemical compositions and operating conditions of the plating bath.

Electrolyte components:	Concentration:
$NiSO_4.7H_2O$, g/l	25
$NaH_2PO_2.H_2O$, g/l	22
CH_3COONa, g/l	20
Lactic acid, g/l	20
Stabilizer 2, mg/l	1
(a commercial product of TU-Sofia)	
Sodium lauril sulphonate (NaLS), g/l	0.01
Operating conditions:	
pH	4.6 - 4.8
Temperature, (˚C)	82
Time, (min)	30-60

ZrO₂ with different size of the particles: 30/60 nm, 1/3 μm and 7/10 μm has been added as dispersoid to this base electrolyte. Their concentration in the electrolyte has been varied within the limits 2.5 ÷ 5.0 g/l, while the particles have been preliminary wetted with SAA (NaLS = 0.01 g/l) and in this form added to the electrolyte.

The disperse coatings have been obtained under continuous air agitation using air flow − 100 ml/ min/ 250 ml electrolyte (with open glass surface ~ 38 cm²).

The deposition speed of the disperse coatings has been determined gravimetrically through the conditional thickness of the obtained coatings δ (μm). At these investigations is used the term "confidential thickness", as the surface of the samples is without determined geometry. The difference of mass of the deposited coating has been measured as a difference in the mass of the substrates after and before metallization.

$$\Delta m = M - M_o,$$

where Δm is the mass of the deposited coating [g], M_o is the mass of the specimen prior to metallization [g], and M – after metallization [g].

The morphology of the composite coating has been determined with scanning electron microscopy (JSM 6390 apparatus, JEOL, Japan).

3. RESULTS AND DISCUSSION
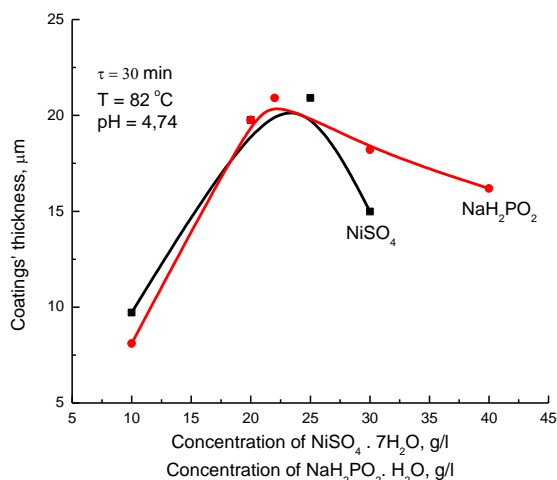
Impact of the main nickel electrolyte components

Fig. 1. Influence of NiSO₄ and NaH₂PO₄ concentration on the Ni-P coatings' thickness.

Fig. 2. Influence of the lactic acid and sodium acetate concentrations on the Ni-P coatings' thickness. Deposition time 30 min at 82 ^{0}C and pH = 4.8.

Usually acid solutions are used for electroless nickel plating of polymers. The concentration of the Sodium hypophosphite is of high importance for the deposition speed and the stability of the electrolytes [1]. In Fig. 1 the deposited Ni-P coatings' thickness upon a change in the NaH₂PO₂.H₂O and NiSO₄.7H₂O content has been established. From the obtained data, shown on Fig.1, it is observed the appearance of the maximum at both components at concentrations 25 g/l for NiSO₄.7H₂O and 22 g/l for NaH₂PO₂.H₂O. The ratio between Ni^{2+} and $H_2PO_2^-$, which should be within 0.25 – 0.6, is of high importance for the electrolytes' operation. For the following studies the used by us electrolyte included: 25 g/l NiSO₄.7H₂O, 22 g/l NaH₂PO₂.H₂O, and the ratio between Ni^{2+} and H₂PO₂$^-$ was 0.41. For concentrations above 30 g/l NiSO₄.7H₂O and NaH₂PO₂.H₂O the solution becomes unstable and a spontaneous reduction of Ni^{2+} within the whole volume is possible. By this reason our studies were carried out with the above mentioned concentrations.

