



Effect of organic impurities on the morphology and crystallographic texture of zinc electrodeposits



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ARTICLE INFO

Article history:

Received 18 December 2015

Received in revised form 6 February 2017

Accepted 19 February 2017

Available online 24 February 2017

Keywords:

Electrowinning

Zinc

Organic impurities

Current efficiency

Texture

ABSTRACT

This work describes the effect of some organic impurities on the quality of zinc deposits and on the efficiency of the electrowinning process. The presence of some organics (*i.e.*, flotation collectors, flocculant and lubricating oil) in the sulfate electrolyte was shown to significantly decrease current efficiency, thereby increasing energy consumption. Microscopic and texture analyses revealed that the individual addition of these organics to the electrolyte leads to the formation of pores on the deposits, variations in their grain size, and orientation changes resulting in crystallographic randomization with a trend to reorient the crystals from a “perpendicular to the plane” to an “in plane” random distribution. The Zn electrodeposit’s features are expected to affect mechanical properties and, in turn, the effectiveness of the stripping operation.

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1. Introduction

It is well-known that residual amounts of organic compounds may contaminate the feed solution of electrowinning tankhouses. The presence of organic impurities in the sulfate electrolyte during the electrowinning of zinc may significantly affect the current efficiency and the quality of the metal electrodeposited on the aluminum cathodes. Previous works, which focused on the effect of organic compounds, such as acid mist suppressants (Hosny, 1993; Mackinnon, 1994; Dhak et al., 2011), extractants (Mackinnon et al., 1980), surfactants added during pressure leaching (Mackinnon et al., 1988; Alfantazi and Dreisinger, 2003), flotation collectors, flocculant and lubricating oil (Majuste et al., 2015), have confirmed these negative effects, which are typically discussed on the basis of the physical and chemical adsorption of organic molecules on the cathode surface and the reactivity of polar organic functional groups to the Zn^{2+} ion. It is well-established that adsorption of organic molecules on the cathode surface may affect the electron transfer to zinc deposition (Eq. (1)) due to the blockage of a fraction of the active sites available for nucleation (Winand, 1992).



Previous works (Mackinnon et al., 1980; Mackinnon et al., 1988; Hosny, 1993; Mackinnon, 1994; Alfantazi and Dreisinger, 2003; Dhak et al., 2011; Majuste et al., 2015) have also described the effects of the organic compounds on the morphology and crystal structure of the metal product only. What has not been clearly established yet is how the morphology and texture of the electrodeposit will affect its mechanical properties and, thus, the effectiveness of the stripping stage. As the metal deposits are bent during stripping by a force applied to the extremity of the deposit, the resulting deformation may lead to the fracture of the material and to the disruption of the stripping process, with consequent implications in the electrowinning performance.

The present investigation is then motivated by the recognition that a better understanding of the effect of contaminants (organics or inorganics) on the electrowinning of metals should include an evaluation of the stripping behavior of the deposit, which allows a more detailed assessment of product quality. The effect of organic impurities on zinc electrowinning has been selected as a case study in this work. Previous work has indicated that the presence of some organic impurities (*i.e.*, flotation collectors, flocculant and lubricating oil) in the sulfate electrolyte affects the morphology and growth pattern of Zn (hexagonal platelets) deposits, which were produced under batch conditions (Majuste et al., 2015). These organics are used in an industrial plant (Votorantim Metais, Três Marias, Brazil) that combines the processing of silicate and sulfide ores. In the present work, the effect of residual organics on the morphology and crystallographic texture of Zn deposits produced in an electrochemical cell with design and flow regime more similar to

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the industrial set-up is evaluated. The mechanical behavior of the deposits obtained under the experimental conditions described here is discussed in another publication (Majuste et al., 2017).

2. Experimental

2.1. Organic compounds

The selected organic compounds are (a) a flocculant, Flonex® (Organic 1), which is added during thickening, (b) a flotation collector for zinc silicate (willemite – Zn_2SiO_4), Tomamine® (Organic 2), (c) a flotation collector for impurities (carbonates), Rice oil (Organic 3), which also acts as anti-foaming agent in the atmospheric leaching of the zinc ore and (d) a lubricating oil, Husoli GS® (Organic 4), which is used in machinery, including cranes (Table 1). The characteristic functional groups of these organic compounds were analyzed by means of Fourier transform infrared spectroscopy and gas chromatography (GC), as described elsewhere (Majuste et al., 2015).

2.2. Electrowinning

The electrowinning experiments were conducted in a continuous three-electrode cell (0.42 mL/min): two lead-silver (0.5% Ag) anodes and a central aluminum (99.5% purity) cathode in the form of vertically aligned plates (6.0 cm length \times 5.6 cm width cathode; 6.0 cm length \times 4.8 cm width anodes). Cathode and anode are distant by 2 cm. In a previous work (Majuste et al., 2015), the effect of organic impurities was investigated under batch conditions and using a set-up consisting of Al cathodes in the form of vertically aligned disks (10 mm diameter) and a central Pt anode in the form of a vertical rod. In this work, the effect of organics was then investigated using electrochemical cell with design and flow regime more similar to the industrial set-up. The electrochemical cell consisted of a 2 L Pyrex® reactor with a Teflon lid. Prior to each experiment, fresh cathode surface was prepared

by wet mechanical polishing (SiC paper, grit size 1200) and rinsing with deionized water (Millipore® Milli-Q). The experiments were carried out at constant current density (530 A m^{-2}) while stirring (350 rpm). The metal was deposited for a short deposition time, 6 h. This time was selected under the assumption that the main features of the Zn deposits (i.e. porosity, crystal type and size) will prevail at longer deposition times. Synthetic electrolyte consisting of $61.7 \text{ g L}^{-1} \text{ Zn}^{2+}$ and 161.7 g L^{-1} sulfuric acid was prepared with deionized water, analytical grade H_2SO_4 96% (FMaia®) and zinc sulfate heptahydrate >99% (Sigma-Aldrich®). The temperature of the electrolyte was kept constant at $38.0 \pm 0.5 \text{ }^\circ\text{C}$ using a temperature-controlled hot plate (IKA® C-MAG HS7). The organic compounds were added to the electrolyte in two concentrations: 50 and 100 mg L^{-1} . All the experiments were conducted in duplicate.

