

Chemical Cobalt Coating of Polyethyleneterephthalate

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The role of the concentration of the components of the alkaline electrolyte for chemical (electroless) coating of cobalt has been investigated with respect to the rate of their deposition on flexible organic support (polyterephthalate). It has been proved that with the increase in the concentration of Co^{2+} ions in the solution the rate of deposition is growing up. The influence of the concentration of NaH_2PO_2 , used as a reducing agent, has been studied in regard to the kinetics of deposition and with respect to the morphology of the cobalt coating, as well as the effect on the quantity of the phosphorus co-deposited in the coating. In the course of the study on the influence of the buffering components (NH_4Cl and H_3BO_3) in the working electrolyte, preventing the undesired liberation of cobalt hydroxide, on the kinetics of reduction of the cobalt ions, their optimal concentrations have been ascertained. It has been found that the increase in pH and in the temperature of the studied electrolyte determined an increase in the rate of reduction of the cobalt ions, whereupon the optimal values have been selected.

Keywords: chemical deposition, cobalt, coating, organic substrate

The chemical metallization is used for the deposition of a thin film of a metal or an alloy on supports of conducting, semi-conducting or dielectric materials. These can be in the form of bulk metal articles, powder particles, fibers or whiskers. The chemical copper-metallization is the most often applied in the practice, but also nickel coating or cobalt coating. The cobalt coating is used to a smaller extent, compared to nickel coating, although the cobalt possesses physico-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. In addition to this consideration, the chemically prepared composites with cobalt matrix represent a promising alternative of a solid chromium coating.

The cobalt coatings, obtained by a chemical method, possess a very high microhardness and wear resistance. They can be used for coating ceramic particles, whiskers or carbon nanotubes.

In a previous work [1] the reduction of cobalt ions using sodium hypophosphite has been studied, which leads to the formation of a compact coating. Unlike the process of chemical nickel coating, which occurs both in acidic, as well as in alkaline medium, the reduction of cobalt requires only alkaline medium. The conducting of the process in acidic solutions is practically unacceptable, due to the very low rate of reduction of the cobalt ions.

A comparative study of the chemical deposition of Ni-P and Co-P, and their composites with co-deposited particles of SiC on copper supports, has been reported in [2]. A comparison is made between chemically deposited from alkaline solutions coating of nickel and cobalt. It has been established that their behavior in the case of chemical deposition is different. Maleic acid has been used as a stabilizer, whose optimal concentration is determined by the nature of the deposited metal. 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.

The morphology of the surface of Ni-P and Co-P coatings is different. While the nickel coating consists of compact and regularly grown spherical globules, the cobalt coating is characterized by better smoothness and a specific needle-like structure. In certain cases the presence of pitting has also been observed.

In [3] the influence of the conditions for chemical metallization has been studied with respect to the magnetic properties and the structure of Co-P films. It has been established that they depend on the ratio between glycine and Co^{2+} , the concentration of the hypophosphate, the pH value and the temperature of the solution. The deposition of coating in a solution at pH 9 and low concentration of the reducing agent or complexing agent leads to low content of phosphorus, which determines the rough crystalline structure of the film and the low value of coercitivity. The coercitivity is increasing with the increase in the phosphorus content in the film, except for the cases, when the glycine or $\text{Co}(\text{OH})_2$ is incorporated into the Co-P film in concentrations higher than those classified as "traces". It has been shown that the inclusion of glycine and $\text{Co}(\text{OH})_2$ in the film coating appears as a result of their adsorption on the crystal modification in the course of its growth.

In [4] 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,

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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 [5] 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.

Hwand and Lin [6] supposed an electrochemical mechanism of deposition during the early stage of formation of the Co-P coating on Pd catalyst. The palladium catalyst has been deposited electrochemically on strongly orientated pyrolysed graphite. In this way some discrete palladium particles are being formed upon the support. The number of the new particles (probably Co-P nuclei) is increasing with the time interval of deposition. This result shows that the oxidation of the hypophosphite is occurring on the Pd nuclei and the electrons are being transferred through the conducting graphite, enabling the reaction of reduction of the Co^{2+} ions and the formation of new nuclei on the insufficiently active catalytically graphite surface. In the course of the process the nuclei are growing up and they merge forming an uninterrupted film.

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 coatings, deposited chemically or electrochemically [7-9]. Depending on the nature of the involved dispersion reagent, the coatings have high microhardness, optimal attrition coefficient and high corrosion resistance.

The aim of the present work was to establish the optimal composition of the electrolyte and the best conditions for chemical deposition of cobalt coating on the material polyethyleneterephthalate by studying the influence of the components of the electrolyte. At the same time the effect of the conditions of occurring of the process on its rate are to be evaluated – the effect is determined on the basis of the thickness of the Co coating per unit of time. The structure, the morphology and the 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 different highly rigid dispersion reagents.

Experimental part

The studies were carried out using samples of wafered polyethyleneterephthalate (PETF) material of dimensions $30 \times 30 \times 0.05$ mm. The samples underwent the following preliminary treatment:

- degreasing and etching in NaOH solution (200 g/L) at a temperature of 60°C and 15 min duration;
- treatment in 3M HCl at room temperature for 3 min;
- treatment in a colloid activating solution, which contains 0.5 g/L PdCl_2 , 20 g/L SnCl_2 and 3M HCl, at room temperature and duration of 3 min;
- accelerating in a solution of NaOH (40 g/L) at room temperature for 3 min.

After this pretreatment the samples were processed further in a solution for chemical cobalt deposition with basic composition (BC):

$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	30 g/L
$\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$	20 g/L
Na citrate	100 g/L
NH_4Cl	50 g/L
pH	9
temperature	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. The influence of adding H_3BO_3 to the solution for coating cobalt has also been studied.

