



The effects of a magnetic field on the morphologies of nickel and copper deposits: the concept of “effective overpotential”

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Abstract: The morphologies of nickel and copper deposits obtained without applied magnetic fields, and with both parallel and perpendicular applied magnetic fields were examined by the scanning electron microscopy (SEM) technique. Changes in the morphologies of the metals caused by the effect of the magnetic fields are explained by the concept of “effective overpotential”. The morphologies of the nickel and copper deposits obtained under parallelly oriented magnetic fields were similar to those obtained at some lower cathodic potentials without an applied magnetic field. The magnetic field with a perpendicular orientation to the electrode surface increased the dispersity of the nickel and copper deposits. Nickel and copper deposits obtained under this orientation of the magnetic field were similar to those obtained at some higher cathodic potentials without an applied magnetic field.

Keywords: electrodeposition, magnetic field, copper, nickel, SEM.

INTRODUCTION

The effects of a magnetic field on electrochemical processes can be divided into three categories, *i.e.*, those relating to mass transport, electrode kinetics and morphology of the metal deposits.^{1–17} The effect of a magnetic field on electrochemical processes is usually observed through the magnetohydrodynamic (MHD) effect. The origin of this effect lies in the Lorentz force, $F_L = i \times B$, where i is the current density and B is the magnetic field.¹ During electrolysis, this force acts on the migration of ions and induces a convective flow of the electrolyte close to the electrode surface. The largest effect of this force and, consequently, the largest MHD effect are achieved with magnetic fields parallelly oriented to the electrode surface (*i.e.*, when the external magnetic field is oriented perpendicularly to the direction of the ion flux). On the contrary, when a magnetic field is applied perpendicular to the electrode surface, the Lorentz force is zero.

In addition to the Lorentz force, magnetically induced forces which have an effect on electrochemical processes are the magnetic gradient force and the para-

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magnetic force. These are gradient forces and they depend on the magnitude of the magnetic field and not on its direction.^{9,17} Other forces of possible significance in magnetoelectrolysis are the gravitational force $\Delta\rho_g$, which drives natural convection, and the damping force (this force depends on the conductivity of the electrolyte and its velocity, v).⁹

The concept of “effective overpotential” was recently proposed in order to explain the morphologies of electrodeposited copper obtained under conditions of strong hydrogen co-deposition.¹⁸ According to this concept, at high overpotentials when hydrogen evolution is sufficiently vigorous, the electrodeposition process actually occurs at an overpotential which is effectively lower (and for that reason, it is called the “effective overpotential” of the electrodeposition process) than that applied. Then, the morphologies of the deposits become, at the macro level, similar to those obtained at some lower overpotentials when hydrogen evolution does not exist. It was estimated¹⁹ that the quantities of evolved hydrogen enabling the validity of the concept of “effective overpotential” correspond to the average current efficiencies of hydrogen evolution above 10.0 % of about 80.0 mA cm⁻². These quantities of evolved hydrogen were sufficient to cause stirring of the solution in the near-electrode layer, decreasing thereby the thickness of the cathode diffusion layer and increasing the limiting diffusion current density, which lead to a change of the hydrodynamic conditions in the solution.

Bearing in mind that both vigorous hydrogen evolution and an applied magnetic field have an effect on the hydrodynamic conditions in a plating solution, it is logical to assume that the concept of “effective overpotential” can be applied for the case of electrodeposition under imposed magnetic fields. The first report on a possible correlation between the effects of a magnetic field and the concept of “effective overpotential” was recently given¹⁶ for the case of iron electrodeposition under a perpendicularly oriented magnetic field. Nevertheless, a detailed analysis of this correlation was necessary and the aim of this study was its investigation. The effect of magnetic fields on the electrodeposition of magnetic (nickel) and non-magnetic (copper) metals, both under imposed parallel and perpendicular fields will be examined.

EXPERIMENTAL

Working conditions

Nickel was electrodeposited from the following solution: NiSO₄·6H₂O, 262.5 g l⁻¹; NiCl₂·6H₂O, 45 g l⁻¹; H₃BO₃, 37.5 g l⁻¹ and coumarin, 0.060 g l⁻¹ at pH 4.5.