Following electrowinning, the Zn deposits were manually stripped from the Al cathode, thoroughly rinsed with deionized water and dried in a furnace at $60 \text{ }^\circ\text{C}$ for 30 min. The average mass of the two Zn deposits produced in each test (one per face of the cathode) was measured by an analytical balance with high degree of precision and readability up to 0.1 mg (Mettler AE200). The current efficiency (CE) was determined according to:

$$CE = \left(\frac{nFm}{ItM} \right) \times 100\% \quad (2)$$

where m represents the total weight of the deposit obtained after 6 h (g), n the number of electrons in the overall deposition reaction (2), F the Faraday constant ($96,485 \text{ C mol}^{-1}$), M the zinc atomic weight (65.39 g mol^{-1}), I the total cell current (C s^{-1}), and t the deposition time (s).

2.3. Characterization of the zinc deposits

2.3.1. Morphology analysis


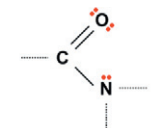


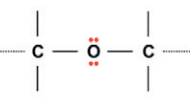

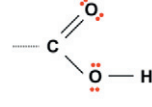
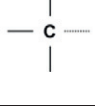
The morphology of the Zn deposits obtained from organic-free and organic-containing electrolytes was analyzed by means of scanning electron microscopy (SEM) coupled to energy dispersive spectrometry (EDS), using a JEOL (JSM 6360 LV) microscope equipped with a Thermo Noran (Quest) spectrometer. The micrographs were obtained using a 15 kV accelerating voltage.

2.3.2. Crystallographic texture analysis

The textures of the Zn deposits were analyzed by X-ray diffraction using a Panalytical MPD diffractometer equipped with $\text{Cu K}\alpha$ radiation, X-ray lens, Euler cradle, graphite monochromator in the diffracted beam and He gas detector. The Schulz reflection method was used and after collection of the main reflection peaks ([001], [100], [101] and [102]) the initial data was corrected for defocusing and further analyzed by WXPpopLA, current W7 implementation of popLA software (Kallend et al., 1991). Orientation Distribution Functions (ODFs) and recalculated pole figures were generated.

Previous works (Dhak et al., 2010; Mackinnon et al., 1990; Tripathy et al., 2004) show various preferential distribution behaviors including intermediate orientations, where neither (001) nor (100) directions seem to be the strongest ones, but always keeping cylindrical symmetry. However, previous works have not measured complete pole figures for characterizing the textures. Only intensity prevalence between different peaks have been taken as a semi-quantitative determination for defining texture characteristics, which is not enough, even in the simplest case of fiber symmetry typically shown by deposition processes. Moreover, poor statistics due to rather coarse grains ($\sim 50 \mu\text{m}$) or a defective evaluation of the machine dependent Lorentz polarization factor, can easily misguide the conclusion. The texture is poorly evaluated, even semi-quantitatively, by that method.

Table 1
Role in the process and functional groups of the selected organic compounds (Majuste et al., 2015).

Organic	Functional groups		
Organic 1 (flocculant)	Alkyl	Amide	
			
Organic 2 (collector for zinc)	Alkyl	Amine	Ether
			
Organic 3 (collector for impurities) ^a	Alkyl	Carboxyl	
			
Organic 4 (lubricating oil)	Alkyl		
			

^aOrganic groups confirmed by gas chromatography.

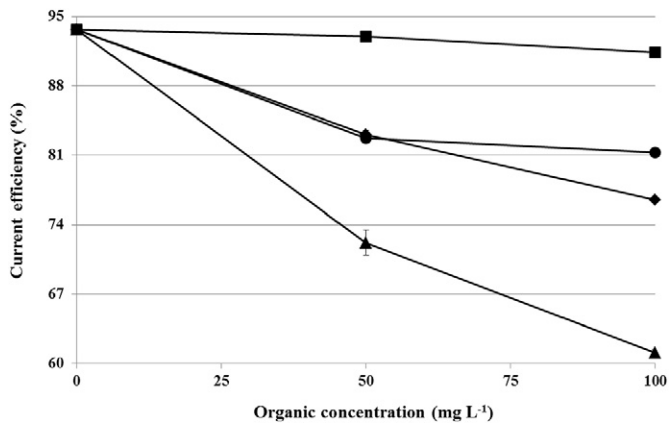


Fig. 1. Zinc electrowinning: effects of the organic compounds on the average values of CE.

3. Results and discussion

3.1. Effect of the organic impurities on the current efficiency

The effect of the organic compounds on the average values of CE is shown in Fig. 1. The CE obtained in the absence of organics in the electrolyte was $93.7 \pm 0.3\%$. The presence of residual amounts of the flotation collector for zinc (Organic 2) in the electrolyte significantly affected the deposition at both concentrations. With the addition of 50 and 100 mg L⁻¹ to the electrolyte, the CE dropped from 93.7 ± 0.3 to 72.2 ± 1.3 and to $61.1 \pm 0.3\%$, respectively. The FTIR analysis of this impurity indicated the presence of non-polar alkyl group and the polar ether (—COC—) and primary amine —NH₂) groups (Majuste et al., 2015). The addition of 50 and 100 mg L⁻¹ of flocculant (Organic 1) decreased the CE from 93.7 ± 0.3 to 83.1 ± 0.4 and to $76.5 \pm 0.2\%$, respectively, while the addition of 50 and 100 mg L⁻¹ of collector for

