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Effect of magnetic flux-densities of up to 0.1 Tesla on copper electrodeposition[(•)]

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Abstract   The effect of magnetic flux densities (B) between 0.0 and 0.1 Tesla on cathode and anode overpotentials, cell voltage and electrodeposit quality was determined for a lab-scale copper electrowinning cell which operates at industrial current density values. Cell voltage decreases with increasing B. The cathodic overpotential decreases by 30 % when B increases from 0.0 to 0.1 T. The anodic overpotential also decreases with increasing B, but this effect is six times less than the corresponding effect on the cathodic overpotential. Cathodic effects can be predicted by an expression derived from electrochemical kinetics and magnetohydrodynamic theory. Anodic effects cannot be predicted in the same way. The size of grains and intergranular voids decreases and the surface of the electrodeposit becomes smoother as B increases, which means that, in the studied conditions, the quality of the produced copper deposits improves.

Keywords   Magnetic field. Electrodeposition. Copper. Kinetics. Microstructure

Efecto de densidades de flujo magnético de, hasta 0,1 Tesla, sobre la electrodeposición del cobre

Resumen   Se determinó el efecto de densidades de flujo magnético (B) de, hasta 0,1 Tesla, sobre los sobrepotenciales catódico y anódico, la tensión de celda y la calidad del electrodepósito en una celda de electroobtención de cobre que opera a valores industriales de densidad de corriente. La tensión de celda decrece al aumentar B. El sobrepotencial catódico disminuye en 30 % cuando B aumenta de 0,0 a 0,1 T. El sobrepotencial anódico también disminuye al crecer B, pero este efecto es seis veces menor que en el caso catódico. Los efectos catódicos pueden predecirse por medio de una expresión deducida de la cinética electroquímica y la magnetohidrodinámica. No es posible realizar una predicción análoga de los efectos anódicos. El tamaño de los granos y de los huecos intergranulares decrece y la superficie del electrodepósito se hace más pareja al aumentar B, lo que implica que, en las condiciones estudiadas, la calidad del depósito de cobre mejora.

Palabras clave   Campo magnético. Electrodeposición. Cobre. Cinética. Microestructura

1. INTRODUCTION

It has been known for decades that magnetic fields affect both the rate of formation and the microstructure of copper electrodeposits. This work aims to advance towards the knowledge needed to develop electrometallurgical cells which make use of magnetic flux densities of 0.0 to 0.1 T (0 to 1000 Gauss) in order to increase production rates and to improve product quality. A study of the effect of such magnetic flux densities on cell voltage, cathodic and anodic overpotentials and the microstructure of copper deposits is reported.

2. PREVIOUS WORK

Magnetic fields affect both the rate of formation[1-4] and the microstructure of electrodeposits[1 and 3-5]. The magnetic effect may be strong enough to generate an electric current in an electrochemical cell without the use of an external power source. This phenomenon is known as 'magnetoelectrolysis' and a detailed mathematical model has been proposed for it[6].

2.1. Magnetic effects on mass transport

The deposition rate is influenced by the combined effects of magnetic and electric fields on ion

velocity. A force is applied on ions and its magnitude is given by the Lorentz equation:

$$\vec{F} = q\left(\vec{E} + \vec{U} \times \vec{B}\right) \qquad (1)$$

On the other hand, the current density (j) is also affected by the presence of a magnetic field. As a result of the Lorentz force, a convective flow is induced in the electrolyte, the mass transport rate increases and so does the limiting current density (j_L) for copper electrodeposition. The magnetic contribution to the limiting current density is given by:

$$\vec{j}_M = \kappa\left(\vec{E} + \vec{U} \times \vec{B}\right) \qquad (2)$$

Processes which are operated under mass transfer control or mixed control (such as industrial copper electrorefining and electrowinning) will be affected by this increase.

Several semi-empirical expressions for the dependence of j_L on B have been proposed, but it is now generally agreed that, in most cases, j_L is proportional to $B^{1/3}$ [4 and 5]. Under the influence of a magnetic field, j_L is also proportional to $c^{3/4}$ [4] where c is the concentration of the reacting species. It has also been suggested that magnetic fields could influence the electrochemical kinetics by inducing an overpotential, decreasing the hydration number of cations or affecting chemisorption at the interface[7-9]. However, other workers[10] have shown that the apparent exchange current density (i_0) variations result from modifications of the morphology of metallic coatings.