Nickel was deposited potentiostatically at room temperature at cathodic potentials of -1000, -1200 and -1300 mV/SCE, with a counter electrode of electrolytic nickel (99.99 %).

Copper was electrodeposited from 0.2 M CuSO₄ in 0.5 M H₂SO₄, (pH 1.5), at room temperature at a cathodic potential of -500 mV/SCE, with a counter electrode of electrolytic copper (99.99%).

The electrodeposition was performed onto copper electrodes. The positions of electrodes in the electrochemical cells were same in the all cases. The quantities of the electrodeposited metals were 16 mA h cm⁻².

Equipment

The deposition of nickel and copper was performed by use of a bipotentiostat, model AFCBP 1, Pine Instruments Company. The electrochemical cell was plunged into a uniform magnetic field of 500 Oe, which was perpendicular or parallel to the electrode surface using the magnetic system model M-50, MMR Technologies, Inc. The nickel and copper deposits were examined by a scanning electron microscope, model Philips SEM-FEG-XL 30.

A schematic illustration of the electrochemical cell, including the field directions, ion velocity, v , and the flux of ions, J , is given elsewhere.¹²

RESULTS AND DISCUSSION

The nickel deposits obtained at a cathodic potential of -1300 mV/SCE without an applied magnetic field, as well as with both a parallelly and perpendicularly oriented applied magnetic field of 500 Oe, are shown in Fig. 1.

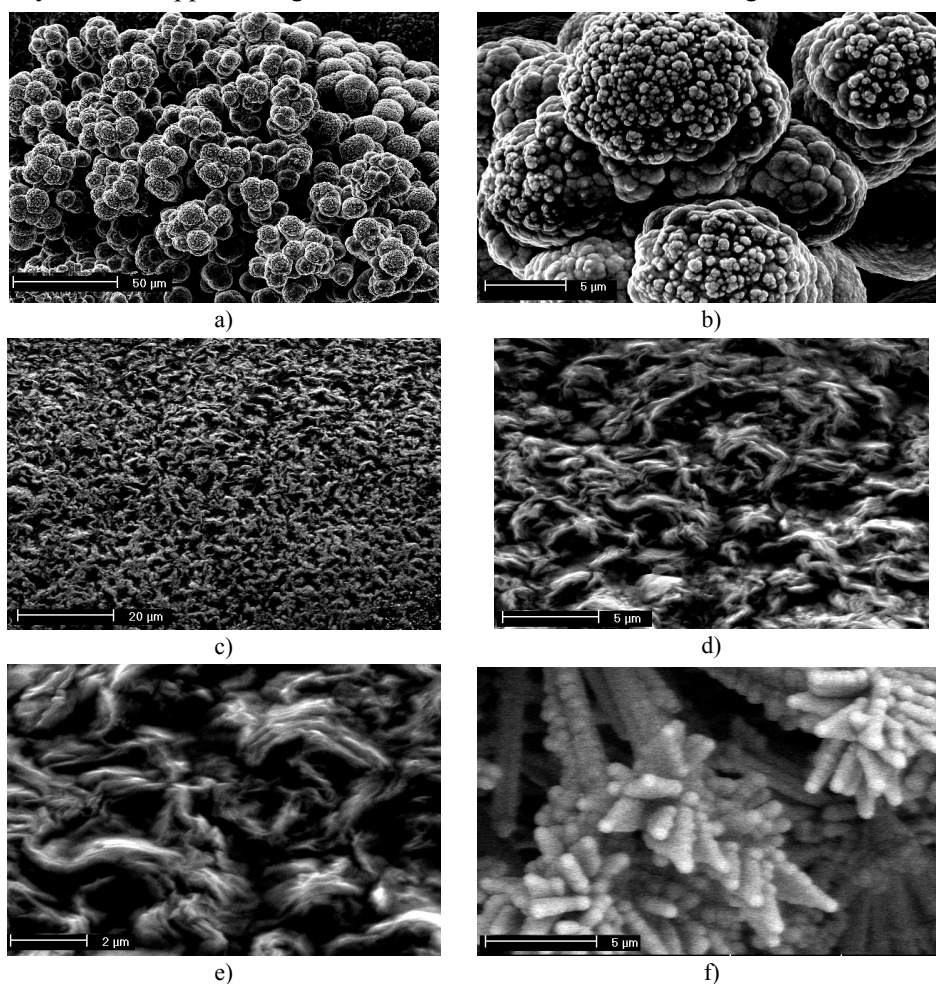


Fig. 1. Nickel deposits obtained at a cathodic potential of -1300 mV/SCE without: a) and b) and with: c), d) and e) a parallelly, and f) a perpendicularly oriented magnetic field of 500 Oe.

