

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

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It is known from the literature that the properties of electrolytic cobalt deposits are closely dependent on the acidity of the electrolyte. Kersten showed as early as 1932 [1] that cobalt sulphate solutions at 30° give hexagonal type (α) deposits if the pH is high and cubic type (β) deposits if the pH is low. These conclusions were later confirmed in [2]. It was shown in [3] that the rate of acid dissolution of cobalt deposits obtained from strongly acidic solutions is not the same as the rate of acid dissolution of deposits obtained at $\text{pH} \approx 5.0$. Polukarov reported [4] that the structural and magnetic properties of cobalt deposits alter radically over the pH interval from 1.9 to 2.6. The deposits obtained at low pH's are mixtures of the two crystalline modifications while deposits obtained above pH 2.6 consist of the α -modification alone. Solov'eva and Abrarov have shown [5] that there is a sharp reduction in cathodic polarization during the electrocrystallization of cobalt from sulfate solutions, change occurring over a narrow interval of pH ranging from 2.7 to 3.3.

The present work is a study of the effect of the acidity of the depositing solution on the microstructure, adsorptional properties, and spontaneous dissolution of the cobalt deposit.

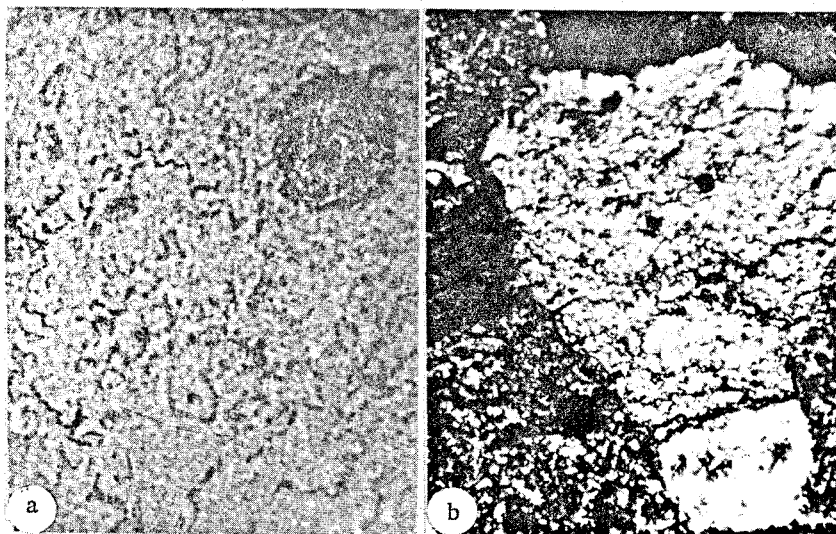


Fig. 1. Microphotograph of cobalt deposits obtained at various pH's (120 $\times$):
a) pH 1.7; b) pH 4.1.

The deposits used here were obtained from a solution containing 500 g $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and 45 g H_3BO_3 per liter, working over the pH interval from 1.5 to 5.1. The solutions were prepared from chemically pure constituents, using doubly distilled water which had been freed of organic contaminants. Electrolysis was carried out in a glass cell at 60°C and was continued for five hours at a current density of 0.015 amp/cm².^{*} A magnetic stirrer was used to keep

^{*} The cobalt deposit obtained under these conditions contained only the hexagonal modification of the metal.

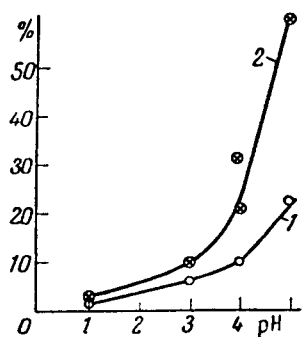


Fig. 2. Dissolution of deposits obtained at various values of the pH. 5 N H_2SO_4 solutions. 1) Time of dissolution, 60 min; 2) 95 min.

quite consistent with the results of [5, 6]. The authors of these latter papers assumed that the alteration of the ionic structure accompanying passage to pH value below two makes for greater ease in the discharge of the cobalt. Increase in the pH entails a replacement of the bound water molecules with OH^- ions, with the result that discharge of the cobalt ions can take place at less negative potentials.

The alterations in the microstructures of cobalt deposits shown in Fig. 1 are similar to the alterations observed with the electron microscope in [4].

The data obtained (Fig. 2) showed a marked increase in the rate of dissolution of cobalt deposits obtained from electrolytes with pH's in excess of 3. It was also observed that the rate of dissolution of such deposits was time dependent. It is seen from Fig. 2 that the amount of cobalt deposit obtained at pH 3 passing into solution in 95 min is one and a half times as great as that passing into solution in 60 min (curve 1) while similar experiments with a deposit obtained at pH 5 showed the 95 min amount to be three times as large as the 60 min amount.

