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PLASMA-CHEMICAL PREPARATION OF NANOSCALE COBALT OXIDE

М.І. Скиба, *О.А. Півоваров*, *А.К. Макарова*, *В.І. Воробйова*. **Плазмохімічне одержання нанорозмірного оксиду кобальту.** На сьогоднішній день все більше розповсюдження викликають золі та нанодисперсні системи оксидів перехідних металів. Завдяки ряду властивостей безсумнівний інтерес для розвитку технологій різних галузей представляє оксид кобальту структури Co_3O_4. В роботі продемонстровано результати досліджень використання контактної нерівноважної низькотемпературної плазми, як інструменту для одержання нанорозмірного оксиду кобальту. ***Мета:*** Метою роботи є одержання оксиду кобальту з використанням як інструменту контактної нерівноважної низькотемпературної плазми. ***Матеріали і методи:*** Дослідження проводили в газорідинному реакторі періодичної дії. Електроди виконано з нержавіючої сталі. Утворений в результаті проби стовп плазми є інструментом обробки. Охолодження реакційної суміші забезпечували безперервною циркуляцією холодної води. Тиск в реакторі становив 80±4 кПа. Для отримання плазмового розряду на електроди подавали напругу 500…1000 В. Силу струму підтримували на рівні 120±6 мА. Оптичні спектри золів реєстрували в діапазоні довжин хвиль 190…700 нм. Термічний аналіз проводили у середовищі повітря зі швидкістю нагріву 10 град/хв у тиглях з кварцу. Одержані зразки досліджували методом рентгенофазового аналізу. Розмірні параметри отриманих сполук досліджували за допомогою електронного мікроскопу. ***Результати:*** Встановлено, що кінцеве значення pH осадження гідроксиду кобальту варіюється в діапазоні 8,2…9,0 і, залежно від величини іонної сили, становить 9 та 8,2 при $I = 0$, $I = 1$ відповідно. Досліджено закономірності зміни окисно-відновного потенціалу та водневого показника розчинів оксиду кобальту при їх обробці низькотемпературною нерівноважною плазмою. Фазовий склад плазмохімічно одержаних сполук кобальту було досліджено за допомогою рентгеноструктурного та термічного аналізу. Основну фазу отриманого продукту представлено оксидом кобальту структури Co_3O_4. За даними мікроскопічного і рентгеноструктурного методів аналізу розміри отриманих сполук кобальту лежать в нанометровому діапазоні.

Ключові слова: плазмовий розряд, одержання, водні розчини, оксид кобальту, наночастки.

M.I. Skiba, *A.A. Pivovarov*, *A.K. Makarova*, *V.I Vorobyova*. **Plasma-chemical preparation of nanoscale cobalt oxide.** As of today, sols and nanodispersed systems of transition metal oxides are increasingly spreading. Due to a number of properties, undoubted interest for the development of technologies in various industries is represented by cobalt oxide Co_3O_4. In this paper, we demonstrate the results of studies on the use of a contact nonequilibrium low-temperature plasma as a tool for obtaining nanoscale cobalt oxide. ***Aim:*** The aim of the work is to obtain cobalt oxide using a contact nonequilibrium low-temperature plasma. ***Materials and Methods:*** The investigations were carried out in a gas-liquid batch reactor. The electrodes are made of stainless steel. The plasma column formed as a result of the test is a processing tool. Cooling of the reaction mixture was ensured by continuous circulation of cold water. The reactor pressure was 80±4 kPa. To obtain a plasma discharge, a voltage of 500...1000 V was applied to the electrodes. The current was maintained at 120±6 mA. Optical spectra of sols were recorded in the wavelength range 190...700 nm. The thermal analysis was carried out in an air medium at a heating rate of 10 deg/min in quartz crucibles. The obtained samples were examined by X-ray phase analysis. The dimensional parameters of the obtained compounds were examined using an electron microscope. ***Results:*** It was found that the final pH value of cobalt hydroxide precipitation varies in the range 8.2...9.0 and, depending on the magnitude of the ionic force, is 9.0 and 8.2 at $I = 0$, $I = 1$, respectively. The regularities of the change in the oxidation-reduction potential and the hydrogen index of cobalt oxide solutions during their processing by a low-temperature nonequilibrium plasma are studied. The phase composition of the plasma-chemical obtained cobalt compounds was investigated by X-ray diffraction and thermal analysis. The main phase of the product obtained is represented by cobalt oxide of structure Co_3O_4. According to the data of microscopic and X-ray diffraction methods of analysis, it is shown that the sizes of the obtained cobalt compounds lie in the nanometer range.