Fig. 1a shows that the nickel deposit obtained without an imposed magnetic field had a shrub-like structure. This shrub-like nickel structure consisted of bunched nickel grains. In addition, every nickel grain consisted of very small, probably nano-sized, nickel grains, as shown in Fig. 1b.

The nickel deposit obtained at the same cathodic potential but with the parallel magnetic field is shown in Figs. 1c–1e. This deposit had a porous structure without bunched nickel grains.

The nickel deposit obtained at the same cathodic potential under the perpendicular magnetic field is shown in Fig. 1f. This nickel deposit had a very developed dendritic 3D structure. The structure of this deposit consisted of thin nickel branches or filaments which terminated in flower like aggregates of nickel. The flower like aggregates of nickel also consisted of thin nickel branches (or filaments) made of small, probably nano-sized nickel grains, like a rosary.

The copper deposits obtained at a cathodic potential of -500 mV/SCE without an applied magnetic field, as well as with both a parallel and perpendicularly oriented applied magnetic field, are shown in Fig. 2.

It can be seen from Fig. 2 that the copper deposits obtained without (Figs. 2a and 2b) and with the perpendicular field (Figs. 2e and 2f) had dendritic structures. The copper deposit obtained with the parallel field (Figs. 2c and 2d) had a cauliflower-like structure.

The application of the concept of “effective overpotential” for the case of a change in the hydrodynamic conditions caused by the effects of a magnetic field means that the morphologies of the nickel and copper deposits obtained under parallel fields (the largest MHD effect) should be, at a macro level, similar to those obtained at some lower overpotentials or potentials without an imposed magnetic field. This assumption will be considered below.

The nickel deposit obtained at a cathodic potential of -1200 mV/SCE without an applied magnetic field is shown in Fig. 3a. It can be seen that there is a similarity at a macro level between the morphology of this nickel deposit and the morphology of the nickel deposit obtained at a potential of -1300 mV/SCE under the parallel magnetic field (Figs. 1c – 1e). Both nickel deposits are without dendritic and globular parts and with clearly visible nickel grains. The only difference lies in the compactness of the deposits, which is a consequence of the larger nucleation rate and more intensive hydrogen evolution at a potential of -1300 mV/SCE than at a potential of -1200 mV/SCE.

Also, the concept of “effective overpotential” can be illustrated by the comparison of the nickel deposit obtained at a cathodic potential of -1200 mV/SCE under the parallel magnetic field with the nickel deposit obtained at -1000 mV/SCE without an imposed magnetic field. The morphologies of these nickel deposits are shown in Figs. 3b and 3c. The morphology of the nickel deposit obtained at a potential of -1200 mV/SCE under the parallel field is shown in Fig. 3b, while the

morphology of the nickel deposit obtained at -1000 mV/SCE without applied magnetic fields is shown in Fig. 3c. From Figs. 3b and 3c, it can be observed that there is similarity at the macro level between these nickel deposits. The boundaries between adjacent nickel grains cannot be observed. Nevertheless, the nickel deposit obtained at -1200 mV/SCE under the parallel field (Fig. 3b) was more similar to that obtained at -1000 mV/SCE without an applied magnetic field than to that obtained at -1200 mV/SCE without an imposed magnetic field (Fig. 3a).

