Nucleation and crystal growth in magnetoelectrodeposition

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Abstract
The aim of this work is to overview effects of a homogeneous magnetic field on the nucleation and growth crystal in electrodeposition processes, according to its amplitude and orientation with respect to the substrate. In this presentation, examination of such interest is given after a brief resume of a model that is generally used to describe the current transients corresponding to the early stages of nucleation and growth. Magnetic field superimposition during electrodeposition generates magnetohydrodynamic (MHD) convection and micro-MHD effect that interact on nucleation and growth phenomena from the very first moment of deposit.

Keywords : electrodeposition, magnetic field, magnetoelectrodeposition, nucleation, growth, magnetohydrodynamic convection.

Introduction
The use of magnetic fields on deposition obtained by electrochemical process makes it possible to modify many parameters among which the deposition rate, the homogeneity, the structure and the physicochemical properties of the deposits. Although the action of magnetic fields on the characteristics of electrochemical deposits has been studied by many authors, the details of the mechanisms involved in their synthesis have concerned a smaller number of papers. The interest of magnetoelectrodeposition lies in developing new materials with specific properties such as catalytic or magnetic and/or the use of electrolytic bath without organic molecules that are introduced as levelling agents. The nucleation and growth during electrodeposition are fundamental in obtaining controlled microstructure deposition with specific properties. The thermodynamics and kinetics aspects are therefore very important in electrodeposition technique. The nucleation depends on the characteristics of the substrate surface such as the crystal structure, the lattice orientation, the crystallographic lattice mismatch between the nuclei and the substrate surface, and also the specific free surface energy and the adhesion energy. In order to achieve information concerning the kinetics of the deposit formation by electrochemical processes, it is usual to analyze the current density transients. This has been done for several materials electrodeposited under magnetic field in order to highlight its influence on the nucleation kinetics and growth control and subsequently on characteristics of deposits. Here early stages of electrodepositions of some metals, alloys, oxides and inorganic materials are examined and compared with other examples from the literature [1-9] to highlight the impact of magnetic field, that is usually more prominent when it is applied perpendicularly to the electric field. Micro-MHD effect, due to a non-uniform distribution of the current lines, caused by the edge effects of the electrode surface and the presence of gas bubbles, is also important in other configurations [1].

Magnetoelectrodeposition
When magnetic field is applied parallel to the cathode surface during electrodeposition, the mass transport of electrolyte ions to this surface is increased and electrochemical reaction can be modified. This MHD effect is due to forces, which increase the convection, among which the most important Lorentz force due to the interaction between the magnetic and electric field (maximal when the magnetic field is imposed perpendicular to the direction of the cathodic current), and the paramagnetic force coming from the potential energy possessed by the magnetic dipoles placed in a magnetic field, which acts inside the diffusion layer during a strong concentration gradient in electroactive species due to the electrochemical reactions at the working electrode [10]. The macroscopic stirring is accompanied by microscopic minute vortexes which emerge inside the boundary layer, called the micro-MHD effect. The forces involved in magnetoelectrodeposition may be of electromagnetic origin (Lorentz force) and / or magnetic (paramagnetic) depending on the nature of the
involved ions. The intensity of these convections varies depending on the relative orientation of the electric fields and imposed magnetic fields, and concentrations of ionic species $c$ in the solution.

The forces involved when the magnetic field $B$ is parallel to a plane electrode are:

- the Lorentz force:  
  \[ \vec{F}_L = j \times \vec{B} \] (1)

where $j$ is the current density and $B$ the magnetic field intensity

- the coulombian force:  
  \[ \vec{F}_C = \rho \times \vec{E}_H \] (2)

where $\rho$ is the local space charge and $E_H$ the tangential electrical field.

The forces involved when the magnetic field $B$ is perpendicular to a plane electrode are:

- the magnetic gradient force:  
  \[ F_B = \chi_m B^2 \nabla c / 2 \mu_0 \] (3)

- the paramagnetic force:  
  \[ F_P = \chi_m B^2 \nabla c / 2 \mu_0 \] (4)

where $\chi_m$ and $c$ are respectively the molar magnetic susceptibility and the concentration of the involved species, $\nabla c$ the concentration gradient, $B$ the magnetic field gradient, and $\mu_0$ the magnetic permeability of free space.

![Fig. 1: Electrolytic current lines in the case of a horizontal upward substrate surface](image)

**Chronoamperometric transients**

Depending on the nucleation process during potentiostatic depositions, some typical relationships between the current and the time can be obtained. The growth type can be one, two, or three dimensional. The origin control can be a kinetic one or a diffusion one and the nucleation type can be instantaneous or gradual that means progressive. The instantaneous nucleation corresponds to a slow growth of nuclei with a quite small number of active sites appearing at the same moment. In this case, nuclei are born before being affected by the spreading of nucleation exclusion zones. The progressive nucleation, corresponds to a fast growth of nuclei on many active sites which are progressively born; in that case the break in nucleation process is dominated by spreading of nucleation exclusion zones.

