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# Influence of solution acidity on growth kinetics, structure and magnetic properties of Co-P films, obtained by chemical deposition

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**Abstract.** The results of studies of the effect of solution acidity on the growth kinetics, structure and magnetic properties of Co-P films obtained by chemical deposition are presented. It was shown that the growth of Co-P films in the low pH region occurs mainly due to the growth of crystallite sizes, and in the high pH region, due to an increase in the nucleation rate. From the analysis of the chemical equilibrium of redox reactions, taking into account the balance of citrate and hydroxyl complexes of Co, a qualitative explanation of the features of the change in the rate and nature of the deposition of Co atoms from pH is proposed.

## 1. Introduction

Currently, materials in which new properties are discovered due to the manifestation of size effects [1-3] are of particular interest, and an intensive search for both new nanostructured materials and technologies for their production is carried out in this direction. Therefore, of undoubted interest is the chemical technology for producing magnetic films, which is based on the reduction reactions of metals from aqueous solutions without using an external source of electric current [4]. It allows you to relatively simply change the composition and/or structure of the films by changing the composition of the solutions from which the reduction of metal ions occurs. Of particular interest are cobalt-containing magnetic films, which is caused, firstly, by the high values of the magnetic parameters of this substance, and also by the fact that the crystal structure of its particles can be modified by changing their geometric dimensions [5, 6]. This is especially pronounced in Co-P films obtained by chemical deposition, in which a change in the pH of the solutions leads to a qualitative change in the magnetic parameters of the samples. When the pH in the films varies from 7.8 to 9, the magnitude of the induced anisotropy constant $K_U$ decreases by an order of magnitude (from $6 \times 10^5$ to $5 \times 10^4$ erg/cm$^3$) and the coercive force decreases by 2-3 orders of magnitude - from 1.5 kOe to units Oe [7,8]).

Despite the fact that by now, progress in the development of this technique for obtaining high-quality thin magnetic films is noticeable, due to the multifactor of the experiment and the difficulty in

describing the redox processes that are taking place, many issues of Co chemical recovery technology from aqueous solutions remain open. The established theoretical concepts of the process of the reduction of Co ions [9–15] during chemical deposition do not make it possible to explain the features of the kinetics of film growth, since based on common approaches to autocatalytic redox reactions.

This paper presents experimental data that determine the effect of pH on the growth rate and grain size of Co-P films during chemical deposition. Based on the analysis of the chemical reactions associated with the reduction of Co, the causes that can affect the kinetics of the formation of the microstructure of the films when the pH of the solution changes are considered. The change in the rate and nature of the growth of crystallites is associated with the presence of citrate complexes of Co, whose concentration in the working solution depends on pH.

## 2. Samples and methods of their research

The films were deposited on glass substrates, which were pretreated according to the procedure usual for chemical metallization [16]. The composition of the working solution consisted of a mixture of 35 mmol / l of cobalt sulfate $CoSO_4 \cdot 7H_2O$, 141 mmol / l of sodium hypophosphite $NaH_2PO_2 \cdot H_2O$, and also 77 mmol / l sodium citrate $Na_3C_6H_5O_7$. The pH value was recorded using a pH-150МИ device with an accuracy of ± 0.05 and set by adding $NaHCO_3$ to the sodium hydrogen carbonate solution. The films were deposited for 180 seconds at a temperature of 100 °C in a constant magnetic field of 2,5 kOe directed parallel to their plane to obtain uniaxial induced magnetic anisotropy in them, studied previously [17]. The magnetic field was created using two permanent magnets connected by a magnetic core.

The microstructure was studied by transmission electron microscopy methods, including the study of the elemental composition of samples on a TEM HT-7700 (Hitachi) equipped with an energy dispersive X-Flash 6T / 60 detector (Bruker). Sample thickness and elemental composition were determined using X-ray spectral analysis. The morphology of the films was determined using an atomic force microscope (AFM). The values of the coercive force and the saturation magnetization were established, respectively, using the meridional Kerr effect on the NANOMOKY and SQUID magnetometer.

