HOW TO IMPROVE THE UNIFORMITY OF METAL DEPOSITION AT VERTICAL ELECTRODES BY ELECTROMAGNETIC FORCES

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Abstract : In electrochemical plating often a uniform deposition is desirable allowing to reduce both energy and material costs. Magnetic fields are well known to influence the mass transfer during electrolysis and offer easy control of the deposition process. In this paper, first, time-constant Lorentz forces are considered which, if properly designed, may considerably im-prove the uniformity of the deposit. Second, time-dependent Lorentz forces are investigated. It is demonstrated that pulsed deposition offers a comparable enhancement of the uniformity.

1. Introduction

Both pulse plating and magnetoelectrolysis are convenient techniques capable of improving the quality of electrochemically deposited layers. Pulse plating is based on the modification of the concentration boundary layers at the electrodes by periodic charging and discharging of the electric double layer. Magnetoelectrolysis, on the other hand, employs a Lorentz force density, $\mathbf{f} = \mathbf{j} \times \mathbf{B}$, resulting from the coupling between the electric current density $\mathbf{j}$ in the electrolyte and the external magnetic field $\mathbf{B}$, to force or to modify the convection of the electrolyte. Despite the different underlying mechanisms, similar effects can be achieved. One of the aims of this work is to ask whether a combination of both techniques leads to synergies when aiming at superior homogeneity of the metal deposits.

Indeed homogeneity of the deposit is one of the ultimate goals of any electrodeposition process. According to Faraday's law, inhomogeneities indicate an inhomogeneous current distribution. A main source of inhomogeneities is natural convection. The electrochemical reactions cause concentration and thus density changes near the electrodes which give rise to a buoyant fluid flow within the boundary layers [5]. Regarding a deposition at a vertical cathode in a large cell, the rising fluid flow is responsible for a thickness δ of the concentration boundary layers that increases in the upstream direction as $y^{1/4}$ [6] where $y = 0$ is the leading edge of the cathode. Since j is proportional to $\partial C/\partial x \approx \Delta C/\delta$, a $j \sim y^{-1/4}$ dependence follows. As a consequence, $\mathbf{j}$ is higher at the bottom of the cathode [7], inducing a bigger deposit thickness there. To improve the homogeneity of the deposit, thus saving time and material, homogenization of the concentration boundary layer is vital.

In the first part of this work we examine how this can be achieved by using static Lorentz forces which significantly affect buoyant fluid layers as they emerge [1,8–10]. The second part is devoted to time-dependent Lorentz forces arising from the combinations of modulated current densities j(t) with static magnetic fields [2-4].

2. Presentation of the problem

The setup considered in both experiment and simulation is shown in Fig. 1a. For the electrochemical deposition a cubic glass cell was used (inner side length H=10 mm) with plane vertical electrodes, the anode being a copper plate and the cathode a glass sheet with a 50 nm Au layer (PVD). The size of the electrodes was 10 mm×10 mm with a distance of 8 mm between them. The cell was placed between two identical pairs of NdFeB permanent magnets, each of them connected via an anchor (Fig. 1a). The two pairs were positioned such that their magnetic fields were horizontal but in opposing directions. This generates a magnetic field $\mathbf{B} = (B_0 \pm b \cdot x)\, \mathbf{e_z}$ with a constant gradient b over the whole cell with positive values at one electrode and negative values at the other, where the absolute values as well as the gradient depend on the distance between the two pairs of magnets [12]. A gap of Δx =20 mm provides a magnetic induction of ±125 mT at the electrodes with a gradient of b=±31 T/m, compared to ±175 mT and ±44 T/m at a distance of Δx = 15 mm.

