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EFFECT OF NICKEL AND MAGNESIUM ON ZINC ELECTROWINNING USING SULFATE SOLUTIONS

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Abstract - Zinc electrowinning is performed with the application of a current through insoluble electrodes (Pb-Ag), causing the electrolysis of zinc sulfate, with or without impurities, and zinc deposition on the cathode of aluminum. The impurities can reduce the current efficiency and increase the energy consumption in zinc electrolysis. In this work, the effect of nickel and magnesium on zinc electrodeposition was studied using the electrochemical techniques of galvanostatic deposition and cyclic voltammetry. Additions of nickel, magnesium or both cations in zinc sulfate electrolyte resulted in a marginal increase in current efficiency. Addition of nickel or magnesium polarizes the cathode; however, the extent of polarization in the presence of magnesium is more than that of nickel. Addition of magnesium to the zinc electrolyte caused zinc reduction at a more negative potential. The addition of nickel to the zinc electrolyte increased the current density of the anodic peaks, thus increasing the dissolution of zinc and hydrogenated phases. The addition of nickel to the zinc and magnesium solutions decreased the nucleation loop, facilitating zinc deposition.

Keywords: Electrolysis; Electrolytic zinc; Nickel; Magnesium; Cyclic voltammetry.

INTRODUCTION

One of the greatest changes in the last forty years concerning the application of steel as a structural element was the use of zinc-coated steels for situations that demand a higher corrosion resistance. Galvanized steel can be applied in all industrial segments that normally use cold rolled steels, such as the automotive industry, auto parts, metallic vehicle bodies, home appliances, electro-electronic equipment, steel furniture, civil construction and containers. Zinc is consumed as zinc oxide by several industries such as rubber vulcanizing, cosmetics, medical, and polymers (Roberge, 1999).

One method of production of electrolytic zinc is electrowinning by using sulfate solutions. A current is applied through insoluble electrodes, which causes zinc deposition on the cathode. Several parameters

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*To whom correspondence should be addressed affect zinc electrolysis and its control, such as the zinc concentration in the electrolyte, temperature, current density, acidity and resistivity of the electrolyte, presence of impurities and additives in the electrolyte, and time of electrolysis (Gurmen and Emre, 2003; Alfantazi and Dreisinger, 2003). Industrial plants in Brazil process zinc sulfide mineral and produce electrolytic zinc from sulfate solutions. The first stage of the industrial plant is to roast the zinc sulfide (ZnS) concentrate in the presence of oxygen to produce zinc oxide (ZnO), the sulfide ion being converted to sulfur dioxide (SO_2) gas. The sulfur dioxide is then further oxidized to sulfur trioxide (SO_3), which is dissolved in water to produce sulfuric acid. Some impurities in the original concentrate such as mercury are carried over with the SO_2 gas and have to be removed in order not to contaminate the sulfuric acid. The impure zinc oxide is then leached with sulfuric acid to dissolve the zinc, producing impure zinc sulfate ($ZnSO_4$). The zinc sulfate thus produced is separated from the remaining solids and passes to the next step, which is purification. The purpose of purification is to remove the impurity metals that have dissolved with the zinc. The principal ones are cadmium, copper, cobalt, nickel, iron, antimony, germanium, manganese, and magnesium. Because zinc is a highly reactive metal, this property can be used to remove them. Upon adding powdered zinc to the solution, the zinc is oxidized and dissolves, with concomitant reduction of the other dissolved metals back to their metallic form. In the industrial plant, the content of magnesium in the electrolyte is kept below 14 $g.L^{-1}$. The values of the nickel and magnesium additions to the electrolyte studied in the present work were selected by a Brazilian zinc industry. Despite that fact that the presence of impurities in the electrolyte is a major problem for the zinc electrowinning industry, literature data are scarce and restricted to specific impurities such as antimony (Tripathy *et al*, 2003; Ivanov and Stefanov, 2002, a, b; Stefanov *et al*, 1997), cadmium, iron and copper (Muresan *et al*, 1996). Cadmium favours zinc deposition by diminishing the nucleation overpotential and is co-deposited with zinc on an aluminum cathode (Muresan *et al*, 1996). The grain size of the deposit is larger than in the absence of cadmium. Iron increases the nucleation overpotential, inhibiting zinc deposition, but has no significant influence on the morphology of the deposit when glue is present (Muresan *et al*, 1996). Copper has a harmful effect on zinc electrowinning. The cathodic deposit is non-adherent, consisting of porous microspheres and a parallel discharge of Cu ions takes place (Muresan *et al*, 1996). Antimony causes zinc redissolution (Tripathy *et al*, 2003; Ivanov and Stefanov, 2002; Stefanov *et al*, 1997).