In order to determine the microhardness of the cobalt layers on micro-level, we deposited cobalt coating on witness-samples for each studied composition and each studied set of conditions, whereupon the supports were cut out of copper foil of thickness 100 microns and the dimensions were 30×30 mm. The copper supports had been etched in advance for 1 min in a solution containing HNO_3 , H_3PO_4 and CH_3COOH at a ratio 1:1:1 at room temperature. The activation was carried out in ionic activator, containing solution of PdSO_4 at room temperature for 1 min.

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 structure 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), and the content of phosphorus in them was evaluated using JSM 6390 apparatus, equipped with an INCA energy-dispersive X-ray spectrometer (EDS).

Results and discussions

An important characteristic of metalized textile materials is the adhesion of the metal coating, deposited on them. 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 [10] showed that the best results are obtained by treatment in alkaline solutions. According to the data [11] in the case of such treatment the following reaction is occurring:



Taking into account some additional investigations, preceding the present study, we have proved that the optimal results, with respect to the adhesion of the metal coating, are achieved by etching the PETF at $40\text{-}60^\circ\text{C}$ in the course of 10-15 min, at 200 g NaOH/L content in the etching solution.

The SEM micrograph of the surface of PETF, after the etching and prior to its metallization, is shown in figure 1. Chemical attack is observed and as a result of it the polymeric surface has become rough, the fibrous structure underneath appears on the surface (fig. 1a) and the ruggedness of the separate fibers is observed (fig. 1b).

This enables good anchoring of the metal coating and improving of the adhesion. This effect is desirable in view of the fact, observed in the case of SiC metallization – for example in [5], that the adhesion between the whiskers of SiC and the cobalt coating is a rather poor one. This appears to be as a result of the electrostatic repulsion between the separate palladium ions, leading to a strong

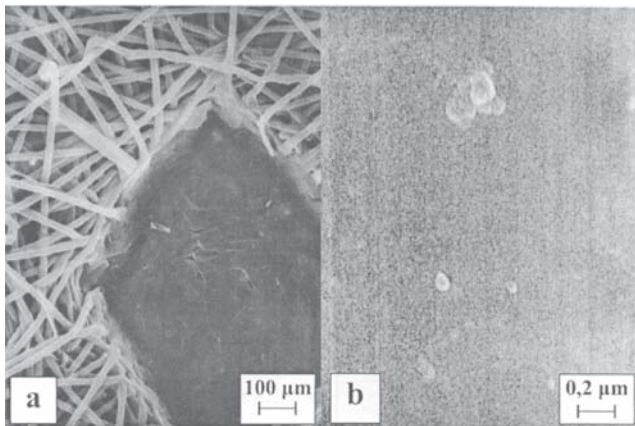
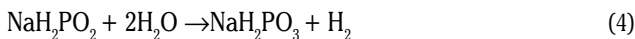
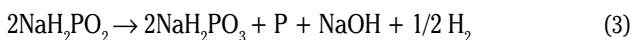
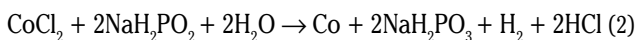


Fig. 1. SEM micrograph of the surface of PETF after etching: a – general view, identifying the fibrous and the matrix components of the material (magnification x100); b – micrograph of the surface of the fiber (magnification x20 000)

decrease in the density of the palladium nuclei in the process of formation on the metalized surface.

In order to avoid such phenomena 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:



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 2.

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. Similar course of the curves “rate of deposition of the cobalt coating as a function of the concentration of CoCl_2 ” has also been reported in [1]. The authors report that the increase in the concentration of cobalt sulfate above 140 g/L, preserving, at the same time, the ratio between the other components, leads to lowering of the rate of the

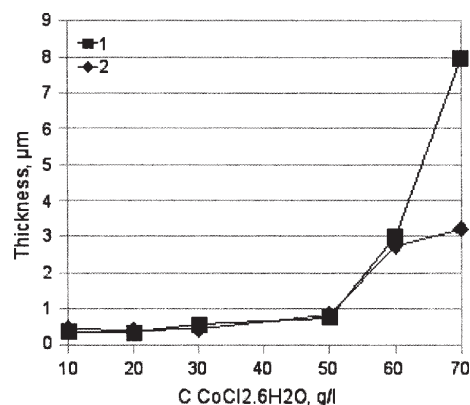


Fig. 2. Influence of the concentration of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in the solution ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ - 20 g/L; Na citrate - 100 g/L; NH_4Cl - 50 g/L; T - 90°C, pH - 9) on the rate of deposition of Co coating; time interval of deposition for each sample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