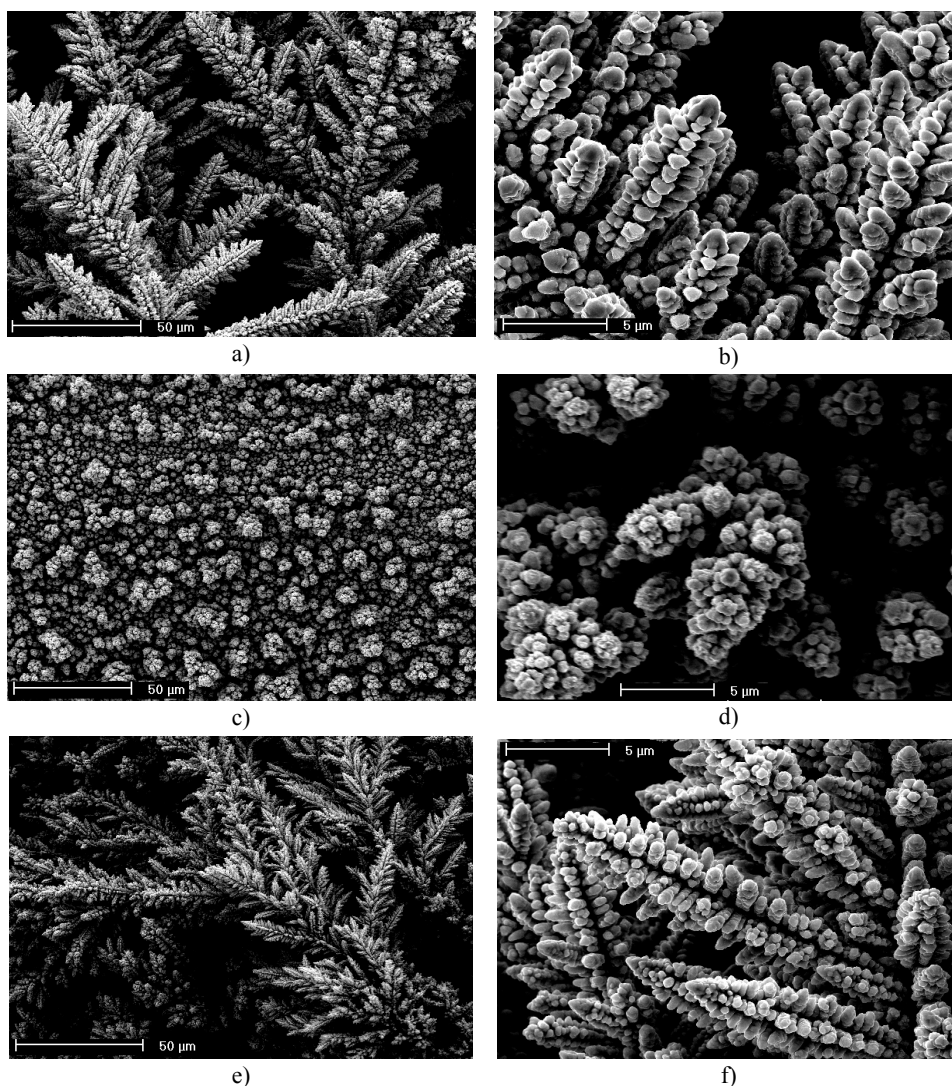


Fig. 2. Copper deposits obtained at a cathodic potential of -500 mV/SCE without: a) and b) and with: c) and d) a parallelly, and e) and f) a perpendicularly oriented magnetic field of 500 Oe.

This concept can also be applied for the case of the electrodeposition of copper. As mentioned earlier, the morphology of the copper deposit obtained at a cathodic potential of -500 mV/SCE under the parallel field had a cauliflower-like structure (Figs. 2c and 2d), while the morphology of the copper deposit obtained without an applied magnetic field had a very dendritic structure (Figs. 2a and 2b). It is known that dendritic structures are main characteristic of electrodeposition under conditions of full diffusion control, while cauliflower-like structures are characteristic of a dominant diffusion control in a mixed control of the electrodeposition process.²⁰