The synergistic interactions between the impurities in the electrolyte determine the quality of the elecrodeposited zinc.

The aim of this work is to study the effect of nickel, magnesium or both on the electrowinning of zinc from sulfate solutions. Cyclic voltammetry was employed to verify the polarization behavior of the cathode and Scanning Electron Microscopy of the zinc deposits was carried out to evaluate the deposit morphology.

MATERIAL AND METHODS

Four types of electrolytes were used: solutions of Zn, solutions of Zn and Ni, solutions of Zn and Mg, and solutions containing cations of Zn, Ni and Mg.

A solution of 60 $g.L^{-1}$ of zinc was prepared by dissolving 262.8 g of $ZnSO_4.7H_2O$ in 1000 mL of distilled water.

Solutions of 60 $g.L^{-1}$ of zinc containing Ni and Mg were prepared by using $NiSO_4.7H_2O$, $MgSO_4.7H_2O$ and distilled water.

The solutions containing Zn and Ni were: 60 $g.L^{-1}$ of Zn and 0.001, 0.004 or 0.008 $g.L^{-1}$ of nickel.

The solutions containing cations of Zn and Mg were: 60 $g.L^{-1}$ of Zn and 5, 10 or 15 $g.L^{-1}$ of Mg.

Solutions of 60 $g.L^{-1}$ of Zn were prepared with the followed associations of Ni and Mg cations: 0.001 $g.L^{-1}$ Ni and 5, 10, or 15 $g.L^{-1}$ of Mg, 0.004 $g.L^{-1}$ Ni and 5, 10 or 15 $g.L^{-1}$ of Mg, 0.008 $g.L^{-1}$ Ni and 5, 10 or 15 $g.L^{-1}$ of Mg.

Electrochemical tests were performed with a Omnimetra PG-29 potentiostat/galvanostat. The electrochemical cell contained three electrodes, an anode of Pb-Ag, a cathode of aluminum, and a reference electrode of Ag/AgCl. Zinc was deposited using galvanostatic deposition, applying a current density of 50.05 $mA.cm^{-2}$. The deposition time was 3 hours. The surface area of the cathode and anode was 1 cm^2. Before testing, cathodes were polished with 600-mesh sandpaper, washed in distilled water and dried. The zinc deposit was removed from the cathode and weighed in a high precision balance.

Applying the Faraday law, the theoretical mass of zinc was calculated:

$$I = nF\frac{dn_i}{dt} \tag{1}$$

where the electric current, in amperes, is given by $I = dQ/dt$ and dn_i/dt represents the rate of reaction in moles per second, n is the number of moles and F is the Faraday's constant. Faraday's Law states that the rate of the electrode reaction is proportional to the magnitude of the electrical current that crosses the electrode-electrolyte interface (Landolt, 1994). The calculated theoretical zinc mass was 184.71 mg. The current efficiency is expressed as the ratio of the deposited zinc mass and the theoretical zinc mass.

Energy consumption (kwh/ton), EC, was calculated by using the equation:

$$EC = \frac{Vm8.4 \times 10^5}{10CE} \tag{2}$$

where Vm is the average potential (V) and CE the current efficiency (%).