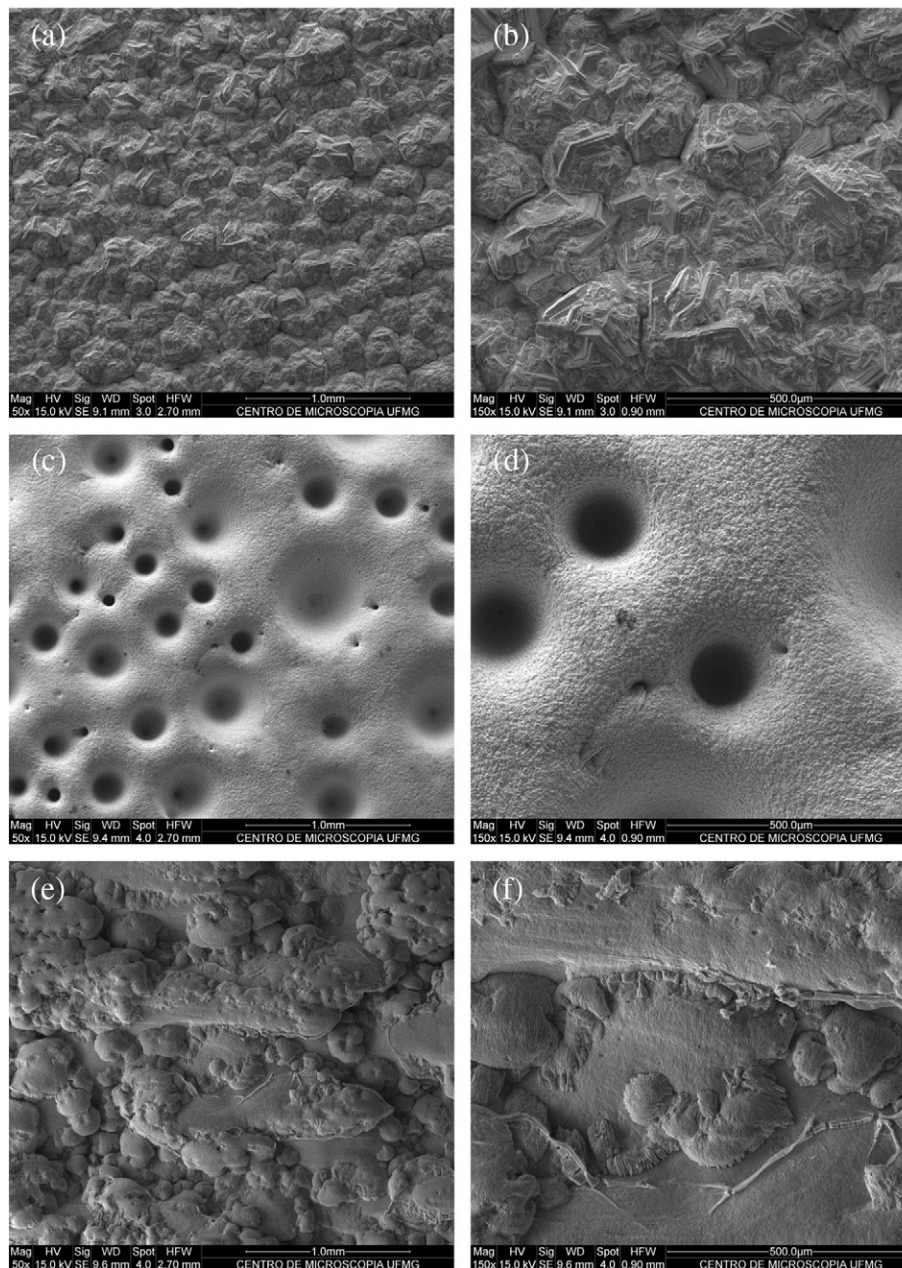


Fig. 2. Typical electron images of Zn deposits (50× and 150×) obtained from (a–b) organic-free electrolyte; (c–d) electrolyte with 50 mg L⁻¹ of collector for zinc (Organic 2); (e–f) flocculant (Organic 1); (g–h) collector for impurities (Organic 3); and (i–j) lubricating oil (Organic 4).