## 3. Experimental results

Figure 1 shows graphs of changes in the growth rate of films, which is determined by the deposition rate of Co and the content of P as a function of pH.
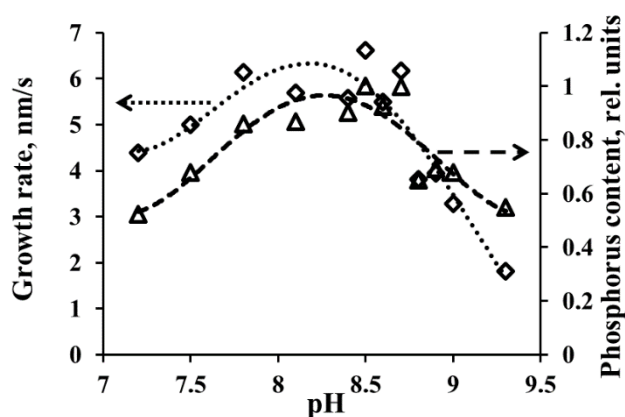


**Figure 1.** Dependence of film growth rate and phosphorus content on pH.

As follows from the above graphs, the dependence of the deposition rate of Co and P on pH is complex. With an changing in the acidity of the solution from 7.2 to 8.1, there is a slight increase in the deposition rate of Co (film thickness), and then, with a further increase in pH, it decreases, which is especially noticeable in the pH range > 8.5. At the same time, due to the difference in changes in the

deposition rate of Co and P, the relative content of P increases with increasing pH, which is shown in figure 2. P concentration increases from 2.2 at. % at pH = 7.2 to 5.8 at. % at pH = 9.3.
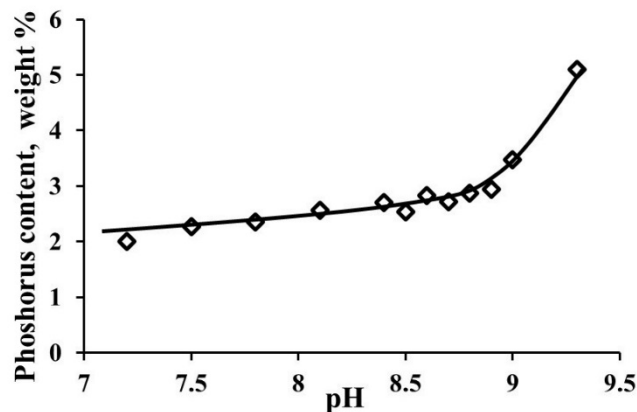


**Figure 2.** Dependence of phosphorus concentration in the film on pH.

The observed changes in the kinetics of film growth from acidity are reflected in its structural changes, on the dimensions of the crystallites constituting it. The typical structure of films obtained at pH < 8.5 is shown in figure 3a; it consists of large crystallites bounded by portions of the amorphous phase of Co-P.

An increase in pH > 8.5 leads to a change in the structure of the films, which is clearly seen in electron microscopic images of the surface (figure 3b). Based on the assumption that particle size is a determining factor affecting the broadening of diffraction lines in the electron diffraction pattern, the crystallite size can be estimated on the basis of the well-known Scherrer formula [18] and amounts to about 2-5 nm. A similar approach was used, for example, in [19]
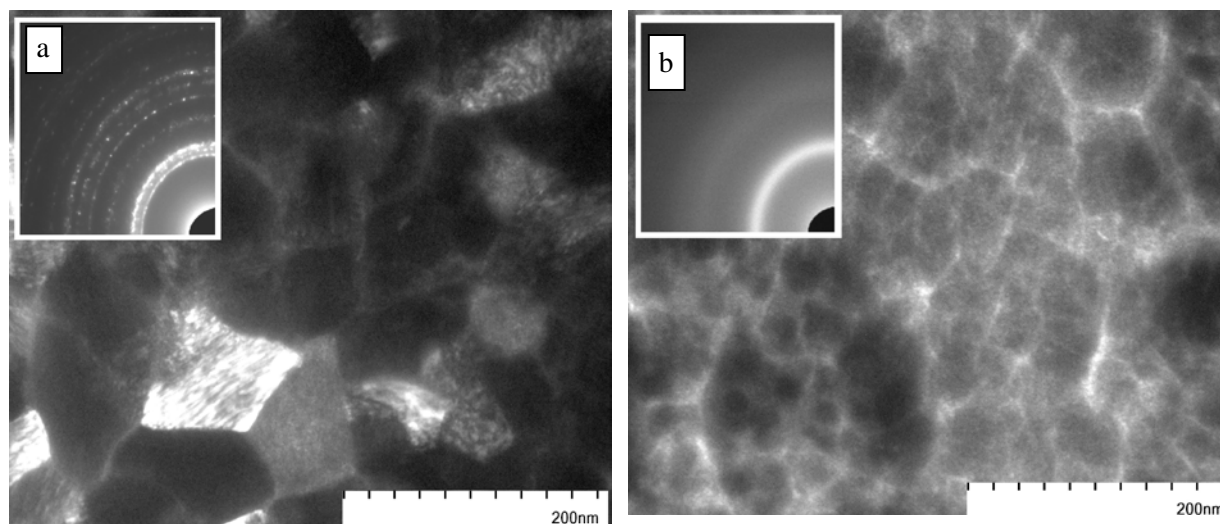