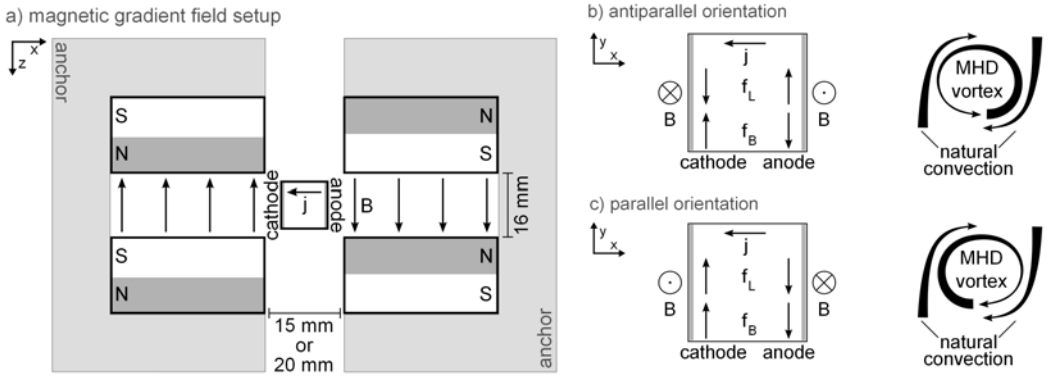

Figure 1: a) Sketch of the setup with magnetic gradient field (top view). (b–c) Scheme of the orientation between the Lorentz and buoyancy force, f and f_B, for antiparallel (b) and parallel (c) configurations along with the resulting convective flow regimes (side view).

Electrodeposition was carried out twice for each flow regime under galvanostatic conditions at 6 mA/cm^2 for 2 h in a 0.05M CuSO4-solution at pH3 (adjusted with H_2SO_4). Subsequently, the cathode was removed from the cell, rinsed with deionized water and EtOH and embedded in acrylic resin (Struers EpoFix). Cutting the specimen into two halves along the vertical centre line produces four samples for each flow regime to be analysed. After polishing and microscopy (TSO long range microscope, 20× magnification, Baumer TXG50 camera, resolution 3.4 px/µm) the thickness of the deposited Cu layer was determined and averaged over the four samples. For the deposition parameters given above, an average layer thickness of d = 16 µm can be predicted according to Faraday's law.

To support the experiments and to develop strategies for an efficient temporal modulation of the Lorentz force, two-dimensional numerical simulations were performed, representing the vertical center plane between the electrodes. For further details of the numerical method we refer to [11, 12, 4].

The relative orientation between the Lorentz force **f** and the buoyancy force $\mathbf{f_b}$ plays a crucial role for the interaction between MHD and natural convection. According to the experimental setup (Fig. 1a), **f** points downward along the y-direction at the cathode and upward at the anode. As a result, a convection roll is established; the axis of which is parallel to the z-axis. The flow of this MHD roll is directed counter-clockwise, i.e. antiparallel to the natural convection as sketched in Fig. 1b. For details, we refer to [13]. Inverting the magnetic field gradient switches the rotation direction of the MHD roll towards a clockwise one, because the Lorentz-force-driven convection is now oriented parallel to the natural convection (Fig. 1c).