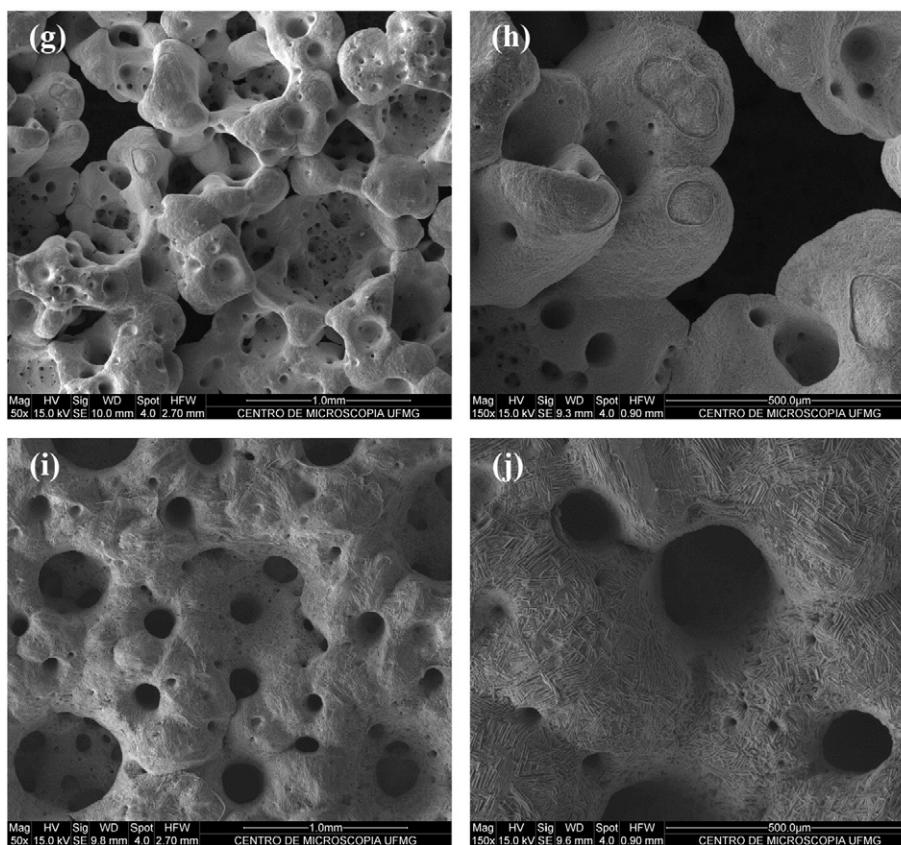


Fig. 2 (continued).

impurities (Organic 3) decreased the CE from 93.7 ± 0.3 to 82.7 ± 0.2 and to $81.3 \pm 0.1\%$, respectively. The FTIR analysis detected the polar primary amide ($-\text{CONH}_2$) and non-polar alkyl groups in the molecule of the flocculant, while the collector for impurities is composed by saturated and unsaturated fatty acids, which contains the polar carboxyl ($-\text{COOH}$) and the non-polar alkyl groups (Majuste et al., 2015). Less pronounced effects were observed when the lubricating oil (Organic 4) was added to the solution (Fig. 1). The average values of CE obtained at 50 and 100 mg L^{-1} are only 0.7 and 2.3 units lower than that determined for the organic-free electrolyte. Only the non-polar alkyl group was detected in the molecule of the lubricating oil. This organic is a saturated hydrocarbon, insoluble in water (Majuste et al., 2015). As discussed later in this paper, Zn deposits obtained from solutions containing this impurity exhibited residual amounts of oil and zinc sulfate (ZnSO_4), which means that the CE values may be slightly lower than the values reported in this paper.

The solubilities of the selected organic compounds are not provided by the manufacturers. In general, the experimental results confirmed that organic molecules with affinity for water may cause strong inhibition of zinc deposition under practical conditions, such as those exhibited by the collector for zinc (Organic 2) and the flocculant (Organic 1). These effects are larger than those observed for the hydrophobic lubricating oil (Organic 4) and the collector for impurities (Organic 3), which is a mixture of fatty acids with relatively low solubility in the electrolyte.

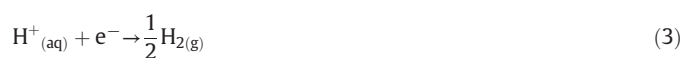
The results obtained with the flocculant (Organic 1) and the collector for impurities (Organic 3) was magnified in the continuous set-up, in comparison with the effects observed by using the mini cell that operates under batch conditions (Majuste et al., 2015). Under flow conditions, a gradual increase of organic molecules at the reaction interface is expected to occur and then a higher impact on the metal deposition rate. The ratio — electrolyte total volume / electrode total area — is equal to 2.28 L cm^{-2} for the continuous cell, while it is equal to

0.42 L cm^{-2} for the mini cell, thus favoring a larger degree of adsorption in the former set-up.

3.2. Characterization of the Zn deposits

3.2.1. Pore

Fig. 2 shows typical electron images of Zn deposits obtained from organic-free electrolyte and organic-containing electrolyte. Only the deposits produced from solutions containing 50 mg L^{-1} of organics were submitted to microscopy analysis. For the organic-free electrolyte, the deposits are apparently smooth with clusters of hexagonal platelets randomly oriented (Fig. 2a and b). Pores were not observed, most likely as a result of the high overpotential for hydrogen evolution (Eq. (3)) on Zn surface. In addition, in the absence of organics in the electrolyte, the metal surface is expected to have a lower metal/electrolyte contact angle (increased wettability), which makes it easier for hydrogen bubbles to detach from the surface.



The electron images of Zn deposits obtained from solutions containing the collector for zinc revealed significant changes in the morphology (Fig. 2c and d). Many pores were observed on the deposit surface, indicating increased hydrogen evolution during the electrowinning, which is consistent with the low values of CE reported in this paper (Fig. 1). The images of Zn deposits obtained from solutions containing the flocculant (Organic 1) (Fig. 2e and f) revealed non-porous deposits consisting of non-homogeneously distributed nodules, of varying sizes and shapes, on layered plateau.

The images of deposits obtained from solutions containing the collector for impurities (Organic 3) show drastic changes in the morphology (Fig. 2g and h). The Zn deposits are highly porous, indicating vigorous

hydrogen evolution, and many areas without metal deposition can also be observed by SEM, which may be ascribed to an initial, physical adsorption of organic molecules, thereby hindering the cathodic reduction of the Zn^{2+} ion. The images of deposits obtained from solutions containing the lubricating oil (Organic 4) also revealed a highly porous deposit (Fig. 2i and j) with fewer areas without zinc deposition. The Zn deposits produced in the presence of Organic 3 are more porous than those produced in the presence of Organic 4 and additionally they include more areas without deposition, which was confirmed in another work (Majuste et al., 2017) through analysis of the fractured surfaces. Thus, it was found that the mass of zinc produced in the presence of the collector for impurities was smaller, as indicated through CE calculations (Fig. 1).

