*ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 5, pp. 846–850. © Pleiades Publishing, Ltd., 2009.*
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## APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

# Effect of the Composition of Pyrophosphate Electrolyte on the Kinetics of Cobalt Electrodeposition

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Received December 29, 2008

**Abstract**—Potentiometric titration was used to study the equilibrium in a solution of the pyrophosphate cobalt complex in a wide range of pH values. The effect of the solution pH and the concentrations of the cobalt complex and the free ligand on the kinetics of cobalt electrodeposition was examined.

**DOI:** 10.1134/S1070427209050188

Cobalt possesses a unique set of properties, which makes this metal irreplaceable in certain fields of new technology. In particular, the areas associated with development of ultrastrong permanent magnets, magnetic recording and digital information storage devices, radio-frequency absorbing materials, miniature lithium-ion batteries, industrial catalysts, micro-electro-mechanical systems (MEMS), and medical diagnostic instruments.

Commonly, electroplated cobalt coatings have a non-equilibrium structure, high internal stresses, lowered corrosion resistance resulting from captured impurities (hydrogen and hydroxides), and through porosity at a thickness of several micrometers. At the same time, modern technology requires deposition of high-quality defect-free coatings with a thickness smaller than 1 μm and equilibrium structure, which could not be done by electrochemical methods so far.

The quality of thin cobalt (and any other) electroplated coatings can only be improved by elucidating the fundamental aspects and the mechanism of both the main and accompanying electrode processes.

Several types of electrolytes, one of which is of the pyrophosphate type, have been suggested for cobalt electroplating. Pyrophosphate electrolytes have been used to deposit numerous metals under similar conditions [1], which is an important advantage in fabrication of multilayered structures. It is noteworthy that the electrodeposition of cobalt is insufficiently understood and only general suggestions have been made about the discharge mechanism of pyrophosphate cobalt complexes.

The aim of this study was to examine the fundamental aspects of discharge of the pyrophosphate cobalt complex at various concentrations of the free ligand and cobalt ions and pH values.

## EXPERIMENTAL

The working solutions were prepared by mixing concentrated solutions of potassium pyrophosphate and cobalt sulfate. The pH value was brought to a required value with a 4.5 M $H_2SO_4$ or 2 M KOH solution. Potassium pyrophosphate and cobalt sulfate of analytically pure grade and other reagents of chemically pure grade were used. The main measurements were performed in a solution of composition 0.24 M $CoSO_4$ + 0.87 M $K_4P_2O_7$, chosen in accordance with the recommendations of [1]. On mixing the components, a pyrophosphate cobalt complex $[Co(P_2O_7)_2]_{\bar{6}}$ is formed in solution in a concentration of 0.24 M, for which 0.48 M of potassium pyrophosphate is consumed, with 0.39 M of $K_4P_2O_7$ remaining free.

The working electrodes with dimensions of 1.0 × 0.6 × 0.7 cm were fabricated from special-purity graphite of GMZ brand, a copper current lead was attached, and all faces except the working surface were insulated with several layers of a polystyrene-based lacquer. The working surface with an area of 0.7 cm$^2$ was polished with emery paper and, then, with filter paper to mirror shine and was cathodically polarized in a 1 M sulfuric acid solution at a current density of 30 mA cm$^{-2}$ for 5 min. Then the electrode was anodically polarized in a fresh portion of the sulfuric acid solution at a current density of 5 mA cm$^{-2}$ for 20 s, washed with distilled water, subjected to a repeated cathodic treatment in a sulfuric acid solution to reduce the intermediate carbon oxides formed in the process, washed, and coated with a 1-μm-thick cobalt layer at a current density of 10 mA cm$^{-2}$ in the course of 5 min. The cobalt electroplating was performed using a sulfate electrolyte of composition (g l$^{-1}$): $CoSO_4 . 7H_2O$ 500, NaCl 15, and $H_3BO_3$ 40; pH 3–4, temperature 20°C [2].

The electrodes could be used many times by easily grinding-off cobalt with an emery paper. For a following run, the whole set of above-described procedures for electrode preparation was repeated once more. This method of electrode preparation made the cobalt surface and the experimental results, on the whole, well reproducible.