Keywords: plasma discharge, production, aqueous solutions, cobalt oxide, nanoparticles.

Introduction. As of today, sols and nanodispersed systems of transition metal oxides are increasingly spreading. Due to a number of properties, undoubted interest for the development of techno-

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logies in various industries is represented by cobalt oxide Co_3O_4. The latter is widely used in the production of lithium ion batteries, as a catalyst in air pollution control to reduce emissions CO, NO_x, organic pollutants from sewage, in the manufacture of batteries, ceramic pigments, etc. [1].

A number of works [2...4] are devoted to the problem of obtaining nanoscale cobalt oxide with help of redox reactions in aqueous and non-aqueous media. Most of these methods are multi-stage and energy-intensive, requiring the use of additional reagents and complex equipment, which increases the cost of production. Therefore, the development of new highly efficient and innovative technologies aimed at obtaining nanoscale inorganic cobalt compounds is still relevant.

The most energy efficient and environmentally friendly, so far, are considered processes based on the use of plasma discharges of various configurations in the gas phase [5, 6]. However, it should be noted that they are mostly insufficiently studied and do not always provide connections with predictable properties. Promising from the point of view of practical application are technologies based on the use of a contact nonequilibrium low-temperature plasma (NLTP). Unlike the existing configurations [7, 8], the NLTP plasma discharge is generated between the electrode in the gas phase and the surface of the liquid in the volume of which the second electrode is located. In general, chemical transformations at the interface are due to a complex effect: electrochemical oxidation-reduction; photolysis reactions initiated by UV irradiation; flow of charged particles from the gas phase to the surface of the liquid medium, which results in the formation of a significant amount of reactive particles and oxidative compounds. By varying the composition of liquid processed phases, it is possible to control the routes of chemical transformations and the composition of the final product. In previous works, the authors have shown the effectiveness of use of a contact nonequilibrium low-temperature plasma for obtaining colloidal solutions of precious metals [9, 10]. In addition, the advantages of using NLTP include new qualitative indicators of the products obtained, simplification of the technological cycle of their production, reduction of material (raw) and energy costs, compactness of technological equipment, high level of technological culture, clean production and modern automatic control of technological stages of production. Therefore, it is of scientific and practical interest to study the plasma-chemical production of nanodispersed cobalt oxide.

The aim of the research is to obtain cobalt oxide using a contact nonequilibrium low-temperature plasma as a tool.

Materials and Methods. The investigations were carried out in a gas-liquid batch reactor of periodic action with volume 100 ml. The electrodes are made of stainless steel, anode (d=4 mm) is located in the liquid part, and the cathode (d=2.4 mm) – at a distance of 10 mm from the surface of the solution. The volume of solution in the reactor was 70 ml. The plasma column formed as a result of the sample is a processing tool. Cooling of the reaction mixture was ensured by continuous circulation of cold water. The reactor pressure was 80±4 kPa. To obtain a plasma discharge, a voltage of 500...1000 V was applied to the electrodes. The current was maintained at 120±6 mA. The solutions were prepared by dissolving "AR" shots precursors in distilled water. Oxidation-reduction potential (ORP) was measured in 30 seconds after the stopping treatment of NLTP solutions. The electrode was kept in the test solutions for at least 1 minute. The ORP value was calculated taking into account the potential of the reference electrode. Optical spectra of sols were recorded on a UV-5800PC spectrophotometer using quartz cuvettes in the wavelength range 190...700 nm. The thermal analysis was carried out using thermal analyzer Derivatograf Q-1500 in an air medium at a heating rate of 10 deg/min in quartz crucibles. The obtained samples were examined by X-ray phase analysis (XRD) using a DRON-3M tool with a standard JCPDS file. The dispersion phase of the precipitate were obtained after plasma-chemical treatment by separation from the liquid and drying in air. The size parameters of the obtained compounds were studied with an FEIE-SEMXL 30 electron microscope.

