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Abstract

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THE EFFECT OF ELECTROLYTE ACIDITY ON THE PROPERTIES OF ELECTROLYTIC COBALT DEPOSITS

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It is known from the literature that the properties of electrolytic cobalt deposits depend strongly on the acidity of the electrolyte. As early as 1932, Kersten established that from acidic cobalt sulfate solutions at high pH and 30° deposits of hexagonal ($-\alpha$) cobalt are obtained, whereas at low pH cubic ($-\beta$) cobalt is obtained (^{1}). Later this was also shown in work (^{2}). In work (^{3}), a difference was observed in the rate of self-dissolution in acids of electrolytic cobalt deposits obtained at pH ≈ 5.0 and in strongly acidic solutions. Polykarov (^{4}) reported that in the pH interval from 1.9 to 2.6 the structural and magnetic properties of the cobalt deposits obtained change sharply: at low pH, deposits are formed that represent a mixture of both cobalt modifications, while at pH above the indicated values only the α-modification is obtained. Solov' eva and Abrarov (^{5}) established a sharp decrease in cathode polarization during the electrocrystallization of cobalt from sulfate solutions in a narrow pH interval (from 2.7 to 3.3).

In the present work, the effect of solution acidity during the electrodeposition of cobalt on the microstructure, adsorption properties, and self-dissolution of the resulting deposits was investigated.

The deposits were obtained from a solution of the following composition: 500 g/l $CoSO_4 \cdot 7H_2O$ + 45 g/l H_3BO_3 at pH from 1.5 to 5.1. The solutions were prepared from chemically pure reagents in twice-distilled water freed from organic impurities. Electrolysis was carried out for 5 h at a current density of 0.015 A/cm^2 in a glass cell at 60°C.* Stirring was carried out throughout the entire electrolysis by means of a magnetic stirrer. The cathode was a platinum plate, the surface of which was several times smaller than the surface of each of the two cobalt anodes between which it was placed. The deposits obtained were washed with water and dried, after which they were studied: their microstructure—by microphotography; self-dissolution in 5 N sulfuric acid at room temperature in air—by weighing; and adsorption of iodine ions from a $4 \cdot 10^{-3}$ N KJ solution labeled with the radioactive iodine isotope (J^{131})—by measurements of the radioactivity of both sides of the deposit.

Figure 2

Figure 1: Figure 2

When deposits were obtained from solutions with pH < 2, an increase in pH by 0.2-0.3 units during electrolysis was observed due to the evolution of hydrogen. At higher pH, no change in it was observed. At pH < 2, deposits with a dense fine-crystalline structure were obtained, while upon transition to pH above 3 a sharp change in the microstructure of cobalt was observed toward the formation of larger crystals with clearly defined faces (Fig. 1). The thickness of the deposits formed at different pH values is greater, the higher its value under otherwise identical conditions, which is associated with a decrease in the overvoltage of cobalt deposition upon transition from more acidic to less acidic solutions. This fact agrees well with the results of works ([5],[6]). The authors of these works assumed that, upon transition from pH < 2 to higher values, the discharge of cobalt ions is facilitated in connection with a change in their structure. As pH increases, water molecules bound to the cobalt ion are replaced by OH^- ions, as a result of which cobalt ions are formed, which are discharged at less negative potentials.

The changes in the microstructure of cobalt deposits presented in Fig. 1 (on the insert, see p. 854) are analogous to the changes observed from electron-microscopic data in work (4).

The data on the self-dissolution of cobalt deposits obtained at different electrolyte pH values (Fig. 2) show that the rate of self-dissolution of cobalt increases sharply for deposits whose pH of formation is above 3. A change in the rate of self-dissolution of such deposits is also observed over the time of dissolution. As is seen from Fig. 2, the amount of cobalt that passed into solution from the deposit obtained at pH 3 is, after 95 min., one and a half times greater than after 60 min. (curve 1), while from the deposit obtained at pH 5 it is three times greater.

Fig. 2. Self-dissolution of deposits obtained at different pH. Solution H_2SO_4 5N. 1 —dissolution time 60 min.; 2 —95 min.