Charge transfer coefficients (α) are not modified when a magnetic field is applied to a $Cu^{2+} \rightarrow Cu^+ \rightarrow Cu^0$ system[11], which indicates that the reaction mechanism is not altered. This is confirmed by the results of other workers: magnetic fields do not alter the exchange current density[10] or the rate-determining step in copper electrodeposition[4 and 12]. Coey and Hinds[4] stated that the magnetic field influences the diffusion rate of copper ions towards the cathode, but not the rate of the charge transfer step which converts cupric ions into neutral copper metal. These authors report a three-fold increase in limiting current density with a magnetic flux density increase from 0.0 to 1.0 T. They also point out that the effect of magnetic fields on the ion diffusion rate can be explained as a result of a decrease in the thickness of the diffusion (depletion) layer adjacent to the cathode. The effect of the field is to induce a slightly stronger convection in the electrolyte. In a specific cell, the diffusion layer thickness decreased from 84 to 28 microns with a magnetic flux density increase from 0.0 to 1.0 T.

For processes under mixed or charge-transfer control operating at constant current density, a magnetic field generates oscillations in the cathode potential[9]. Depending on field strength, the deposition process is inhibited or accelerated. Similar oscillations have been observed in copper anode dissolution[12]. In this case, certain values of magnetic flux density can stop the oscillating behaviour altogether. This phenomenon has the potential of being used as a corrosion control method[1].

2.2. Magnetic effects on deposit microstructure

Electric and magnetic fields interact in a complex fashion to influence the shape and size of metal grains as they grow to form the deposit. This effect is heavily dependent on the relative positions of the electrodes and on the relative orientation of electric and magnetic fields[1 and 13] and remains a matter of controversy.

Early work pointed out that the presence of a magnetic field of 0.54 T, either parallel or perpendicular to the cathode, had no effect on crystal morphology in Fe, Ni and Co deposits[14]. On the other hand, it was shown[15] that the magnetic field enhanced the preferred growth direction in Cu-Ni alloys. This could be explained by means of a proposed theory[9], according to which certain values of the magnetic field influence the quality of the deposits while other values have no effect. Growth of dendrites was inhibited by an applied magnetic field in the case of Zn deposition[15].

Under carefully chosen conditions, magnetic fields can promote the following effects on the deposit: a more uniform morphology, inhibition of dendrite growth, change in macrostress, increased hardness, more uniform current distribution, increased corrosion resistance and composition shift in alloy plating[1]. These effects are more pronounced at low deposition current densities.

Magnetic effects on nickel deposition from Watt's solution (an aqueous solution of nickel sulfate, nickel chloride and boric acid at pH = 4.5) have been recently discussed[5]. The applied magnetic field was parallel to the substrate. In the

absence of a magnetic field, nickel deposits exhibit a mixture of <211> and <100> textures. When a magnetic field of 0.3 to 0.9 T was applied, the <211> orientation became predominant. When an organic inhibitor was added, magnetic effects on the deposit microstructure became more marked.

The authors conclude that the magnetic field acts indirectly on nickel electrodeposition, affecting hydrogen evolution and inhibitor adsorption. They also state that the observed morphological changes are due to an increase in the surface concentration of inhibiting species caused by enhanced mass transport by the magneto-hydrodynamic effect.

2.3. Magnetic effects on the rate of copper electrodeposition

Magnetic fields have an effect on the rate of reactions involving paramagnetic species, in particular, copper ions[6]. The copper/acidic copper sulfate system, typical of copper electrometallurgical processes, has been studied by several authors[2, 11 and 16-18].

For copper electrodeposition, the limiting current density at constant copper concentration was shown to be dependent on B according to $j_L = j_L^0 + 10.916 \, B^{1.6435}$ [19], where j_L^0 is the limiting current density in the absence of a magnetic field. The electrodes were made of non-magnetic material and the magnetic field was parallel to the electrodes. Rotating disc electrode experiments showed that j_L is proportional to the product $B^{1/3} \, c_b^{4/3}$ [11], where c_b is the copper concentration in the bulk solution.

Slow sweep potentiodynamic experiments, showed that the application of a 0.6 T magnetic field clearly increased the cathodic current density in the copper deposition range, while it did not have a noticeable effect on the more cathodic hydrogen evolution range. Anodic copper dissolution remained equally unaffected[2]. These workers found that the cathodic current enhancement depended strongly on the pH of the solution. Current density increase was less than 20 % in the 1.5 to 2.5 pH range, while it sharply increased at pH < 1.0, reaching nearly 120 % at pH = 0.7. These effects were independent of the position of the electrodes with respect to the orientation of the magnetic field.