**Figure 3.** TEM image and electron diffraction pattern of Co-P films obtained in the pH range < 8.5 (a) and pH ~ 9 (b).

As follows from figure 4, obtained using AFM, the surface of the films has a hilly appearance; the appearance of such sections is associated with the specifics of film growth from the liquid phase, with the formation of separate nuclei of crystallites in the initial stage and their further growth [20].
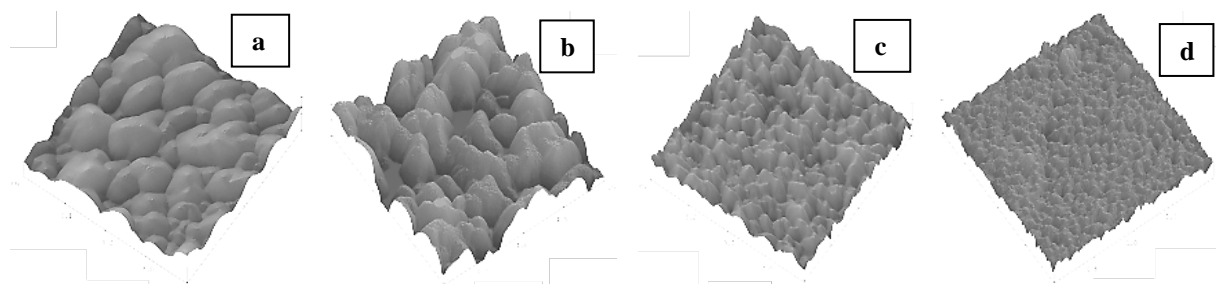
**Figure 4.** AFM images of the surface of the obtained films: a - pH = 7.2; b - pH = 8.7; c - pH = 8.9; d – pH = 9.3.

The characteristic size of inhomogeneities on the surface of the film, determined by means of AFM, correlates well with the change in crystallite size, determined using TEM, figure 5. In either case, a monotonous, almost linear, decrease in the size of structural elements with increasing pH is observed.
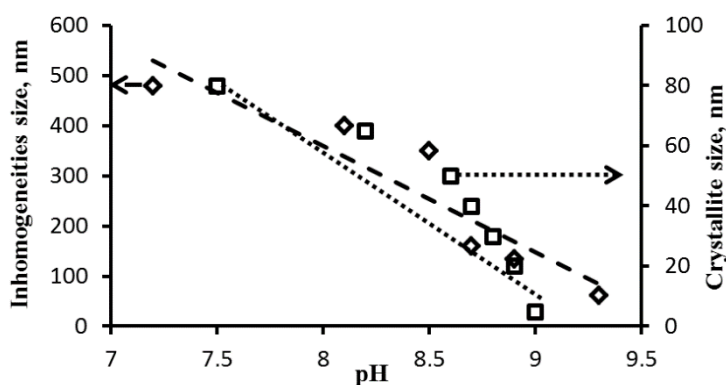


**Figure 5.** Dependence of the average crystallite size (according to the TEM data) and the average value of the surface inhomogeneities (according to the AFM data) on the pH value.