Results and Discussion. Analysis of the chemical properties of cobalt compounds indicates that the production of sols and dispersed cobalt oxides is fundamentally possible. The simplest method is hydrolysis of cobalt followed by oxidation of the products in the presence of an additional oxidizing agent (hydrogen peroxide and/or oxygen). Now the authors of the work have reliably established that when treating water and aqueous solutions with a contact nonequilibrium low-temperature plasma, a significant amount of reactive particles is formed in the system, leading to the formation of oxidative compounds and hydrogen polyhydroxide (H_nO_n). Thus, studies of plasma-chemical production of oxygen-containing cobalt compounds were carried out in two stages. First, the parameters of the deposition of cobalt hydroxide in aqueous solutions were established, and then the phase composition and characteristics of the solutions obtained under the action of NLTP and their dispersed phase were studied.

One of the main technological parameters characterizing the expediency of using the proposed technology is the degree of conversion of the raw material to the final product. To optimize the process of plasma-chemical production of compounds, it is necessary to achieve the maximum possible degree of conversion of the cobalt salt during hydrolysis process.

Precipitation of cobalt hydroxide is associated with the formation of various hydroxo complexes in the solution. The composition of these complexes and the transformations that occur during the formation of cobalt hydroxide play an important role in the formation of both the cobalt hydroxide structure and, subsequently, cobalt oxide. Based on this study, the hydrolysis process requires theoretical and practical research.

Nowadays, the process of cobalt hydrolysis has been studied by both foreign and domestic researchers [11]. It is found that the process proceeds in two stages with the intermediate formation of $CoOH^+$ in a solution of cobalt chloride in the second stage of hydrolysis, which then passes into an insoluble form of cobalt hydroxide and has a blue color. However, in the scientific literature there is almost no data on the effect of ionic force on the degree of solubility of low soluble precipitates. Therefore, to determine the effect of ionic force on the solubility of the precipitate, the composition of the precipitate and the rate of its deposition at various ionic forces were calculated. Calculation of the equilibrium composition of precipitated cobalt hydroxide was carried out by a constant method taking into account the following components in solution: Co^{2+}, $CoOH^+$, $Co(OH)_2$. For the calculation the hydrolysis constants and the product of the solubility of the hydrolysis of cobalt chloride with the dependence on the value of the ionic strength of 0 and 1 by the Debye-Hückel equation were used [12].

The hydrolysis equation Co (II) can be written in the general form:

$$xCo^{2+} + yH_2O = Co_x(OH)_y + yH^+,$$

where x – number of atoms of cobalt complex;
y – number of hydroxyl groups.

The general equation of the hydrolysis constant will be:

$$K_{x0-y} = \frac{[Co_x(OH)_y][H^+]^y}{[Co^{2+}]^x},$$

where K_{x0-y} – hydrolysis constant of the corresponding hydroxide complex;
$[Co_x(OH)_y]$, $[H^+]$, $[Co^{2+}]$ – ion concentrations.

The expression for determining the solubility of cobalt and their complexes in solution is calculated using the balance equation:

$$S_{gen} = [Co^{2+}] + [CoOH^+] + [Co(OH)_2] = \sum 10^{\lg[Co_x(OH)_y]}$$

where S_{gen} – general solubility of cobalt.

For a quantitative description of the hydrolysis process Co^{2+} was calculated and built dependence of concentration and solubility of the components from the pH value at different values of ionic force (Fig. 1).

