INFLUENCE OF THE CONDITIONS FOR DEPOSITION ON MECHANICAL PROPERTIES OF CHEMICALLY DEPOSITED THIN COBALT LAYERS

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Abstract: Cobalt layers with the thickness of 0.5 – 1,5 μm are deposited on a copper foil substrates varying the concentration of the cobalt ions ($CoSO_4$), the reducer (NaH_2PO_2), as well as the pH of the electrolyte. The influence of the conditions for deposition on the morpholgy, structure, and mechanical properties (hardness, modulus of elasticity, adhesion, etc.) of the layers is studied. On the basis of the obatined results, conclusions for the influence of the conditions for formation of the metal-plastic properties of the layers are made.

Keywords: COBALT LAYERS, ELECTROLESS DEPOSITION, MECHANICAL PROPERTIES

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. 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. It is important to point that the properties of the chemically deposited Cu and Ni coatings with different functional application are studied relatively well, but the date for Co are not enough. Insufficient are the investigations about the application of cobalt as a metal matrix for fabrication of composite materials, containing different co-deposited dispersed particles. 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 (diamond, cubic or hexagonal boron nitride, carbides of transitions metals – Ti, W, Nb, Ta, etc) nano- and microparticles for preparation of different abrasive tools [2-4]. In this aspect the knowledge of mechanical properties of electroless deposited thin Co layers determines serious practical interest.

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 [5-7]. 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 investigate the influence of the components of an optimized electrolyte and the regime [8] of electroless deposition on the structure and mechanical properties of cobalt layers.

2. *Experimental*

The studies were carried out using samples-supports of copper foil of dimensions 30 x 30 x 0.100 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. After this pretreatment the samples were processed further in a solution for chemical cobalt deposition with basic composition, in g/l: $CoCI_2.6H_2O$-30; $NaH_2PO_2.H_2O$-20; Na citrate-100; NH_4Cl-50; gpH 9; T-90^oC [8]. With this electrolyte we studied the influence of the concentrations of the main components ($CoCI_2.6H_2O$ – 10-70 g/l and $NaH_2PO_2.H_2O$ – 10-60 g/l), as well as the pH (8-10.5) of the solutions.

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). Structural and textural effects in deposited coatings were investigated by a four-circle Philips PW 1050 diffractometer with texture goniometer attachment using CuK_α radiation. They were manifested by comparing the peak intensities of a standard ICDD (International Centre for Diffraction Data) data base sample and the prepared samples as normalized intensities.

Investigation of mechanical properties of Co films was realized by nanoindentation experiments [9], using Nano Indenter G200 (Agilent Technologies). This indenter is equipped with a Berkovich three-sided diamond pyramid with centerline-to-face angle 65.3º and 20nm radius at the tip of the indenter. The minimum load possible to be applied is 10 mN, and the maximum load is 500 mN. Displacement recording resolution is 0.01 nm and the load recording resolution is 50 nN. The device is equipped with an optical microscope with 2 objectives of magnification respectively 250x and 1000x. We realized series of 25 indentations on each sample probe in order to have better statistics. We used method of indentation with fixed maximum displacement 200nm, which guarantee us that we are far from the substrate. This method prescribes a single load/unload cycle to a specified depth. Indentation hardness H_{IT} and indentation modulus E_{IT} are determined using the stiffness as calculated from the slope of the load-displacement curve during unloading. Basic input parameters used in this indentation method are given in Table 1.

Table 1: Input parameters for nanoindentation experiments

Parameter	Unit	Values
Percent To Unload	%	90
Surface Approach Velocity	nm/s	10
Depth Limit	nm	200
Delta X For Finding Surface	μm	-50
Delta Y For Finding Surface	μm	-50
Approach Distance To Store	nm	1000
Peak Hold Time	s	10
Surface Approach Distance	nm	5000
Poisson's Ratio	-	0.3

3. *Results and discussion*

3.1. Influence of the concentration of $CoCl_2$, NaH_2PO_2 and pH of the electrolyte on their structure, composition and thickness

In [8] it has been found out that within the interval of concentrations of $CoCI_2.6H_2O$ 10 – 60 g/l the rate of deposition of cobalt 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.

