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INITIAL STAGES OF COBALT ELECTRODEPOSITION FROM SULPHATE BATHS

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Abstract

The electrodeposition of cobalt from sulphate baths has been studied during its initial stages, due to the recent interest on cobalt and cobalt alloy electrodeposits. Potentiostatic and potentiodynamic electrochemical techniques have been applied using a three-electrode cell and a vitreous carbon electrode. The influence of pH and potential in the voltammetric and chronoamperometric response has been analysed, and nucleation and growth models have been tested under the experimental conditions of the work and in the absence of hydrogen evolution. An instantaneous nucleation under diffusion control occurs at pH=4 while at pH=6.5 progressive nucleation under diffusion control has been obtained.

KEYWORDS: COBALT ELECTRODEPOSITION, SULPHATE BATH, NUCLEATION MODEL, CRITICAL NUCLEUS.

1. Introduction

The interest of cobalt and cobalt alloy electrodeposition is increasing because their magnetic properties have high technical applications [1-2]. Cobalt alloys present high resistance to corrosion [3-5] and recently have achieved commercial interest as a non-contaminant economic way to provided attractive and functional finishing [6, 7].

They are not many studies on cobalt electrodeposition in the literature, comparing to other metals as nickel or copper. Cobalt electrodeposition has been studied from chloride and sulphate Co(II) aqueous solutions [5, 8-10] or 30% KOH with tris-ethylenediammine cobalt(III) chloride solutions and cobalt(II) thiocyanate in N,N-dimethylformamide solutions [11, 12]. In these studies it has been found that the structure and properties of cobalt deposits are closely related to electroplating

conditions as pH, bath composition, and deposition potential. However, the mechanism of nucleation and crystal growth of cobalt deposits has received much less attention because cobalt electrodeposition onto a foreign substrate takes place normally with simultaneous hydrogen evolution, which makes difficult the analysis of the current transients.

In this study, we investigate the initial stages of cobalt electrodeposition from a sulphate bath at different pH using potentiodynamic and potentiostatic electrochemical techniques, in order to establish the influence of plating variables on cobalt electrodeposition and hydrogen evolution processes. We also perform a kinetic study of the nucleation process of cobalt electrodeposition by applying the typical models that describe the early stages of the electrocrystallization processes [13-15].

2. Experimental

The electrochemical measurements were performed in a three electrode cell using a Tacussel vitreous carbon electrode inserted in a Teflon support as working electrode (area=0.071 cm^2), a platinum wire as counter electrode and Ag/AgCl /KCl (3 M), inserted in a Luggin capillary, as reference electrode. All potentials reported in the text are referred to this electrode. An AUTOLAB PSTAT10 controlled by a microcomputer was used as potentiostat. Different sets of voltammetric and chronoamperometric experiments were done. Voltammetric experiments were carried out at 50 mV s^{-1}, scanning at first to negative potentials, and running only one cycle in each experiment. Chronoamperometric experiments were carried out in a wide range by stepping from an initial potential of –300 mV to the selected final potential.

Chemicals used were $CoSO_4 \cdot 7H_2O$, sulphuric acid, sodium hydroxide and Na_2SO_4 analytical grade. All solutions were freshly prepared with water, first distilled and then treated with a Millipore Milli Q system. The acidic sulphate bath contained 1 M H_2SO_4 as supporting electrolyte. The baths at pH=2, 4 and 6.5 contained, respectively, 0.2 M, 1M and 0.2 M Na_2SO_4 as supporting electrolyte. Sulphuric acid and sodium hydroxide were used to adjust the pH. In all cases the $CoSO_4$ concentration was 0.01 M. Before each experiment the solution was deaerated with argon. The working electrode was polished mechanically with alumina powder of 3.75 and 1.87 µm, ultrasonicated and thoroughly rinsed with deionised water before each experimental series. Then, the working electrode was submitted to an electrochemical conditioning before each experiment.

3. Results and Discussion

Voltammetric study.