Fig. 1 shows the theoretical calculations of the distribution of cobalt ions, its constituents and the solubility of cobalt hydroxide, depending on the pH value. Consequently, in solution till a pH = 8.9 cobalt exists in the form Co^{2+} and $CoOH^+$ (Fig. 1, *a*), and, since pH = 9, it goes to a soluble hydroxide $Co(OH)_2$. Similar calculations were performed for the distribution of cobalt compounds at the ionic strength $I = 1$ (Fig. 1, *b*). The obtained data indicate that at pH = 8.2 the solution precipitates into soluble cobalt hydroxide. Therefore, when the electrolyte is added to the ionic force equal to 1 (Fig. 1, *b*, curve 4), the solubility of the precipitate can be increased. Thus, it is confirmed that, when adjusting the ionic force of the solution, it is possible to reduce or increase the solubility of a poorly soluble precipitate. Analysis of the calculated data shows that the final pH of the precipitation of cobalt hydroxide varies in the range 8.2...9.0 and, depending on the magnitude of the ionic strength, is 9.0 and 8.2 at $I = 0$, $I = 1$, respectively.

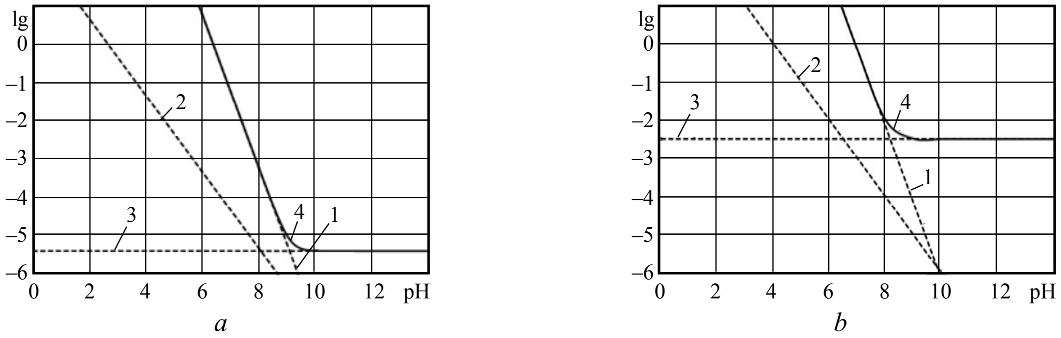


Fig. 1. Distribution dependence Co^{2+} *(1), cobalt hydroxo complex* $CoOH^{+}$ *(2), cobalt hydroxide* $Co(OH)_2$ *(3) and overall solubility (4) of the pH at: a –* $I = 0$*, b –* $I = 1$

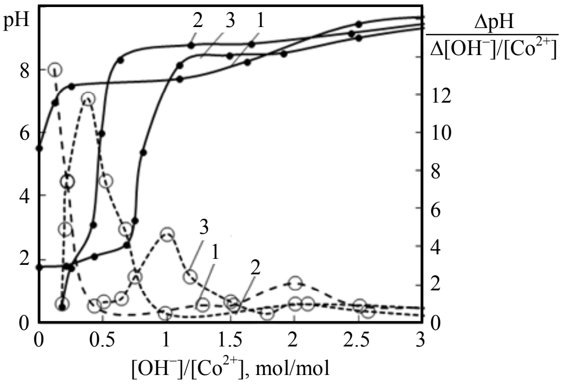


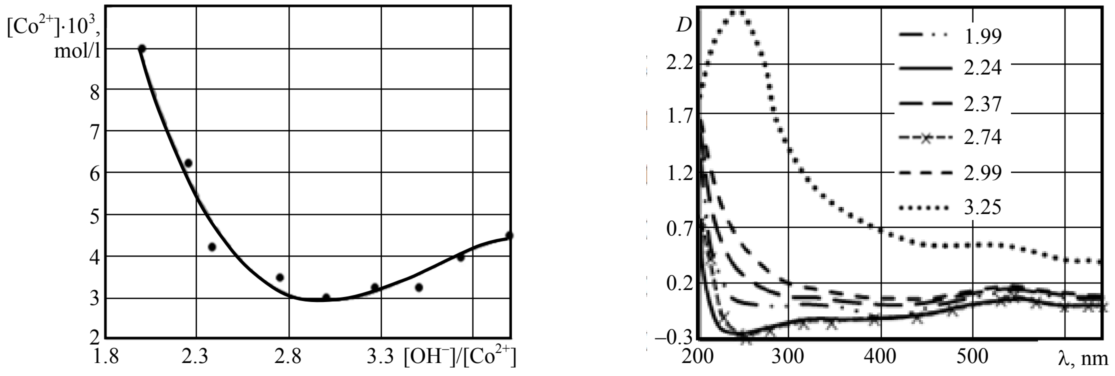
Fig. 2. Integral (•) and differential (○) titration curves of a cobalt chloride solution $[Co^{2+}]/[OH^-]$*, mol/l: 1 – 0.04/1.0; 2 – 0.02/0.49; 3 – 0.25/0.98*