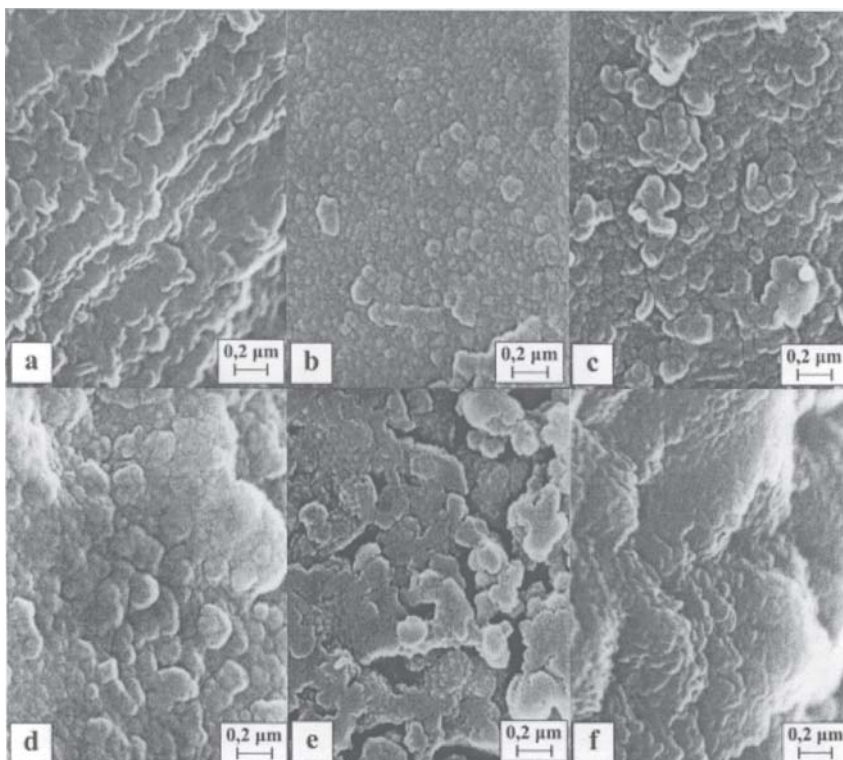


Fig. 3. SEM micrographs (50 000x) of the surface of PETF support after coating cobalt chemically in solutions of different concentrations of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$: a - 10 g/L; b - 20 g/L; c - 30 g/L; d - 50 g/L; e - 60 g/L; f - 70 g/L

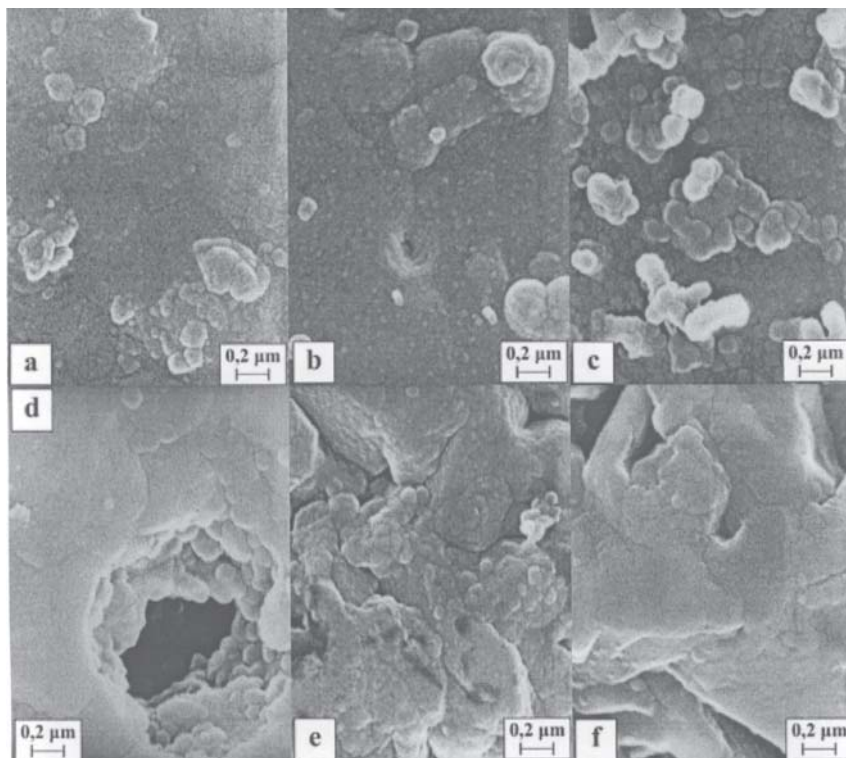


Fig. 4. SEM micrographs (50 000x) of the surface of copper support after coating cobalt chemically in solutions of different concentrations of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$: a - 10 g/L; b - 20 g/L; c - 30 g/L; d - 50 g/L; e - 60 g/L; f - 70 g/L

reduction process of the cobalt ions. 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 figures 3 and 4.

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, respectively on the copper support, are the following:

- there exist differences in the growth of the cobalt coating on the two kinds of supports. 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. 3a). 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. 3b). Increasing further the concentration of Co^{2+} ions (fig. 3c, 3d) 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. 3) 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. No such effect is observed in the case of cobalt coatings, deposited on copper support (fig. 4);

- the nature of the support exerts also influence on the appearance of pitting defects (fig. 4d). In the case of Cu supports these defects, owing to the hydrogen liberated during the reduction process, are much more strongly expressed, whereupon their amount is increasing with the increase of the CoCl_2 concentration in the working solution;

- the substantial differences in the growth of the cobalt coatings on rigid metal (copper) and on flexible non-metal

(polyethyleneterephthalate) supports, respectively the differences in the uniformity of distribution of Co coatings on them, will determine the different options for co-deposition of solid dispersion agents in them. As in the case of the flexible non-metallic materials (supports), which consist of threads, each thread is covered in separate forming a skeleton of cobalt-coated fibers, the co-deposition of the dispersion agents will be favored to a greater extent.

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 figure 5. 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.

