Electrodeposition of cobalt from citrate containing baths

A.C. Frank *, P.T.A. Sumodjo

Instituto de Química, Universidade de São Paulo C.P. 26077, 05513-970, São Paulo–SP, Brasil

ARTICLE INFO

ABSTRACT

The kinetics of the initial stages of cobalt electrodeposition on glassy carbon from a chloride bath containing citrate was studied using different electrochemical techniques. Cyclic voltammetry was used to characterize the deposition and the stripping processes. Cobalt films were galvanostatically deposited and potentiodynamically stripped. Complex species distribution in solution functional to the bath composition and pH were used to explain the observed deposition and stripping features. Current transients were analyzed using the models by Scharifker and Hills to describe the general behavior of the nucleation in Cobalt/citrate systems. It was concluded that Co electrodeposition in citrate mediums occurs via an instantaneous nucleation followed by a tridimensional growth under mass control mechanism. It is remarkably different from what other authors have found for Co deposition from solutions with no additive or containing ammonia. Thus, the choice of additive can change the reaction mechanism. Deposition parameters such as number of active sites, critical nucleus size and average diffusivity were estimated.

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1. Introduction

It is known that the physical properties and morphology of an electrodeposit strongly depend on several parameters of the electrodeposition process, such as the solution composition, pH, temperature, potential and current density. The first stages of the electrodeposition play a very important role in the electrochemical phase formation and therefore in the properties of the final deposit, specially as the dimensions of the structures continue to scale down. For example, in general, to deposit a flat and homogeneous film it is desirable that the process undergoes an instantaneous nucleation mechanism so that the few nuclei have approximately the same size as they slowly grow at their former positions on the uncovered substrate surface. In other cases, usually the final deposit obtained via progressive nucleation is coarse, because whereas the first nuclei grow, others appear, so the crystals have different sizes.

Cobalt electrodeposition has received much attention because of the ferromagnetic nature of cobalt and its potential applications in storage media devices and magnetic sensors [1,2]. With respect to the electrocrystallization mechanisms, it has been found that, in aqueous sulfate solutions, cobalt deposits preferably via a progressive nucleation followed by 3-D growth, but the mechanism changes to instantaneous nucleation when the applied overpotential is high or in solutions with high cobalt concentration [3].

This general behavior is common for many other metallic ions (e.g. tin [4]). Furthermore, the substrate and the nature of the anions constituent of the plating bath were also reported to affect the nucleation and growth mechanism [3,5–7]. Most of the studies using glassy carbon as substrate [5,6,8] have been done in chloride [5,6] or sulfate [3,7,8] containing baths. Most studies indicate that cobalt electrodeposition in acidic solutions occurs similarly to that of other iron-group metals by involving two successive single electron transfer steps [9], with the first step involving the formation of an intermediate adsorbed ion. Depending on the pH and on the applied potential or current, the hydrogen evolution reaction (HER) occurs simultaneously with cobalt electrodeposition [3].

An interesting way to change and control the electrocrystallization mechanism is by modifying the coordination sphere of the metal by introducing an additive to the aqueous solution. This can generate new complex species in solution, changing the diffusion of the electroactive species present and/or causing partial or complete loss of the solvation sheath, which can therefore affect the rate limiting step of the process [10–12]. Also, it is recognized that the presence of organic additives in electrodeposition baths is often necessary to produce adherents and homogeneous deposits, to stabilize the plating solution or to allow thermodynamically unfavorable reactions to occur [13–15]. Although the importance of use of additives in plating baths is recognized, there are few reports in the literature on studies of the effect of additives on the mechanism of cobalt electrodeposition. Ammonia has received some attention [6,16–18]. Palomar-Pardavé et al., [6] demonstrated that the mechanism involved in cobalt electrodeposition depends on the

* Corresponding author. Tel.: +55 11 3091 2154; fax: +55 11 3091 2154.
E-mail addresses: frank@iq.usp.br, anfrank@ig.com.br (A.C. Frank).

nature of the metal/ammonia complex in the solution, which in turn depends on pH. Using Scharifker and Hills [19] models to analyze chronoamperometric data, Palomar-Pardavé *et al.*, [6] found that cobalt nucleation onto glassy carbon follows either a progressive nucleation mechanism or a combination of various mechanisms, depending on the complex species present. Grujicic *et al.*, [18] also studied this system, using electrochemical techniques together with a morphological study with Atomic Force Microscopy (AFM). With the electrochemical studies, they also concluded that cobalt undergoes a progressive nucleation mechanism onto glassy carbon. However, the AFM study apparently indicated that instantaneous nucleation also occur, a contradiction justified by the authors as due to the formation of three different types of cobalt nuclei, each with its own rate of growth and reaction surface area. Therefore, although there is still some room for discussion, it seems that ammonia does not alter significantly the cobalt nucleation mechanism, which occurs via a progressive mechanism in solutions with no additive [3].