Table 1 shows the effect of the pH of the solution on the magnetic parameters of the studied samples. An increase in pH leads to a decrease in grain size and, consequently, to a radical decrease in $H_C$. The magnitude of the saturation magnetization ($M_S$) at the same pH values can vary widely and does not correlate with the change in pH The observed variation in $M_S$ values is likely due to technological reasons that lead to an uncontrolled variation in the density of packages of grains inside the film.

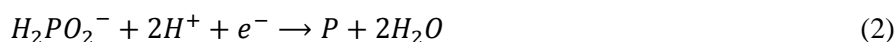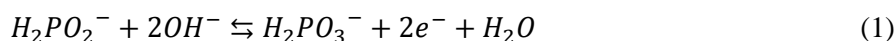**Table 1.** Parameters of the obtained films.

| pH | d, nm | $H_C$, Oe | $M_S$, G |
|----|-------|-----------|----------|
| 7.2 | 90 | 850 | 1342 |
| 8.7 | 40 | 900 | 819 |
| 8.9 | 20 | 70 | 1380 |
| 9.3 | 3 | 30 | 986 |

## 4. Discussion of the results

As was established earlier [17], the growth of a Co-P film during chemical deposition occurs with the formation of islands of isolated Co crystallites on a substrate. During the subsequent deposition, the island structure of the film becomes continuous due to the growth and fusion of crystallites. In accordance with this, the kinetics of film growth can be described using two mechanisms: the formation of nuclei and an increase in their size. From the above data, we can conclude that the growth of Co-P films in the low pH region occurs mainly due to the growth of crystallites, and in the high pH region, due to nucleation. In order to understand the causes of such changes in the mechanisms of film

growth, it is necessary to consider the chemical processes associated with the reduction of the Co and P atoms and the effects on them of the acidity of the solution.

Chemical reactions of oxidation of the reducing agent, the reduction of phosphorus and cobalt are determined by the following equations:

$$H_2PO_2^- + 2OH^- \leftrightarrows H_2PO_3^- + 2e^- + H_2O \tag{1}$$

$$H_2PO_2^- + 2H^+ + e^- \longrightarrow P + 2H_2O \tag{2}$$

$$Co^{2+} + 2e^- \to Co \tag{3}$$

With increasing pH, reaction (1) tends to accelerate, and competing reactions (2) and (3) - to slow down. At the same time, reaction (2) is accelerated directly, and reaction (3) is slowed down due to the formation of cobalt complexes with a high stability constant of the type $Co(OH)_3^-$ [21], which reduces the number of ions $Co^{2+}$ in solution.

From the conditions of chemical equilibrium, it is possible to establish the ratio of Co complexes with high and low stability constant depending on pH. With an increase in pH, cobalt sequentially passes from the ionized form of $Co^{2+}$ through the forms $CoH_2Cit^+$, $CoHCit$ and $CoCit^-$ to the form $Co(OH)_3^-$, as shown in figure 6.
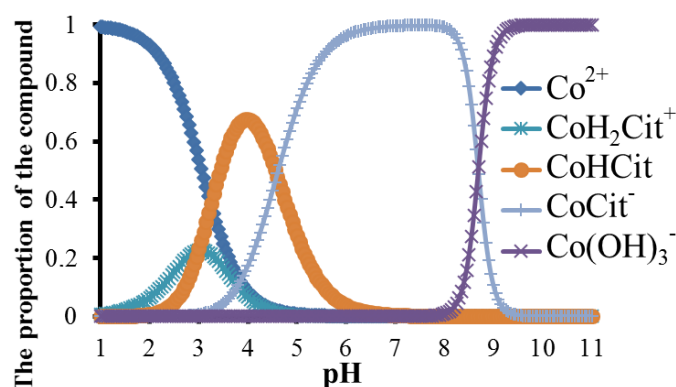