The potentiometric titration of the solutions was performed with a pH-150M pH-meter ion-meter, with the solution agitated with a magnetic stirrer. The volume of the solution being analyzed was 50 ml.

The electrochemical measurements were made at a temperature of 20 ± 2°C in a three-electrode Pyrex cell with separated spaces in air, with a saturated silver chloride electrode serving as reference.

Polarization curves (PCs) were measured from the zero-current potential in the cathodic direction at a potential sweep rate of 60 mV min$^{-1}$ to a potential at which the current density reached a value of 100 mA cm$^{-2}$ (forward PCs) and then backwards, to the zero-current potential (reverse PCs). This procedure made it possible not only to analyze electrochemical characteristics of the cobalt electroplating process, but also to obtain additional important information about changes in the state of the electrode surface.

The results of the potentiometric titration of solutions of potassium pyrophosphate and pyrophosphate cobalt complex are shown in Fig. 1. In titration of a 0.87 M $K_4P_2O_7$ solution with 4.5 M $H_2SO_4$, the pH value first rapidly decreases by approximately one unit and then, upon further addition of the acid, a more gradually sloping portion is observed (Fig. 1a, curve *1*). In the process, a white crystalline precipitate starts to be formed in the solution and its amount gradually grows. Upon addition of 9.7 ml of the acid, the titration curve exhibits a sharp bend corresponding to introduction of a mole of sulfuric acid per mole of the pyrophosphate, i.e., formally corresponds to the formation of potassium dihydropyrophosphate. Raising the amount of $H_2SO_4$ results in a slower variation of pH; the originally formed precipitate dissolves in this portion of the titration curve. Upon addition of 20 ml and more of $H_2SO_4$, the whole amount of the pyrophosphate is formally in the protonated form [3].

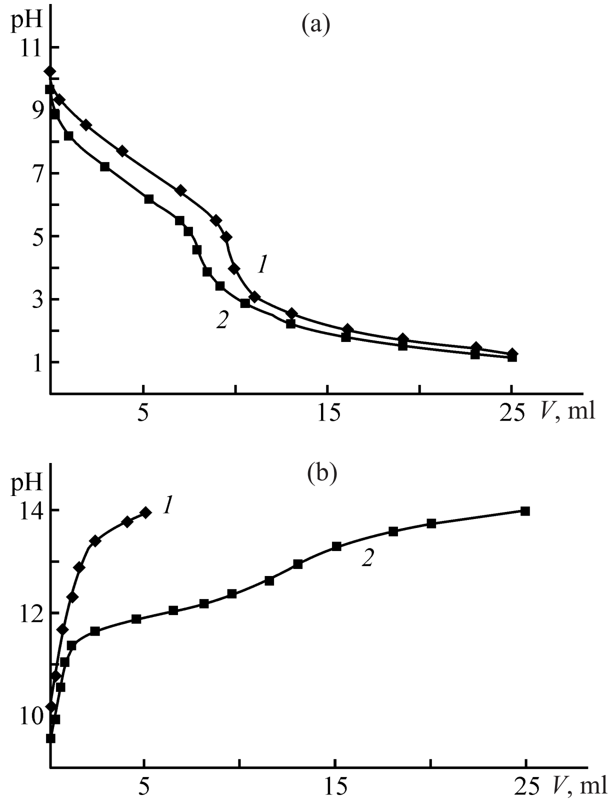

**Fig. 1.** Curves of potentiometric titration of (1) 0.87 M $K_4P_2O_7$ and (2) 0.24 M $CoSo_4$ + 0.87 M $K_4P_2O_7$ solutions with (a) 4.5 M $H_2SO_4$ and (b) 2 M KOH.

The titration curve of the pyrophosphate cobalt complex has a similar shape (Fig. 1a, curve *2*). Upon addition of first drops of the acid, the pH value rapidly shifts in the acid direction and a pink precipitate of, presumably, cobalt hydropyrophosphates starts to be formed. The amount of the precipitate is at a maximum at the bending point (8.0 ml of a 4.5 M $H_2SO_4$ solution); upon further increase in the amount of the acid, the precipitate dissolves and the solution takes on a pink color characteristic of cobalt aqua complexes $[Co(H_2O)_6]^{2+}$ [4–6].