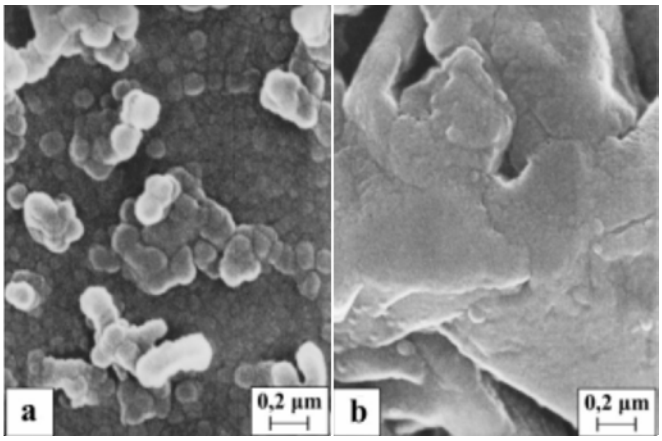

Fig.1. SEM micrographs (50 000x) of the surface of copper support after coating cobalt chemically in solutions of different concentrations of $CoCI_2.6H_2O$: a - 30 g/l; b - 70 g/l

The influence of the concentration of $CoCl_2$ in the working electrolyte on the morphology and structure of the deposited cobalt coatings is illustrated in Fig. 1. On the base of these data was established that with increasing of Co^{2+} ions concentration in the electrolyte the sizes of cobalt crystals changed significantly – from 100-300 nm at 20 g/l to 20-50 nm at 70 g/l. According as probably 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.

The dependence of the thickness of the deposited cobalt coating on the concentration of NaH_2PO_2 in the solution show, that the increasing 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 [8].

The influence of the quantity of the reducing agent (NaH_2PO_2) on the structure of the cobalt coatings at constant content of $CoCI_2.6H_2O$ in the solution (30 g/l) is shown in Fig. 2.

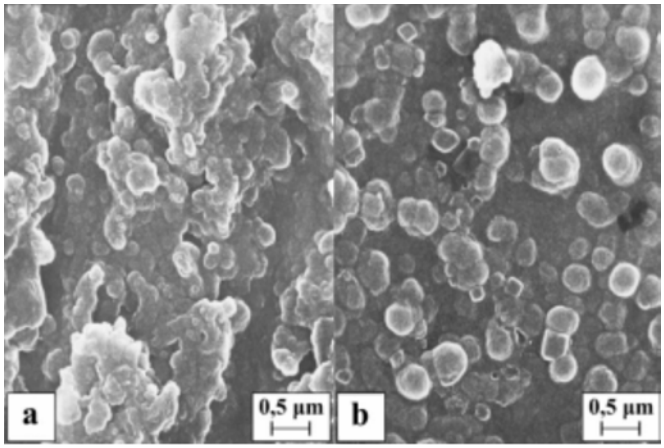

Fig.2. SEM micrographs (20 000x) of the surface of copper support, after coating cobalt chemically in solutions of different concentration of $NaH_2PO_2.H_2O$: a - 10 g/l; b - 60 g/l

A characteristic feature of the initial stages of growing of the cobalt coating on copper support (Figure 2 a), at low concentration of hypophosphite (10 g/l) is the fact that a clearly expressed orientation of the growing crystallites is observed which 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 smaller grains (Figure 2,b).

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 and microhardness. The changes in the thickness and in the content of phosphorus in the cobalt coating, within the range of NaH_2PO_2 concentrations in the solution, studied by us, are shown in Table 2.

***Table 2**: Dependence of the tickness (δ) of the cobalt coatings and the content of phosphorous (P) on it on the concentration of $NaH_2PO_2.H_2O$ in the electrolyte. Time of deposition of the Co coatings – 30 min*

$C_{NaH2PO2.H2O}$, **g**/l		δ, μm		P, **%**
10		0,24		0,63
20		0,42		3,42
30		1,14		3,75
50		1,42		4,43
60		0,33		1,75

It follows from Table 2 that there exists a definite proportionality between the thickness of the deposited cobalt coatings and the quantity of co-deposited phosphorus, which gives evidence for uniform inclusion of the phosphorus inside the thickness of the layer in the course of co-deposition.

Upon increasing the pH of the electrolyte the rate of reduction of Co ions is growing up reaching the highest value at pH 10.5 [8]. The study of the influence of pH on the structure established that the increase in the pH of the working electrolyte determines an uniform granular structure of layers without any significant differences in the sizes of crystals.

3.2. Texture of the chemically deposited cobalt layers

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. Figure 3 illustrate some of the results, obtained by us, throwing some light on this aspect of the investigation.

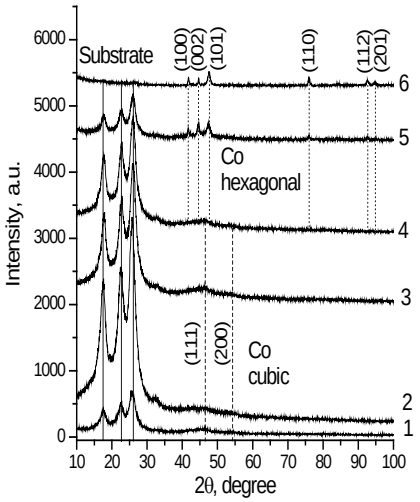

Fig.3. XRD diffraction patterns of chemically deposited cobalt coatings, illustrating the influence of their texture on:

- 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 - $C_{NaH2PO2}$ = 20 g/l; 4 - $C_{NaH2PO2}$ = 50 g/l;

- pH of the electrolyte (3 – pH = 9 ; 5 - pH = 10,5).