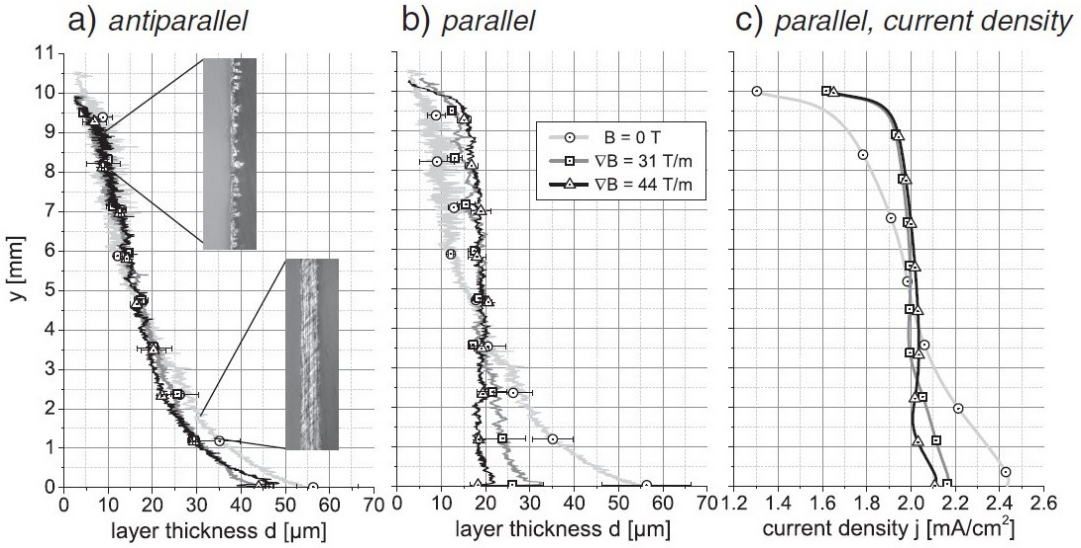

Figure 2: (a,b) Layer thickness measured along the cathode for different orientations of the Lorentz force after 120 min (j=6 mA/cm^2), c) Current density (computed) along the cathode for parallel orientation of Lorentz force and buoyancy force after t=10 min (j=2 mA/cm^2) [1].

Since own previous work showed that the relative orientation of the involved forces substantially affects the flow characteristics and hence the mass transport, the deposit thickness for both regimes is analyzed and compared with the case of pure natural convection.

3. Results for a time-constant Lorentz force

For the reference case without **B** (Fig. 2a, light grey line) it is obvious that the copper deposition is very inhomogeneous, ranging from a thickening at the bottom up to d=55µm toward a decrease to about 10 µm in the upper part. Additionally, dendritic growth structures can be observed within this region (insets in Fig. 2a). When the Lorentz and buoyancy forces are aligned in antiparallel mode (Fig. 1b), only marginal deviations in the shape of the resulting deposit are observed (Fig. 2a, dark-grey and black line). Only the thickening at the bottom is about 5 µm smaller for forced convection, and even a region of dendritic growth can be found between y = 7 and 10 mm.

In contrast to the antiparallel case, the layers deposited when Lorentz force and buoyancy force are oriented *parallel* to each other (Fig. 1c) exhibit a much more uniform shape, shown in Fig. 2b. In this case, the two effects support each other, and the strongly depleted fluid layer in front of the cathode is removed. Cu-ion rich electrolyte is advected from the anode and pushed upwards along the cathode where it serves as a reservoir for deposition. This in turn leads to uniform concentration boundary layers and hence to a homogeneous deposit thickness of about d = 20 µm in a large central part of the electrode.

The improved homogeneity of the deposit layer due to the Lorentz force is also supported by the numerical simulations (Fig. 2c). Qualitatively, the current density resembles the experimental results of deposit thickness discussed above even for this low value of **j**. For both values of the magnetic field gradient, the homogeneity of the current density distribution is improved considerably.

4. Results for pulsed deposition

The main part of the results presented here employs a temporal modulation of the current density with reversal as depicted in Fig. 3. Beside, although not shown, also time-periodic

modulations of the current density without reversal and superimposed temporal modulations of the magnetic field amplitude were considered [4].

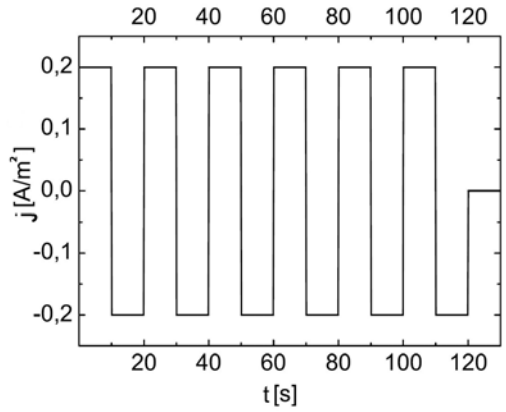

Figure 3: Temporal modulation of the current density j(t) with reversal.

