

ELECTROLESS DEPOSITION OF COBALT MATRIX FOR CO-DEPOSITION OF HIGH-HARD NANO- AND MICROPARTICLES

D. Stoychev^{1*}, N. Koteva², M. Stoycheva³, E. Velkova⁴, D. Dobrev⁵

¹*Institute of Physical Chemistry-Bulgarian Academy of Science, Acad.G.Bonchev str., Bl.11, 1113 Sofia, Bulgaria*

²*Technical University of Sofia, St. Kl.Ohridsky Blvd. 8, 1000 Sofia, Bulgaria*

³*Institute of Electrochemistry and Energy Systems-Bulgarian Academy of Science, Acad.G.Bonchev str., Bl.10, 1113 Sofia, Bulgaria*

⁴*Institute of Chemical Engineering-Bulgarian Academy of Science, Acad.G.Bonchev str., Bl.103, 1113 Sofia, Bulgaria*

⁵*Institute of Mathematics and Informatics-Bulgarian Academy of Science, Acad.G.Bonchev str., Bl.8, 1113 Sofia, Bulgaria*

Abstract: The composition and regime for chemical deposition of cobalt layers on non-metal, as well as metal substrates are investigated and determined. Within our investigation, we are studying the affect of the concentration of the cobalt ions (CoCl_2) and the reducer (NaH_2PO_2) on the kinetics of deposition of the cobalt layer. In addition, the influence of the pH and the temperature of the electrolyte is examined. The optimal conditions for the deposition of the cobalt matrix at which the quantity of the co-deposited dispersoid, i.e. most needed in the production of abrasive instruments for surface treatment and other applications is also defined.

Keywords: COBALT LAYERS, ELECTROLESS DEPOSITION, COMPOSITE MATERIALS

1. Introduction

The chemical/electroless metallization is used for deposition of a thin metal or alloy films on supports of conducting, semi-conducting or dielectric materials. These can be in the form of bulk metal articles, powder particles, fibers, whiskers or carbon nanotubes. The chemical copper-metallization is the most often applied in the practice, but also nickel or cobalt coatings [1]. The cobalt coating is used to a smaller extent, compared to nickel coating, although the cobalt possesses physical-mechanical properties, similar to those of nickel. The cobalt coatings are preferred most often in the cases, when it is necessary to utilize their magnetic properties. Due to the contamination of the environment with Cr(IV) salts during the last years intensive investigations are carried out to replace the solid chromium coatings by nickel- or cobalt-based nanometer thickness composite coatings, deposited electroless or electrochemically [2-4]. Depending on the nature of the involved dispersion particles, these coatings have high microhardness, wearresistance and high corrosion resistance.

A very prospective area for application of electroless obtained composite layers, based on electroless deposited Co matrix, are these included high and super high-hard nano- and microparticles for preparation of different abrasive tools. A comparative study of the electroless deposition of Ni-P and Co-P, and their composites with co-deposited particles of SiC on copper supports, has been reported in [5]. A comparison is made between chemically deposited from alkaline solutions coating of nickel and cobalt. It has been ascertained that the chemical stability of the solution for coating cobalt is greater than that for coating nickel. At the same time, the effectiveness of chemical deposition from nickel bath is better than that of the cobalt from cobalt bath.

In ref. [6] the disperse coating based on Co-P/PTFE is considered and it has been prepared by a chemical method. The cobalt matrix is preferable in view of its structure, the properties of the surface and the adhesion of cobalt to a steel support. The PTFE is included in the matrix in order to attribute better anti-friction properties to the composite. The studies have shown that the coating has a high microhardness and good adhesion to the matrix after the metallization. The composite crystallizes in a hexagonal texture and the size of the cobalt crystals does not change except for the increase in the constant of the crystal lattice, especially after heating. In the coating the fluorine exists in the form of PTFE, while the cobalt and the phosphorus - in the form of P and Co^{3+} .