The calculated data are confirmed by experimental studies of the boundary conditions for the precipitation of cobalt hydroxide (Fig. 2). Consequently, the formation of a cobalt hydroxide precipitate occurs in two stages in the pH range from 8.0 to 9.5; the second stage of hydrolysis is completed at a molar ratio $[OH^-]/[Co^{2+}] \approx 3$ and with a value greater than 8, that is consistent with the literature data [13].

The expediency of using the molar ratio of reagents $[OH^-]/[Co^{2+}] = 3$ during the hydrolysis confirm the study of the content of cobalt ions in the supernatant after precipitation of the hydroxide (Fig. 3). Analysis of the obtained data shows that at a molar ratio $[OH^-]/[Co^{2+}] < 3$ there is a decreasing in the concentration of cobalt ions in the supernatant and an increasing in the degree of precipitation; at $[OH^-]/[Co^{2+}] > 3$ The concentration of cobalt ions increases due to the formation of complex cobalt compounds. This is largely confirmed by the absorption spectra of the supernatant obtained at different molar ratios $[OH^-]/[Co^{2+}]$. As it can be seen from the obtained data (Fig. 3, *b*), with an increase in the molar ratio above 2 in the absorption spectra, there is no pronounced maximum characteristic for the ion $[Co(H_2O)_6]^{2+}$ (λ_2=510 nm), which indicates an increase in the degree of precipitation.

Samples of solutions were obtained. They have been treated with a plasma discharge with different initial concentrations of $[Co^{2+}]$ at $[OH^-]/[CO^{2+}]=3$, constant value of the current and pressure. The gross characteristic of the reactions is the oxidation-reduction potential characterizing the content of oxidized and reduced forms of all redox pairs present in the solution. Fig. 5 shows the results of measuring the ORP of oxygen-containing solution of cobalt compounds as a function of the concentration of cobalt ions and the duration of plasma discharge treatment.

For all studied time intervals, a regular change in the ORP is observed: firstly, the ORP increases to a certain “concentration limit”, and with a further increase in the content of cobalt ions the ORP remains almost unchanged. Obviously, the yield of a product of the oxidation-reduction transformation of H_2O and CO^{2+} is determined by a combination of a large number of factors (for example, the plasma-chemical yields of their radical particles, redox potentials, concentrations, acidity of solutions, temperature). Therefore, this process is difficult to predict and requires additional research.



a *b*

Fig. 3. Dependence of the concentration of cobalt ions (a) and absorption spectra (b) in the supernatant, depending on the molar ratio of reagents [OH⁻]/[Co^{2+}] during the hydrolysis process

Fig. 5 shows the results of studies for determination of the acidity of plasma-chemically treated solutions, depending on their concentration and the time of exposure to a plasma discharge.

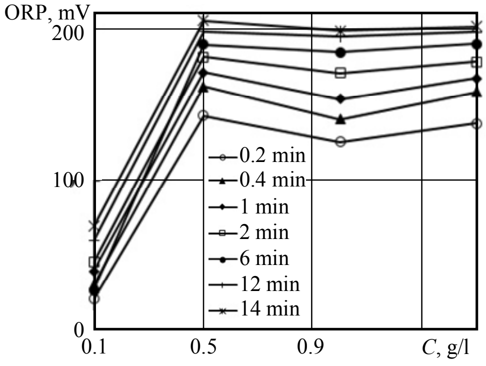


Fig. 4. Collating of oxidation-reduction potentials with the concentration of solutions as a function of the duration of plasma treatment