In titration of the $K_4P_2O_7$ solution with 2 M KOH, pH rapidly shifts in the alkaline direction (Fig. 1b, curve *1*), with the outward appearance of the solution remaining unchanged.

In titration of a 0.24 M $CoSO_4$ + 0.87 M $K_4P_2O_7$ solution with a KOH solution, an ample blue precipitate of cobalt hydroxide is formed. To this process corresponds an extended plateau in the potentiometric curve (Fig. 1b, curve *2*). The bending point in curve *2* at 12 ml of the KOH solution corresponds to introduction of two moles of KOH per mole of $K_4P_2O_7$, i.e., to completion of the $Co(OH)_2$ formation. The precipitate is not dissolved in an excess amount of KOH.

Analysis of the potentiometric titration curves shows that the pyrophosphate cobalt complex is stable at 20°C in the pH range 8.7–11.6. Further study was carried out just within these limits. According to B. Purin's data [1], the stability range of the complex is at pH 7.0–12.0; however, it can be readily shown experimentally that, in an attempt to prepare solutions with pH 7–12, a precipitate is rapidly formed.

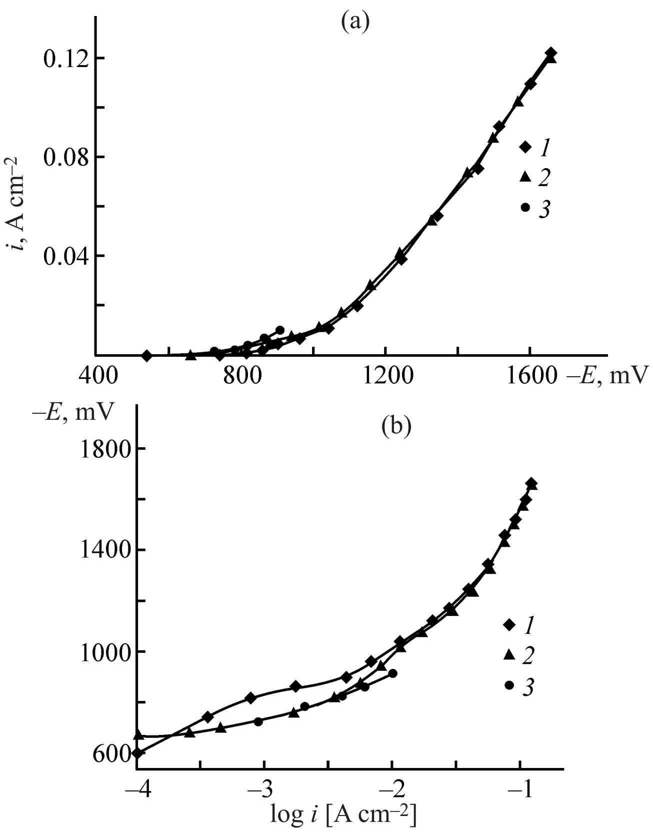

**Fig. 2.** (a) Cathodic potentiodynamic polarization curves in a 0.24 M $CoSO_4$ + 0.87 M $K_4P_2O_7$ solution at pH 10 on a cobalt electrode and (b) the same curves plotted in semilog coordinates. (*i*) Current density and (*E*) potential; the same for Figs. 3, 4. PC: (*1*) forward run and (*2*) reverse run; (*3*) Purin's data for a 0.2 M $CoSO_4$ + 1.0 M $K_4P_2O_7$ solution at pH 10 in the alvanostatic mode.

The forward and reverse potentiometric polarization curves obtained in a 0.24 M $CoSO_4$ + 0.87 $K_4P_2O_7$ solution are shown in Fig. 2a. The forward and reverse polarization curves are closely similar (curves *1* and *2*). The same figure presents Purin's data [1] (curve *3*) for a solution with about the same composition.