In ref. [7] SiCw/Co composite particles are successfully prepared by chemical metallization and the changes in the microstructure of the cobalt coating have been studied. During the first stage of the chemical metallization the surface of the whiskers is being uniformly covered with separate clusters. Further, as a

consequence of this, they grow up and form a uniform cobalt coating. After establishing contact between the clusters the cobalt forms a plate-like structure. These results show that the growth of the cobalt coating on inert surface is evolving from cluster structure into a continuum. The cobalt coating is transformed from amorphous state into crystalline state and aggregates of clusters during the heating at 500°C in hydrogen atmosphere.

The aim of the present work was to establish the optimal composition of the electrolyte and regime for chemical deposition of cobalt coatings on different substrates by studying the influence of the components of the electrolyte. The structure, morphology and chemical composition of the deposited cobalt are to be determined, respectively to find options of applying the cobalt coating as matrix for co-depositing in it diamond particles with different sizes.

2. Experimental

The studies were carried out using samples of wafered polyethyleneterephthalate (PETF) material of dimensions 30 x 30 x 0.05 mm. The samples underwent the preliminary treatment described in [8]. After this pretreatment the samples were processed further in a solution for chemical cobalt deposition with basic composition, in g/l: $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ -30; $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ -20; Na citrate-100; NH_4Cl -50; pH 9; T-90°C. With this solution we studied the influence of the time interval of metallization on the thickness of the deposited cobalt coating. In the rest of the experimental runs we changed the concentrations of the main components, as well as the temperature and the pH of the solutions.

On the basis of the carried out investigations, the optimal content to which the diamond particles (with sizes of 0.5 – 70 μm) had been added with the concentration of 5 g/l had been determined. Using this electrolyte, the possibilities to obtain composite (Co-diamond particles) layer on the polyethylene terephthalate substrate was studied.

The adjusting of the pH value of the solutions was carried out with a 10% solution NaOH. The thickness of the deposited cobalt coatings was determined gravimetrically.

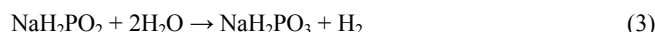
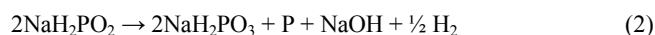
The morphology, structure and the number of co-deposited diamond particles of the obtained cobalt coatings was studied by means of scanning electron microscopy (SEM) using a JEOL 200CX scanning microscope under conditions secondary electron image (SEI).

3. Results and discussion

In the course of elaborating the appropriate technology for metallization, the adhesion depends mainly on the composition of

the etching solution and on the conditions during the treatment. Our previous investigations showed that the best results are obtained by treatment in alkaline solutions.

We used the colloidal method of activation, in which the colloidal palladium Pd-Sn sol particles are being adsorbed on the surface of the polymeric fibers, stabilized by $[\text{SnCl}_3]^-$. During the acceleration stage the hydrolyzed products of tin and of the stabilizing shell of most of the Pd-Sn nuclei are being removed. Actually, it is on these nuclei that the deposition of cobalt from the solution is starting to occur according to reactions:



3.1. Influence of the concentration of CoCl_2

A systematic investigation was carried out with respect to the influence of the concentration of CoCl_2 in the operating solution upon the rate of the process of chemical deposition of cobalt. Some of the obtained results are shown in Figure 1.