The cyclic voltammograms were obtained with up to six cycles at a scanning rate of 0.01 $V.s^{-1}$ according to the literature (Muresan *et al*, 1996). The range of potential was -1600 mV to 0 mV versus Ag/AgCl. For the cyclic voltammetry tests, the cathode of aluminum (0.70 cm^2 in area) was polished with 600 mesh sandpaper, washed in distilled water, and dried. The anode was Pb-Ag and the reference electrode was $Ag/AgCl_{sat}$.

Characterization of the electrodeposited zinc was performed by using scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and X-ray diffraction analysis (XRD). The equipment used was a Jeol model JSM-35 with, 25 kV of accelerating potential and a lateral resolution of 3 µm. The equipment used in the XRD analysis was a Rigaku Geigerflex series, with copper radiation, a step time of one second, and a step size of 0.02°.

RESULTS AND DISCUSSION

Current Efficiency and Energy Consumption

Table 1 shows results for the current efficiency as a function of nickel addition to the zinc sulfate electrolyte. There was an increase in the current efficiency as the nickel content increased, favoring zinc deposition.

However, according to the literature (Stefanov and Ivanov, 2002), the presence of nickel in the acid electrolyte inhibits zinc deposition and causes redissolution of the zinc. Nickel can deposit on the cathode and act as a cathode in microcells, where hydrogen reduction occurs (Stefanov and Ivanov, 2002). The electrodeposited zinc then acts as an anodic region, where oxidation with zinc dissolution occurs. However, in this study, in the pH range from 4.5 to 5.0, hydrogen reduction was minimized. The nickel content of 0.008 $g.L^{-1}$ Ni was insufficient to promote zinc dissolution, with a decrease in current efficiency. One factor which contributes to reduce zinc dissolution is that the anode area was larger than the cathode area (electrodeposited nickel).

Initially, there was an increase in the current efficiency as the magnesium content increased (Table 1). This result is explained by the increase of the electrolyte conductivity. The addition of 15 $g.L^{-1}$ of magnesium caused a decrease of the current efficiency, due to the increase of the viscosity and resistivity of the electrolyte. The high concentration of magnesium cations formed a physical barrier, which hindered zinc diffusion and deposition. The addition of magnesium sulfate to the electrolyte also decreased the solubility of zinc sulfate, decreasing the concentration of zinc ions in the solution. Magnesium, which has a low reduction potential, did not deposit with zinc, remaining in solution.

The addition of nickel to the electrolyte of zinc sulfate with 5 $g.L^{-1}$, 10 $g.L^{-1}$, and 15 $g.L^{-1}$ (Table 1) of magnesium caused an increase in the current efficiency. It is interesting to note that, when nickel is added to the zinc solution in the presence of magnesium, depolarization occurs, facilitating zinc deposition. This indicates that the presence of nickel, even at very low concentrations, affects the zinc deposition behavior and dominates over the effect of magnesium. The nickel addition was not sufficient to generate microcells where the deposited nickel could act as a cathode and the deposited zinc as an anode, favoring zinc dissolution. Another effect of nickel addition is to increase the conductivity of the solution and to optimize electrolysis. Industrial electrolytes contain up to 180-200 $g.L^{-1}$ of H_2SO_4 in order to increase the conductivity. The addition of Ni and Mg ions to the electrolyte plays the same role as acid addition, increasing the conductivity of the solution and the zinc mass deposited.

The addition of nickel to the zinc sulfate electrolyte caused an increase in the current efficiency, causing a decrease in the energy consumption of the process, as shown in Table 2. The addition of nickel cations in the electrolyte generated depolarization and an increase in the conductivity of the solution, increasing the current efficiency and decreasing the energy consumption.

The reduction of energy consumption of an industrial process is very important for environmental and economic reasons, so nickel addition was beneficial to zinc electrolysis.