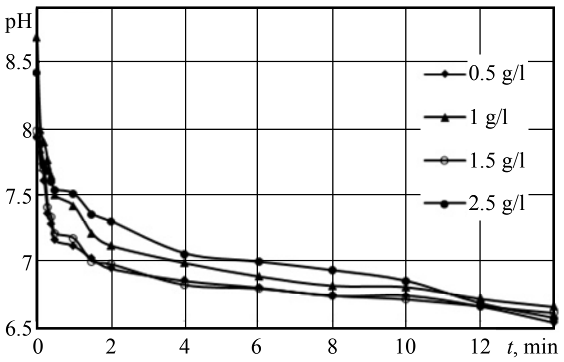


Fig. 5. Dependence of pH of solution on duration of plasma treatment and concentration of cobalt ions (I=120 mA, P=0.08 MPa, [OH⁻]/[Co^{2+}]=3)

As it is known [13], the change in the acidity of aqueous solutions during their processing by NLTP is explained by the combined effect of the cathodic process of hydrogen evolution on the surface of the electrode immersed in the solution and the anodic process of water oxidation on the surface of the solution in the zone of action of the plasma flame.

During plasmochemical treatment of distilled water its pH rapidly decreases to 2...3 units, which is due to the accumulation of hydrogen polyoxides in water. The obtained data indicate that an increase in the duration of the action of the NLTP discharge on solutions of various concentrations contributes to a decrease in the hydrogen index. This is probably due to the consumption of OH radicals on the formation of hydrogen and/or H_2O_2 and on the transfer of electrons from radicals H to the solution. Also, the change in acidity of the observed solutions may be due to the participation of H^+ and OH^- ions in the oxidation of cobalt hydroxide ions and redox reactions of its oxidation products with hydrogen peroxide.

Identification of the dispersed phase of the solution obtained as a result of plasma-chemical treatment of cobalt hydroxide (I=120 mA, P=0.8 MPa, τ=14 min., $C_{[Co2+]}$=1.5 g/l, $[OH^-]/[Co^{2+}] = 3$, air drying at 25°C) performed by X-ray analysis. The received data (Fig. 6) indicates the presence of reflections of crystallographic planes (111), (311), (422), (440) which maxima are located at the corners 20.0318; 38.1(7); 59.87(7); 65.17 respectively, corresponding cobalt oxide of structure Co_3O_4. Quantitative analysis of X-ray diffraction data indicates that the content of cobalt oxide is 79...80 % by weight. The average size of the crystallites is conveniently estimated by the Debye-Scherrer formula [14…17]:

$$D = \frac{K\lambda}{\beta\cos\theta},$$

where K – constant, which is assumed to be 0.94;

λ – wavelength of X-rays,

β – broadening of peaks;

θ – Bragg angle.

The obtained calculation data show that the average particle size in the sample under study is 20…30 nm.

The phase composition of the plasmochemically obtained compounds was additionally investigated by thermal analysis in a static air atmosphere, the results of which are shown in Fig. 7.

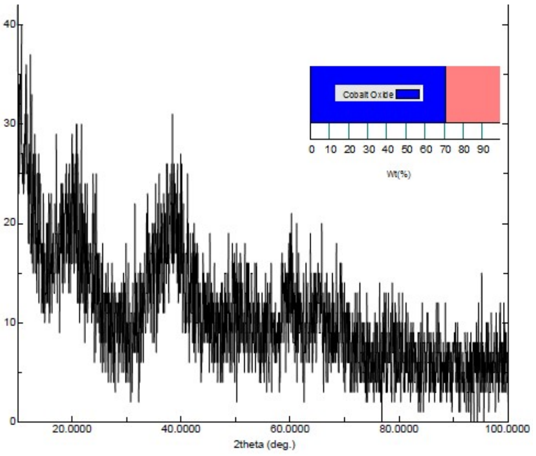


Fig. 6. X-ray diffraction pattern of a dispersed phase of a solution of oxygen-containing cobalt compounds obtained using a contact nonequilibrium low-temperature plasma (I=120 mA, P=0.8 MPa, τ=14 min., $C_{[Co2+]}$=1.5 g/l, $[OH^-]/[Co^{2+}]$=3)