Influence of the organic additives

During reduction of the nickel ions with sodium hypophosphite the concentration of the hydrogen ions in the solution continuously increases – i.e. pH decreases. This leads to a change in the deposition speed. Therefore, organic acids and their salts are added to the electrolyte for nickel plating that exercises buffering effect and do not allow quick
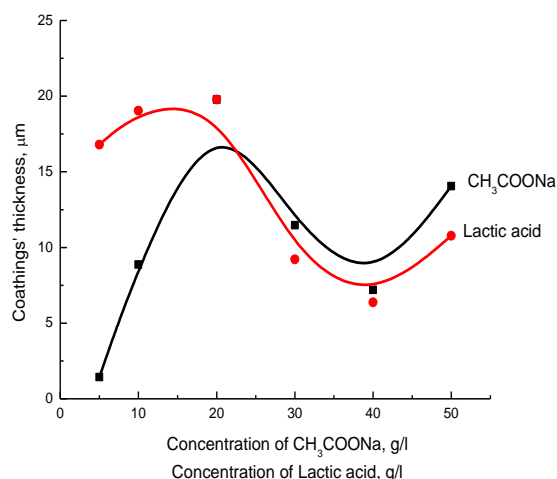
change of pH during operation. The anions of the organic acids, respectively of their salts, participate in the formation of different, sufficiently sustainable complex nickel ions and decrease the concentration of the free Ni^{2+} ions. Thus the electrolyte stability is increased.

Petrov [1], as well as Shalkayskas & Vashkialis [14] recommend as complexing agent in the acid solutions to use the following acids /or their salts/: lactic, aminoacetic (glycocol), citric, glycolic, etc. The complex formers can possess buffer properties as well. Such is the lactic acid, which at relatively low temperature possesses both properties. The organic additives exercise big influence on the speed of nickel reduction. For many of them the dependence of the nickel plating speed on the additive concentrations passes through a maximum.

The process acceleration is explained with the buffer action of the organic additives, and the speed reduction at high concentration of the additive is due to the blocking of the catalytic surface of the adsorbed organic substances.

According to Badet [15] the action of the accelerators can be explained with the loosening of the bond between the hydrogen and phosphorous in the sodium hypophosphite molecule. It should be noted that the majority of the accelerators are efficient buffers.

With aim of increasing the reduction speed of the nickel ions, we have studied the influence of the following buffering and complexing compounds: Sodium acetate and Lactic acid. From the obtained data, shown on Fig. 2, we had chosen 20 g/l as

optimal concentration for both organic additives used for the next investigations from us.

Influence of pH

The change in the acidity of the nickel plating bath exercises big influence on its operation and stability, as well as on the phosphorous contents in the obtained coating.

For pH values below 4 the dissolution of the nickel coating in the acid medium is possible, which shows that uncovered sections are obtained.

content of P in the coating is seen, which decreases with the pH increase of the solution [1].

Influence of the surface active agents (SAA) and the stabilizers

According to the reference [1] SAA can also play the role of stabilizers of the electroless nickel plating.

The results from the dependence of the deposited nickel coating thickness on the different SAA (veranol H-10, sodium lauryl sulfonate(NaLS)

Table 2. Influence of pH solution on the Ni-P coatings' thickness. Deposition time 30 min at 82 ^{0}C.

pH	3.8	4.0	4.8	5.0	5.5
δ, μm	13.63	20.52	38.57	37.85	37.31
(Δm, g)	(0.1067)	(0.1607)	(0.3021)	(0.2964)	(0.2922)
EDS, wt %					
C K	5.39		8.70		8.89
O K	0.78		1.03		2.79
P K	7.07		5.94		5.38
Ni K	86.76		84.33		82.94

Besides that during the reduction of the nickel ions high-soluble nickel phosphite is formed.