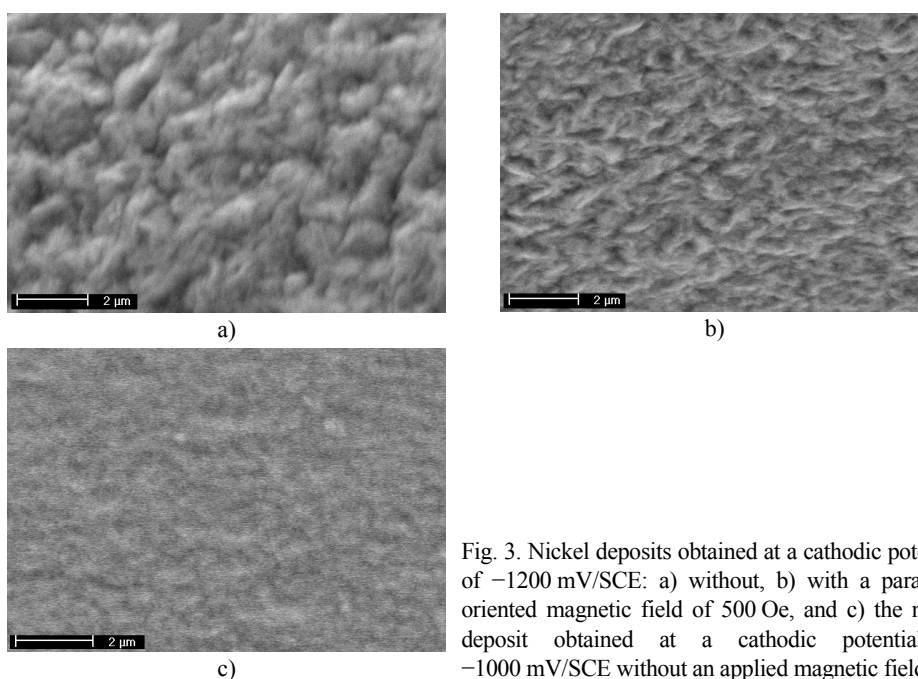


Fig. 3. Nickel deposits obtained at a cathodic potential of -1200 mV/SCE: a) without, b) with a parallelly oriented magnetic field of 500 Oe, and c) the nickel deposit obtained at a cathodic potential of -1000 mV/SCE without an applied magnetic field.

Thus, it can be seen that the application of a parallel magnetic field of 500 Oe led to a shifting of the formation of characteristic morphological forms toward lower cathodic potentials by about 100 – 200 mV. Hence, the obtained morphologies of the nickel and copper deposits can be explained by the concept of “effective overpotential” in the manner below.

The deposition overpotential, η , in the region of mixed activation/diffusion control is given by Eq. (1):²⁰

$$\eta = \frac{b_c}{2.3} \ln \frac{i}{i_0} + \frac{b_c}{2.3} \ln \frac{1}{1 - (i/i_L)} \quad (1)$$

where b_c is the cathodic Tafel slope and i_0 and i_L are the exchange and the limiting current densities, respectively. The activation part of the deposition overpotential required for the charge transfer, η_a , is given by Eq. (2):

$$\eta_a = \frac{b_c}{2.3} \ln \frac{i}{i_0} \quad (2)$$

and the remaining overpotential, η_{diff} , given by Eq. (3):

$$\eta_{\text{diff}} = \frac{b_c}{2.3} \ln \frac{1}{1 - (i/i_L)} \quad (3)$$

is due to mass transfer limitations (diffusion limitation primarily).

The influence of magnetic field appears to be restricted to the diffusion-limited regions. During electrolysis under parallel fields, the Lorentz force induces convective flow of the electrolyte close to electrode surface. A magnetically stimulated convection leads to a decrease in the thickness of the diffusion layer, thus the diffusion-limited current is increased. This will lead to a decrease in the degree of diffusion control of the electrodeposition process, because the current density of the electrodeposition process increases with increasing limiting diffusion current density at a fixed value of overpotential η , and then, η_a should be larger in the presence than in the absence of the effect of a magnetic field. If the applied overpotential remains the same, η_{diff} must decrease. This is only a qualitative analysis, while a quantitative analysis of the change of hydrodynamic conditions has been given elsewhere.¹⁸

As a rule, it was adopted that the limiting diffusion current density depends on magnetic field, as $i_L \propto B^{1/3}$.³ According to Eqs. (1) and (3), increasing the limiting current density leads to a decrease of the degree of diffusion control of the deposition process (a decrease of diffusion part in Eqs. (1) and (3)), and then, the electrodeposition process occurs at some overpotential which is effectively lower. This overpotential at which a metal electrodeposition occurs when the change in the hydrodynamic conditions is caused by the effect of an imposed magnetic field (*i.e.*, by the magnetohydrodynamic effect) represents the "effective overpotential" of the electrodeposition process.