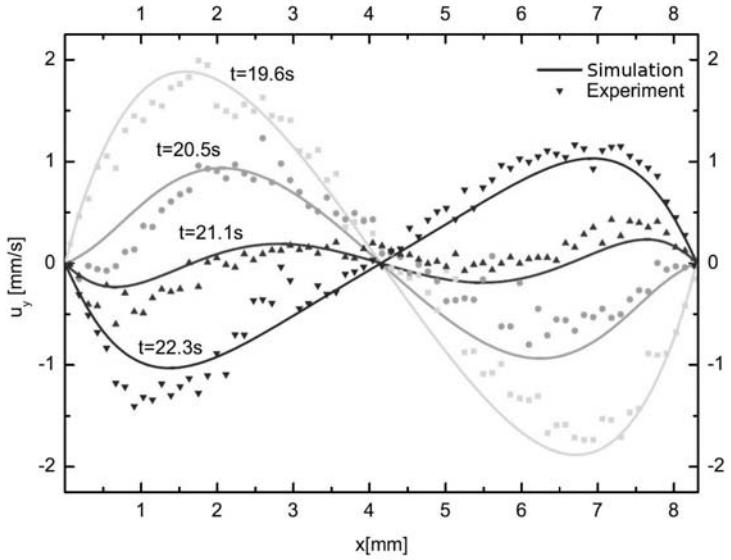

Figure 4: Comparison of measured velocity profiles from [3] with numerical simulations [4].

Fig. 4 shows snapshots of the vertical velocity profiles between the electrodes (placed at x=0 and x = 8.4 mm) near the instant t=20 s where the current density switches from j(t)=-0.2 A/m^2 (squares) to j(t)=+0.2 A/m^2 (triangles), equivalent to a reversal of the direction of **f** at both electrodes. The reversal process in the velocity profiles is nicely seen, and a good agreement between simulation and experiment can be stated. In order to define an electrode-averaged measure for the deviation from uniform deposition $\delta_{cu}(y)$ which locally depends on height y, a mean value and a standard deviation can be defined as

$$\bar{\delta}_{cu} = \frac{1}{L_y}\int_y \delta_{cu}(y)\,dy, \qquad \sigma_r = \int_y \frac{\sqrt{(\delta_{cu}(y)-\bar{\delta}_{cu})^2}}{\bar{\delta}_{cu}}\,dy \tag{1}$$

Fig. 5 shows the temporal evolution of these quantities versus time. The insert highlights the temporal growth of the standard deviation which cannot be avoided in this configuration. The mean value follows a sawtooth behaviour as the net deposition periodically vanishes.

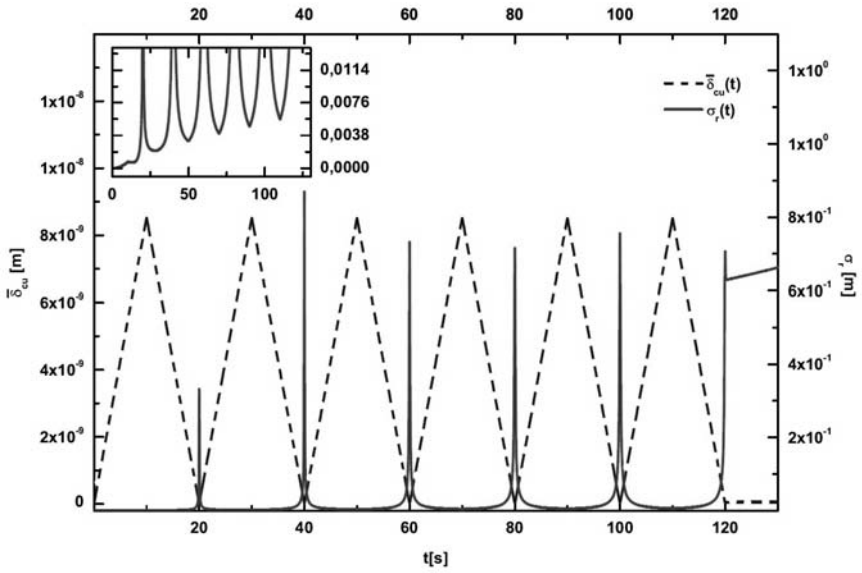

Figure 5: Temporal evolution of the deviation from uniform deposition [4].

5. Conclusion and Outlook

The results presented in this paper clearly show that a properly designed Lorentz force can considerably improve the homogeneity of a metal deposit at vertical electrodes in natural convection conditions. In the case of a nearly time-independent Lorentz force this effect is most pronounced when the latter is orientated in the same direction as the buoyancy force at the electrodes [1]. Furthermore, proper time-dependent Lorentz forces with periodic cell currents are proven to deliver comparable uniformity [2]. A further delay of the build-up of the vertical density stratification which prevents uniform deposition can be achieved when the magnetic field amplitude is used for control in addition. Further results of an advanced temporal management of the current density and of the magnetic field are described in [4] and will be published elsewhere.

6. References

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