Fig. 3 shows the difference in the kinetics of self-dissolution of cobalt obtained at different pH values. The rate of self-dissolution of cobalt obtained at pH 1.5 is small and practically constant throughout the entire experiment (curve 1), whereas for cobalt obtained at pH 5.1 it increases rapidly with time (curve 2). The change in the rate of self-dissolution with dissolution time apparently reflects a temporary change in the structure of cobalt deposits obtained at pH > 2. The disordering of the structure of cobalt obtained at pH 5.0—6.4 was

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* Under these conditions, only hexagonal cobalt is obtained.

Figure 3

Figure 2: Figure 3

indicated in work (4), in which a change over time was observed in the magnetic characteristics of deposits obtained at such pH values.

Fig. 3. Kinetics of self-dissolution of cobalt obtained at different pH values. 1 –pH 1.5; 2 –pH 5.1

When explaining the differences in the dissolution of cobalt deposits obtained at different pH values, it should also be borne in mind that the stationary potential of cobalt obtained at pH < 3 is more positive than in cases where it is obtained at higher pH values, which indicates a lower overvoltage of the anodic process in the latter case during the self-dissolution of cobalt in sulfuric acid. This, as well as the course of the anodic polarization curves for deposits obtained at different pH values, shows that, electrochemically, the surface of cobalt obtained at pH < 2 corresponds to a less active state than the surface of cobalt obtained at pH < 3.

The difference in the properties of cobalt deposits obtained at different pH values was also revealed by studying their adsorption properties with respect to surface-active iodine ions. Using labeled iodine ions, it was shown that deposits corresponding to the structure at pH > 3 possess a greater sorption capacity than deposits obtained at low pH values. The adsorption time is also very significant in this respect. With short-term adsorption (5 min.), the difference in sorption capacity of the various deposits is comparatively small (~ twofold), whereas with prolonged adsorption it is much greater. After 5 h the sorption values already differ by almost an order of magnitude. These results make it possible to assume that the absorption of iodine ions occurs not only on the outer surface of the deposit, but also extends into its interior. Such an assumption is confirmed by the phenomenon, found for the deposits studied, of penetration of ions

of iodine inward, which is more pronounced for cobalt deposits obtained at pH 5. Such a phenomenon was first discovered on platinum (^{7}). In the present work it was observed on cobalt deposits with adsorbed iodine from the increase in their radioactivity after partial dissolution and subsequent exposure in air (emergence from the interior to the outer surface), and also from the decrease in the radioactivity of the deposits before dissolution after washing out the potassium iodide solution from which sorption had been carried out (migration inward). The magnitude of the observed penetration effect increased with increasing contact time of cobalt with the KI solution.

Fig. 4. Effect of J^- ions on the self-dissolution of cobalt obtained at pH 5.0. 1 –deposit obtained without J^-; 2 –J^- ions adsorbed; 3 –J^- ions incorporated into the deposit

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Figure 3: Fig. 4. Effect of J^- ions on the self-dissolution of cobalt obtained at pH 5.0. 1 —deposit obtained without J^-; 2 —J^- ions adsorbed; 3 —J^- ions incorporated into the deposit

On the basis of the data obtained, it may apparently be assumed that cobalt deposits obtained at high (~ 5) pH have a disordered structure with a developed internal surface accessible to J^- ions.

This assumption is also confirmed by the fact that the amount of J^- ions absorbed by the surface of cobalt deposits exceeds that required for the formation of one monolayer, calculated for the visible surface. For deposits obtained at pH 5 this excess is several times greater than for those obtained at pH < 2, and it increases with increasing sorption time of iodine ions.

Iodine ions sorbed on cobalt deposits obtained at different pH values exert an inhibiting effect during dissolution of cobalt in sulfuric acid. This effect, however, is especially strong when iodine ions are incorporated into the deposit during its electrocrystallization. When electrolysis is carried out in the presence of J^- ions, dark-colored deposits are obtained with a microstructure analogous to that of deposits obtained in the absence of J^- at low pH. Sorbed iodine ions, unlike those incorporated during electrolysis, have no effect on the color or microstructure of the deposit. Such an effect of iodine ions during electrocrystallization of cobalt is determined by an increase in the overvoltage of discharge of its ions, as shown in ([8]), which is analogous to the phenomenon observed in the absence of J^- when the pH is lowered ([5]).

The results obtained show that the corrosion resistance of cobalt deposits can be increased both by lowering the acidity of the solution and by incorporating inhibiting iodine ions into the deposit during its electrocrystallization.

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