The morphological differences observed between Zn deposits produced under batch conditions (Majuste et al., 2015) and under flow

conditions (this work) are likely associated with the differences reported for the calculated CE values, as previously discussed. The characterization of the Zn deposits produced under batch conditions revealed the formation of pores in deposits obtained from solutions containing the collector for impurities (Organic 3) or the lubricating oil (Organic 4), and different growth pattern was identified when the collector for zinc (Organic 2) was added to the solution. The Zn deposits consisted of hexagonal platelets perpendicularly oriented to the electrode surface, suggesting that only nucleation occurs, which was ascribed to the interaction between the polar amine group detected in this compound and the Zn^{2+} ion. Under flow conditions, the gradual increase of organic molecules at the reaction interface lead to the development of even more porous deposits (case of Organic 3 and Organic 4), while the use of a much larger cathode area may favor the product growth (case of Organic 2).

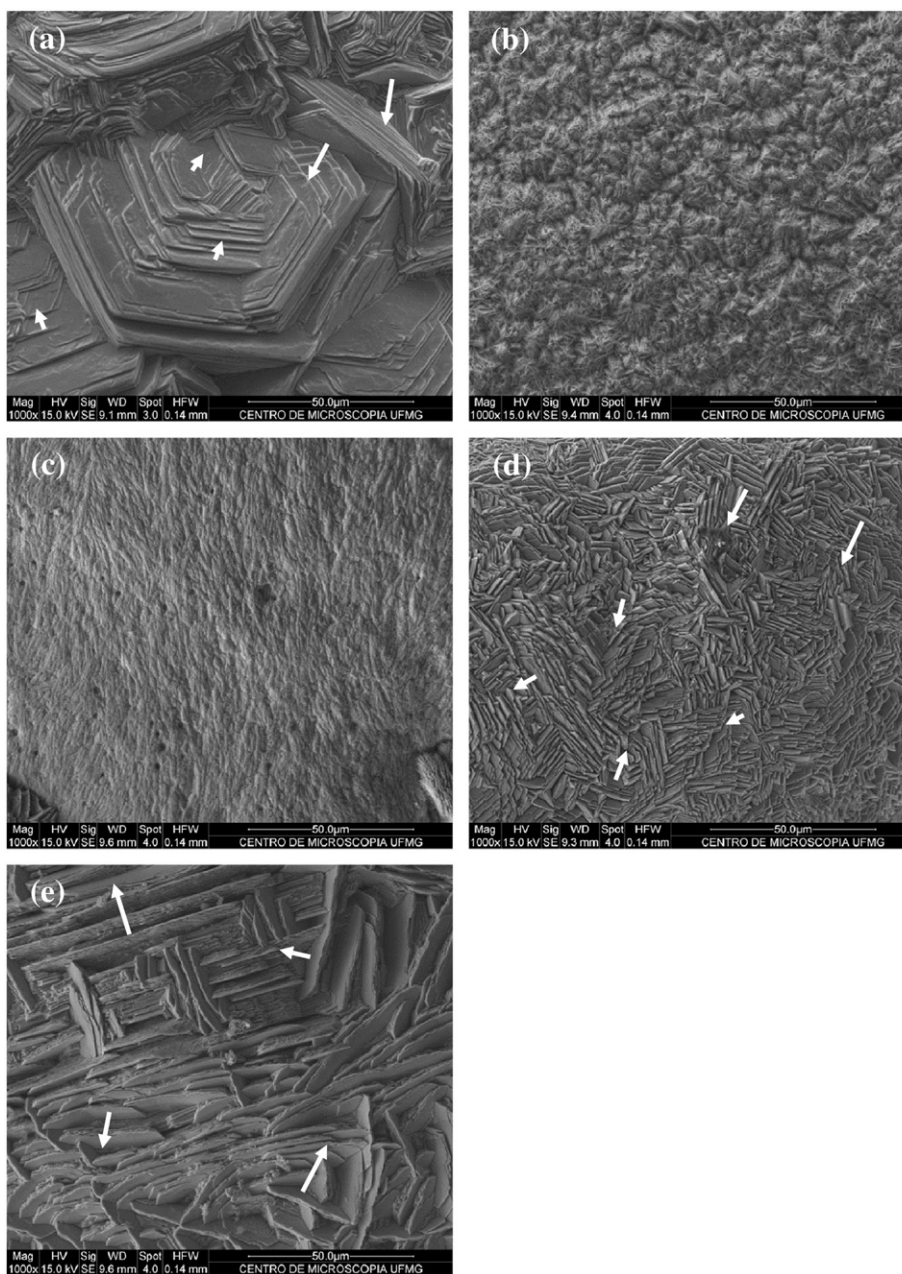


Fig. 3. Typical electron images of Zn deposits ($1000\times$) obtained from (a) organic-free electrolyte, (b) electrolyte with 50 mg L^{-1} of collector for zinc (Organic 2); (c) flocculant (Organic 1); (d) collector for impurities (Organic 3); and (e) lubricating oil (Organic 4). The white arrows show schematically the $\langle c \rangle$ axes direction, with lengths proportional to the inclination with respect to the perpendicular to the platelet: longest arrows indicate that the $\langle c \rangle$ axes are contained on the specimen plane.

It is well-established that the hydrogen bubbles attached to the cathode surface lead to the formation and growth of pores, as the metal deposit is formed around the bubbles within the interval they remain attached to the electrode (Gabe, 1997). The porosity of the Zn deposits may be related to the different degrees of adsorption of each organic on the surface and their effect on the adhesion of hydrogen bubbles. The diminution of the reaction area (i.e. surface partially covered by physically or chemically adsorbed molecules) may also lead to local increase of current density and, as a result, a higher hydrogen evolution rate, thus explaining the negative effects of the organics on current efficiency.

