MHD AND MAGNETIC CONVECTIVE EFFECTS ON ELECTROCHEMICAL REACTIONS

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Introduction. If the phenomena concerned with magnetohydrodynamic (MHD) effects in electrochemistry have been largely studied for long [1-3], one can note that the bibliography on the other magnetic field influences in this research field is much more scattered, although rapidly raising during the very last years [4-8]. The first encountered problem is essentially to recognize the nature of the convective forces that a magnetic field creates on the solutions during the electrochemical reaction. If the main forces: the Lorenz force F_L, the paramagnetic force $\mathrm{F}_{\nabla C}$, andthe magnetic gradient force $\mathrm{F}_{\nabla B}$, are now well-known, their respective magnitude remains a problem before being able to discriminate the acting forces and know which of them are dominating. Our present work concerns experimental results allowing a deeper insight on the comparison between MHD and paramagnetic forces to be made.

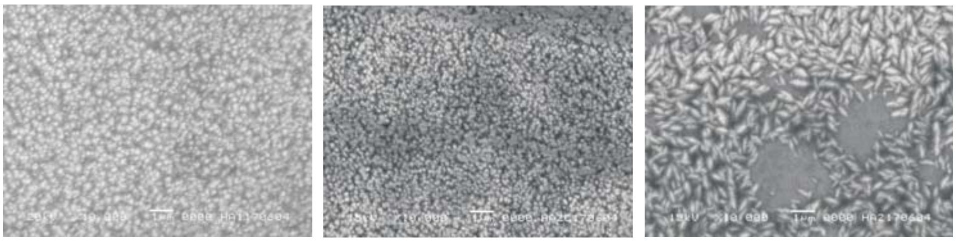
(1) (2) (3)

Fig. 1. SEM micrographies (scale bar 1 μm) of electrodeposited Fe-Co alloys. Magnetic field $B = 0.9$ T. (1) parallel. (2) and (3) perpendicular to the electrode. (2) edge, (3) center of the electrode. Electrolyte: pH = 2.8. ($\mathrm{FeSO_4}$) = 0.05 M; ($\mathrm{CoSO_4}$) = 0.2 M. $T = 25$°C.

1. Experimental.

Experiments have been carried out with a classical three electrode cell that was thermostated (25°C). The electrolyte was a sulfate copper solution (0.1 M or 0.05 M) in dilute sulfuric acid (0.5 M). The working electrode was a flat disc ($\varnothing = 5$ mm) and the counter-electrode was a flat copper foil parallel to the working electrode, either at a long distance for measuring the limiting current or placed to a small distance (≤ 1 cm) for oscillation phenomenon investigations. In the Reims laboratory (DTI), the magnetic field was obtained by the means of an electromagnet (Drusch EAM 20G) controlled by a Hall probe to deliver a constant, homogeneous horizontal magnetic field up to 1.6 T. In the Grenoble High Magnetic Field Laboratory (GHMFL, CNRS) the magnetic field was in the vertical upward direction.

2. Results.

The mean limiting currents for the Cu(II) species reduction are reported in Fig. 2 for two different magnetic field directions and a vertical working electrode. For an horizontal magnetic field parallel to the electrode, according to the magnetic field direction, the Lorenz force acts either in the same

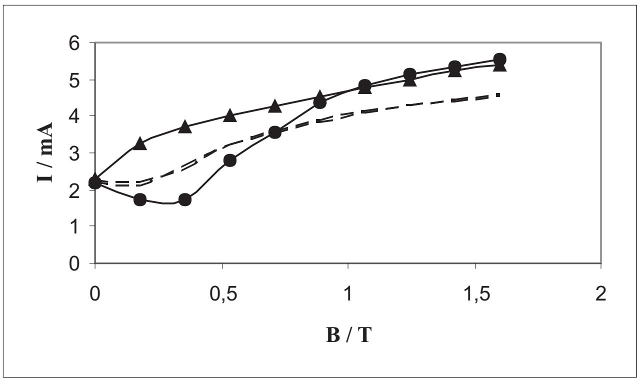

Fig. 2. Limiting current vs. magnetic field for electrodeposition of copper. $CuSO_4$ 0.1 M, H_2SO_4 0.5 M. Vertical working disc electrode (∅ = 5 mm). Horizontal magnetic field **B**: dotted line for **B** perpendicular to the electrode; solid lines for **B** parallel to the electrode with both possible directions: ▲ MHD force in the *g* direction ● MHD force in the opposite direction.

or in the opposite way that the gravitational force g. In the first case, the current increases for any magnetic field value, whereas in the second case, a minimum current is reached because of the opposite convective effects of magnetic field and gravitation. For higher magnetic field amplitudes, the magnetic field effects are predominant in both cases and the current is the same whatever the magnetic field direction.