These studies were asked to establish the most appropriate pH - values for which the selected by us nickel electrolytes have the biggest deposition speed, stability and utilization. The dependence of the deposition speed on different pH values of the electrolyte is shown in Table 2.

From the obtained data it is seen that with pH increase the speed of reduction is increased, but during previous work at pH – value above 5.0 sediments of insoluble compounds are obtained and the probability for spontaneous reduction of the nickel ions within the whole electrolyte volume is increased. Due to this reason during our later studies we worked with pH within the range 4.6 ÷ 4.8. From the data in the table the change of the %

and PEG-4000) concentration on Fig. 3 were shown. The obtained results show that PEG-4000, which is non-ionogenic SAA, reveals constant values, but at high electrolyte concentrations. For anion-active surfactant such as NaLS, the deposition speed is the highest but at low concentrations in the electrolyte. The veranol, from one side, is environmentally danger and is forbidden from the EU because it contains polyphenol. From the other side, the obtained results from us show diminishing of the deposition speed. Therefore, we preferred to work with NaLS within the range 0.01÷0.1 g/l and by financial point of view also.

With the aim to optimize the electrolyte composition the influence of the coating thickness has been studied in relation of presence of preliminary selected by us optimal SAA (NaLS) concentrations and of the following stabilizers: Na₂S₂O₃, Stabilizer 1 (a commercial product of TU-Sofia) and Stabilizer 2 (a commercial product of TU-Sofia).

Table 3. Influence of the Stabilizer type on Ni-P coatings' thickness in the presence of 0.01 g/l NaLS in electrolyte to electroless plating. Deposition time: 30 min.

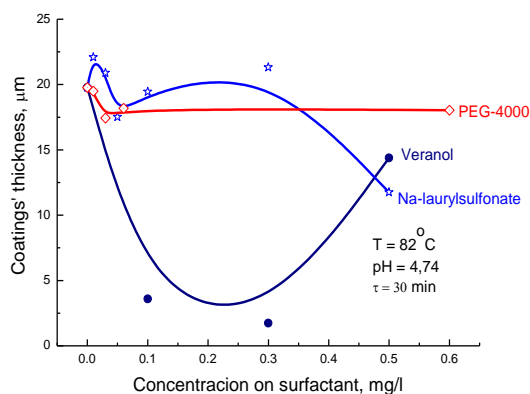| Type of Stabilizer, 1 mg/l	δ, μm (Δm, g)
NaLS + Na₂S₂O₃	22.08 (0.1729)
NaLS + Stabilizer 1	23.73 (0.1858)
NaLS + Stabilizer 2	26.04 (0.2039)

Fig. 3. Influence of the type and concentration of Surfactants on Ni-P coatings' thickness.

The obtained data in Table 3 has showed that in the presence of NaLS and Stabilizer 2, the deposition speed, respectively the thickness of the obtained coatings is the highest, due to which all further studies have been conducted using this combination.

Obtaining of composite Ni-P/ZrO₂ coatings

The data on Fig. 4 show the change in the thickness of the composite Ni-P coating in the presence of different size ZrO₂ particles. The studies have been conducted for two different
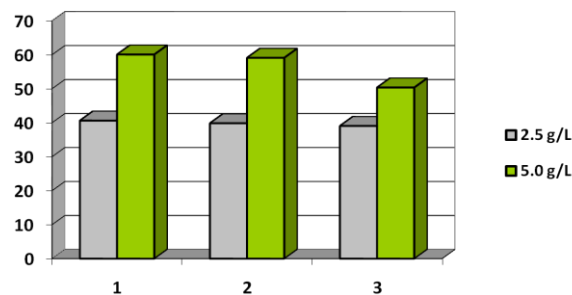