According to ref. [1], in the case of reduction of cobalt ions with sodium hypophosphite a metal coating is obtained, which contains phosphorus. Its amount depends on the conditions of carrying out the process. The inclusion of phosphorus exerts substantial influence on the structure and on the properties of the coating, especially on its magnetic characteristic features. The change in the content of phosphorus in the coating, within the range of NaH_2PO_2 concentrations in the solution, studied by us, are shown in table 1, while the influence of the quantity of the reducing agent on the structure of the cobalt coatings, deposited on polyethyleneterephthalate support and on copper support

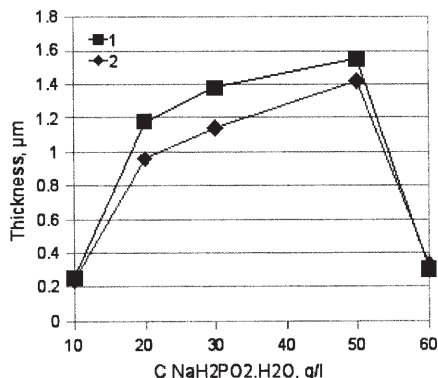


Fig. 5. Influence of the concentration of $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ in the solution ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ - 30 g/L; Na citrate - 100 g/L; NH_4Cl - 50 g/L; T - 90°C, pH - 9) on the rate of deposition of Co coating; time interval of deposition for each sample - 30 min; 1-■- PETF substrate; 2-◆- Cu substrate

at constant content of cobalt in the solution is shown in figure 6.

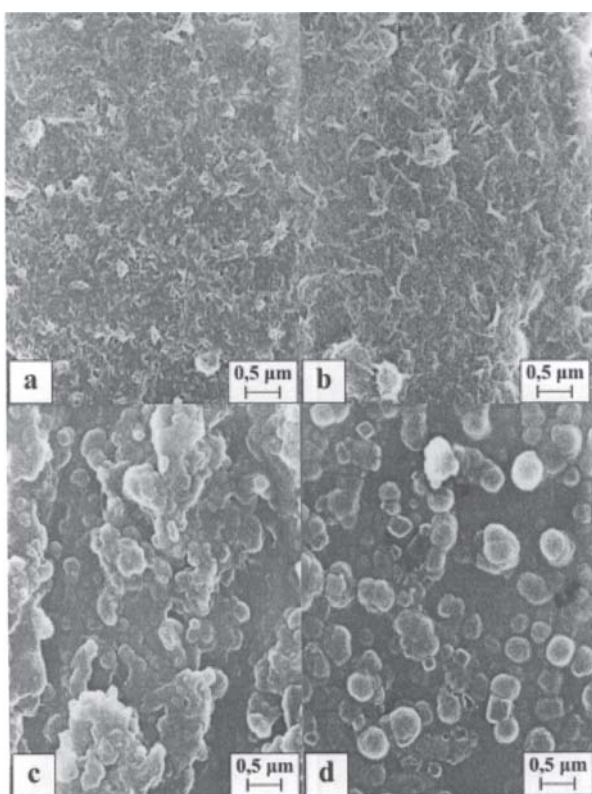


Fig. 6. SEM micrographs (20 000x) of the surface of PETF support, after coating cobalt chemically in solutions of different concentration of $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$: a - 10 g/L; b - 60 g/L, and of copper support: c - 10 g/L; d - 60 g/L

It follows from table 1 that there exists a definite proportionality between the thickness of the deposited cobalt coatings and the quantity of co-deposited phosphorus on both types of supports, which gives evidence for uniform inclusion of the phosphorus inside the thickness of the layer in the course of co-deposition. It is remarkable, however, that in the case of copper support the quantity of co-deposited phosphorus is considerably smaller, especially at the lower concentrations of $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$.

From the results, obtained by the SEM investigation of chemically deposited coatings of cobalt on flexible support, built of PET fibers (fig. 6), 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 $\sim 0.15 \mu\text{m}$;

- upon increasing the concentration of the sodium hypophosphite, the size of the Co grains, contained in the coating, grows up twice (fig. 6b) - 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;

- a characteristic feature of the initial stages of growing of the cobalt coating on copper support (fig. 6 c), at low concentration of hypophosphite (10 g/L) is the fact that a clearly expressed orientation of the growing crystallites is observed. This effect can be associated with the influence of the formed orientated micro-roughness in the course of rolling the sheets of the copper support, which determines the direction of growing of the cobalt grains. At increased content of hypophosphite in the solution (60 g/L) the structure of the deposited coating is large grains (fig. 6d). What is also making impression in this case is the fact that on the copper support the structure of the cobalt coating differs substantially from that on the terephthalate tissue. Spheroidal and cubic agglomerates are growing on the copper support, whose dimensions are much larger than those of the pyramidal formations appearing on the PETF support.

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. This influence is specific and it differs in the cases of non-

Concentration of $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ in BC, g/l	Thickness of the coating on PETF support, μm	Thickness of the coating on Cu support, μm	P content (%) in the Co coating on PETF support	P content (%) in the Co coating on Cu support
10	0,25	0,24	2,12	0,63
20	0,55	0,42	4,01	3,42
30	1,38	1,14	5,18	3,75
50	1,55	1,42	5,87	4,43
60	0,50	0,33	2,33	1,75

Table 1
DEPENDENCE OF THE THICKNESS OF THE COBALT COATING AND THE CONTENT OF PHOSPHOROUS ON IT ON THE CONCENTRATION OF $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ IN THE ELECTROLYTE. TIME INTERVAL FOR DEPOSITION OF THE COBALT COATING - 30 min

metallic and metallic supports. In the case of fibrous support of polyethyleneterephthalate, at the lower rates of reduction of the cobalt ions (when the concentrations of the sodium hypophosphite are lower), a relatively uniform and small-size crystalline deposited cobalt coating is formed on the fibers of PTEF and there is accumulation of bulk cobalt phase in the areas between the fibers. At high concentration of the reducing agent on the fibers of terephthalate large-grain Co layers are formed and their thickness is not uniform. At the same time in the case of metal (copper) support, at low concentrations of the reducing agent the cobalt layers are orientated in the direction of rolling treatment of the copper sheet support. In contrast to the fibrous support, however, the cobalt coating obtained both at low concentrations, as well as at high concentrations of the reducing agent, is characterized by large-grain structure, formed along screw-like dislocation mechanism of growing.

