Hydrometallurgy 169 (2017) 393–398

Contents lists available at ScienceDirect

Hydrometallurgy

journal homepage: www.elsevier.com/locate/hydromet

Technical note

A novel device for testing the mechanical behavior of metal electrodeposits during cathode stripping

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ARTICLE INFO

Article history:
Received 6 February 2017
Accepted 21 February 2017
Available online 03 March 2017

Keywords:
Electrowinning
Zinc
Organic impurities
Bending behavior
Stripping

ABSTRACT

The effect of the morphology and the crystallographic texture on the mechanical behavior of zinc electrodeposits is described. The mechanical behavior was assessed with a customized bending device and correlated to the main features of the deposit. The methodology proposed in this paper allows a better assessment of the effect of impurities (organics/inorganics) or additives on the quality of metal deposits, thereby assisting industry to optimize conditions and increase productivity. Bending tests carried out up to a bending angle of 50° revealed that the organic contaminants affect the mechanical properties of the zinc deposit differently. These properties were found to be strongly correlated to the electrodeposit's features. Highly porous deposits showed low ductility, which in turn caused the fracture of the sample at small bending angles, thus impeding effective stripping. The results obtained from the bending tests allowed a semi-quantitative prediction for the behavior of different zinc deposits during the stripping operation.

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. However, these previous works have 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.

A schematic representation of the industrial stripping of Zn deposits is illustrated in Fig. 1. Fig. 1a displays the Zn deposit adhered to the cathode and Fig. 1b illustrates the situation where the adhesion of the deposit to the cathode is not strong, and the penetration of the stripping wedge triggers a generalized separation of the deposit from the cathode, leading to a detachment point far ahead of the wedge. Under these circumstances, the deposit is submitted to a very low bending strain. On the other hand, if the adherence of the deposit is strong, the detachment point between the cathode and the deposit is close to the wedge, as displayed in Fig. 1c. The detail in Fig. 1d indicates that in this situation, the deposit is bent with an angle (θ) close to that of the wedge (in the range from 30° to 50°). The industrial stripping procedures can thus be replicated under laboratory conditions using a bending test able to bend the Zn deposits up to angles similar to that of the stripping wedge.

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 the product quality. In the present work, the effect of residual organics in the sulfate electrolyte on the mechanical behavior of Zn deposits is assessed with a customized bending device and correlated to their morphology and

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http://dx.doi.org/10.1016/j.hydromet.2017.02.018
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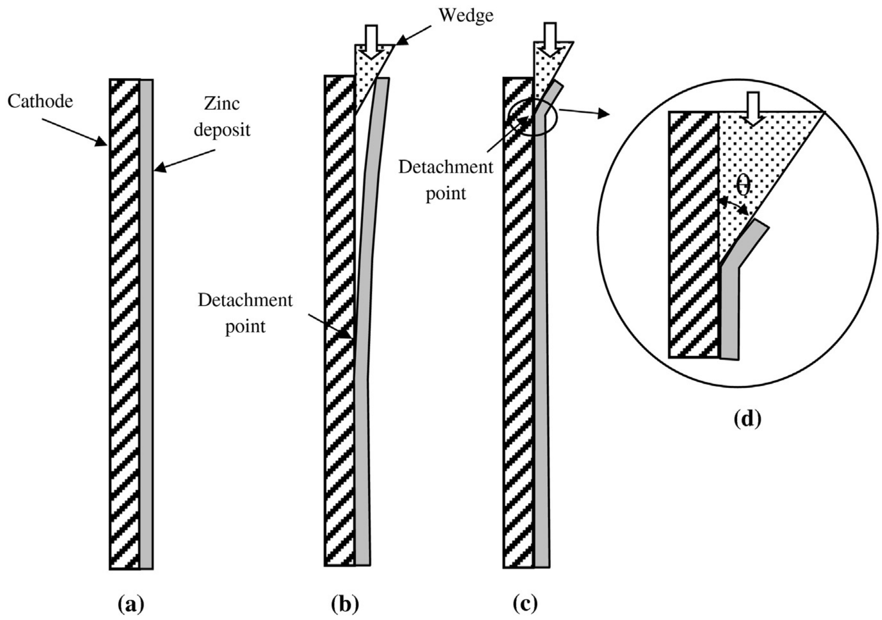