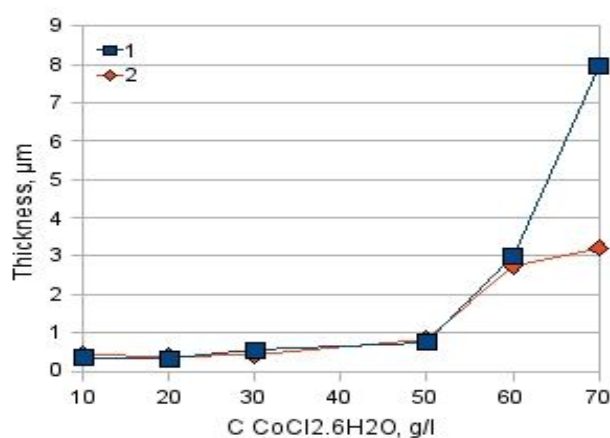


Fig. 1. Influence of the concentration of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in the solution ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ - 20 g/l; Na citrate - 100 g/l; NH_4Cl - 50 g/l; T - 90°C, pH - 9) on the rate of deposition of Co coating; time interval of deposition for each sample - 30 min; 1-■ - PETF substrate; 2-◆ - Cu substrate.

It has been found out that within the interval of concentrations of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ 10 – 60 g/l the rate of deposition of cobalt does not depend on the nature of the support. It is growing up gradually upon increasing the concentration of the cobalt ions up to the value of 50 g/l, and thereafter it is increased sharply at concentrations 60 and 70 g/l. At this point the increase becomes more than 2.5 times higher at concentration 70 g/l for the PETF supports, in comparison to the copper supports. At the higher concentrations (the results are not shown in the figure) the rate of deposition continues to increase, but afterwards it drops down. Here at this point, however, the appearance of pitting is observed, accompanied by formation non-compact Co coatings of lower quality. The deterioration of the quality and/or the absence of cobalt coating at CoCl_2 concentration in the solution of about and above 100 g/l is explained by the great increase in the Co^{2+} amount near the surface of the metalized support and insufficient quantity of the reducing agent, which removes the charge of Co^{2+} .

The influence of the concentration of CoCl_2 in the working electrolyte on the morphology and on the structure of the deposited coating is illustrated in Fig. 2.

The conclusions, which can be drawn upon comparing the changes in the surface morphology and the structure of the deposited cobalt coatings on the terephthalate support are the following - at low concentrations of the cobalt in the solution the Co deposited on the separate fibers of the polyethyleneterephthalate support is orientated and it is epitaxially influenced by the fibers of the support (Fig. 2a). Upon increasing the concentration of Co^{2+} (20

g/l), as a consequence of the increased rate of nuclei formation processes, the size of the growing cobalt crystallites is decreased considerably (Fig. 2b). Increasing further the concentration of Co^{2+} ions (Fig. 2c, 2d) the size of the cobalt crystallites starts to grow up - an effect, which is probably connected with shortage of the reducing agent - whereupon reaching concentrations 60 and 70 g/l (Fig. 2) several times larger Co agglomerates are being formed. In this case the epitaxial influence of the support is not observable - the agglomerates are orientated in a way characteristic of the cobalt structure;