The polarization curves plotted in semilog coordinates are shown in Fig. 2b. It can be seen that the forward PC has a complex shape and is constituted by several portions. At potentials lower than –800 mV, i.e., at current densities lower than $7 \times 10^{-4}$ A $cm^{-2}$, cobalt is not deposited. This portion was not considered in this study. At current densities in the range from $1 \times 10^{-3}$ to $4 \times 10^{-3}$ A $cm^{-2}$, a short portion with a Tafel slope of approximately 120 mV is observed. In this portion of the PC, high-quality dense cobalt deposits can be obtained, with the current efficiency by cobalt, measured in separate experiments in the potentiostatic mode, being 91–95%, i.e., with nearly zero evolution of hydrogen. At potentials higher than –900 mV (current densities exceeding $4 \times 10^{-3}$ A $cm^{-2}$), the slope of PC gradually increases. This portion corresponds to deposition of cobalt with simultaneous hydrogen evolution, with the contribution of the latter process increasing with the current density. Under these conditions, dark gray electroplated cobalt coatings are formed with cracks and clearly pronounced traces of cobalt hydroxide.

Thus, cobalt is mainly deposited in a short portion with a slope of 120 mV, i.e., this portion is, in fact, a portion of the partial curve of metal deposition, which can be used to judge about the effect of various factors on the

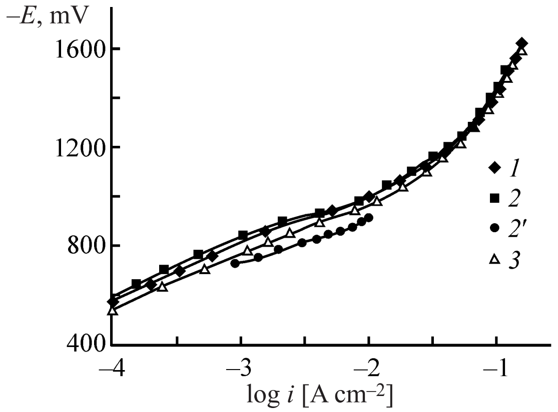

**Fig. 3.** Effect of the pH value on the polarization of the cobalt electrode. Solution composition 0.24 M $CoSO_4$ + 0.87 M $K_4P_2O_7$. pH: (*1*) 9.0, (*2*) 10.0, (*3*) 11.4, and (*2′*) curve from [1], obtained in a 0.2 M $CoSO_4$ + 1.0 M $K_4P_2O_7$ solution at pH 10.

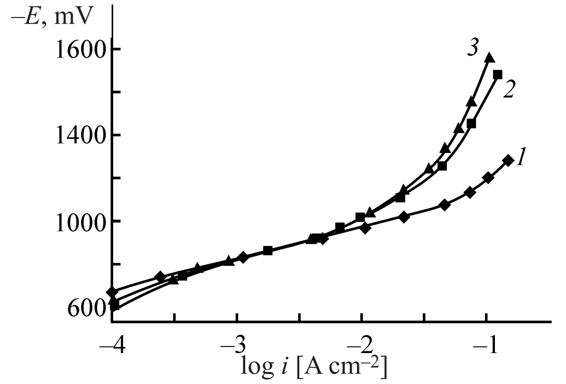

**Fig. 4.** Effect of the free potassium pyrophosphate concentration on the polarization of the cobalt electrode. $CoSO_4$ concentration 0.24 M, pH 10.0. Free $K_4P_2O_7$ concentration (M): (*1*) 0.66, (*2*) 0.39, and (*3*) 0.2.

process kinetics. At high current densities, the hydrogen evolution is superimposed on the main process, which probably leads to alkalization of the near-electrode layer to a pH value of 11.6, at which the pyrophosphate cobalt complex begins to decompose to give cobalt hydroxide and the electrode surface starts to be blocked. In more detail, the electrode surface blocking by the forming metal hydroxide was considered in [7] for the example of cathodic hydrogen evolution from weakly acid solutions of aluminum salts.

