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Identification of Different Cobalt Nucleation on Glassy Carbon

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Abstract: The nucleation mechanisms of cobalt from sulfate solutions were studied by utilizing the electrochemical technique, chronoamperometry. It was found that the recorded current-time transients introduced from 1.0 mol/L $CoSO_4$ solution were complexes with unusual shapes. All characteristic features were identified as separate process. The instantaneous or progressive nucleation with 2D or 3D growth exists during the cobalt deposition, depending on the applied potentials.

Keywords: Cobalt, current transient, nucleation mechanism.

Electrodeposited cobalt is widely used in the computer industry and the multilayer (Co/Cu) of GMR recently. However, only a few studies have been made on the electrochemical nucleation mechanisms of Co electrodeposition[1-4]. Chronoampero- metry is a technique being suitable for electrochemical nucleation mechanisms studies because it provides the current-time transients (CTTs), which give the direct information about the nucleation kinetics and crystal growth process. CTTs resulted from electrocrysyallization for different substrates commonly present only one maximum. This characteristic feature indicates that the mechanism of electrocrystallization is related to one kind of nucleation process. As for CTTs with complex shapes, a rather few studies concerning the electrocrystallization were reported[1,2,5]. In this paper, we reported the nucleation mechanism of cobalt based on the CTTs with complex shapes by using a glass carbon electrode in acidic cobalt electrolyte.

Experimental

A conventional three-electrode cell, equipped with a big area platinum foil counter electrode and a saturated calomel electrode (SCE), was used. All the potentials were quoted with respect to the SCE. The glass carbon electrode was a rod, 3 mm in diameter. The disc electrode was carefully polished with successively finer grades of alumina slurry down to 0.05 μm, and then cleaned ultrasonically in distilled water to remove any residues from the polishing process. It was then rinsed with distilled water *prior to* each

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experiment.

1.0 mol/L $CoSO_4$ solution was prepared from analytical grade reagents using triply distilled water and deaerated *prior to* each experiment. Solution was unstirred during the experiment. The current transients were performed with a single negative potential step from the open-circuit potential to the potential that deposition of Co would occur. All the current transients were carried out on a CHI660 Electrochemical Analysis System (CH Instruments) at ambient temperature.

Results and Discussion

The BFT model [6] and the Scharifker-Hills model [7] are suitable for treating CTTs with a well-defined maximum. The BFT model described the 2D growth determined by the lattice incorporation of adatoms to the periphery of growing nuclei. The Scharifker-Hills model described the 3D growth under diffusion control. A comparison of the experiment data with theoretical current transients in a non-dimensional form by plotting (I/I_m) *vs* t/t_m and $(I/I_m)^2$ *vs* t/t_m, the nucleation process with 2D and 3D growth can be revealed, respectively. The theoretical transients in non-dimensional form for instantaneous and progressive nucleation with 2D were given by Eq.(1) and Eq.(2), and with 3D growth by Eq.(3) and Eq.(4).

$$\frac{I}{I_m} = (t/t_m)\exp\{-1/2[(t^2 - t_m^2)/t_m^2]\} \qquad \text{(2DI)} \qquad (1)$$

$$\frac{I}{I_m} = (t/t_m)^2\exp\{-2/3[(t^3 - t_m^3)/t_m^3]\} \qquad \text{(2DP)} \qquad (2)$$

$$\frac{I^2}{{I_m}^2} = \frac{1.9542}{t/t_m}\{1 - \exp[-1.2564(t/t_m)]\}^2 \qquad \text{(3DI)} \qquad (3)$$

$$\frac{I^2}{{I_m}^2} = \frac{1.2254}{t/t_m}\{1 - \exp[-2.3367(t/t_m)^2]\}^2 \qquad \text{(3DP)} \qquad (4)$$

A family of current transients obtained for 1.0 mol/L $CoSO_4$ at different potentials was shown in **Figure 1**. The shapes of these CTTs were complex and depended on the applied potential. More than one maximum (M) within the CTTs clearly showed that the cobalt electrocrystallization consists of two or more consecutive nucleation steps. The CTTs also showed that the nucleation rate became fast and the mechanism became more complex with the increase of the potential. A non-linear fitting method showed that the nucleation and growth process actually overlapped during the electrocrystalliza- tion. The Scharifker-Hills and BFT model were used at the same time to identify and interpret the nucleation steps by analyzing the data associated M_1 and M_2 maximum. All the calculated results were shown in **Figure 2**. It can be concluded that the 2DP-2DP nucleation and growth occurred at -0.8 V. However, the experimental data did not fit the theoretical curve well at a given high overpotentials. Such discrepancies had been explained in some references[8]. In our case, the occurrence of hydrogen evolution reaction (HER) may be the main reason [2]. Although the detailed nucleation mechanism was difficult to clarify, it can be deduced that the 2DP-2DP/2DP-3DP nucleation and growth predominated at -1.0V; and 3DI-3DP nucleation and growth at -1.2V.