Table 1: Current efficiency (%) as a function of the addition of nickel and magnesium

	60 $g.L^{-1}$ of Zn	60 $g.L^{-1}$ of Zn and 5 $g.L^{-1}$ Mg	60 $g.L^{-1}$ of Zn and 10 $g.L^{-1}$ Mg	60 $g.L^{-1}$ of Zn and 15 $g.L^{-1}$ Mg
60 $g.L^{-1}$ of Zn	96.82±0.20	97.75±0.35	98.01±0.69	96.96±0.67
60 $g.L^{-1}$ of Zn and 0.001 $g.L^{-1}$ Ni	97.63±0.24	99.04±0.95	98.86±0.90	97.31±0.43
60 $g.L^{-1}$ of Zn and 0.004 $g.L^{-1}$ Ni	97.81±0.25	97.90±0.40	99.58±0.87	98.33±0.71
60 $g.L^{-1}$ of Zn and 0.008 $g.L^{-1}$ Ni	98.27±0.83	99.71±0.52	99.46±0.65	99.93±0.55

Table 2: Energy consumption and cell voltage as a function of the addition of nickel and magnesium.

Solution	60 $g.L^{-1}$ of Zn	60 $g.L^{-1}$ of Zn and 5g. L^{-1} Mg	60 $g.L^{-1}$ of Zn and 10 $g.L^{-1}$ Mg	60 $g.L^{-1}$ of Zn and 15 $g.L^{-1}$ Mg	60 $g.L^{-1}$ of Zn and 0.001 $g.L^{-1}$ Ni	60 $g.L^{-1}$ of Zn and 0.004 $g.L^{-1}$ Ni	60 $g.L^{-1}$ of Zn and 0.008 $g.L^{-1}$ Ni
Energy Consumption/ $KWh.ton^{-1}$	1804.65	1782.81	1761.95	1803.26	1771.96	1761.27	1751.26
Cell Voltage/mV	2184	2178	2159	2185	2060	2051	2048

A trend of reduction of the potential was observed with magnesium addition at 5 and 10 $g.L^{-1}$ (Table 2). The effect on the current efficiency and energy consumption due to the addition of 5 $g.L^{-1}$ and 10 $g.L^{-1}$ of Mg was an increase of the conductivity of solution. These concentrations were not sufficient to promote a steric effect of magnesium ions inhibiting zinc diffusion. Addition of 15 $g.L^{-1}$ of magnesium to the electrolyte promoted an increase of the resistivity and viscosity of the electrolyte and an increase of the potential and the energy consumption. The size of magnesium ions (0.072nm) is close to that of zinc ions (0.074nm) and the high concentration of magnesium ions hinders the diffusion of zinc ions in solution and zinc deposition on the cathode. Krupkowa and Rudy (1972) also observed a potential decrease upon addition of magnesium cations to the electrolyte.

Cyclic Voltammetry

The cyclic voltammograms obtained for the zinc sulfate solutions showed a cathodic peak due to zinc deposition and hydrogen reduction (Saba and Elsherif, 2000) or the formation of hydrogenated phases (Munford, 1998). The onset of depostion occurs at -1040 mV vs.(Ag/AgCl) occurs. Because the metal of the cathode was different from the deposited metal, the beginning of nucleation required more energy to produce the first nucleus. This energy consumpton is evident in the first scan. The cyclic voltammograms exhibited a hysteresis loop of nucleation (Saba and Elsherif, 2000; Munford, 1998).

Cyclic voltammograms were obtained with six potential scanning cycles. The current density of the anodic peak increased until cycle four. As the scanning was performed, an increase of the zinc deposit was observed and, in the anodic region, the complete dissolution of zinc did not occur. However, in the fifth and sixth cycles, the current density decreased. Munford (1998) reported that the removal of the hydrogenated phase occured simultaneously with zinc dissolution and that this removal decreased as the thickness of the zinc deposit increased. The fact that complete removal of zinc did not occur was confirmed by the decrease of the nucleation loop. Thus, the thickness of the zinc deposit increased as the number of cycles increased.