Fig. 1. (a) Initial situation: Zn deposit attached to Al cathode; (b) stripping of the Zn deposit when the adhesion between the deposit and the cathode is low; (c) stripping of the Zn deposit when the adhesion between the deposit and the cathode is high; (d) detail of the stripping region in Fig. 1c.

crystallographic texture. This device is able to bend the zinc deposits up to angles close to that of the stripping wedge (in the range of 30° to 50°). The organics (*i.e.*, flotation collectors, flocculant and lubricating oil) are used in an industrial plant (Votorantim Metais, Três Marias, Brazil) that combines the processing of silicate and sulfide ores.

2. Experimental

2.1. Zinc deposits

The Zn deposits were produced using a continuous electrowinning cell in sulfate electrolyte containing a flocculant, Flonex® (Organic 1), which is added during thickening, a flotation collector for zinc silicate (willemite – Zn_2SiO_4), Tomamine® (Organic 2), 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 or a lubricating oil, Husoli GS® (Organic 4), which is used in machinery, including cranes. The main chemical groups of the organic compounds were identified and the deposits were characterized by means of morphological and crystallographic texture analyses, as better described elsewhere (Majuste et al., 2017).

2.2. Bending test

The Zn deposits (20 mm width × 50 mm length) were subjected to two-point bending test in a customized device shown in Fig. 2a, which reproduces the bending of the metal sheet during the stripping stage (Fig. 2b). The device is placed on a universal testing machine (INSTRON 5582), where a controlled vertical force (F_V) is applied to the punch of the device, which in turn transmits the force to the sample. One end of the sample is fixed by a locking device that applies a compression force, while the punch moves vertically at a constant speed of 0.2 mm s^{-1}, bending the sample. The weight of the punch was considered in the calculations. This approach takes into account all geometric factors (Fig. 2c) related to the experimental set-up. The variables measured here were the vertical displacement of the punch (L_V) and F_V. As the angle of contact θ between the sample and the punch changes throughout the test and the net force F that causes bending is perpendicular to the sample, F will be larger than F_v when $\theta > 0°$ (Eq. (1)). The horizontal force component (F_H) is also applied to the sample by the punch and can be readily calculated using simple trigonometry (Eq. (2)).

$$F_V = F \cdot \cos(\theta) \tag{1}$$

$$F_H = F \cdot \sin(\theta) \tag{2}$$

Even though F_H is not directly measured in the test, it tends to push the punch horizontally, increasing the distance between the support and the load application point. However, due to the rigidity of the test system, the horizontal elastic deflection of the punch can be assumed negligible and safely ignored in the analysis. The angle θ between the bent sample and its original position can be readily calculated if the geometry of the test system is simplified: the sample was assumed to be straight. The horizontal distance between the punch and the support (L_H) is kept constant during the test. Thus, as the angle between L_H and L_V is 90°, a right triangle is formed, where the bending angle θ can be calculated (Eq. (3)). When L_H is reduced, the same value of θ is reached for a lower value of L_V. Thus, the use of θ instead of L_V as a measurement of the ductility of the sample unifies all testing conditions. The total distance between the support and the load application point (L) can be calculated (Eq. (4)).

$$\theta = \mathrm{arctg}(L_V/L_H) \tag{3}$$

$$L = \sqrt{\left(L_V{}^2 + L_H{}^2\right)} \tag{4}$$

During the bending test, L increases as the punch moves down and bends the sample. Therefore, the moment of the force applied to the sample also increases, as given by:

$$M = F \cdot L \tag{5}$$

The magnitude of the moment and bending angles reported here are related to a thinner Zn deposit, produced for a short deposition time