The voltammetric response of cobalt(II) electrodeposition in a sulphate bath is strongly dependent on pH media. In a highly acidic bath, at pH corresponding to 1 M H_2SO_4 solution (fig 1, curve a), the cobalt electrodeposition takes place around –1050 mV but it can not be separated of hydrogen evolution. Then the efficiency of the electrodeposition process is very low (in the anodic scan no oxidation peak is observed, and the measured Q. and Q$_+$ are –1.09x10^{-2} and 4.1x10^{-6} C, respectively). If the pH is increased to 2 the electrodeposition process starts at practically the same potential, appearing a cathodic peak at around –1300 mV with signs of hydrogen evolution. In the anodic scan a single oxidation peak is observed at around –250 mV (fig 1, curves b and c), that increases when the cathodic scan limit is made more negative. For curve 1b the measured Q. and Q$_+$ are –8.16x10^{-3} and 4.17x10^{-4} C, meanwhile for curve 1c the measured Q. and Q$_+$ are –1.19x10^{-2} and 1.02x10^{-3} C, respectively.
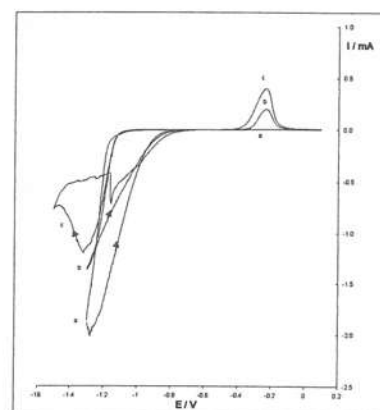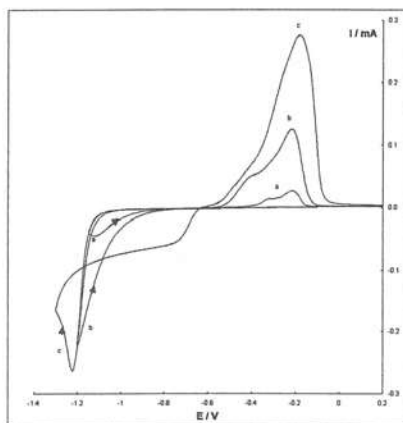

Figure 1. Cyclic voltammograms at 50 mV s^{-1} from a vitreous carbon electrode in the following solutions and cathodic potential limits: a) 0.01 M $CoSO_4$, 1M sulphuric acid, E= –1300 mV; b) 0.01 M $CoSO_4$, 0.2 M sodium sulphate, pH=2, E= –1300 mV; c) 0.01 M $CoSO_4$, 0.2 M sodium sulphate, pH=2, E= –1500 mV.
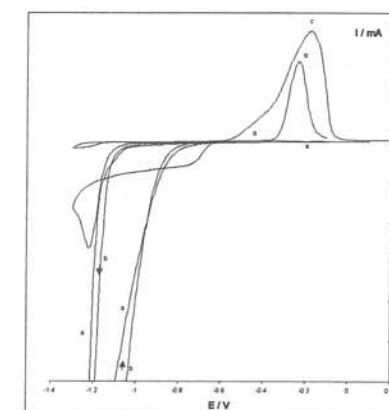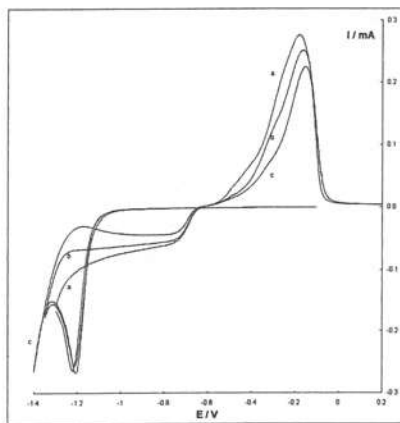
Figure 2. Cyclic voltammograms at 50 mV s^{-1} from a vitreous carbon electrode in solution 0.01 M $CoSO_4$ and: a) 1M sulphuric acid; b) 0.2 M sodium sulphate, pH=2; c) 1 M sodium sulphate, pH=4; d) 0.2 M sodium sulphate, pH=6.5. Cathodic potential limit = –1300 mV.

When the pH is increased to 4, the reduction of cobalt(II) takes also place around –1050 mV but the hydrogen evolution is displaced at around –1300 mV; then cobalt deposits can be obtained with a minimised hydrogen evolution if the cathodic limit is less negative than –1300 mV. Figure 2 also shows that the reduction current at pH=4 (curve c) is much lower than reduction currents at pH=2 (curve b) or at more acidic pH (curve a), and the measured Q_- and Q_+ for curve 2c are -1.64×10^{-3} and 1.28×10^{-3} C, respectively. These values indicate a very important decrease in hydrogen evolution. Also a reduction peak at around –1225 mV is presented for the curve at pH=4. In the anodic scan two oxidation peaks are obtained at pH=4 (fig 2, curve c), their shape depending on the cathodic potential limit (figure 3); at lower cathodic potential limits the double oxidation peak is better defined. It can be observed that for limit potentials more negative than –1300 mV the oxidation current decreases (fig 3b) due to a loss of efficiency in the electrodeposition since hydrogen starts to evolve significantly.


Figure 3a. Cyclic voltammograms at 50 mV s^{-1} from a vitreous carbon electrode in solution 0.01 M CoSO$_4$, 1 M sodium sulphate at pH=4 and different cathodic limits: a) –1150, b) –1200, c) –1300 mV.