Potentiostatic chronoamperometric transient modelling is usually used to study nucleation process. A classical treatment of the experimental data leads to numerous models [11-14], reviewed by Hyde and Compton [15], that considers that the nuclei are formed according to the equation:

\[ \frac{dN}{dt} = AN_0 e^{-At} \quad \text{or} \quad N = N_0 (1 - e^{-At}) \] (5)

where $t$ is the time since the overpotential is applied to the electrode, $N$ is the number of nuclei, $N_0$ is the saturation nucleus density corresponding to the number of active sites and $A$ is the nucleation rate constant. In order to consider the overlap of diffusion zones, the Avrami’s theorem can be applied. It considers collisions and overlaps of the growing centres in a process of multiple nucleations and growth. According to the Scharifker and Hills’ model [16] considering that the nuclei have a hemispherical form, and with diffusion process during the nucleation, two limiting nucleation mechanisms instantaneous and progressive are described. Normalized transients (corresponding to the ratio of the total current $I$ per the maximum current $I_m$ versus the ratio of the time $t$ per the time $t_m$) are used to discriminate nucleation kinetics.
These curves are representations of some expressions summarized in Table 1 which are typical for the different nucleation processes.

### Tab. 1: Expressions resulting from the analysis of the current maxima from [14].

| Instantaneous nucleation | Progressive nucleation |
|--------------------------|------------------------|
| \( t_n = \frac{1.2564}{NnkD} \) | \( t_n = \left( \frac{4.6733}{ANkD} \right)^\varphi \) |
| \( I_w = 0.63832zFDCF(kN)^{\frac{1}{2}} \) | \( I_w = 0.4615zFDCF(kAN)^{\frac{1}{2}} \) |
| \( I_w^2 t_n = 0.1629(zFc)^{2}D \) | \( I_w^2 t_n = 0.2598(zFc)^{2}D \) |

\[
\frac{I}{I_n} = \frac{1.9542}{I_n} \left\{ 1 - \exp\left[ -1.2564\left( \frac{I}{I_n} \right)^{\varphi} \right] \right\}^{\gamma} \\
\frac{I}{I_n} = \frac{1.2254}{I_n} \left\{ 1 - \exp\left[ -2.3367\left( \frac{I}{I_n} \right)^{\varphi} \right] \right\}^{\gamma}
\]

This model was used in different studies concerning potentiostatic deposition of materials under the superimposition of magnetic field. Usually, the nucleation rate of crystals increases with magnetic flux density as for Nickel or Hydroxyapatite [2-3] or sometimes decreases as for Zinc deposition in overpotential regions [4]. For Ag, Fe and CoFe or CoNiMn alloys electocrystallisation, no effect of a magnetic field on the nucleation processes has been noticed while the growth of nuclei can be affected [5-6]. Cu2O crystal nucleation seems to become instantaneous in the presence of the magnetic field whereas it appears progressive with no magnetic field [7] as it can be seen in figure 2 compared with normalized transients of the two limiting nucleation mechanisms.

**Fig. 2:** Normalized potentiostatic transients for cuprous oxide electrodeposition on horizontal upward stainless steel electrode // B (B ⊥ j).

In a potentiostatic regime and for discrete germs without coalescence, a set of current-time relations for a nucleation independent from the substrate surface state and a growth of germs controlled either by the mass transport, or by the electronic transfer kinetics, has been proposed by Thirsk and Harrisson [17]. The general expression of the current that depends only on the reaction mechanism takes then the following shape:

\[
I = kF^n, \quad (6)
\]

where \( k \) is a constant that depends on the deposited material characteristics and on the reduction mechanism, \( n \) depends on the nucleation/growth type, and on the electrochemical regime control as presented in Table 2. In the case of Mn doped Cu2O deposition, two opposite effects on nucleation are observed considering doping or magnetic field superimposition: Mn2+ ion promotes progressive mode, and magnetic field promotes instantaneous mode.
Tab. 2: Value of the exponent $n$ corresponding to the chronoamperometric curves according to the mechanism of the electrodeposition from [17].

| $n$    | Instantaneous | Gradual | Diffusion |
|--------|---------------|---------|-----------|
| 1      | 2D            | 2D      | 3D        |
| 2      | 3D            | 2D      | 3D        |
| 1/2    | Instantaneous | Gradual | Diffusion |
| 3/2    | Gradual       | 3D      | 2D        |

Concerning the growth process, the MHD convection could principally act on the branching growth without modifying the Cu$_2$O crystal habit (Figure 4) [8]. Due to forces and induced convection, magnetic field can act on the mass transport process at the very beginning of nucleation process and modify the mechanism of crystal or grain growth. Also magnetic field could influence the kinetics of chemical reactions in the electrical double layer [9].

**Conclusion**

Both magnetohydrodynamic convection and micro-MHD effect induce modifications from the very beginning of the growth process.

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