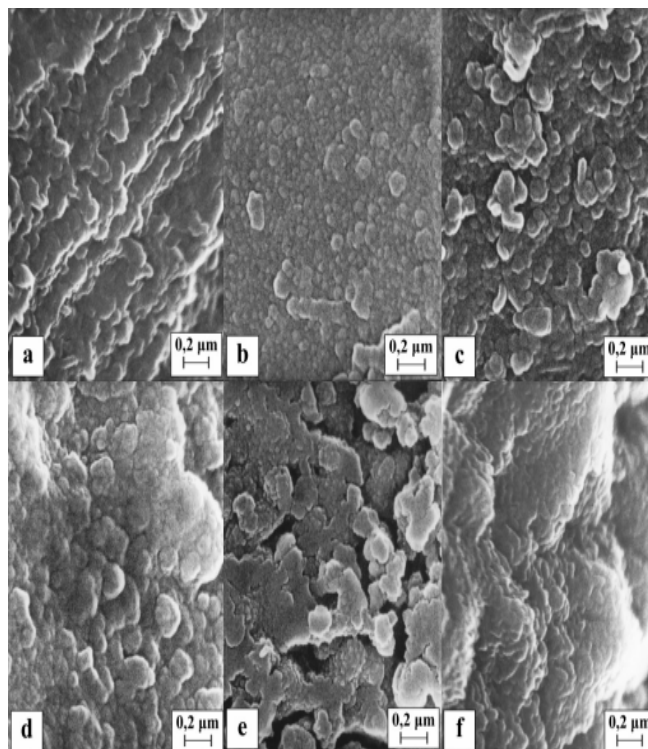


Fig. 2. SEM micrographs (50 000x) of the surface of PETF support after coating cobalt chemically in solutions of different concentrations of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$: a - 10 g/l; b - 20 g/l; c - 30 g/l; d - 50 g/l; e - 60 g/l; f - 70 g/l

3.2. Influence of the concentration of NaH_2PO_2

The dependence of the thickness of the deposited cobalt coating on the concentration of NaH_2PO_2 in the solution is shown in Fig. 3. The obtained results show that the increase in the concentration of the reducing agent up to 50 g/l leads to an increase in the rate of the process, respectively to obtaining a thicker coating per unit of time. At higher concentrations of the reducing agent and permanent ratio between the remaining components, the rate of the process is decreasing. This is probably due to the shortage of cobalt ions, whose amount has to correspond to the increase in the concentration of the reducing agent in the immediate vicinity of the metalized surface. In spite of these obtained results, in the rest of the experimental runs we used solutions with lower concentration of NaH_2PO_2 (20 g/l), because in these cases the solutions are much more stable and there is no spontaneous reduction of the cobalt ions observable within the entire bulk of the solution.

From the results, obtained by the SEM investigation of chemically deposited coatings of cobalt on flexible support, built of PET fibers (Fig. 4), one can draw the following conclusions:

- upon adding 10 g/l sodium hypophosphite (and 30 g/l CoCl_2 content) into the solution a compact Co coating is deposited (at lower concentrations, which are not represented by micrographs, the coating is not compact and the quality is rather poor), which is highly dispersed. The sizes of the crystallites composing it are about ~ 0.15 μm;

- upon increasing the concentration of the sodium hypophosphite, the size of the Co grains, contained in the coating, grows up twice (Figure 4b) - whereupon the separate fibers of the

terephthalate flexible support become rough. In this case one can observe strengthening of the epitaxial influence of the fiber structure on the structure of the cobalt coating and at the same time an increase in the quantity of deposited cobalt in the zones between the fibers, in comparison with the amount of cobalt deposited on the fibers. This effect is most probably due to the considerably higher quantity of Pd-nuclei, which are anchored more easily in the more deeply etched zones (in comparison with the surface of the fibers) between the fibers of PETF flexible support;

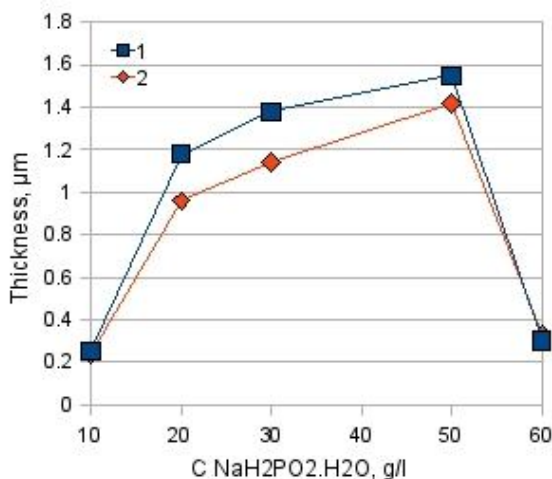


Fig. 3. Influence of the concentration of $\text{NaH}_2\text{PO}_2\cdot\text{H}_2\text{O}$ in the solution ($\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ - 30 g/l; Na citrate - 100 g/l; NH_4Cl - 50 g/l; T - 90°C, pH - 9) on the rate of deposition of cobalt coating; time interval of deposition for each sample - 30 min; 1-■ - PETF substrate; 2-◆ - Cu substrate