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 2θ=42-48°; 76° and 93-98°), characteristic of the α modification of the cobalt. This change is investigated in details in [8], where is established 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).

3.3. Mechanical properties of investigated Co films

We investigate influence of concentration of the cobalt ions ($CoSO_4$), concentration of the reducer (NaH_2PO_2), as well as the pH of the electrolyte on indentation hardness and indentation modulus of Co films.

The indentation hardness is calculated from the maximum force divided by the projected area:

$$H_{IT} = \frac{P_{\max}}{A} \qquad 1)$$

The indentation modulus can be determined as:

$$E_{IT} = \frac{\left(1-\nu^2\right)}{\left\{\frac{2\beta\sqrt{A}}{S\sqrt{\pi}} - \frac{1-\nu_i^2}{E_i}\right\}} \qquad 2)$$

where (defined from "Load-displacement" curve) stiffness $S = \beta\frac{2}{\sqrt{\pi}}E_{eff}\sqrt{A}$,

the effective elastic modulus E_{eff} is defined by $\frac{1}{E_{eff}} = \frac{1-\nu^2}{E_{IT}} + \frac{1-\nu_i^2}{E_i}$,

ν is the Poisson's ratio of the probe,

β is a constant , which depends of geometry of the indenter,

E_i and ν_i are the indenter's elastic parameters [10].

Figures 4 and 5 show alteration of indentation hardness and indentation modulus depending on concentration of the cobalt ions. It's obviously from these figures, that increasing of the cobalt ions concentration leads to increasing of indentation hardness and modulus. This could be explained by the fact that increasing of concentration of cobalt ions leads to decreasing of grain sizes, but according to Hall-Petch relationship [11]- hardness of the layer is generally observed to increase as the grain size decreases:

$$H = H_0 + kD^{-1/2}, \qquad 3)$$

where D is average grain size, H_0 and k are constants.

Figures 6 and 7 show increasing of indentation hardness and alteration of indentation modulus depending on concentration of the reducer (NaH_2PO_2). It's obviously from these figures, that increasing of concentration of the reducer leads to increasing of indentation hardness and decreasing of indentation modulus. This result could be explained by the fact that increasing of concentration of the reducer leads to obtaining of thicker films, as well as the incorporation of phosphorous around of crystal grains (as shown in Table 2) which have higher hardness.

Figures 8 and 9 show alteration of indentation hardness and indentation modulus depending on pH of the electrolyte. It's obviously from these figures, that increasing of pH of the electrolyte leads to decreasing of indentation hardness and indentation modulus. The reason for this result could be well known inverse Hall-Petch effect-below a critical grain-size, hardness decreases with decreasing grain size [12]. Other possible reason for this could be codeposition of hydroxides.