Fig. 4. Influence of ZrO_2 concentration and type on the conditional thickness of the composite coatings: 1 - ZrO_2 30/60 nm; 2 - ZrO_2 1/3µm; 3 - ZrO_2 7/10 µm.
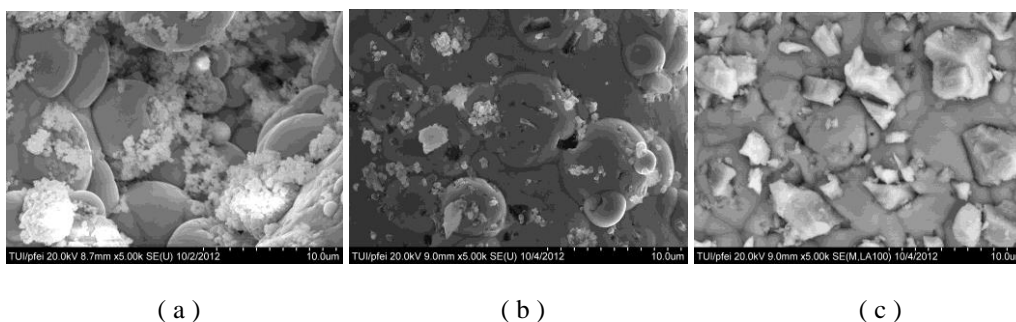

(a)   (b)   (c)

Fig. 5. SEM micrographs of the composite Ni-P/ZrO_2: a) ZrO_2 30/60 nm; b) ZrO_2 1/3 µm; c) ZrO_2 7/10 µm.

concentrations (2.5 g/l and 5.0 g/l) of the dispersoid in the electrolyte. No significant change in the thickness of the coatings depending on the particle sizes is observed. With the increase of the concentration of the dispersoid in the electrolyte the thickness of the composite coating is also increasing. With increasing of the particles' size in the electrolyte, their number in the composite coating diminishes.

The results for the increasing of ZrO_2 in the composite coating have been confirmed by the taken SEM-micrographs of the surface morphology of the three disperse coatings on Fig. 5 for equal concentration of the dispersoids in the electrolyte, and EDS-analysis, showing the contents of Zr incorporated in the coatings as follows: 1 (ZrO_2 30/60 nm) – 30.60 wt. %, 2 (ZrO_2 1/3 µm) - 20.30 wt. % and 3 (ZrO_2 7/10 µm) - 18.44 wt. %.

CONCLUSIONS

In connection with the obtaining of electroless composite Ni-P/ZrO_2 coatings preliminary optimization of the electrolyte composition and of the electroless nickel plating has been conducted. For this purpose the influence of $NiSO_4$, NaH_2PO_2, SAA, stabilizers and pH has been studied.

The inclusion of disperse ZrO_2 particles in metal Ni-P matrices, on flexible substrates has led to the obtaining of composite materials, characterized by

definite chemical and physical properties, wich will be studied at our following investigations.

The obtained materials are implementable for raising the wear resistance of machine elements, as well as for restoration of worn working surfaces of rubbing parts.

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ПОЛУЧАВАНЕ НА ХИМИЧНИ КОМПОЗИТНИ Ni-P/ZrO₂ ПОКРИТИЯ ВЪРХУ ГЪВКАВИ ПОДЛОЖКИ ОТ ПОЛИЕТИЛЕН ТЕРЕФТАЛАТ

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(Резюме)

Включването на дисперсни частици в метални матрици, постигнато чрез процеса на химично съотлагане, доведе до получаването на ново поколение композитни материали, характеризиращи се с определени химични и физични свойства.

Целта на тези изследвания е получаването на химични композитни Ni-P/ZrO₂ покрития върху гъвкави подложки от полиетилен терефталат (PET). С тези покрития се постигат по-добри механични характеристики, в сравнение с такива, в които няма включени частици.

Във връзка с получаването на тези композитни покрития предварително е проведено оптимизиране на електролита за химично никелиране. За тази цел е изследвано влиянието на основните му параметри, а именно NiSO₄, NaH₂PO₂, ПАВ и pH.