Influence of the temperature

The dependence of the rate of chemical cobalt coating on the temperature of the solution is represented in figure 7. It is seen from the figure that upon increasing the temperature of the electrolyte the rate of cobalt ions reduction is accelerated.

Thereupon its change is practically independent of the nature of the support up to about $\sim 90^{\circ}\text{C}$, 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 ($90 - 95^{\circ}\text{C}$) temperature interval.

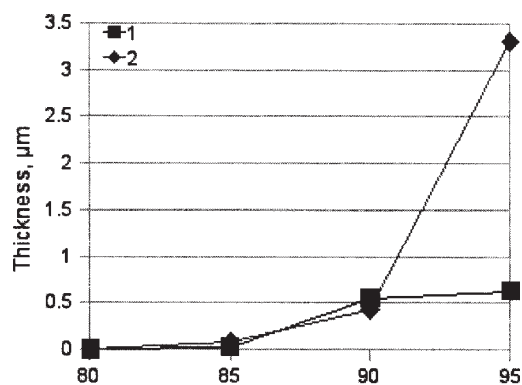


Fig. 7. Dependence of the rate of chemical deposition of cobalt coating on the temperature of the electrolyte on supports of PETF (1-■-) and Cu (2-◆-) from electrolyte, containing: $\text{CoCl}_2 \cdot 6\text{H}_2\text{O} - 30 \text{ g/L}$; $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O} - 20 \text{ g/L}$; Na citrate - 100- g/L; $\text{NH}_4\text{Cl} - 50 \text{ g/L}$; T - 90°C , pH - 9. Time interval of deposition for each sample - 30 min.

Influence of pH

The influence of the pH factor of the electrolyte for coating cobalt upon the rate of deposition of the cobalt film and on its morphology are illustrated in figures 6 and 7. It is seen from figure 6 that in the case of PTEF support, with the increase of pH, the rate of coating cobalt is growing up and a maximum is observed at $\text{pH}=9.5$.

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 $\text{pH} 10.5$.

The influence of pH on the structure of the deposited coatings was studied both on flexible polyethyleneterephthalate support, as well as on copper support (fig. 9).

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 (fig. 9b). The Co coating, deposited under these conditions on copper support, is characterized by uniform granular structure and non-compact, non-cracked layers (fig. 9c). 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.

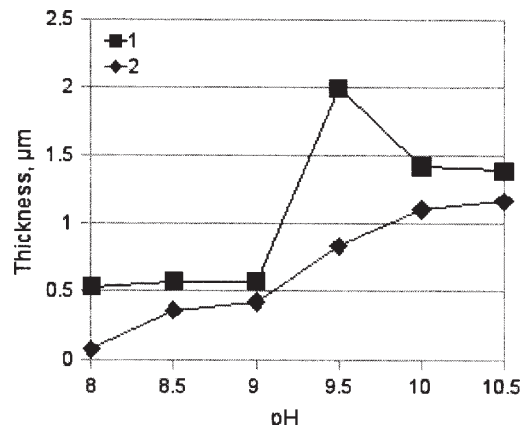


Fig. 8. Dependence of the rate of chemical deposition of cobalt coating on the pH of the electrolyte ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O} - 30 \text{ g/L}$; $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O} - 20 \text{ g/L}$; Na citrate - 100 g/L; $\text{NH}_4\text{Cl} - 50 \text{ g/L}$; T - 90°C) on supports of PETF (1-■-) and Cu (2-◆-). Time interval of deposition for each sample - 30 min.

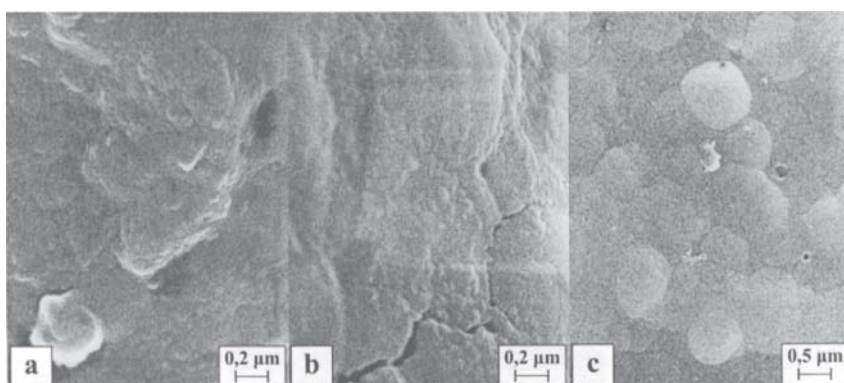


Fig. 9. SEM micrographs of the surface of PETFsupport, after coating cobalt chemically in solutions of different pH: a - 8.5; b - 9.5, and on Cu supports at pH 9.5 - c. Composition of the electrolyte: $\text{CoCl}_2 \cdot 6\text{H}_2\text{O} - 30 \text{ g/L}$; $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O} - 20 \text{ g/L}$; Na citrate - 100 g/L; $\text{NH}_4\text{Cl} - 50 \text{ g/L}$; T - 90°C . Time interval of deposition for each sample - 30 min.