The reverse polarization curve (Fig. 2b, curve *2*) coincides with the forward PC, but exhibits a certain hysteresis at low polarizations. This may be due to a change in the state of the electrode surface: formation of a cobalt deposit with a developed surface and also formation and adsorption of a colloid film of cobalt hydroxide and basic salts of cobalt on the cathode. No bend is observed in the reverse PC at a potential of –800 mV, and, therefore, the bend at the same potential in the forward PC is presumably due to reduction of oxide films and adsorbed oxygen.

To examine the effect of pH on the kinetics of the cathodic processes, several PCs were measured in the 0.24 M $CoSO_4$ + 0.87 M $K_4P_2O_7$ solutions at pH values of 9.0 to 11.4. The polarization curves measured in solutions with pH 9 and 10 and plotted in the semilog coordinates (Fig. 3, curves *1* and *2*) almost coincide, whereas at pH 11.4 (curve *3*), a somewhat weaker polarization is observed, especially in the PC portion with a slope of about 120 mV. In the electrolyte of the last type, high-quality cobalt coatings cannot be obtained. Presumably, the decomposition pH of the pyrophosphate cobalt complex to give a hydroxide is reached in the electrolyte with pH 11.4 even at low current densities. Figure 3 also shows Purin's data [1] obtained in a solution with pH 10 (curve *2'*).

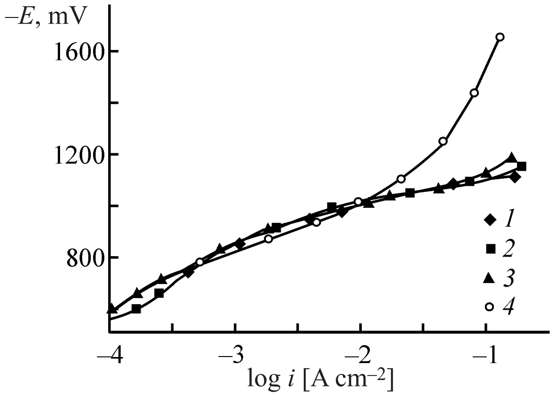

**Fig. 5.** Cathodic polarization curves measured in solutions with different cobalt sulfate concentrations. Free potassium pyrophosphate concentration 0.39 M, pH 10.0. $CoSO_4$ concentration (M): (*1*) 0.024, (*2*) 0.05, (*3*) 0.1, and (*4*) 0.24.

The cathodic polarization in electrodeposition of metals from complex electrolytes is strongly affected by the free ligand concentration, and, therefore, the effect of the concentration of free potassium pyrophosphate on the electrodeposition of cobalt was studied. The concentration of cobalt and the solution pH were maintained constant. As can be seen in Fig. 4, all the semilog PCs have a portion with a Tafel slope of approximately 120 mV; however, in the solution with the highest concentration of potassium pyrophosphate, this portion is the longest: one-and-a-half orders of magnitude in current, from $1 \times 10^{-3}$ to $3 \times 10^{-2}$ A $cm^{-2}$. In this range of current densities, high-quality cobalt coatings can be obtained without traces of cobalt hydroxide, i.e., an increase in the concentration of free potassium pyrophosphate markedly facilitates the cathodic process and lowers the polarization, which is particularly noticeable at high current densities.

In all probability, a high free ligand concentration hinders formation of cobalt hydroxide and precludes passivation of the cathode surface, thereby lowering the polarization. From the theoretical standpoint, the metal complex should become more stable, and the polarization, stronger, as the free ligand concentration increases [8, 9]. In the case under study, the high free ligand concentration exerts a markedly stronger depassivating influence than does the increase in the stability of the pyrophosphate cobalt complex. The increase in the cathodic polarization and the shortening of the PC portion with a slope of 120 mV in solutions with low free ligand concentration are possibly due to a decrease in the dissolution rate of cobalt hydroxide formed in the parallel reaction of hydrogen evolution leading to alkalization of the near-electrode layer and to blocking of the electrode surface. It should be noted that PC portions with slopes close to 120 mV almost coincide, irrespective of the free ligand concentration.