Figure 3b. Cyclic voltammograms at 50 mV s^{-1} from a vitreous carbon electrode in solution 0.01 M CoSO$_4$, 1 M sodium sulphate at pH=4 and different cathodic limits: a) –1300, b) –1350, c) –1400 mV.

If the pH is increased to 6.5, the intensity of the electrodeposition and oxidation processes is strongly decreased (fig 2, curve d). In the cathodic scan the reduction potential is displaced to more negative values, around –1150 mV, and in the anodic scan a very wide oxidation peak is obtained. The measured Q_- and Q_+ for curve 2d are -7.63×10^{-5} and 2.69×10^{-5} C, respectively.

Chronoamperometric study.
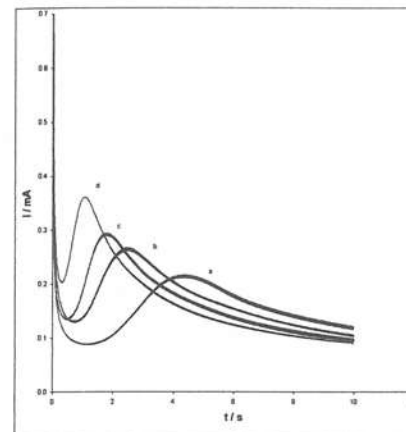
Figure 4a. Potentiostatic transients from a vitreous carbon electrode in solution 0.01 M CoSO$_4$, 1M sodium sulphate at pH=4. The potential step transients were made from $E_o=$ -300 mV to: a) –1050, b) –1075, c) –1100, d) –1125 mV.
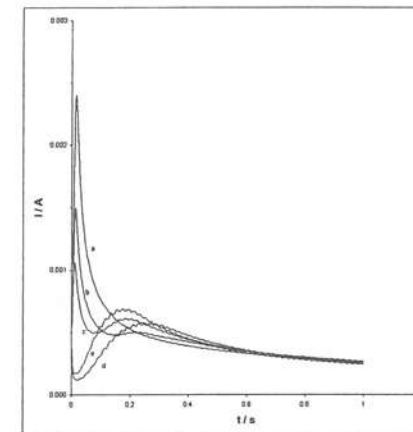
Figure 4b. Potentiostatic transients from a vitreous carbon electrode in solution 0.01 M CoSO$_4$, 1 M sodium sulphate at pH=4. The potential step transients were made from $E_o=$ -300 mV to: a) –1175, b) –1200, c) –1250, d) –1275, e) -1300 mV.

A family of current transients obtained at different electrodeposition potentials has been analysed. In the bath at pH=4, two sets of current responses have been obtained depending on whether the hydrogen evolution process takes place. For electrodeposition potentials equal or less negatives than –1200 mV (fig 4a), the analysis of the raising part of current transients gives a dependence with $(t-t_o)^{1/2}$, where t_o is the induction time (the slope of log i vs. log(t-t$_o$) is ½, see curves a-d in fig 6). Then, an instantaneous nucleation (IN) process controlled by diffusion describes the initial stages of cobalt electrodeposicion at potentials where hydrogen evolution doesn't take place. The nuclei density can be determined using equation 1 [13-16] for a IN process under hemispherical diffusion:

$$I = k\, t^{1/2} \tag{1}$$

$$k = \frac{\pi z F M^{1/2} (Dc)^{3/2} A N^*}{\rho^{1/2}}$$

In equation 1 the following parameter values have been used: $\rho = 8.9$ g/cm^3, $z = 2$, $M = 58.93$ g/mol, $F = 96485$ C/mol e$^-$, $D = 1 \times 10^{-5}$ cm^2/s, $c = 1 \times 10^{-5}$ mol/cm^3 and $A = 0.071$ cm^2. Table 1 shows the nuclei density, N*, at different potentials.

Table 1. Nuclei density, N*, at different potentials for cobalt electrodeposition in a sulphate bath at pH=4.

-E / mV	k / A s$^{-1/2}$	N* / cm^2
1075	2.29×10^{-4}	2.07×10^6
1100	3.17×10^{-4}	2.86×10^6
1125	3.81×10^{-4}	3.44×10^6
1175	2.19×10^{-2}	1.98×10^8
1200	1.21×10^{-2}	1.09×10^8
1250	9.42×10^{-3}	8.50×10^7

For potentials more negative than −1200 mV, a second electrodeposition process takes place (fig 4b), with signs of hydrogen evolution at higher negative potentials. The analysis of the raising part of these second current transients gives a dependence with t, indicating that an instantaneous nucleation with bidimensional crystal growth is obtained for this second electrodeposition process.
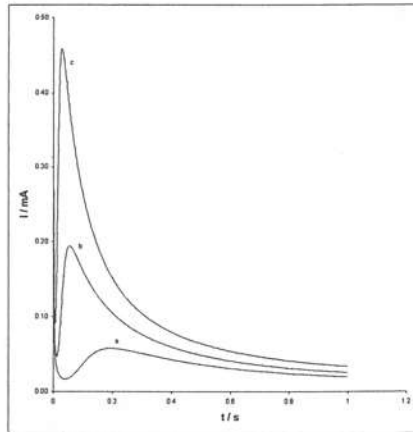
Figure 5. Potentiostatic transients from a vitreous carbon electrode in solution 0.01 M CoSO$_4$, 0.2 M sodium sulphate at pH=6.5. The potential step transients were made from E$_o$= -300 mV to: a) −1200, b) −1300, c) −1400 mV.