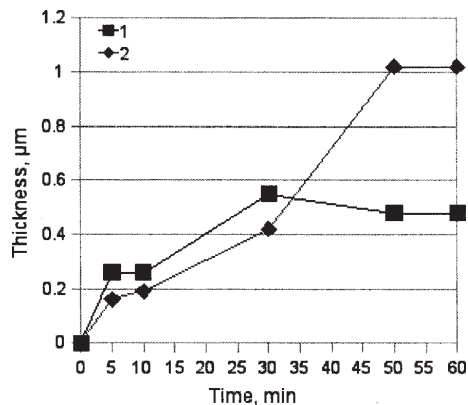


Fig. 10. Dependence of the rate of chemical deposition of cobalt coating on the time interval of deposition on supports of PETF (1-■-) and Cu (2-◆-). Composition of the electrolyte and conditions of the chemical deposition: $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ - 30 g/L; $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ - 20 g/L; Na citrate - 100 g/L; NH_4Cl - 50 g/L; T - 90°C, pH - 9.

Influence of the time interval of metallization

The duration of coating cobalt in the solutions, studied by us, influences in a specific way the rate of cobalt deposition, respectively the thickness of the obtained coating, the specific cases of different supports (fig. 10).

From the results represented in figure 10 one can see that at time intervals of deposition 5, 10 and 30 min the rate of cobalt deposition, respectively the thickness of the deposited Co coating (the technologically important parameter "thickness" is depicted along the ordinate axis i.e. the amount of deposited Co related to unit of surface area) is growing up with the time interval, whereupon on PETF support the rate is exceeding with respect to Cu support. This fact could be due to the greater actual surface of PETF in comparison to that of the copper support, on which a greater amount of catalyst is adsorbed. After the 30th min the rate of deposition on PETF support practically does not change any more, while on Cu support it continues to grow up. The reaching of a steady state value of the rate of deposition on Cu support is accomplished after reaching the 50th min of deposition.

In [1], considering the results, which characterize the structure of relatively thick cobalt coatings, the authors have found out that the sizes of the crystallites and their orientation is determined mainly by the quantity of phosphorus, which has been included in the coating. In this connection the authors claim that the co-deposited phosphorus possesses and inhibiting effect in regard to the process of growing of the cobalt layers. In our opinion, the results represented in figure 10, registering dependence of the rate of deposition with the time on the nature of the support, can also be associated with inhibiting influence of the co-deposited phosphorus. This is one of the possible reasons to reach steady state rate of cobalt deposition on the two types of supports after the 30th min (for PETF), respectively the 50th min of deposition (for Cu). In support

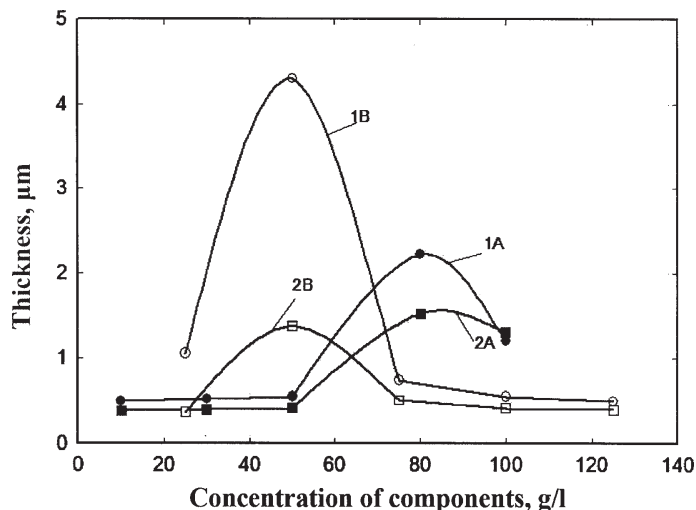


Fig. 11. Dependence of the rate of chemical deposition of cobalt coating on the concentration of NH_4Cl (curves 1A and 2A) and of Na-citrate (curves 1B and 2B) on supports of PETF (curves 1A and 1B) and Cu (curves 2A and 2B). Composition of the electrolyte and conditions of chemical deposition: $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ - 30 g/L; $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ - 20 g/L; T - 90°C, pH - 9. In case of varying the concentration of NH_4Cl - the concentration of Na-citrate in the electrolyte is fixed at 100 g/L, upon varying the concentration of Na-citrate then the concentration of NH_4Cl is fixed at 50 g/L.

of such a supposition are also the results on the amount of co-deposited phosphorus in the Co coating, deposited on both kinds of supports (table 1). It can be seen from the table that the phosphorus content in the Co coating, when the support is copper, is considerably smaller compared to the Co coating, deposited on PETF support.

Influence of the additives to the solution for coating cobalt - influence of sodium citrate

In the course of the process of coating cobalt chemically in alkaline medium it becomes necessary to add some substances to the working solution, which should prevent the liberation of cobalt hydroxide. They should form some complex compounds and decrease the concentration of the free cobalt ions down to a value, at which the cobalt hydroxide does not reach its solubility product value in the working solution. Such kinds of compounds appear to be the salts of citric acid, tartaric acid, glycine etc. In the experimental runs, carried out by us, we used as complexing agent sodium citrate, whose concentration was varied from 25 up to 125 g/L (fig. 11). Lower concentrations of citrate could not be used because of the danger of formation of insoluble products of hydrolysis of the cobalt salts.