Figure 1 CTTs for the electrocrystallization of cobalt onto GCE from 1.0 mol/L $CoSO_4$

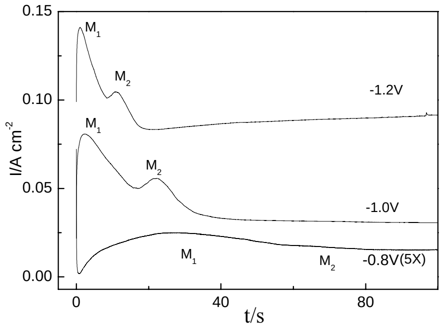
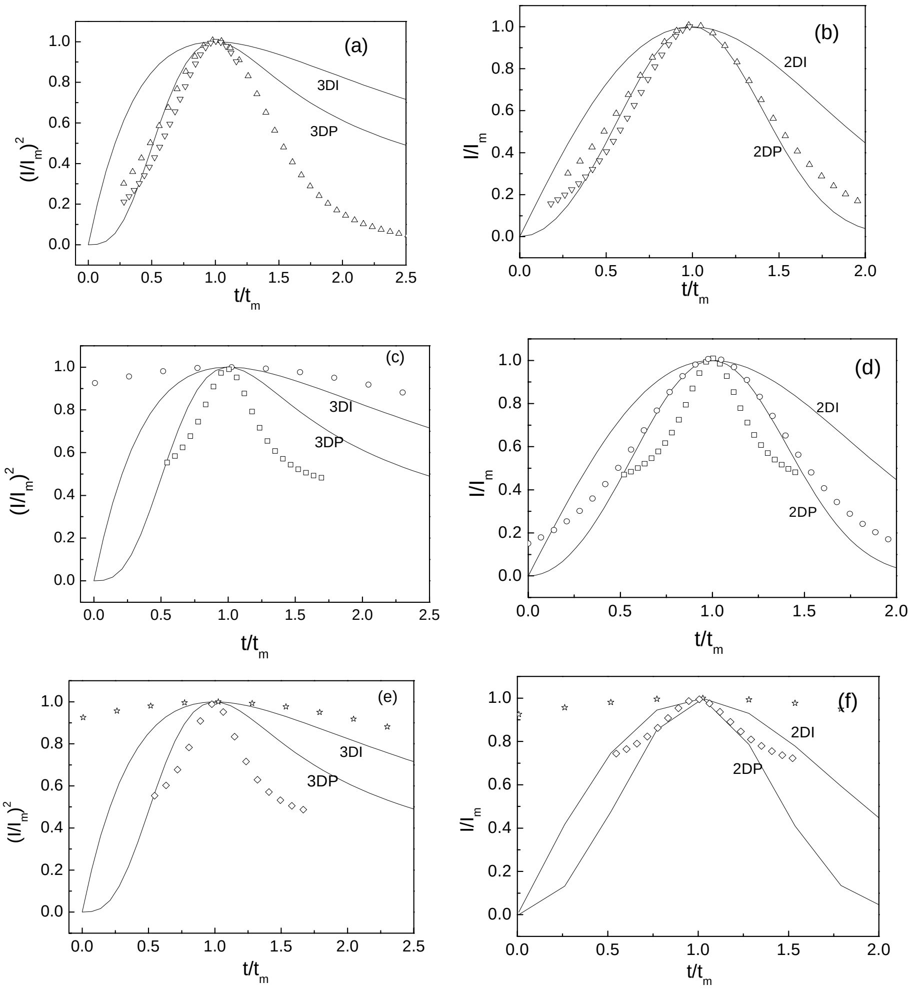


Figure 2 Non-dimensional plots of experiment data (point) and the theoretical curve (lines) associated with M_1 and M_2 maximums at different potentials



(a) and (b) correspond to 3D and 2D models associated with M_1 (△) and M_2 (▽) recorded at –0.8V;
(c) and (d) correspond to 3D and 2D models associated with M_1 (○) and M_2 (□) recorded at –1.0V;
(e) and (f) correspond to 3D and 2D models associated with M_1 (☆) and M_2 (◇) recorded at –1.2V

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