Figure 1 shows the effect of magnesium addition to the zinc sulfate electrolyte. The morphology of the cathodic peak was due to the high concentration of zinc cations and the simultaneous hydrogen reduction reaction. Addition of magnesium inhibits reduction of the zinc. The results of galvanostatic deposition showed that the current efficiency decreased as the magnesium content in the electrolyte increased up to 15 $g.L^{-1}$. The current efficiency obtained using zinc sulfate as electrolyte is similar to the value obtained using zinc sulfate with 15 $g.L^{-1}$ Mg. The deposition occurred at a more negative potential with magnesium addition than in the absence of magnesium. Magnesium addition decreased the potential at which the oxidation peak occurred. Magnesium addition favored zinc dissolution.

The addition of nickel to the electrolyte of zinc sulfate increased the oxidation potential relative to the anodic peak in the cyclic voltammograms, in comparison with the cyclic voltammogram of zinc sulfate (Figure 2). The anodic peak occurred at -521 mV vs.(Ag/AgCl) in the cyclic voltammogram of the zinc sulfate solution and at -374 mV vs.(Ag/AgCl) in the cyclic voltammogram of zinc sulfate with 0.008 $g.L^{-1}$ Ni. The inihibition of zinc deposition was highest for zinc sulfate with addition of 0.004 $g.L^{-1}$ Ni (Figure 2). The effect on zinc deposition was similar in the cyclic voltammograms obtained using zinc sulfate electrolyte without nickel addition and with addition of 0.001 g.L^{-1} and 0.008 g.L^{-1} of Ni. The results of galvanostatic deposition show that the mass of electrodeposited zinc obtained using zinc sulfate with 0.004 g.L^{-1} Ni is lower than that with 0.008 g.L^{-1} Ni. However, the values of the current efficiency obtained using the electrolyte with 0.001 g.L^{-1} Ni and 0.004 g.L^{-1} Ni were similar and higher than the current efficiency obtained for zinc sulfate without nickel addition.

The effect of the addition of nickel on the voltammogram of zinc sulfate with 5 g.L^{-1} of magnesium was studied (Figure 3). An increase of the nickel content in the zinc sulfate eletrolyte with 5 g.L^{-1} Mg increased the current density of the anodic peak. The addition of nickel facilitated zinc deposition. The results of galvanostatic deposition confirmed this result. The addition of 0.001 and 0.008 g.L^{-1} of nickel to the zinc sulfate electrolyte with 5 g.L^{-1} of magnesium increased the mass of electrodeposited zinc and the current efficiency.

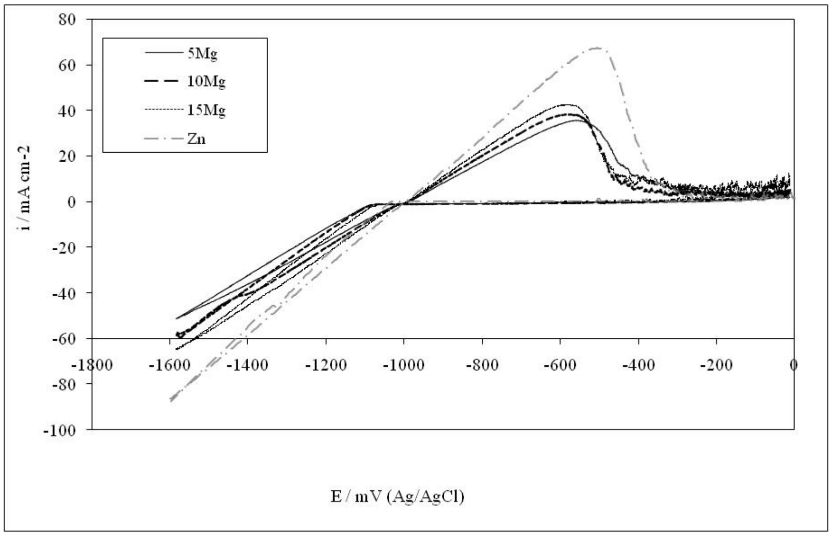

Figure 1: Effect of magnesium addition (5, 10 and 15 g.L^{-1}) on the cyclic voltammograms of 60 g.L^{-1} zinc sulfate electrolyte; scan rate of 0.01V.s^{-1} at room temperature