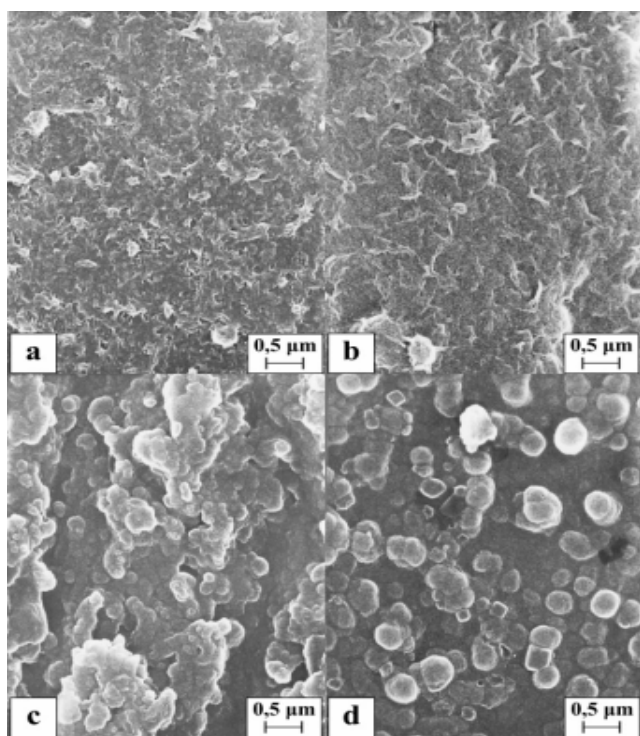


Fig. 4. SEM micrographs (20 000x) of the surface of PETF support, after coating cobalt chemically in solutions of different concentration of $\text{NaH}_2\text{PO}_2\cdot\text{H}_2\text{O}$: a - 10 g/l; b - 60 g/l, and of copper support: c - 10 g/l; d - 60 g/l

Obviously, the concentration of the reducing agent exerts substantial influence both on the rate of deposition, as well as on the structure of the deposited cobalt layers.

3.3. Influence of the temperature

The dependence of the rate of chemical cobalt coating on the temperature of the solution is represented in Figure 5. It is seen

from the figure that upon increasing the temperature of the electrolyte the rate of cobalt ions reduction is accelerated.

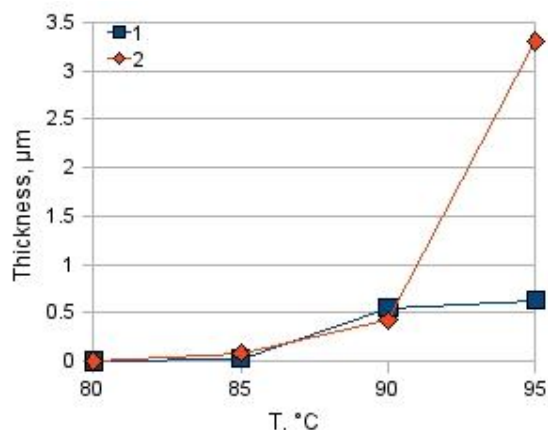


Fig. 5. Dependence of the rate of chemical deposition of cobalt coating on the temperature of the electrolyte on supports of PETF (1-■) and Cu (2-◆) from electrolyte, containing: $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ - 30 g/l; $\text{NaH}_2\text{PO}_2\cdot\text{H}_2\text{O}$ - 20 g/l; Na citrate - 100 g/l; NH_4Cl - 50 g/l; T - 90°C, pH - 9. Time interval of deposition for each sample - 30 min.

Thereupon its change is practically independent of the nature of the support up to about 90°C, but thereafter it grows up sharply on the metal support (Cu), in comparison to the non-metal (PETF) support. The obtained results prove that the composition, chosen by us, is efficient with respect to coating cobalt on the PETF support within a narrow (90 - 95°C) temperature interval.