3.2.2. Grain size

The addition of the organic compounds to the electrolyte caused grain refinement as well. Zn crystallites with smaller sizes were observed by SEM at higher magnifications (Fig. 3). The largest Zn

crystallites are observed for samples obtained from organic-free electrolyte and solution containing the lubricating oil (Organic 4), with hexagonal platelets of approximately 50 μm in diameter and 2–3 μm in thickness, while the smallest ones (approximately <5 μm) are observed for samples obtained from solutions containing polar molecules (i.e. the flocculant, Organic 1, and the collector for zinc, Organic 2). Intermediate sizes are observed for the sample produced in solution containing the collector for impurities (Organic 3), with platelets of approximately 5–10 μm in diameter and <1 μm in thickness.

It is well-known that the grain size of metal deposits is affected by the number of grain-producing dislocations during the electrocrystallization (Oniciu and Mureşan, 1991). Thus, factors that promote disorder in the growing crystal contribute to reduce the grain size of the deposit. The adsorption of organic molecules on the cathode surface, for instance, inhibits the surface diffusion of the ad-atoms towards the growing centers, creating disorder during the incorporation of the ad-atoms

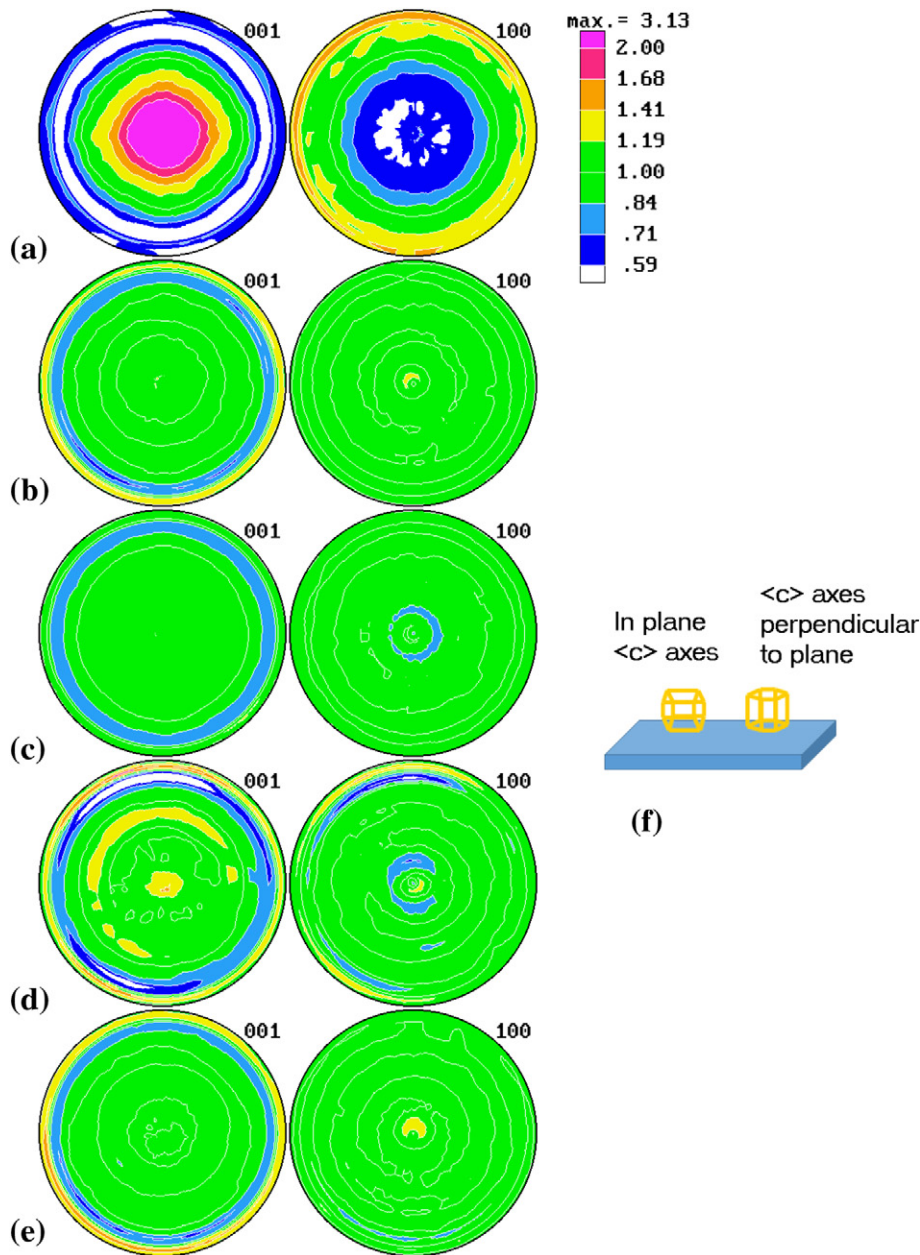


Fig. 4. Recalculated (001) and (100) pole figures for Zn deposits obtained from: (a) organic-free electrolyte; (b) electrolyte with 50 mg L^{-1} of collector for zinc (Organic 2); (c) flocculant (Organic 1); (d) collector for impurities (Organic 3); (e) and lubricating oil (Organic 4); (f) schematic representation of the “in plane” $\langle c \rangle$ axes and “perpendicular to the plane” $\langle c \rangle$ axes.