A characteristic feature of the process is that after increasing the concentration of Na-citrate up to 50 g/L the rate of deposition is increasing sharply, but thereafter it drops down. In spite of this fact, we used higher

Table 2
DEPENDENCE OF THE THICKNESS OF THE COBALT COATING ON THE CONCENTRATION OF H_3BO_3 IN THE ELECTROLYTE. TIME INTERVAL FOR DEPOSITION OF THE COBALT COATING - 30 min

Concentration of H_3BO_3 in BC, g/l	Thickness of the coating, μm, PETF support	Thickness of the coating, μm, Cu support
10	4,65	1,74
20	1,68	0,99
30	0,59	1,1
40	0,16	0,92

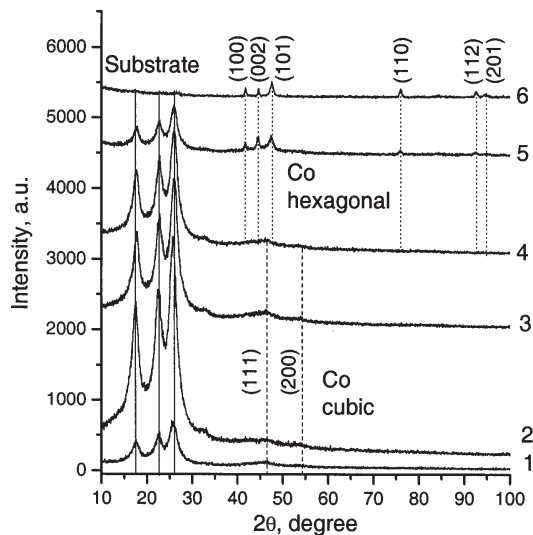


Fig. 12. XRD diffraction patterns of chemically deposited cobalt coatings, illustrating the influence of their texture on:
 - the concentration (in g/L) of the cobalt ions in the working electrolyte (1 - $C_{Co^{2+}} = 10$ g/L; 2 - $C_{Co^{2+}} = 30$ g/L; 6 - $C_{Co^{2+}} = 70$ g/L);
 - the concentration (in g/L) of the reducing agent in the working electrolyte (3 - $C_{NaH_2PO_2} = 20$ g/L; 4 - $C_{NaH_2PO_2} = 50$ g/L);
 - pH of the electrolyte (3 - pH = 9; 5 - pH = 10,5).

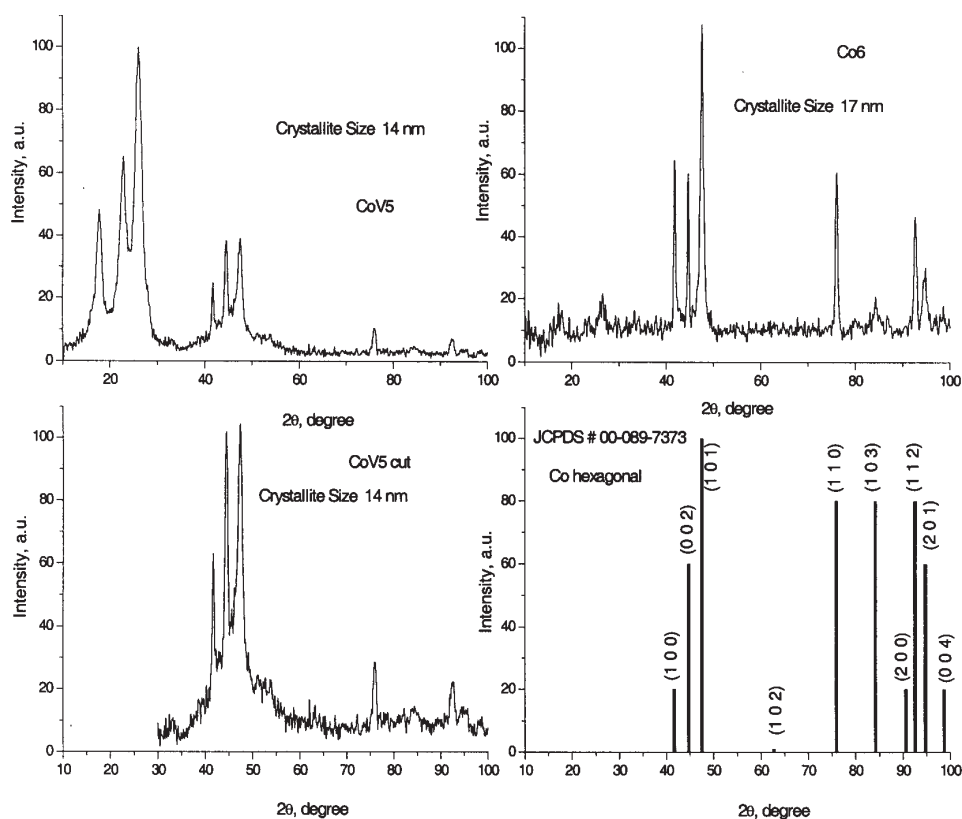


Fig. 13. Powder diffraction patterns of chemically deposited cobalt coatings (samples No.5 and No.6 in fig. 11), compared with a standard reference non-structured sample)

concentration of citrate (100 g/L), in order to avoid spontaneous reduction of the cobalt ions in the entire bulk of the solution.

- influence of NH_4Cl , $(NH_4)_2SO_4$ and H_3BO_3

Substantial influence on the reduction of the cobalt ions was exerted by the buffering additives. Such additives are most often NH_4Cl and $(NH_4)_2SO_4$, but also H_3BO_3 . The ammonium salts are known to play not only the role of buffering additive but also to be complexing agents [1]. The boric acid, in the presence of salts of the tartaric and citric acids is forming mixed complexes with the cobalt, whose composition involves the anions of the organic acid and of the boric acid. These substances, in addition to being buffers and complexing agents, are also known to exert influence on the composition and on the properties of the coating.

The use of ammonium salts as buffering additive has also certain disadvantages, determined by the volatility of ammonia at high temperatures, as well as the formation of very stable complexes with the Cu^+ ions in the solution for coating cobalt.

In our experimental runs we used solutions with concentrations of NH_4Cl from 10 up to 100 g/L. Upon increasing the concentration of NH_4Cl (up to 80 g/L) the rate of the process is promoted at first, but then it is decreasing (fig. 11).