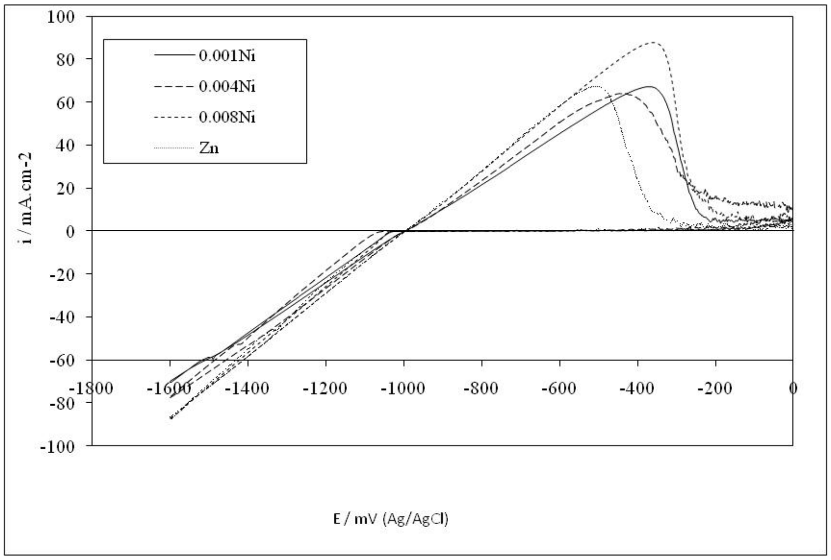

Figure 2: Effect of nickel addition (0.001, 0.004 and 0.008 g.L^{-1}) on the cyclic voltammograms of 60 g.L^{-1} zinc sulfate electrolyte; scan rate of 0.01V.s^{-1} at room temperature

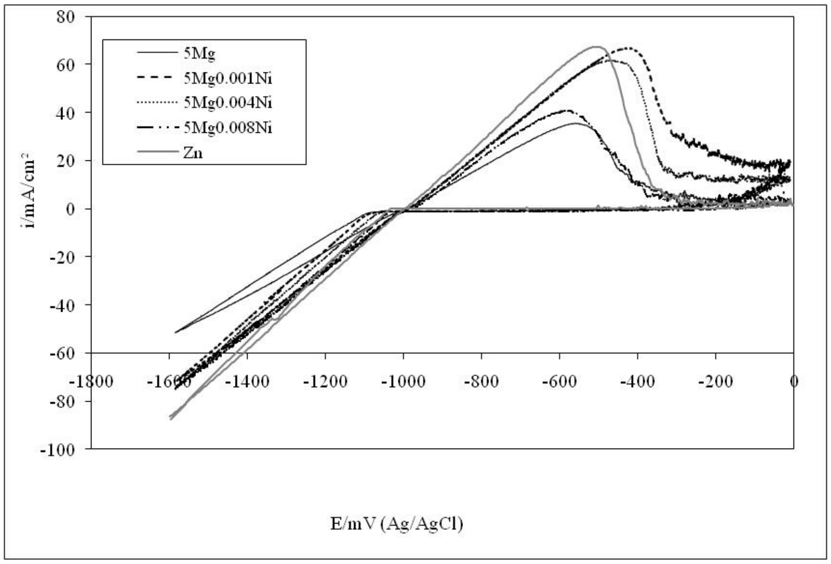

Figure 3: Effect of nickel addition (0.001, 0.004 and 0.008 g.L^{-1}) on the cyclic voltammograms of 60 g.L^{-1} zinc sulfate electrolyte with 5 g.L^{-1}Mg; scan rate of 0.01V.s^{-1} at room temperature

Morphology of the Electrodeposited Zinc

The morphology of the zinc electrodeposited from zinc sulfate was hexagonal, with crystal agglomerates with the same orientation (Figure 4).