Figure 3 shows the variation of the kinetics of dissolution of cobalt with the deposition pH. The rate of dissolution of cobalt obtained at pH 1.5 was low and remained essentially constant during the entire course of the experiment (curve 1) while the rate of dissolution of cobalt at pH 5.1 rose rapidly with the passage of time (curve 2). The fact that the rate of dissolution altered as dissolution proceeded is clear indication of a time dependent change in the structure of deposits obtained at pH's in excess of 2. It has been pointed out in [4] that cobalt deposits obtained at pH 5.0-6.4 have disordered structure and time dependent magnetic properties.

In attempting to obtain an understanding of the differences in the dissolution of cobalt deposits prepared at various pH's, it should be remembered that the stationary potential for deposition at $\text{pH} < 3$ is more positive than the potential for deposition at high pH. This is indication of a lower overvoltage for the anodic processes involved in

the dissolution of the latter type of cobalt in sulfuric acid. This, together with the form of the anodic polarization curves for deposits obtained at various values of the pH, gives proof that the surface of cobalt prepared at $\text{pH} < 2$ is less active, electrochemically speaking, than the surface of cobalt prepared at $\text{pH} < 3$.

The difference in the properties of cobalt deposits obtained at various pH's was also brought out by a study of the adsorption of surface active iodide ions by these substances. Labeled iodide ions were used to show that the adsorption capacity of deposits obtained at lower pH's. The time of adsorption was a very significant factor here. The difference in the adsorption capacity of the various deposits was relatively small (approximately two-fold) in short-term adsorption of the order of 5 min, but much more pronounced in long-term adsorption. There was a difference of almost an entire order in the magnitude of the adsorption over a five-hour period. On this basis it could be assumed that the absorption of iodide ions occurs not only on the external surface

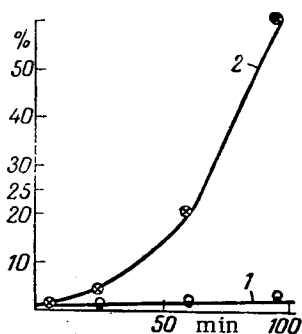


Fig. 3. The kinetics of dissolution of cobalt obtained at various values of the pH. 1) pH 1.5; 2) pH 5.1.

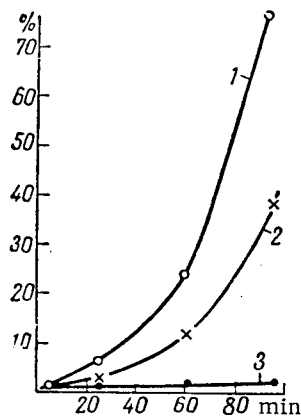


Fig. 4. The effect of I^- ions on the dissolution of cobalt obtained at pH 5: 1) deposit without I^- ; 2) with adsorbed I^- ; 3) I^- ions occluded in deposit.

but in the interior of the deposit as well. This assumption was confirmed by the fact that iodide ions were observed to penetrate into the deposits, the penetration being most pronounced in the case of deposits obtained at pH 5. Effects of this kind were first reported for platinum in [7]. The effect observed in the present work was that of an increase in the radioactivity of a cobalt deposit carrying adsorbed iodine after the deposit had been partially dissolved and then held in the air (passage from the interior to the external surface) and a decrease in the radioactivity of the deposit (prior to dissolution) after washing away the potassium iodide solution from which sorption had taken place (passage inward). The magnitude of the observed penetration increased with the time of contact between the cobalt and the KI solution.

These results justified the conclusion that cobalt deposits obtained at high pH (~ 5) are structurally disordered and have a highly developed internal surface which is available for I^- ion sorption.

This assumption was confirmed by the fact that the amount of I^- ion taken up by the cobalt deposit exceeded that required for the formation of a monolayer, calculation being made on the basis of the apparent surface area. This excess was several times greater for deposits obtained at pH 5 than for deposits prepared at pH < 2 , and increased with the time of iodide ion sorption.

Iodide ions sorbed on deposits obtained at various values of the pH exerted an inhibiting effect on the dissolution of the cobalt in sulfuric acid. This effect was especially marked in ions which had been occluded in the deposit during electrodeposition. The deposit obtained by electrolysis in the presence of I^- ions had a dark color and a microstructure similar to that observed in deposits obtained at low pH in the absence of I^- . The sorbed ions differed from the ions occluded in electrolysis insofar as they exerted no effect on the color or microstructure of the deposit. It has been shown in [8] that this action of the iodide ions in the electrocrystallization is the result of an increase in the overvoltage for cobalt ion discharge, the effect being analogous to the increase observed at low pH in the absence of I^- ions [5].

The results obtained here indicate that the corrosional stability of cobalt deposits can be enhanced by a reduction of the acidity of the depositing solution and by the occlusion of inhibiting iodide ions in the deposit during electrocrystallization.

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