Weight difference tests showed that, at pH = 0.8, the copper deposition rate more than doubled when a 0.6 T magnetic field was applied compared to the absence of a magnetic field. In a multi-electrode cell, current densities 3 to 4 times higher than normal copper refining c.d.'s were achieved. Solenoidal fields created by winding current carrying wires around the electrochemical cell can increase mass transport to an even greater extent[20-22].

As to the reaction mechanism in copper electro-deposition, in the previous section it was stated that magnetic fields did not affect the exchange current density, the charge transfer coefficient or the rate-determining step (rds), but other workers take a different view[2]. They seem to believe that their results contain large errors due to uncompensated voltage drops in the electrolyte. These authors agree with Mattson and Bockris, proposing the following reaction mechanism for copper electrodeposition in acidic solution:

$$Cu^{2+}(aq) \quad + e \quad \rightarrow \quad Cu^+(aq) \quad \text{slow (rds)}$$
$$Cu^+(aq) \quad + e \quad \rightarrow \quad Cu^0(s) \quad \text{fast}$$
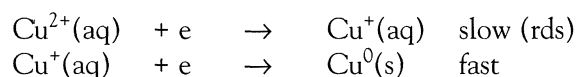
The same workers conclude that the primary effect of the magnetic field is to alter the rate of transport of ions to the cathode surface. The mass transfer coefficient (k) is defined as k = D/δ, where D = diffusivity, m^2/s and δ = diffusion layer thickness, m. It is thereby influenced by the magnetic field. A k change should, in turn, affect the rate of processes under mass transfer or mixed control.

Copper electrorefining cells naturally produce a magnetic field in two ways: first, via the current transported by ions in the electrolyte and second, via the current transported through the bus bars. The generated B value ranges from 10^{-4} to 10^{-2} T [23]. Both the magnitude and direction of B vary in a complex way at different points in and around the cell. The same author points out that the B = 10^{-4} T value can influence the hydrodynamics of the system, while the B = 10^{-2} T value can also influence the electrode processes. The linear velocity of the magnetically induced electrolyte movement is within the 1 to 20 mm/s range. These values are comparable, in order of magnitude, to the linear velocity of the electrolyte movement caused by convection and diffusion.

The same work indicates that a vertically directed B vector causes a slight improvement in the purity and microstructure of copper cathodes and also a better distribution of current during deposition. However, it is pointed out that the magnetic field can also perturb the sedimentation of anodic slimes.

The need for further research in this area has been pointed out in a major review by Fahidy[3]: "... the exact role of magnetism in modifying microscopic as well as macroscopic behavior is not completely understood. Consequently, there exists at present no overall mathematical framework or model that can explain various magnetic field effects within a single cohesive physical or mathematical paradigm...". On the same subject, Coey and Hinds[4], have pointed out: "...(magnetic) fields influence the deposition rate and the morphology of electrodeposits. In some respects these effects are not well understood. (...) If magnetic field effects on the transport of ions in solution prior to crystallization can be better understood, there are prospects for some quite novel practical applications of magnetism...".
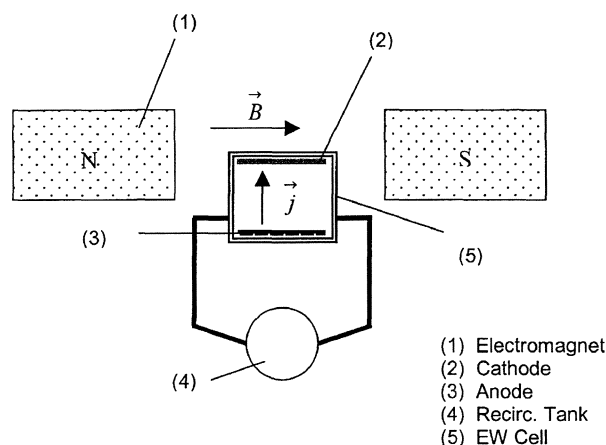
3. EXPERIMENTAL

3.1. Choice of flux density range

In electrometallurgical studies, magnetic flux densities have covered an extremely wide range, which stretches from 0.0 to 5.0 T [24]. The authors have chosen to work at the lower end of the said range. A value of 0.1 T applied to the test cell has been adopted as the upper limit for the present study for two main reasons: a) most of the published work regarding magnetic field effects in electrometallurgy, use magnetic flux densities higher than 0.1 T; b) magnetic flux density values lower than 0.1 T have been shown to affect electrode processes, so their effects are metallurgically significant.