On the other hand, there is no difference for a magnetic field perpendicular to the electrode. Only a magnetic field threshold can be highlighted that can be ascribed to the gravitational force, which is predominant for low magnetic field amplitudes when the paramagnetic force (that acts on the susceptibility gradient due to the Cu(II) species gradient) is not very effective. Actually, these experiments do not allow us to discriminate between the paramagnetic force and the Lorenz force that could be produced on the edges of the electrode where the current and the magnetic lines are no more parallel and one can even argue that no paramagnetic force occurs in the diffusion layer. The only point that defends any paramagnetic force involvement is the current amplitude increase that seems too

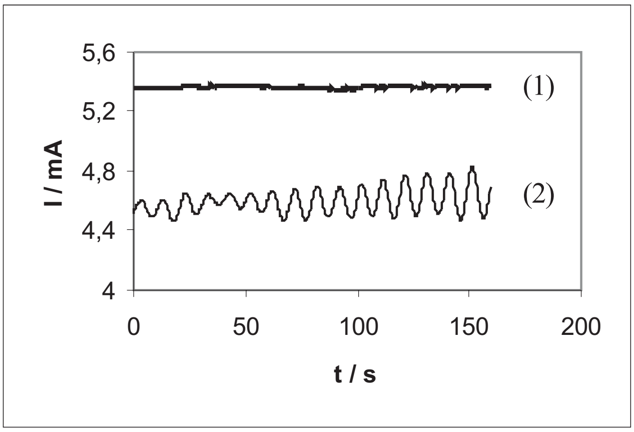

Fig. 3. Chronoamperometric curves for copper electrodeposition (limiting current). Same solution as in Fig. 2. Working electrode (WE) copper ∅ = 5 mm. The counter-electrode (CE) is a copper plate (20 × 20 mm). WE – CE distance = 6 mm. Electrodes are vertical. Horizontal magnetic field **B** = 1 T. (1) **B** is parallel to both electrodes. (2) **B** is perpendicular.

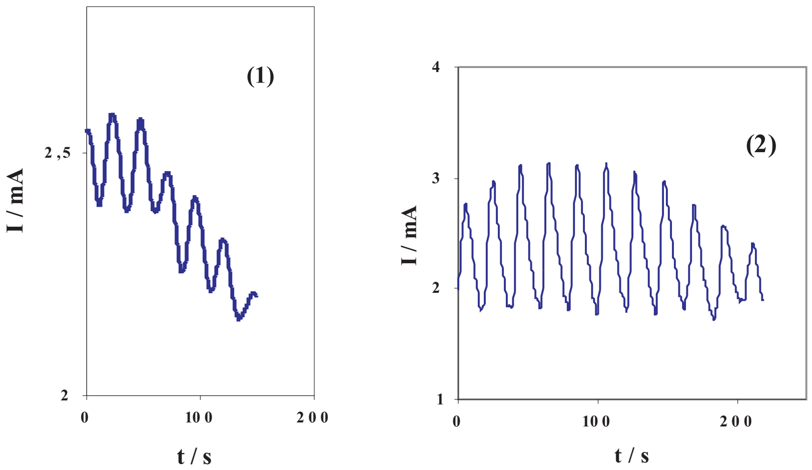

Fig. 4. Chronoamperometric curves for copper electrodeposition. Same electrolyte and electrodes as in Fig. 3. Distance = 1 cm. The magnetic field is perpendicular to the horizontal electrodes. (1) **B** = 1 T; (2) **B** = 1.7 T.

high for edge effects only.

A more pronounced phenomenon arises when magnetic field lines are perpendicular to the working and counter-electrodes that are put face to face. Depending on the distance between both electrodes, their orientation (vertical or horizontal) and the magnetic field amplitude, some oscillations take place. This phenomenon does not occur for a parallel magnetic field [all other conditions being similar (Fig.3)] or when the electrode distance is too large. Up to now, it is not possible to correlate the amplitude of the oscillations with the magnetic field amplitude or with the geometric conditions, nevertheless it is obvious that the oscillation shape and period depend on both parameters (Fig.4).

Oscillations need a threshold magnetic field amplitude and the periode is decreasing with increasing magnetic field (Table 1). With vertical electrodes and all other conditions similar, the periode is twice smaller than for the horizontal case (Fig.4).

Such an effect, that cannot be related to chemical phenomenon as a precipitation – dissolution mechanism of a salt on the electrode surface, is actually due to an interaction of convective processes where an overlap of hydrodynamic layers can be suspected. The present experimental work can provide numerical results to elucidate the relationship between magnetic field and current for paramagnetic convective effects and discriminate the actual relevant parameters of this phenomenon.

Table 1. Periods of the oscillations for electrodeposition of copper. Same electrolyte and electrodes as in Fig. 2. Electrode distance = 1 cm.

B/T	T/s
0.62	11.5
0.88	9.5
0.98	7
1.16	4.5
1.42	4
1.6	3.5

3. Conclusion. The limiting current of copper electrodeposition has been analysed with a magnetic field superimposed in parallel or perpendicular direction. If the mean limiting current values do not allow to compare correctly the involved forces (Lorenz and paramegnetic forces), some oscillations that occur in specific experimental conditions can be the solution to discriminate these forces, thus explaining the microeffects than can be highlighted during alloy (or metal) electrodeposition.

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