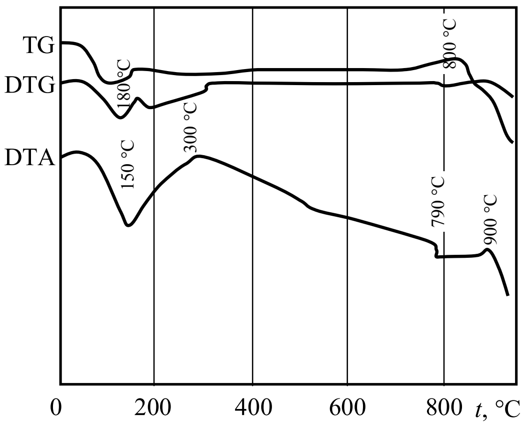


Fig. 7. Thermogram of the dispersed phase of a plasma-chemically produced solution of oxygen-containing cobalt compounds:
TG – Thermogravimetric curve; DTA – Differential thermal analysis curve; DTGA – Differential thermogravimetric analysis curve

The loss of mass, which is accompanied by an endothermic effect, is in good agreement with the course of the reactions of the removal of water molecules from the structure of the $Co(OH)_2$ compound upon its dehydration to Co_3O_4, that is present in the obtained samples from X-ray diffraction studies of the reaction:

$$6Co(OH)_2+O_2 \rightarrow 2Co_3O_4+6H_2O.$$

The peak in the temperature range 800...900 °C identifies the presence of cobalt oxide of the Co_3O_4 structure and corresponds to the process of its decomposition:

$$2Co_3O_4 \rightarrow 6CoO+O_2.$$

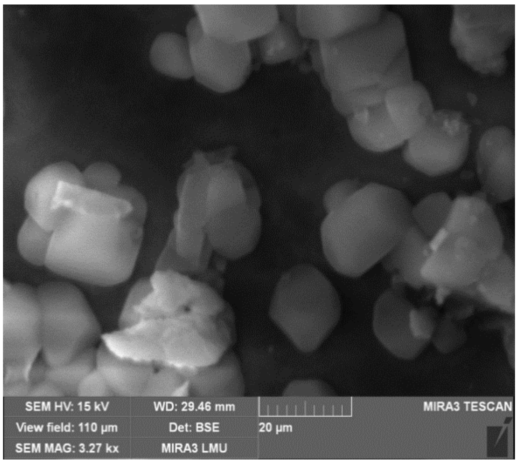


Fig. 8. Images of a dispersed phase (SEM) of a plasma-chemically produced solution of oxygen-containing cobalt compounds ($I=120$ mA, $P=0.8$ MPa, $\tau=14$ min., $C_{[Co2+]}=1.5$ g/l, $[OH^-]/[Co^{2+}]=3$)

By varying the parameters of the plasma chemical process, it is possible to influence the size and physico-chemical properties of the produced particles. When carrying out the process in an aqueous medium, it is possible to obtain disperse systems characterized by a given shape and morphology of nanoparticles, a narrow range of their sizes and a constant chemical composition. To characterize cobalt oxide obtained using a contact nonequilibrium plasma, a sample of the dispersed phase was examined using electron microscopic analysis.

According to electron microscopy, a dispersed phase is formed in the liquid under the action of NLTP from aggregated and discrete nanoparticles (Fig. 8). We can observe particles on the images whose diameter is in the nanoscale range up to 10...60 nm.

Conclusions. This paper presents the results of theoretical and experimental studies of the hydrolysis process of cobalt chloride as a preliminary stage in the production of cobalt oxide. It is shown that the formation of cobalt hydroxide precipitate occurs in two stages in the pH range from 8.0 to 9.5; the second stage of hydrolysis finishes with a molar ratio of reagents $[OH^-]/[CO^{2+}] = 3$ at pH greater than 8. Using the X-ray diffraction and thermal studies, the phase composition of the plasma-chemically obtained compounds was established. It is shown that the main formed phase is cobalt oxide of the Co_3O_4 structure. According to X-ray phase analysis, the average size of the formed particles is calculated. According to the data of microscopic analysis, it is established that the sizes of the obtained cobalt compounds lie in the nanometer range. The regularities of the change in the oxidation-reduction potential and the hydrogen index of solutions of cobalt oxide are investigated when they are "activated" by a low-temperature nonequilibrium plasma.

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