3.2. Experimental procedure

Experiments were conducted in an acrylic copper electrowinning (EW) cell (6 × 6 × 6 cm^3) with electrodes of 5.8 × 5.8 cm^2 surface area. The angle between electric and magnetic field lines was 90° in all cases. The anode was made of lead and the cathode, of electrolytic copper. The backsides of both electrodes were covered with epoxy resin to ensure that only the front faces generated the electric field and sustained the electrochemical reactions. The applied magnetic field was produced by a magnetic field generator (see Fig. 1) formed by two 800-turn-coils made of copper wire of 2.93 mm diameter on an iron body of rectangular cross section (12 × 12 cm^2).

Figure 1. Experimental layout showing the position of magnet, electrowinning cell and recirculation tank.

Figura 1. Esquema experimental que muestra la posición del electroimán, la celda de electroobtención y el estanque de recirculación.

Three series of experiments were conducted in order to establish the effect of magnetic flux density and cell current density on: a) the cell voltage; b) the values of cathodic and anodic overpotentials and c) the microstructure of copper electrodeposits.

The magnetic field generator was fed by two Seegom 40 A, 60 V power sources. The cell current density was generated by a Kenwood PD 35-20 rectifier (20 A, 40 V) and the cell voltage was measured by means of a Hydra computerized multichannel data acquisition unit. For all experiments, one half of the cell is placed between the two end faces of the iron core, which generates a uniform magnetic field (see Fig. 1); this half contains the cathode. The other half of the cell, which contains the anode, is placed outside the uniform magnetic field. The electrolyte is aqueous copper sulfate (40 g/L Cu) and sulfuric acid (180 g/L). It also contains 3 ppm of guarfloc, an additive to improve the quality of the deposit. The solution is recirculated to an ad hoc tank at a low flow rate (about 5 cm^3 per min) and its temperature is kept constant at 21±1 °C.

The studied cell current densities (nominal values, as there were slight variations in surface area from electrode to electrode) were 200, 350 and 500 A/m^2 for the first series and 350 A/m^2 for the second and third series. The studied magnetic field densities were 0, 0.025, 0.05 and 0.1 T. Anode and cathode potentials were measured against a copper / saturated copper sulfate

electrode with Luggin capillary and recorded by means of a Hydra computerized multichannel voltmeter.

Values of the magnetic flux density were measured in the EW cell using an MPS analogue gaussmeter. The measurements were taken while the EW cell was in operation and the magnetic field generator was on. One of the measurements was carried out next to the cathode, in the middle of the highest B, uniform magnetic field zone, and the second one was carried out 6 cm away, next to the anode, in the lower B, non-uniform magnetic field (see Fig. 1). These measurements were carried out for magnetic flux densities of 0.025, 0.05 and 0.1 T in the uniform field zone.

The metallographies were carried out by polishing 0.5×0.3 cm^2 specimens with 600 micron sand paper, 5 micron alumina paste and, finally, 1 micron alumina paste. The specimen was then etched with a 1 g potassium dichromate, 4 ml sulfuric acid and 50 ml distilled water solution to which two drops of hydrochloric acid were added just before etching. The specimen was then washed with distilled water and ethyl alcohol. The metallographs were obtained by means of a Nikon Labophot microscope with an attached photographic camera. The magnification was 20 x.

4. RESULTS

4.1. Effect of the magnetic flux density on cell voltage and overpotentials

Table I gives the results for the cell voltage (V_{cell}) as a function of magnetic flux density (B) and cell current density (j_{cell}). At constant B, the cell voltage increased with increasing j_{cell} for all the studied values. On the other hand, the cell voltage

Table I. Cell voltage (V_{cell}) as a function of magnetic field flux density (B) and cell current density (j_{cell})

Tabla I. Tensión de celda (V_{cell}) en función de la densidad de flujo magnético (B) y la densidad de corriente de celda (j_{cell})

j_{cell}, A m^{-2}	200	350	500
B, T			
0.000	2.232	2.589	2.988
0.025	2.128	2.432	2.903
0.050	2.126	2.421	2.792
0.100	2.112	2.415	2.786

decreased with increasing B for all the studied current densities values.