**Figure 6.** Distribution of complex forms of cobalt in the working solutions used, depending on pH.

The working range of the pH of the process ranges from 7 to 9.5, which coincides with the presence of cobalt citrate $CoCit^-$ complexes in the solution, and the termination of the precipitation process is associated with an increase in the concentration of the hydroxide complex $Co(OH)_3^-$. This is due to the processes of dissociation of these complexes, taking into account their stability constant. For cobalt citrate and cobalt hydroxide, the dissociation equations are:

$$CoCit^- \leftrightarrow Co^{2+} + Cit^{3-}, \tag{4}$$

$$Co(OH)_3^- \leftrightarrow Co^{2+} + 3OH^-, \tag{5}$$
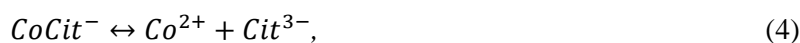
The stability constant determines the ratio of the concentration of the complex form of a substance to the product of the concentrations of dissociated ions:

$$K_{CoCit^-} = \frac{[CoCit^-]}{[Co^{2+}]\cdot[Cit^{3-}]} = 10^{4.83} \tag{6}$$

$$K_{Co(OH)_3^-} = \frac{[Co(OH)_3^-]}{[Co^{2+}]\cdot[OH^-]^3} = 10^{10.5} \tag{7}$$

Given that $[OH^-] = 10^{(14-pH)}$, the expressions for the concentration of cobalt ions take the form:

$$[Co^{2+}] = \frac{[CoCit^-]}{10^{4.83}\cdot[Cit^{3-}]}, \tag{8}$$

$$[Co^{2+}] = \frac{[Co(OH)_3^-]}{10^{10.5}\cdot 10^{(42-3pH)}} = \frac{[Co(OH)_3^-]}{10^{(52.5-3pH)}} \tag{9}$$

From equations (8–9), it follows that the hydroxide complexes $Co(OH)_3^-$ are less likely to dissociate into ions, in contrast to the citrate Co $CoCit^-$ complexes. The calculated dependences of the relative concentrations of citrate and hydroxide complexes of Co are presented in figure 6. In accordance with them, at pH> 8.1, a decrease in the concentration of cobalt ions is observed, which leads to a decrease in the rate of the recovery process until the complete cessation of film growth in the region of pH ~ 9.5.

The established ratios of the concentrations of the complexes correlate very well with the actual data on the dependence of the growth rate of the films on the pH shown in figure 1: the decrease in the cobalt reduction rate is directly related to the decrease in the $CoCit^-$ concentration.

The predominance of one or another film growth mechanism by reaction (3) is well explained by the lack of either electrons produced by reaction (1) or cobalt ions. With a shortage of electrons, Co ions, recovering, tend to be embedded in the crystal lattice of already existing crystallites, and with a lack of cobalt ions, tiny crystallites form on the surface of the film.

Thus, the dependence of the growth rate of cobalt films on the pH value can be described by the influence of two limiting factors: the lack of electrons in the pH range <8.1 and the lack of cobalt ions in the pH range> 8.7. In the intermediate region, apparently, there is compensation for a decrease in the amount of cobalt ions by an increase in the number of electrons.

A concomitant Co-reduction reaction is the reduction of P, which occurs as a result of reaction (2). This reaction is associated with the use of sodium hypophosphite as a reducing agent and is not independent, since it does not proceed in the absence of reaction (3). It is known that an increase in the concentration of phosphorus leads to amorphization of the film at a concentration of P above 9 at.% [11]. However, structural transformations in the samples studied by us occur at significantly lower concentrations of P. The high saturation magnetization values of the studied films, as follows from table 1, indicate a low P content in samples obtained at high pH. This fact confirms the assumption that the presence of P is not the main cause of structural changes in the films under study. Therefore, to explain them, it is necessary to take into account the mechanisms described above associated with the kinetics of the reduction of Co ions as a result of chemical reactions.

## 5. Conclusion

Based on the data obtained, it follows that a change in the structure of Co-P films during chemical deposition is associated with the specific growth kinetics of Co crystallites, depending on the acidity of the solutions. The change in the growth rate of crystallites can be described by the influence of two limiting factors: the lack of electrons in the pH range < 8.1 and the lack of cobalt ions in the pH range > 8.7.

## Acknowledgments

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