Citrate is one of the most utilized additives in electrodepositions [12], as it is a strong complexing agent to many metals, such as cobalt, nickel, copper, iron and tungsten [12,20–23]. It is also reported to be a stabilizer agent in plating baths [23] and is widely employed in electrodeposition of alloys [24–26]. In addition, citrate can form some polymeric species that partially block the surface of the electrode, inhibiting the hydrogen evolution reaction and increasing the deposition efficiency [27]. Regarding electrodeposition of Co, cobalt oxides or cobalt based alloys from citrate baths, some studies have been reported. El Rehim et al., [28] reported a work on the deposition of Co onto steel from citrate or citric acid solutions. They concluded that citric species provoke an increase in the overpotential of the deposition and that the current efficiency could reach very high values ($\sim$88%), but there are no details regarding the influence of the complex species present in these solutions or any analysis on the mechanism of the electrodeposition. It has also been reported that the rate of deposition of cobalt oxide is lowered as the citrate concentration is increased, as it can block the some active sites of the electrode [29]. When used to deposit alloys, citrate may allow the deposition of alloys that are not predicted thermodynamically (as the CoCu [26]) or, together with ammonia, to control the composition and morphology of alloys (as the CoMo [25], although the current efficiency is low). Cobalt and citrate complex species have also been used in the synthesis of cobalt-based nanoparticles, tuning the size of the nanostructures (between 20 and 70 nm) [30] or also its shape, morphology and properties by the control of the complex species present [31].

However, to our knowledge, there are no reported studies discussing the mechanisms of cobalt electrodeposition from citrate solutions. This study focuses on the first stages of cobalt electrodeposition on a glassy carbon electrode from chloride plating baths containing citrate as additive. The effect of the additive on the electrodeposition process was analyzed using the species distribution curves. The employed electrochemical techniques were chronoamperometry, chronopotentiometry and cyclic voltammetry. Different plating solutions were studied in the sense that composition and pH were varied. The main kinetic parameters were determined when possible. We were able to show that the presence of citrate alters the chemistry of the solution, changing the cobalt deposition mechanism when compared to the already established mechanism for the deposition from a solution without additive or from an ammonia containing bath.

2. Experimental

The Co^{2+} concentration in the chloride solutions was maintained fixed at $0.15 \, mol \, L^{-1}$. Two different metal:additive molar ratios

Table 1
Baths composition and pH.

System	pH	$[Co^{2+}]/mol \, L^{-1}$	[citrate]/mol L^{-1}
C1	4.8	0.15	0.15
C2	4.8	0.15	0.30
C3	7.0	0.15	0.15
C4	7.0	0.15	0.30

were studied, 1:1 and 1:2, and, for each system, baths with different pHs were tested: 4.8 and 7.0. Table 1 shows the compositions of the studied baths. The pH of the solutions was adjusted using $HCl_{(conc)}$ or $NH_{3(conc)}$ and the ionic strength was kept constant at $2.2 \, mol \, L^{-1}$ with the addition of NaCl. Experiments were run at room temperature and oxygen was purged from the solutions by nitrogen bubbling before the experiments.

The electrochemical experiments were carried out using a conventional three-electrode cell; a glassy carbon disc (surface area = $0.0924 \, cm^2$) was used as the working electrode and a platinum wire as the counter electrode. A Ag|AgCl electrode was the reference electrode and all potentials (E) are referred to this electrode. The glassy carbon electrode was mechanically polished prior to every experiment with files of different grades (120, 280, 400 and 1500) and with alumina (1 μm). This is especially important to assure that the surface has approximately the same morphology for all the experiments, as it has been shown that glassy carbon surfaces well mechanically polished have active sites for nucleation randomly located on the surface [32]. Electrochemical measurements were controlled using a potentiostat/galvanostat (Perkin-Elmer, Princeton Applied Research - EG&G 273A).

Cyclic voltammetry experiments were run to determine parameters such as deposition and crossover potentials for the different studied baths. Hence, potentiodynamic E/I profiles were initially obtained by running the potential scan at a fixed rate of $10 \, mV \, s^{-1}$. Subsequently, the scan rate was varied from $10 \, mV \, s^{-1}$ to $200 \, mV \, s^{-1}$. The initial potential was set at 0.0 V, close to the open circuit potential of the systems.

Galvanostatic depositions followed by linear voltammetric stripping experiments were carried out to determine the ratio between the charge correspondent to the anodic stripping of the cobalt deposit and the total cathodic charge applied to the system (ce). The Co films were galvanostatically electrodeposited by application of an unvarying cathodic charge of 450 mC to the system, only varying the applied current density and the deposition time accordingly. The films were anodically stripped by linear scan voltammetry ranging from -0.40 V to +1.40 V in H_2SO_4 $0.5 \, mol \, L^{-1}$. The species distribution curves were constructed based on the literature values [33,34] of formation constants of the complex species present in each system using the softwares Hydra and Medusa [35].

Potentiostatic current transients were obtained by the application of different potentials, selected from the analysis of the cyclic voltammograms, and the data analysis followed some of the basic models for treating nucleation and growth I x t curves (t is the time).

3. Results and Discussion

3.1. Cyclic Voltammetry Experiments and Galvanostatic Electrodepositions

Fig. 1 shows a cyclic voltammogram of system C1, representative of the citrate systems, at potential scan rate, v, of $10 \, mV \, s^{-1}$. During the initial potential scan towards the negative direction, the cathodic current density (j_c) starts to rise when nucleation starts (around -0.78 V). Subsequently in the cyclic voltammogram, j_c continues to increase due to the bulk Co metallic phase formation. A broad cathodic peak, CP, appears at -1.00 V, so which indicates the