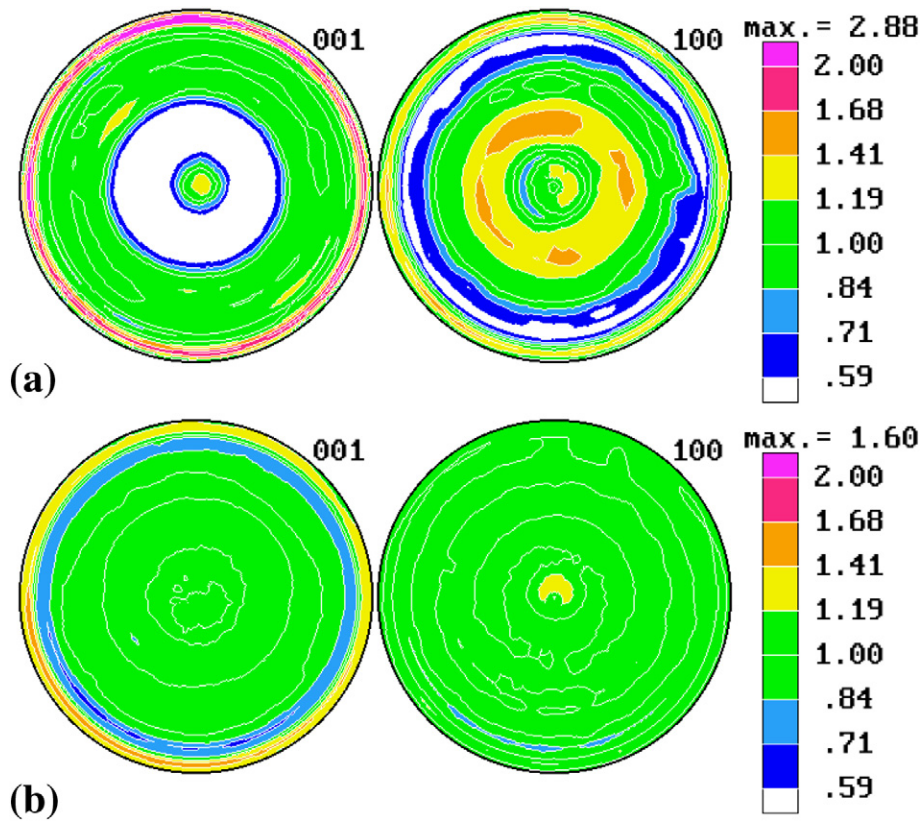


Fig. 5. Partial switching of $\langle c \rangle$ axes from “perpendicular to the plane” direction to “in plane” direction in Zn deposits obtained from electrolytes with 50 mg L⁻¹ of (a) floculant (Organic 1) and (b) lubricating oil (Organic 4). It can be seen that different samples produced by the same method differ widely on texture severity. Panel a differs from Fig. 4c although the general behavior of having $\langle c \rangle$ axes contained randomly distributed on the planes of the platelets is a constant.

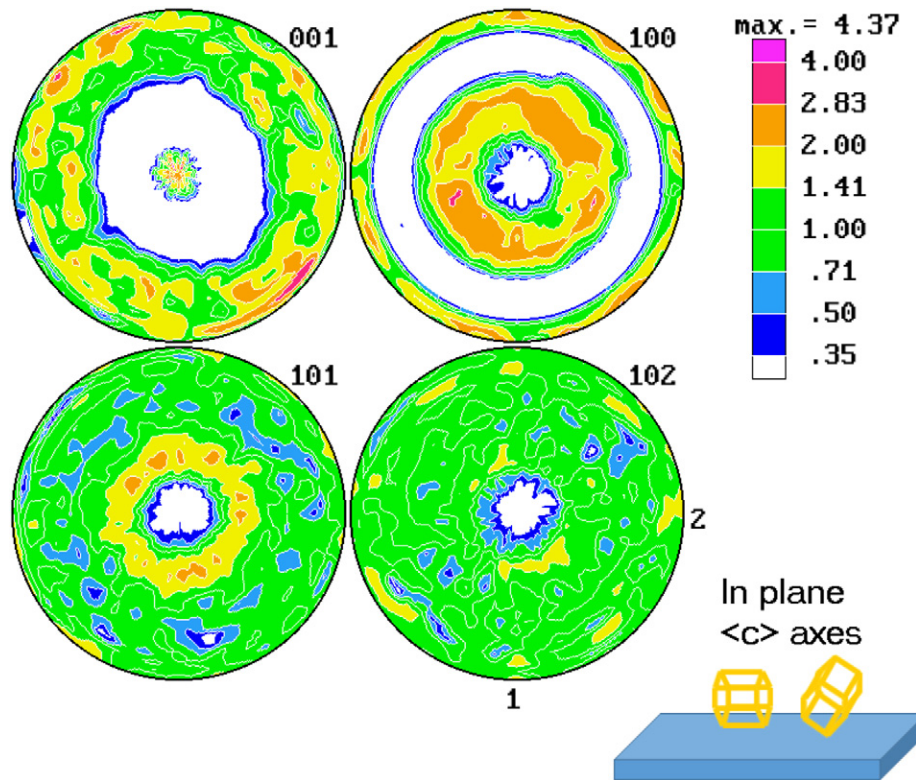


Fig. 6. Evidence of large grain size structure, together with $\langle c \rangle$ axes orientation switching phenomenon, on a Zn deposit obtained from electrolyte with 50 mg L⁻¹ of lubricating oil (Organic 4). $\langle c \rangle$ axes are contained randomly distributed in the platelet plane, with a distribution spread of 20°–30°, although some “perpendicular to the plane” component is also present.

Table 2Main effects of the organic compounds (50 mg L⁻¹ of organic) on the current efficiency and on the features of the Zn deposit.

Organic	Current efficiency	Morphology	Texture	Bending (Majuste et al., 2017)
Organic 1 (floculant)	Major decrease	Nodular, smaller crystallite size	Cylindrical, random distribution, trend for <c> axes reorientation	Flexible deposit
Organic 2 (collector for zinc)	Largest decrease	Porous, smaller crystallite size	Cylindrical, random distribution	Flexible deposit
Organic 3 (collector for impurities)	Major decrease	Highly porous, holes	Cylindrical, random distribution, trend for <c> axes reorientation	Very brittle deposit
Organic 4 (lubricating oil)	Minor decrease	Highly porous, holes	Cylindrical, random distribution, trend for <c> axes reorientation	Brittle deposit

into the crystal lattice. The present investigation revealed that interaction between the electroactive species and the organic molecules may also significantly affect the crystallite size of the metal electrodeposit.