3.4. Influence of pH

The influence of the pH factor of the electrolyte for coating cobalt upon the rate of deposition of the cobalt film is illustrated in Fig. 6. It is seen from Fig. 6 that in the case of PETF support, with the increase of pH, the rate of coating cobalt is growing up and a maximum is observed at pH = 9.5.

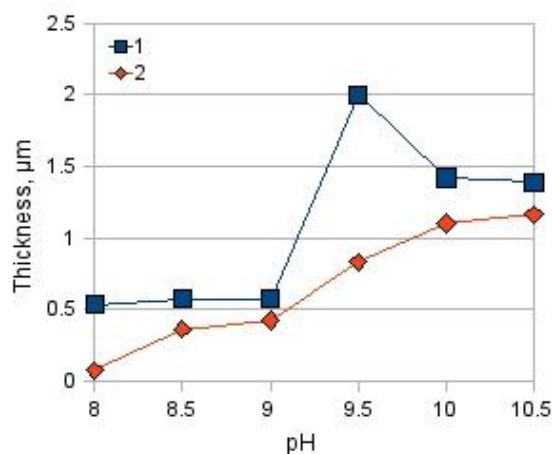


Fig. 6. Dependence of the rate of chemical deposition of cobalt coating on the pH of the electrolyte ($\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ - 30 g/l; $\text{NaH}_2\text{PO}_2\cdot\text{H}_2\text{O}$ - 20 g/l; Na citrate - 100 g/l; NH_4Cl - 50 g/l; T - 90°C) on supports of PETF (1-■) and Cu (2-◆). Time interval of deposition for each sample - 30 min.

At higher values of pH the rate of deposition of Co, respectively the thickness of the coating obtained per unit of time, is decreasing and then it remains practically constant. In the case of copper support upon increasing the pH the rate of reduction of Co ions is growing up reaching the highest value at pH 10.5. The influence of pH on the structure of the deposited coatings was studied both on flexible polyethyleneterephthalate support, as well as on copper support. The following peculiarities are observed: the increase in the pH of the working solution determines a decrease in the size of the agglomerates, building the cobalt coating, respectively obtaining more homogeneous and smooth layers. At the same time, the

sharply increasing rate of deposition leads to appearance of micro-cracking in the coating on PETF support. The Co coating, deposited under these conditions on copper support, is characterized by uniform granular structure and non-compact, non-cracked layers. Obviously, although the higher pH of the working solution is increasing the rate of cobalt deposition still it is not optimal in the case of cobalt coating on flexible supports. Therefore in this case it is purposeful to work at lower pH of the working solution.

3.5. Example of applying the cobalt coating as matrix for co-depositing in it diamond particles

The discussed above results were used to choose an optimal for

the rate of deposition electrolyte. Diamond particles with different sizes and concentration of 5g/l were added to the electrolyte. The ability of the electrolyte to co-deposit diamond particles with sizes: 0.5-7 μm , forming composite Co-diamond layer on a flexible polyethylene terephthalate substrate is illustrated in Fig. 7. The obtained results show that the chemically deposited cobalt matrix successfully incorporates a large number of diamond particles and presents a perspective for production of composite materials containing dispersoids with high hardness.