Table II presents the results for the absolute value of the overpotential (η_c) of the cathodic reaction ($Cu^{2+} + 2e \rightarrow Cu^0$) as a function of magnetic flux density. The absolute value of the cathodic overpotential decreased steadily with B. Its reduction was nearly 30 % for the highest B value.

Table III gives the results for the overpotential (η_a) of the anodic reaction ($2 H_2O \rightarrow O_2 + 4 H^+ + 4e$) as a function of magnetic flux density. It decreased steadily with B. Its reduction was 5 % for the highest B value.

It is worth noting that the variation of the absolute value of the cathodic over-potential with B was about six times larger than the variation of the anodic overpotential with B. Non-uniform magnetic fields have a much more marked effect on mass transport than uniform fields[11]. Results for the variation of magnetic flux density with position in the EW cell are given in table IV and they show that the cell is placed within a non-uniform field, as discussed above. Depending on the applied magnetic flux density, the B gradient ranges from 0.16 to 0.86 T m^{-1} between anode and cathode.

Table II. Cathodic overpotential (η_c) as a function of magnetic flux density (B) at $j_{cell} = 350$ A m^{-2}

Tabla II. Sobrepotencial catódico (η_c) en función de la densidad de flujo magnético (B) a $j_{cell} = 350$ A m^{-2}

B, T	$|\eta_c|$, V
0.000	0.133
0.025	0.130
0.050	0.123
0.100	0.095

Table III. Anodic overpotential (η_a) as a function of magnetic flux density (B) at $j_{cell} = 350$ A m^{-2}

Tabla III. Sobrepotencial anódico (η_a) en función de la densidad de flujo magnético (B) a $j_{cell} = 350$ A m^{-2}

B, T	η_a, V
0.000	0.557
0.025	0.550
0.050	0.543
0.100	0.529

Table IV. Magnetic flux density (B) and its gradient as a function of position in the magnetic field

Tabla IV. Densidad de flujo magnético (B) y su gradiente en función de la posición en el campo magnético

B (cathode)*	B (anode)*	$\dfrac{\partial B}{\partial x}$
T	T	T m^{-1}
0.100	0.045	0.86
0.050	0.022	0.44
0.025	0.015	0.16

* 'Anode' and 'cathode' refer to positions close to the surfaces of the electrodes shown in figure 1.

* Las palabras 'ánodo' y 'cátodo' se refieren a posiciones cercanas a la superficie de los electrodos en figura 1.

4.2. Effect of the magnetic flux density on deposit microstructure

Figures 2 to 4 present the results for the microstructure of the copper electrodeposit as a function of the magnetic flux density. It is patently clear that the grain size decreases with increasing B and the compactness of the deposits increases likewise.

It is also noticeable that the size of voids within the deposit-with the resulting capacity for electrolyte entrapment and deposit contamination - markedly decreases with increasing B.

5. DISCUSSION

5.1. Cell voltage and overpotentials

The results for the dependence of the cell voltage with cell current density (see Table I) were as expected, as the equations of electrochemical kinetics predict that the overpotential of both the cathodic and anodic reactions increase with increasing current density. In addition, the IR_{el} potential drop in the electrolyte also increases with current.

On the other hand, table I shows that the cell voltage decreased with increasing magnetic flux density. This is also borne out by table II, where the cathodic overpotential decreases by 30 % with a magnetic flux density increase from 0.0 to 0.1 T.

Table III shows that the effect of the applied magnetic field on the overpotential of the anodic reaction is far less important. For a magnetic flux
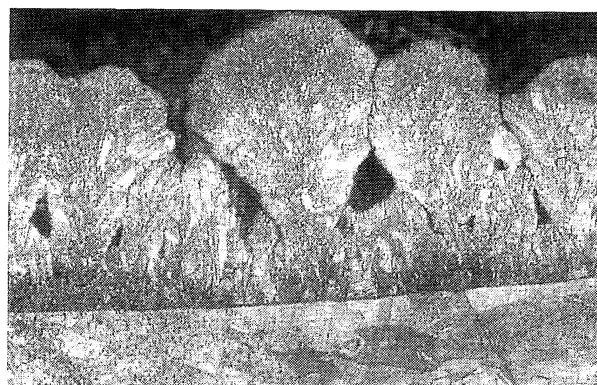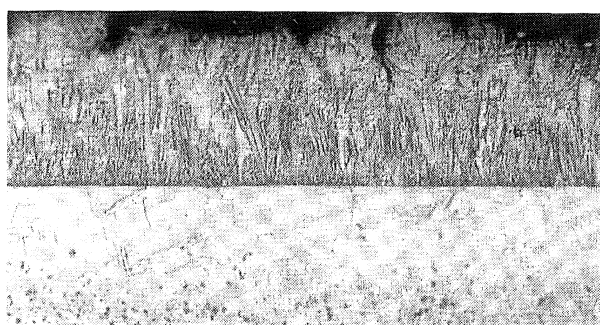

Figure 2. Metallograph for j_{cell} = 350 A m^{-2}, B = 0.0 T, 20 X magnification.