3.2.3. Contamination

The SEM/EDS analysis indicated residual amounts of organics and ZnSO₄ on metal deposits produced from electrolytes containing the organics. It is possible that entrapped ZnSO₄ electrolyte was not fully rinsed, likely due to residual amounts of organic (spots or droplets) attached to the deposit. Thus, this residual ZnSO₄ crystallizes during the drying of the Zn deposit and appears as needle-shaped crystals, as visualized at high magnifications by SEM/EDS. The presence of residual ZnSO₄ and organics on the final product may lead to a larger generation of slag during the smelting. Additionally, trace contamination of the Zn deposits with lead (Pb) and silver (Ag) was also observed by SEM/EDS, which is possibly related to precipitation, due to their low solubility. The presence of Pb and Ag in the cathode can be ascribed to anode corrosion in the absence of manganese ion in the solution.

3.2.4. Crystallographic texture analysis

Direct pole figures for the Zn deposits obtained from organic-free electrolyte and solutions containing 50 mg L⁻¹ of organics are shown in Fig. 4, where the basic circle corresponds to the plane of the Zn deposit and only directions [001] and [100] are presented because they represent the two main extreme texture components obtained for the analyzed samples. All the samples exhibited cylindrical (fiber) texture characteristics. A relatively random distribution of crystals has been observed, except for the sample obtained from organic-free electrolyte, which displays a well-developed 3-times random preferential orientation of the <c> ([001]) axes perpendicular to the plane of the sample, with a distribution cone of about 20° from the vertical. The texture analysis also revealed that the samples obtained in the presence of the floculant (Organic 1) or lubricating oil (Organic 4) in the solution exhibit a trend to switch the orientation of the <c> axes from the “perpendicular to plane direction” to the “in plane” direction with a random distribution along the directions in that plane, as shown in Fig. 5.

The texture analysis also revealed the growth of slightly larger grain size for the Zn deposit obtained in the presence of 50 mg L⁻¹ of lubricating oil in the electrolyte, in comparison to the Zn deposit produced from the organic-free solution, as shown in Fig. 6. In addition to the trend for <c> axes reorientation (Fig. 5), a “spotty” aspect was displayed for such sample, which is ascribed to the detection of large grains. In fact, a relatively high intensity (>4-times the random intensity) is caused by the large grains impinging during measurement, with a small influence from the “in plane” orientation of the <c> axes.

The texture results were also found to be compatible with the images obtained by SEM, that is:

- The deposition of platelets with hexagonal symmetry and with the <c> axes almost perpendicular to the sample plane can be observed (as shown in Fig. 3a), in agreement with the measured 3-times random texture;
- The platelets are oriented approximately perpendicularly to the deposition plane, confirming the partial reorientation of the <c> axes

from “perpendicular to the plane” to “in plane” orientation (as shown in Fig. 3d and e);

- Fig. 2a and e show that the grains are quite large and flat crystals, close to approximately 50 μm dimension, which is more or less the size where the “spotty” pattern in the pole figures usually appears.

The above-mentioned modifications in the growth pattern of the Zn deposits support the hypothesis that the adsorbed organic molecules affect the electrocrystallization of the metal ion. These molecules prevent the growth of platelets in one specific direction possibly by hindering the diffusion of ad-atoms, thus inducing different growth rates for different crystal planes. There might be even a tendency to facilitate the growing of crystals in such way that the orientation switches to an “in plane” <c> axes preferential distribution. These changes, coupled with the formation of pores on the Zn deposits, led to significant changes of the mechanical properties of this material.

Table 2 summarizes the main findings of this work. As discussed in another work (Majuste et al., 2017), porosity appears to be the key cause for the low ductility of a metal deposit. The mechanical deformation of Zn deposits produced from electrolytes contaminated with residual amounts of insoluble or poorly soluble organics (hydrocarbon and fatty acids, respectively) may lead to the fracture of the metal sheet and to the disruption of the stripping process, with serious implications in the electrowinning performance.

4. Conclusions

The role of some organic compounds in the porosity, grain size and texture of Zn electrodeposits and on the efficiency of the electrowinning process is discussed in this paper. The individual additions of floculant, collector for zinc, collector for impurities to the electrolyte, which may be present at residual amounts when zinc silicate ores are treated, caused significant reductions in the current efficiency of the electrowinning process, thereby increasing energy consumption. The addition of the organics to the electrolyte also changed the features of the metal deposit. Microscopy analysis showed that the addition of organics to the electrolyte may lead to the formation of pores on the deposit surface and variations in the grain size. Orientation changes ending up in randomization, with a trend to reorient the crystals from a “perpendicular to the plane” to an “in plane” random distribution, were determined by texture analysis. These changes affected the mechanical behavior of the material, as confirmed by means of bending tests using a customized device (Majuste et al., 2017).

Acknowledgements

The authors would like to thank Votorantim Metais – Zinc for providing organic samples and technical support; Centre of Microscopy/UFMG (Breno B. Moreira), Laboratory of Ceramic Materials/UFMG (Prof. Eduardo H.M. Nunes and Prof. Wander L. Vasconcelos) and Laboratory of X-rays/IFIR-CCT Rosario for the analyses. D. Majuste and V.S.T. Ciminelli thank the sponsoring companies of the AMIRA P705B Project (Improved anode and cathode processes in the electrowinning of base metals) for their financial support and permission to publish this paper.

The partial financial support from the Brazilian agencies (CAPES/PROEX, CNPq, and FAPEMIG), Agencia Nacional de Promoción de la Ciencia y la Tecnología and CONICET, Argentina, is acknowledged as well.

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