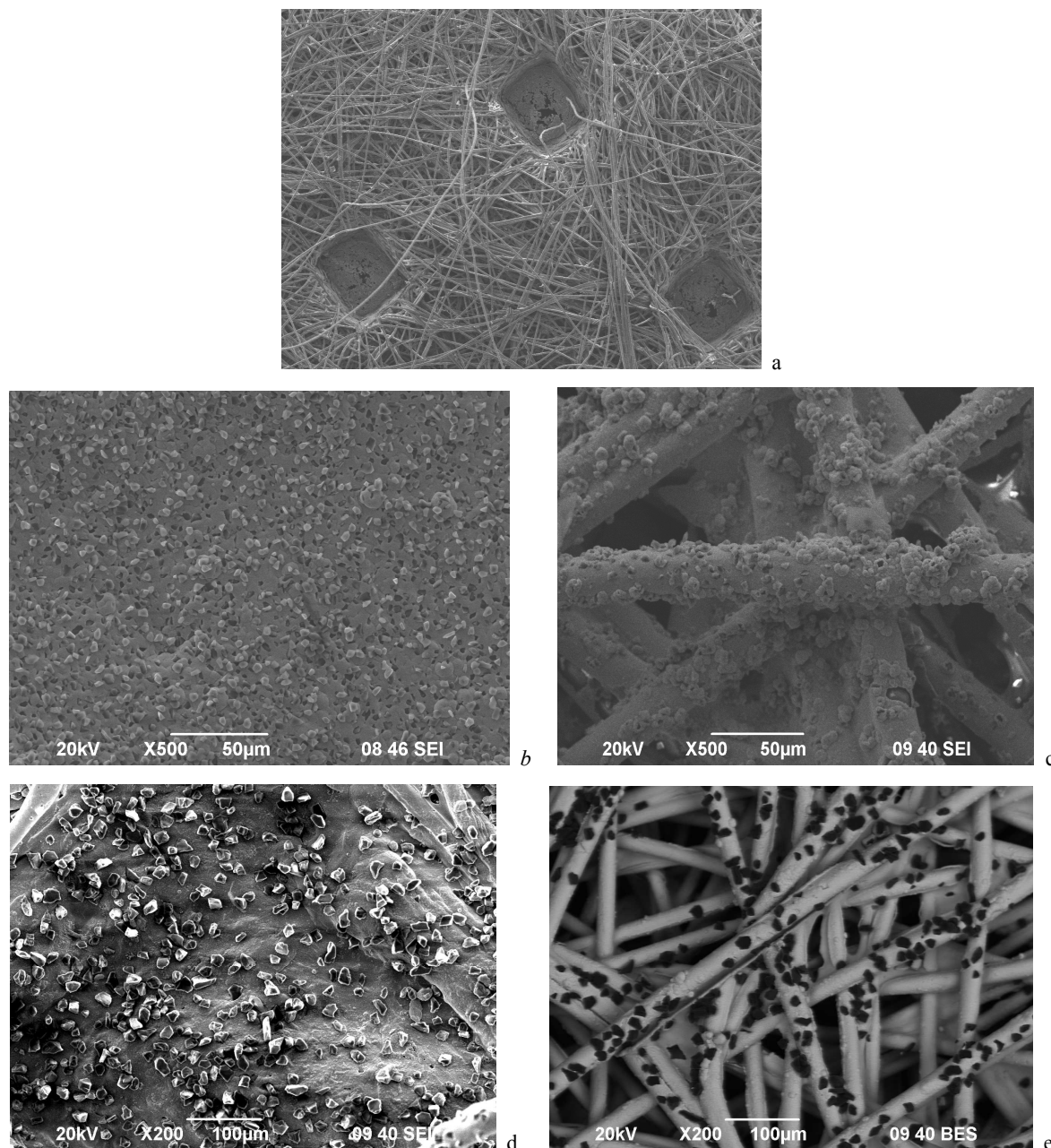


Fig. 7. SEM micrographs of the PETF substrate surface (a), after electroless deposition of cobalt-diamond composite coatings (in the matrix (b,d) and on the fibrous (c,e) zones of the substrate) in solutions containing 5 g/l diamond particles with different sizes: b and c - 5 μm ; d and e- 10 μm . Composition of the electrolyte: $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ - 30 g/l; $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ - 20 g/l; Na citrate - 100 g/l; NH_4Cl - 50 g/l; pH 9.5; T - 90°C. The time interval of deposition for each sample - 30 min.