In the bath at pH=6.5 only one set of current transients are obtained (fig 5), and the analysis of their raising parts gives a (t-t$_o$)$^{3/2}$ dependence (the slope of log i vs. log(t-t$_o$) is 3/2, see curves A-C in fig 6). Then a progressive nucleation (PN) controlled by the diffusion to the growing crystallites takes place at this pH. The nuclei density can be determined using equation 2 [13, 14], for a PN process under hemispherical diffusion, and the parameter values before indicated. Table 2 shows the nuclei density, N*, at different potentials.
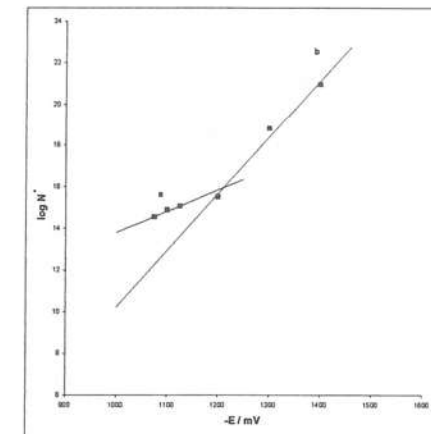
$$I = k\, t^{3/2} \tag{2}$$

$$k = \frac{4\pi z\, F\, M^{1/2}\, (Dc)^{3/2}\, A\, N^*}{3\rho^{1/2}}$$

Table 2. Nuclei density, N*, at different potentials for cobalt electrodeposition in a sulphate bath at pH=6.5.

-E / mV	k / A s$^{-3/2}$	N* / cm^2
1200	8.10×10^{-4}	5.40×10^6
1300	0.022	1.47×10^8
1400	0.19	1.27×10^9
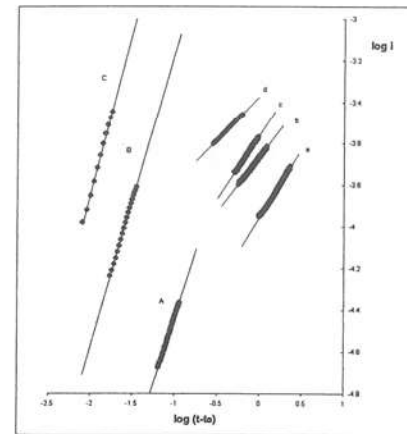
Figure 6. Plot of log i vs. log (t-t$_o$) for curves a-d in figure 4a (small letters) and curves a-c in figure 5 (capital letters).

Figure 7. Plot of ln N* vs. potential, E, for values of table 1 (curve a) and table 2 (curve b).

The plot of ln N* versus the potential gives a straight line for experiments at pH=6.5 (figure 7), and also for the lower potentials of experiments at pH=4. According to equation 3 [17-19] the calculated critical nucleus size is between 0-1 atoms, in both cases. This result is in agreement with others studies that also have determined very low values for the critical nucleus size in electrodeposition [20-24]. It means that the electrode surface-active centres play the role of the critical nucleus [25], and when the necessary overpotential is reached nucleation occurs at these centres and the growth of the nucleus proceeds.

$$\frac{d\,lnJ}{dE} \approx \frac{d\,ln\,N^*}{dE} = -\frac{zF}{RT}N_{crit} \tag{3}$$

Soto et al. [5] have reported that in a 1 M ammonium chloride solution, pH=4.66, cobalt electrodeposition proceeds via a progressive nucleation with hemispherical diffusion. These authors have also found that the critical nucleus size is practically zero, in agreement with our results.

4. Final comments

The reduction of cobalt depends on pH media, and is shifted to more cathodic potentials when pH increases at 6.5, presenting also an important decrease in the current intensity. Working at pH=4 a significant cobalt electrodeposition can be obtained in a wide range of potentials without hydrogen evolution. The electrodeposition process occurs, in its initial stages, through an instantaneous nucleation and diffusion control at pH=4, but through a progressive nucleation and diffusion control at pH=6.5. From the calculated nuclei density and its dependence on the potential, a critical nucleus size of 0-1 atoms is obtained. This result indicates that the atomistic model of nucleation will be more realistic for its description, and that the electrode surface-active centres play the role of critical nucleus.

Acknowledgements

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