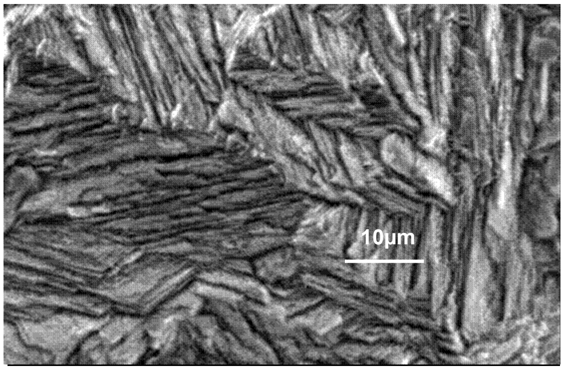

Figure 4: Zinc electrodeposited from zinc sulfate electrolyte.

Addition of magnesium and nickel caused changes in morphology and hexagonal crystals of zinc were not observed. Figure 5 shows a SEM micrograph of zinc deposited from a zinc sulfate solution with 15 g/L Mg and 0.008 g/L Ni. Magnesium (3.1% wt), sulfur (5.9% wt), chlorine (1.9% wt), and potassium (0.8% wt) were identified in the zinc layer (Zn – 88.3% wt) by using energy dispersive spectroscopy analysis (EDS).

The electrodeposited zinc was analyzed by using XRD and only the zinc phase was identified in all samples studied.

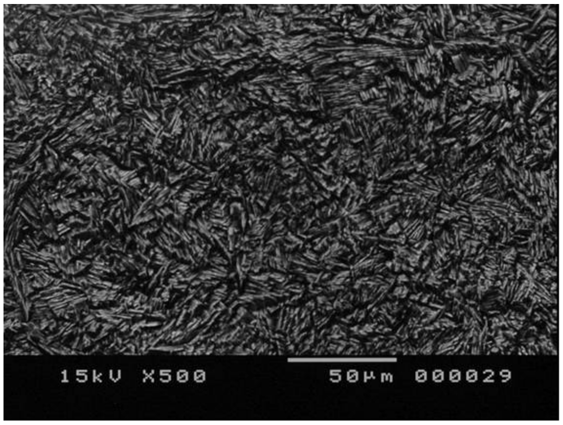

Figure 5: Zinc electrodeposited from the electrolyte with 15 g.L^{-1} Mg and 0.008 g.L^{-1} Ni

CONCLUSIONS

- Additions of nickel to the zinc sulfate solution increased the current efficiency and decreased the energy consumption.
- Addition of nickel to the zinc sulfate electrolyte with magnesium addition up to 15 g.L^{-1} was beneficial to zinc electrolysis, increasing current efficiency.

- The addition of nickel to the electrolyte of zinc sulfate increased the oxidation potential relative to the anodic peak in cyclic voltammograms, in comparison with the cyclic voltammogram of zinc sulfate.
- The increase of nickel content in the zinc sulfate eletrolyte with 5 g.L^{-1} Mg increased the current density of the anodic peak.
- Addition of magnesium to the zinc sulfate solution up to 10 g.L^{-1} increased the current efficiency and decreased the energy consumption.
- The addition of magnesium to the zinc electrolyte caused the occurrence of zinc reduction at a more negative potential.
- Nickel and magnesium addition changed the electrodeposited zinc morphology.
- The morphology of hexagonal crystals of zinc was only observed in the zinc layer electrodeposited from zinc sulfate electrolyte without the addition of nickel and magnesium.

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NOMENCLATURE

BCD region	hysteresis loop of nucleation	
CE	current efficiency	%
dn_i/dt	rate of reaction	Moles per second
EC	energy consumption	Kwh/ton
EDS	energy dispersive spectroscopy	
F	Faraday's constant	Coulomb
I	electric current	Ampere
N	number of moles	Moles
SEM	scanning electron microscopy	
Vm	average potential	Volt

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