4. Conclusions

The optimal compositions have been investigated and ascertained as well as optimal conditions have been selected for the chemical deposition of cobalt coatings on organic materials

(polyethylene terephthalate). In the course of this study the role of the concentration of the cobalt ions in the electrolyte has been elucidated in regard to the kinetics of deposition of the cobalt layers both on flexible organic polyterephthalate substrate (as well as on a hard, inorganic substrate of copper). It has been found out that upon

increasing the concentration of the Co^{2+} ions in the solution the rate of deposition is growing up. Thereupon the rate of deposition on PETF is increasing exceedingly in comparison to the copper support. In view of the rate of coating cobalt on both types of supports the optimal CoCl_2 concentrations are of the order of 60-70 g/l. In our opinion, however, the most suitable concentration from the point of view of the technological process is the concentration of 20-30 g/l. The increase in the concentration of CoCl_2 up to values of 50g/l exerts a slightly positive effect on the rate of deposition, while at the higher concentrations a deterioration of the quality of the deposited coating is observed. At this concentration the stability of the electrolyte is also higher.

The influence of NaH_2PO_2 , used as reducing agent, has been studied in regard to the kinetics of the deposition process and with respect to the morphology of the cobalt coating, as well as the influence on the quantity of phosphorus co-deposited in it. It has been established that with the increase in the concentration of the reducer the course of the dependence of the reduction rate passes through a maximum. The concentration of the reducer, which is close to this maximum, is accepted to be the optimal one for the electrolyte, studied by us. This optimum corresponds also to the maximal co-deposited amount of phosphorus inside the cobalt coatings.

The increase in the pH and in the temperature of the coating electrolyte, selected by us, has been found to determine an increase in the rate of reduction of the cobalt ions. Optimal values for pH and for the operating temperature of the working electrolyte have been found, at which the following factors have been estimated: stability, productivity (bulk capacity), rate of deposition and economic expedience.

Our preliminary results show that the chemically deposited cobalt matrix successfully incorporates a great number of diamond particles and presents a perspective for production of composite materials containing dispersive particles with high hardness.

Acknowledgment: This work is supported by the Bulgarian National Science Fund under Project ID 02/102/07.2009 (Contract DID 02/28/12.2009).

References

1. GORBUNOVA, K.M., NIKIFOROVA, A.A., SADAKOV, G.A., MOISEEV, V.P., IVANOV, M.V., *Fiziko-chimicheskie osnovy processa chimicheskogo kobaltirovaniya (Physico-chemical Basics of Electroless Cobalt Plating)*, , Nauka, Moscow, 1974 (in Russian)
2. BROOMAN, E.W., *Journal of Applied Surface Finishing*, **1**, no.1, 2006, p. 38
3. BROOMAN, E.W., *Galvanotechnik*, **104**, no. 1, 2006, p.58
4. KLINGENBERG, M.L., BROOMAN, E.W., *Plating and Surface Finishing*, **92**, no. 4, 2005, p. 42
5. RUDNIK, E., KOKOSHKA, K., LAPSA, Y., *Surface and Coatings Technology*, **202**, 2008, p. 2584
6. TANG, Y., ZHOU, S., XTE, Y., *Plating and Surface Finishing*, **95**, no. 10, 1998, p. 241
7. JIANG, J.T., ZHEN, L., XU, C.Y., SHAO, W.Z., *Surface and Coatings Technology*, **201**, 2007, p. 6059
6. HVAND, B., LIN, S., *J. Electrochem. Soc.*, **142**, 1995, p. 3749
7. BROOMAN, E.W., *Journal of Applied Surface Finishing*, **1**, no. 1, 2006, p. 38
8. STOYCHEV, D., KOTEVA, N., STOYCHEVA, M., VELKOVA, E., DOBREV, D., *Materiale Plastice – in press*.