To determine the effect of the cobalt concentration on the cathodic polarization, several PCs were measured at a constant free pyrophosphate concentration (0.39 M) and pH, with the concentration of the pyrophosphate cobalt complex in solution varied from 0.024 to 0.24 M. The data obtained (Fig. 5) demonstrate that the polarization curves nearly coincide at potentials in the range from –800 to –1000 mV, irrespective of the content of cobalt in the solution. At higher cathodic potentials, the PCs measured in solutions with cobalt concentrations of 0.024 to 0.1 M are closely similar, and only at a cobalt concentration of 0.24 M, a sharp increase in the polarization is observed, which occurs because conditions are created under which cobalt hydroxide is formed, and the electrode surface, blocked. It is important to note that, at a cobalt concentration of 0.024 M in solution, high-quality cobalt coatings are deposited at a cathode current density of 0.1 A $cm^{-2}$, with no traces of hydroxides observed. The process is accompanied by vigorous hydrogen evolution; however, the small slope of the PC (Fig. 5, curve *1*) shows that there is no blocking of the cathode surface even at a so high current density. This is due to the large excess of free potassium pyrophosphate (0.39 M) over the concentration of the cobalt complex (0.024 M). At a cobalt concentration of 0.24 M and current density of 0.1 A $cm^{-2}$, the coating quality is unsatisfactory and the polarization is very strong (Fig. 5, curve *4*).

Thus, analysis of polarization curves makes it possible to determine the conditions in which high-quality cobalt coatings can be obtained. The decisive factor affecting the cathodic polarization and the coating quality is the ratio between the cobalt and pyrophosphate concentrations in solution.

## CONCLUSIONS

(1) The pH range of a stable existence of the pyrophosphate cobalt complex is 8.7–11.6.

(2) The polarization curve portion in which high-quality cobalt coatings are deposited has a Tafel slope close to 120 mV, which corresponds to a stage-by-stage occurrence of the electrochemical event with a decelerated transfer of the first electron.

(3) Changes in the solution pH and in the cobalt and free pyrophosphate concentrations have no effect on the rate of the cathodic process in the polarization curve portion with a slope of 120 mV. However, the length of this portion strongly depends on the solution composition.

(4) High-quality cobalt coatings are deposited with a current efficiency exceeding 90% in the polarization curve portion with a Tafel slope of approximately 120 mV, and strained coatings with unsatisfactory quality and trace amounts of nonmetallic impurities are obtained in the polarization curve portion with a large slope.

## REFERENCES

1. Purin, B.A., *Elektroosazhdenie metallov iz pirofosfatnykh elektrolitov* (Electrodeposition of Metals from Pyrophosphate Electrolytes), Riga: Zinatne, 1975.
2. Mel’nikov, P.S., *Spravochnik po gal’vanopokrytiyam v mashinostroenii* (Reference Book of Electroplated Coatings in Machine-Building), Moscow: Mashinostroenie, 1979.
3. Kravtsov, V.I., *Ravnovesie i kinetika elektrodnykh reaktsii kompleksov metallov* (Equilibrium and Kinetics of Electrode Reactions with Complex Metals), Leningrad: Khimiya, 1985.
4. Freemanttle, M.H., *Chemistry in Action*, Thomson Learning, 2nd ed., 1995.
5. Remy, H., *Lehrbuch der anorganischen Chemie*, Leipzig: Geest and Portig, 1961.
6. Pyatnitskii, I.V., *Analiticheskaya khimiya kobal’ta* (Analytical Chemistry of Cobalt), Moscow: Nauka, 1965.
7. Krasikov, V.L. and Aleksandrova, G.S., *Zh. Prikl. Khim.,* 2009, vol. 82, no. 5.
8. Vyacheslavov, P.M., *Elektroliticheskoe osazhdenie splavov* (Electrodeposition of Alloys), Leningrad: Mashinostroenie, 1986.
9. Rotinyan, A.L., Tikhonov, K.I., and Shoshina, I.A., *Teoreticheskaya elektrokhimiya* (Theoretical Electrochemistry), Leningrad: Khimiya, 1981.