This effect of the parallel field is equivalent to those achieved by vigorous hydrogen evolution,¹⁸ rotating the electrode⁹ or vigorous stirring of the electrolyte.⁹

The second special case is that of a magnetic field perpendicular to the plane surface of the electrode. According to MHD theory, for this orientation of a magnetic field to the electrode surface, the Lorentz force is zero, and then, changes in growth processes are not expected (*i.e.*, the expected MHD effect is zero). In this set-up the observed effects can result either from the non-homogeneity of the magnetic field (magnetic field gradient or a ferromagnetic electrode in magnetic induction, or an electrode composed of a magnetized material), or from an effect of the magnetic forces on the concentration gradients of electrochemical species.¹⁷ Hence, the main forces involved when magnetic fields are applied perpendicular to the electrode surface are the magnetic gradient force (which depends

on the field gradient, ∇B) and the paramagnetic force (this force is caused by concentration gradients, ∇c , of paramagnetic ions, Cu^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , *etc.*).

The difference between the morphologies of nickel and copper deposits obtained with the perpendicular field (Fig. 1f and Figs. 2e and 2f, respectively) and those obtained without an applied magnetic field (Figs. 1a and 1b, and Figs. 2a and 2b, respectively) is clearly visible. This difference is larger in the case of the electrodeposition of nickel than in case of copper electrodeposition. The nickel deposit obtained under the perpendicular field had a very developed 3D dendritic structure (Fig. 1f), unlike shrub-like nickel structure (Figs. 1a and 1b) obtained without an applied magnetic field. On the other hand, although both copper deposits had dendritic structures, there was a difference in the ramification of these copper dendrites. The copper deposit obtained under the perpendicular field had a somewhat more ramified structure (Figs. 2e and 2f) than the copper deposit obtained without the imposed magnetic field (Figs. 2a and 2b).

The concept of "effective overpotential" applied to the case of electrodeposition under perpendicular fields means that the electrodeposition process occurs at an overpotential which is effectively higher than the overpotential without an applied magnetic field.

There is the opposite effect to the case of metal electrodeposition under parallel fields. The changes in the morphologies under perpendicularly oriented magnetic fields were similar to those obtained when limiting diffusion current density was decreased. In fact, the possibility of decreasing limiting currents with a perpendicular field was reported recently.²¹ Grant *et al.*²¹ showed that a uniform magnetic field perpendicularly oriented to the microelectrode surface in order to induce rotational flow of the electrolyte causes either an increase or a decrease in the voltammetric limiting currents (from -37 to $+119\%$), depending solely on the size of the electrode. For inlaid disc electrodes with radii less than $100\ \mu\text{m}$, the magnetic field driven flow results in a decrease of the transport limited current, as a consequence of rotational solution flow adjacent to the surface, preventing gravity-driven natural convection. Some similar local effects on electrodeposition on a small scale profile can probably be expected in the case of electrodeposition of both, nickel and copper, similar to the change of mass transfer conditions described by Bockris *et al.*^{22,23}

In the absence of the MHD effect, it is clear that the main forces responsible for the change of morphologies of nickel and copper deposits under perpendicularly oriented magnetic fields are the paramagnetic and magnetic gradient forces. As already mentioned, the paramagnetic force is caused by concentration gradients of paramagnetic Cu^{2+} and Ni^{2+} ions and the effect of this force does not depend on the direction of the magnetic field. The obtained morphologies of nickel and copper deposits under perpendicular fields are similar to those obtained by electrodeposition processes from solutions with lower concentrations of the depositing ions without an applied magnetic field.

The cause of larger change in the morphology of the nickel deposit under the perpendicular field than the change in the morphology of the copper deposit is probably the magnetic character of metallic nickel. Changes in the morphologies of ferromagnetic electrodeposits under perpendicularly oriented magnetic fields are ascribed to some magnetic properties, such as, for example, magnetoresistance^{11,12,15,16} or magnetic anisotropy.⁸

The possible reason for the change in the morphologies of the nickel and copper deposits under perpendicularly oriented magnetic fields is the vigorous evolution of hydrogen at -1300 mV/SCE and -500 mV/SCE, respectively. The fact that the change in the morphology of the nickel deposit under the perpendicular field is only observed by electrodeposition of nickel at -1300 mV/SCE¹⁵ (and not at lower cathodic potentials) clearly indicates to the contribution of the vigorous hydrogen evolution to the change in the morphologies of nickel and copper deposits at high potentials. It can be concluded that the growth of these very developed dendritic deposits is controlled by convective phenomenon caused by the magnetic field and diffusion effects.