Figura 2. Metalografía para j_{cell} = 350 A m^{-2}, B = 0.0 T, magnificación de 20 X.
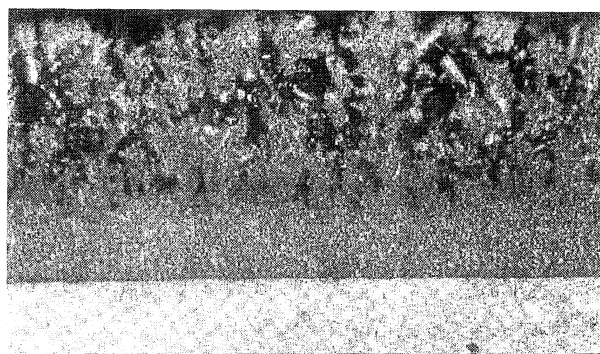
Figure 3. Metallograph for j_{cell} = 350 A m^{-2}, B = 0.05 T, 20 X magnification.

Figura 3. Metalografía para j_{cell} = 350 A m^{-2}, B = 0.05 T, magnificación de 20 X.

Figure 4. Metallograph for j_{cell} = 350 A m^{-2}, B = 0.1 T, 20 X magnification.

Figura 4. Metalografía para j_{cell} = 350 A m^{-2}, B = 0.1 T, magnificación de 20 X.

density increase from 0.0 to 0.1 T, the anodic overpotential decreases by 5 %, i.e. six times less than the effect of B on the overpotential of the cathodic reaction. This is explained by two facts:

a) that in the present work, the anode was placed outside the zone of strongest magnetic force, so that the magnetic effect on anodic processes was weaker (see Table IV) and b) the anodic reaction is under charge transfer control, which means that any effect from the magnetic field on the mass transport rate does not significantly affect its rate. However, it could affect the processes of evolution and adsorption of oxygen bubbles on the anode surface, thereby modifying the value of the cell voltage.

5.2. Microstructure of the electrodeposits

Figures 2, 3 and 4 show metallographs of copper deposits obtained at 350 A m^{-2} in increasing order of the applied magnetic flux density (0.0, 0.05 and 0.1 T).

In figure 2 (no applied magnetic field), both the grain and intergranular void size are the largest. In figure 3 (B = 0.05 T) the grain size is smaller and so is the void size, but the number of voids has increased compared to the no-field case. In figure 4 (B = 0.1 T), the grain size is the smallest and no voids are observed; the deposit is the most compact of the three.

In other words, the figures show that, in the 0.0 – 0.1 T magnetic flux density range: a) the grain size decreases as the magnetic flux density increases; b) the compactness of the deposits also increases with increasing magnetic flux density; c) the deposit surface becomes smoother as the magnetic flux density increases.

Fewer and smaller voids mean that a smaller amount of electrolyte can be trapped in the deposit, thus reducing the amount of impurities in the cathode. This may result in improved chemical quality. At the same time, a higher degree of compactness may result in better mechanical properties for the produced copper. Then, it is possible to conclude that the application of a magnetic field in the studied range may improve the quality of electrodeposits.

5.3. Theoretical aspects

Copper electrowinning is normally carried out under mixed control, i.e., within a cell current density range where the charge transfer and mass transfer rates for copper electrodeposition are similar. In this case, the reaction rate (current density) for the cathodic reaction ($Cu^{2+} + 2e \rightarrow Cu^0$) is given by an expression derived from Butler-

Volmer and Fick equations and a relationship which links them both[25] to give:

$$j_{cell} = \frac{j_{o,c}^b |j_{L,c}|}{j_{o,c}^b + |j_{L,c}| exp\left(\frac{\alpha_c F}{RT}\eta_c\right)} \qquad (3)$$

The cathodic overpotential is then

$$|\eta_c| = \frac{RT}{\alpha_c F} \ln\left(\frac{j_{o,c}^b \left(|j_{L,c}| - j_{cell}\right)}{j_{cell}|j_{L,c}|}\right) \qquad (4)$$