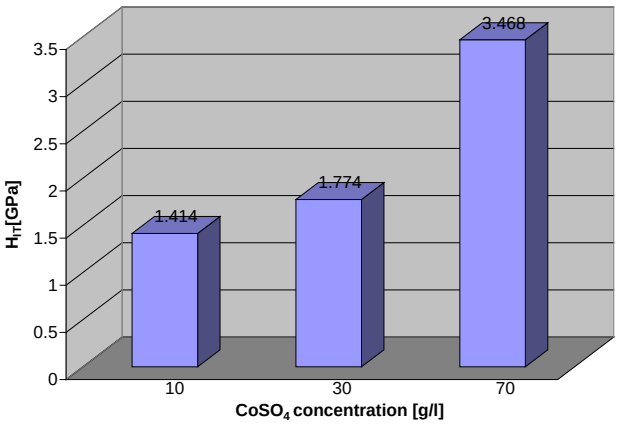

Fig.4

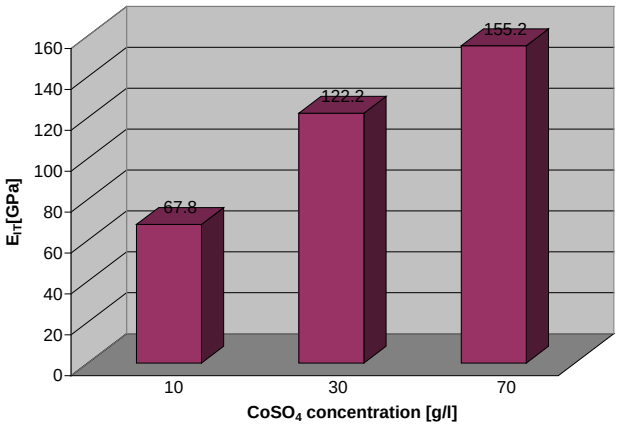

Fig.5

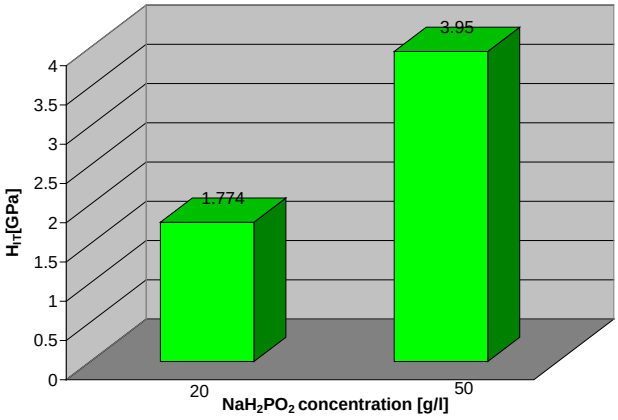

Fig.6

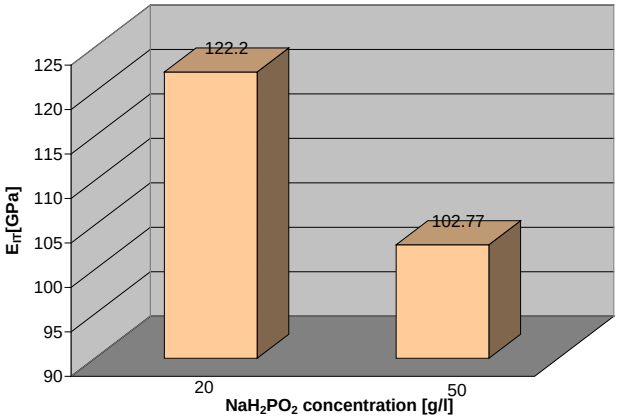

Fig.7

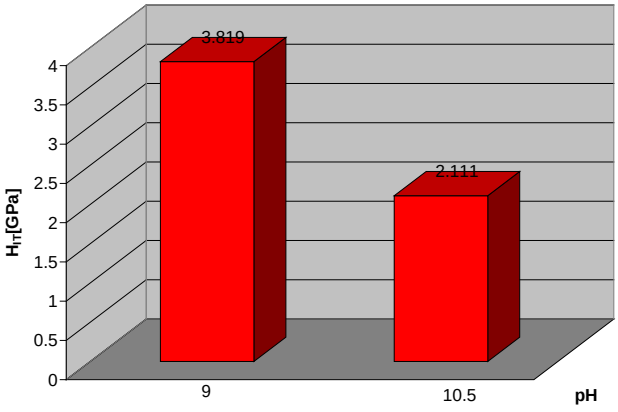

Fig.8

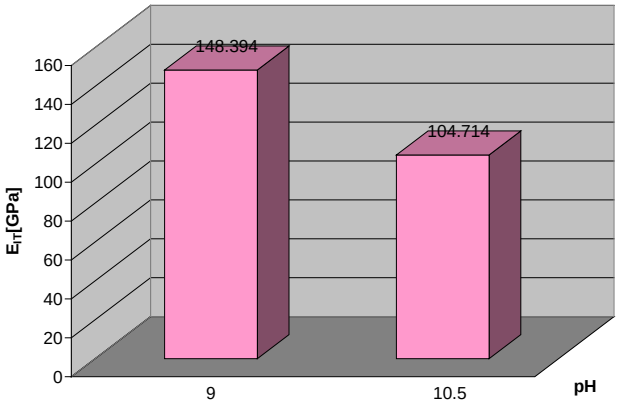

Fig.9

4.Conclusion

On the base of realized investigations were established that with increasing of Co^{2+} ions concentration in the electrolyte the sizes of cobalt crystals of deposited Co layers decreased significantly – from 100-300 nm at 20 g/l to 20-50 nm at 70 g/l. Analogous influence has the increasing of the concentration of the reducing agent (NaH_2PO_2). Simultaneously the applying of NaH_2PO_2 leads to uniform inclusion of phosphorus inside the thickness of the layers in the course of co-deposition.

These results correspond on the established influence of these components of the working electrolyte on the changing of the mechanical properties of deposited Co coatings:

- increasing of the cobalt ions concentration leads to increasing of indentation hardness and modulus which could be explained by the fact that increasing of concentration of cobalt ions leads to decreasing of grain sizes (according to Hall-Petch relationship);

- increasing of concentration of the NaH_2PO_2 leads to increasing of indentation hardness and decreasing of indentation modulus which could be explained by the fact that increasing of concentration of the reducer leads to obtaining of thicker films, as well as the incorporation of phosphorous around of crystal grains which have higher hardness.

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