For example, Shannon *et al.*⁷ also showed that for a weak value of an applied magnetic field, a change in the morphology of nickel deposits is possible with both parallel and perpendicular fields. This change was ascribed to the existence of a metastable hydrodynamic condition in the plating solution. This metastable condition is subjected to local disturbances *via* the applied magnetic fields and gas evolution. The magnetic field, in addition to acting on the paramagnetic Ni ions, influences the flow dynamics and stability of the evolved gas bubbles.

The larger change in the morphology of the nickel deposit than the change in the morphology of the copper deposit obtained under perpendicular fields can also be ascribed to some other processes characterised only for electrodeposition of nickel. For example, the electrodeposition of nickel was performed from neutral solutions²⁴ and there is a possible effect of local changes of the pH in the vicinity of the electrode due to the co-deposition of the corresponding hydroxides with nickel. In the case of electrodeposition of metals from acid solutions (which is the case of copper from a sulphate solution), there is no effect of local changes of the pH on the morphology of the electrodeposited metals because hydrogen evolution causes only a small change of the pH in the vicinity of the electrode.

In any case, the changes in the morphologies of the nickel and copper deposits caused by the effect of the perpendicularly oriented magnetic field clearly indicate that there was some additional energy introduced by the magnetic field of this orientation. In the case of nickel, this energy was larger than in the case of copper, which is probably the consequence of the magnetic properties of nickel (*i.e.*, the fact that nickel is a ferromagnetic metal).

Finally, the subject of this work was only the analysis of the morphologies of the nickel and copper deposits obtained without and with both parallelly and per-

pendicularly oriented imposed magnetic fields. The obtained metal morphologies are explained very well by the concept of “effective overpotential”. The possible kinetic reasons for the change in the morphologies of the metals under the imposed magnetic fields were not considered.

CONCLUSIONS

Analysis of the morphologies of nickel and copper deposits obtained without and with both parallel and perpendicular fields showed that the concept of “effective overpotential” can be applied for the case when a change of the hydrodynamic conditions is caused by the effect of the magnetic fields (*i.e.*, by the magnetohydrodynamic effect).

The nickel and copper deposits obtained under a parallel magnetic field were similar, at the macro level, to those obtained at lower deposition overpotentials without an applied magnetic field. For example, the nickel deposits obtained at -1200 mV/SCE and -1300 mV/SCE with the parallel field were similar to those obtained at -1000 mV/SCE and -1200 mV/SCE without an applied field, respectively.

On the other hand, the analysis of the morphologies of the nickel deposits obtained under the perpendicularly oriented magnetic field showed that the morphologies of these deposits were similar, at the macro level, to those obtained at some higher overpotentials, but without an applied magnetic field.

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ИЗВОД

УТИЦАЈ ПРИМЕЊЕНИХ МАГНЕТНИХ ПОЉА НА МОРФОЛОГИЈЕ ТАЛОГА НИКЛА И БАКРА: КОНЦЕПТ “ЕФЕКТИВНЕ ПРЕНАПЕТОСТИ”

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Техником скенирајуће електронске микроскопије (СЕМ) су биле испитане морфологије талога никла и бакра добијене без примењеног, као и са паралелно и вертикално оријентисаним магнетним пољима. Промене морфологија талога никла и бакра под утицајем примењених магнетних поља су објашњене концептом “ефективне пренапетости”. Морфологије талога никла и бакра добијене у паралелно оријентисаном магнетном пољу су биле сличне онима добијеним на неким нижим катодним потенцијалима без примењених магнетних поља. Примена магнетног поља са вертикалном оријентацијом према електродној површини је повећала дисперзност талога никла и бакра. Талози никла и бакра добијени под овом оријентацијом магнетног поља су били слични онима добијенима на неким вишим катодним потенцијалима без примењеног магнетног поља.

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