The anodic reaction ($2H_2O \rightarrow O_2 + 4H^+ + 4e$) takes place under charge transfer control and its rate is given by:

$$j_a = j_{0,a}^s exp\left(\frac{\alpha_a F}{RT}\eta_a\right) \qquad (5)$$

The cell voltage is calculated as:

$$V_{cell} = \Delta E_e + \eta_a + |\eta_c| + IR_{el} \qquad (6)$$

where the electrolyte resistance is given by,

$$R_{el} = \frac{1}{\kappa}\frac{l_{ac}}{A} \qquad (7)$$

It has been established that the effect of magnetic fields is to enhance the mass transfer rate of the reacting species towards the reaction site, i.e., the limiting current density is increased by a magnetic term j_M, represented by equation (2).

From equations (2) and (3) an expression which links electrochemical kinetics with magnetohydrodynamics is thus obtained,

$$|\eta_c| = \frac{RT}{\alpha_c F} \ln\left(\frac{j_{cell}|j_{L,c} + j_M|}{j_{o,c}^b|j_{L,c} + j_M - j_{cell}|}\right) =$$

$$= \frac{RT}{\alpha_c F} \ln\left(\frac{j_{cell}|j_{L,c} + \kappa\left(\vec{E} + \vec{U} \times \vec{B}\right)|}{j_{o,c}^b|j_{L,c}| + \kappa\left(\vec{E} + \vec{U} \times \vec{B}\right) - j_{cell}}\right) \qquad (8)$$

The effect of a magnetically-induced limiting current density increase on the cathodic overpotential is qualitatively shown in figure 5 by means of an Evans diagram[26]. When the limiting current density increases from $|j_{L1}|$ to $|j_{L2}|$, the cathodic overpotential decreases from η_1 to η_2. As
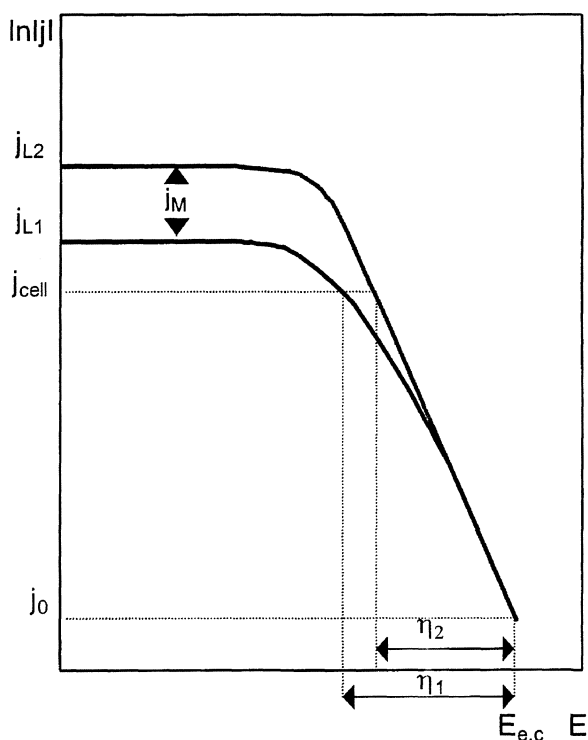
Figure 5. Evans diagram showing the effect of an applied magnetic field on the cathodic overpotential (η). As j_L increases by a magnetically induced current density (j_M), η decreases from η_1 to η_2.

Figura 5. Diagrama de Evans que muestra el efecto de un campo magnético aplicado sobre el sobrepotencial catódico (η). Mientras j_L aumenta debido a una densidad de corriente magnéticamente inducida (j_M), η decrece de η_1 a η_2.

Table V. Data for relevant parameters

Tabla V. Datos para parámetros relevantes

Variable	Value	Unit
$\vec{E}$	40	$V\,m^{-1}$
F	96500	$C\,eq^{-1}$
d_{ac}	0.06	m
R	8.314	$J\,mol^{-1}\,K^{-1}$
T	294	K
$\vec{U}$	$0.5 \cdot 10^{-3} - 1.0 \cdot 10^{-3}$	$m\,s^{-1}$*
j_{cell}	350	$A\,m^{-2}$
$j_{L,c}$	558.8	$A\,m^{-2}$
$j_{0,c}$	34.43	$A\,m^{-2}$
α_c	0.465	-
k	53	$\Omega^{-1}\,m^{-1}$

* Range taken from ref.[4].