The influence of the boric acid upon the rate of the process of coating cobalt chemically is illustrated in table 2. It is reported in [1] that boric acid accelerates the process only in alkaline solutions, containing tartaric or citric acid. It is supposed that one of the reasons for the accelerating action of boric acid is not only its buffering ability, i.e. the maintaining of constant pH value for long time, but also the formation of complexes between the cobalt ions and the anions of the organic acids. The data in table 2 show that at low concentrations of the boric acid (10 g/L) the rate of the process of coating cobalt is very high, but afterwards with the increase of its concentration the rate of the process becomes lower, as a consequence of the binding the greater part of the cobalt ions in the complex.

The obtained results on the effect of boric acid in the electrolyte, studied by us, gives us the reason to include H_2BO_3 at low concentrations in the next optimization step of the electrolyte composition. This step will be undertaken during the following stage of our research work, when it is foreseen to add highly rigid dispersion agents to the electrolyte for coating cobalt chemically in view of their co-deposition.

Texture of the chemically deposited cobalt coatings

Data are practically missing in the current literature with respect to the influence of the composition of the electrolyte and in regard to the conditions of chemical deposition of the cobalt coatings on their texture. Figures 12 and 13 illustrate some of the results, obtained by us, throwing some light on this aspect of the investigation.

It follows from the represented XRD patterns that the cobalt layers, obtained from electrolytes, in which the concentration of the cobalt ions is up to 30 g/L and the pH value is up to 9, are amorphous. Very slightly expressed reflexes are noticeable in them at 2θ around 47 and 54°, which are indicative of the fact that an insignificant part of the crystallites, building up the chemically deposited cobalt coating, have cubic packing, i.e. the so called β modification of the cobalt, with poorly expressed texture in the directions (111) and (200). In the cases of layers, obtained from electrolytes with high concentration of the cobalt ions (XRD pattern 6) and at high pH value (XRD pattern 5), the reflexes from the β modification of the cobalt practically disappear, whereupon a comparatively larger part of the crystallites appears, which have hexagonal packing (the reflexes at $2\theta=42-48^\circ$; 76 and 93-98°), characteristic of the α modification of the cobalt. This change is illustrated in details in figure 13. There it is seen that under the conditions of preparation of sample 5 (increased pH) the predominating directions in the orientation of the crystallites are (101), (002) and (100), while under the conditions of preparation of sample 6 (high concentrations of the cobalt ions in the working electrolyte) additionally appear the directions (110), (112) and to a smaller extent the direction (201).

It is important to note that the dimensions of the elementary building units, determined by XRD – the blocks building up the obtained cobalt coatings, practically do not depend on the change in the conditions for their preparation and the dimensions vary within the interval 14 – 17 nm.

Obviously the changes in the conditions for chemical deposition of cobalt coatings determine only some insignificant changes in the orientation and in the size of the crystallites building up the coatings. These coatings have a rather amorphous structure and under specific conditions the appearance of hexagonal and/or cubic crystalline phases becomes possible, which could possibly influence to a certain extent the capacity of the growing cobalt layers to co-deposit different dispersion agents inside them.

Micro-hardness of the chemically deposited cobalt coatings

The influence of the concentration of the cobalt ions being reduced in the electrolyte was studied as well as the concentration of the reducing agent and the effect of pH of the electrolyte upon the micro-hardness of the cobalt layer. Thereupon it has been found that with the increase in the concentration of the cobalt ions the micro-hardness based on the Wickers scale (measured with micro-hardness tester "Leitz Wetzlar" (Germany)) is growing up for the concentration interval studied by us (10-70 g/L) from about ~ 140 kg/mm² up to ~ 370 kg/mm². The increase in the

concentration of the reducing agent (within the interval - 10-60 g/L NaH_2PO_4) influences even more strongly – from values of HV ~ 180 kg/mm² (at 10 g/L) up to values of about ~ 400 kg/mm² (at 50 g/L). The increase in the pH of the electrolyte for coating cobalt decreases the micro-hardness of the cobalt layers – from values of HV ~ 380 kg/mm² (at pH =9) to values ~ 210 kg/mm² (at pH =10.5).

The established tendencies in the process of changing the micro-hardness of the chemically deposited cobalt coatings correlate well with the changes registered in their micro-structure as well as with the observed changes in the content of phosphorus co-deposited in them (table 1), forming solid solution with the cobalt [12]. On the other hand the obtained results, showing the options for altering the micro-hardness of the cobalt matrix within wide limits, give us the reason to suppose that it can be applied successfully for incorporating hard and super-hard dispersion agents in it. In the course of forming the composite materials for polishing and grinding, for example, the variation of the hardness of such supporting matrix can play a very essential role by creating more favorable possibilities in view of evacuation the material to be removed.

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 support, as well as on a hard, inorganic support 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 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_4 , 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 effect of the buffering components (NH_4Cl and H_2BO_3), preventing the liberation of cobalt hydroxide in the alkaline working electrolyte, has also been studied with respect to the kinetics of reduction of the cobalt ions. Optimal concentrations have been found for them also, at which the rate of reduction of the Co^{2+} ions is the maximal one. The obtained results have also shown that these substances have not only buffering action, but they are

complexating agents at the same time, which influence in a specific way the structure and the morphology of the cobalt coating.

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.

The influence of the time interval of deposition has been studied with respect to the change in the rate of chemical deposition. It has been shown that up to the 50th min of deposition the rate of the process is increasing, but thereafter it reaches a steady value. Thereupon, depending on the nature of the support, this steady rate has a different value. A supposition is put forward that the established effect is owing to inclusion of phosphorus in the coating, which exerts an inhibiting effect on the rate of the process.

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