* Rango tomado de ref.[4].

the cell voltage is given by equation (6), then a decrease in $|\eta_c|$ leads to a cell voltage reduction.

5.4. Quantification of magnetic effects on the cell voltage

Equation (8) was quantified in order to check its validity in the studied range of magnetic flux densities. Table V presents values for relevant parameters.

For B = 0.0 T, the cathodic overpotential was $|\eta_1|$ = 0.180 V; for B = 0.1 T, it decreased to $|\eta_2|$ = 0.134 V. This represents a confirmation of the predicted decrease in cathodic overpotential with increasing magnetic flux density. Moreover, the calculated value for the cathodic overpotential decrease is 0.046 V, which is close to the measured 0.038 V decrease (see Table II).

A different situation arises when the effect of B on the anodic overpotential is considered. As the anodic reaction is charge-transfer controlled, mass transport phenomena are absent from the

equations of electrochemical kinetics (see eq.5) so that magnetic effects cannot be included. As a result, it is not possible to derive an electrochemical kinetics – based equation for the cell voltage which takes into account all possible magnetic effects, e.g., their influence on the structure of the double layer, on oxygen evolution, chemisorption, adsorption and other anode surface phenomena. However, an empirical equation of the form:

$$V_{cell} = a \left(\frac{j_{cell}}{[Am^{-2}]} \right)^b \left(\frac{B}{[T]} \right)^c + d \qquad (9)$$

with a = $1.482 \cdot 10^{-3}$ V; b = 1.384; c = - 0.066; d = 1.838 V affords good predictions for the cell voltage in the studied B and j_{cell} ranges, with the only restriction that B and j_{cell} must be greater than zero.

6. CONCLUSIONS

For magnetic flux densities in the 0.0 – 0.1 T range applied on a lab-scale copper electrowinning cell operating at industrial-scale values for the cell current density, the conclusions are:

– The copper electrowinning cell voltage decreases with increasing magnetic flux density (B).

- As B increases from 0.0 to 0.1 T, the absolute value of the overpotential of the cathodic reaction decreases by 30 %.
- The overpotential of the anodic reaction also decreases with B, but this effect is six times less than the decrease of the cathodic overpotential for the same B increase.
- The effect of the magnetic flux density on the cathodic overpotential can be predicted and quantified by an equation derived from electrochemical kinetics and magnetohydrodynamics.
- The effect of B on the anodic overpotential cannot be explained using an equation such as the one mentioned in the previous conclusion. An empirical expression has been proposed for the cell voltage as a function of magnetic flux density and cell current density.
- The morphology of the electrodeposits is affected by the magnetic field. Grain size decreases, the size of voids between the grains also decreases and the deposit surface becomes smoother as the magnetic flux density increases. This means that the application of magnetic fields to the studied cell improves the quality of the produced copper cathodes.

Acknowledgments

List of symbols

A : cathode surface area, m^2
$\vec{B}$: magnetic flux density, T [1 T = 10^4 Gauss]
c_i : concentration of species i, mol L^{-1}
D : diffusivity, $m^2\ s^{-1}$
d_{ac} : anode-cathode distance, m
$\vec{E}$: electric field strength, V m^{-1}
$\vec{F}$: Laplace or Lorentz force, N
F : Faraday's constant, 96500 C eq^{-1}
$\vec{j}$: current density, A m^{-2}
j_a, j_c : anodic and cathodic current densities, A m^{-2}
j_{cell} : cell current density, A m^{-2}

j_L : limiting current density, A m^{-2}
j_M : magnetically induced current density, A m^{-2}
j_0^b : exchange current density referred to concentrations in the bulk solution, A m^{-2}
j_0^s : exchange current density referred to concentrations at the electrode surface, A m^{-2}
I : current, A
q : charge, C
R : gas constant, J K^{-1} mol^{-1}
R_{el} : electrolyte resistance, Ω
T : absolute temperature, K
$\vec{U}$: linear velocity of electrolyte, m s^{-1}
V_{cell} : cell voltage, V
z : charge number
α_a, α_c : anodic and cathodic charge transfer coefficients
δ : diffusion layer thickness, m
ΔE_e : difference between the equilibrium potentials of the cathodic and anodic reactions, V
η_c, η_a : overpotentials of cathodic and anodic reactions, V
κ : electrical conductivity of electrolyte, $\Omega^{-1}\ m^{-1}$

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