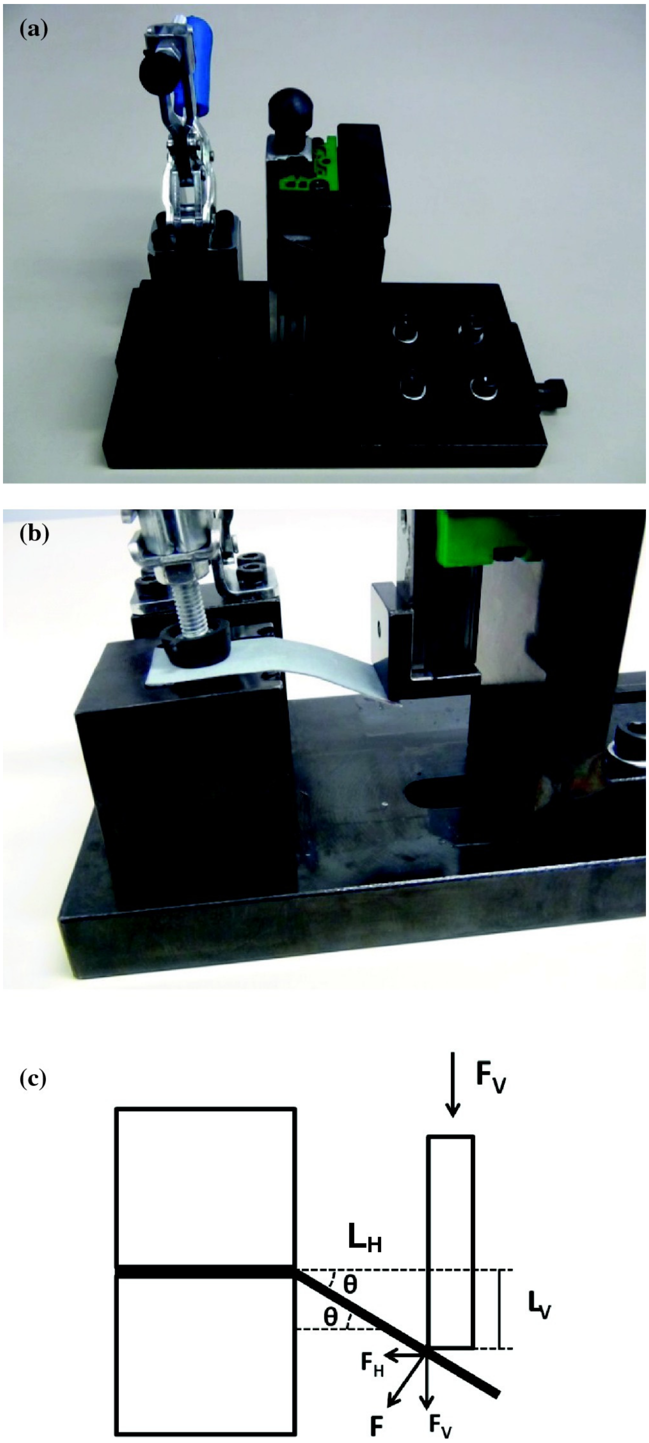

Fig. 2. Photographs of the device used in the bending test of the Zn deposits (a) and (b); and geometry of the bending test, after significant bending of the sample (c).

(6 h) in comparison with the industrial condition. A deposit produced under industrial conditions (plating time of 24–36 h) will be thicker, and this is expected to affect the parameters measured by the device.

2.3. Fracture surface analysis

The fracture surface analysis of Zn deposits obtained from organic-free and organic-containing electrolytes was analyzed by means of scanning electron microscopy (SEM) using an ASPEX Explorer microscope operating at 15–20 kV.

3. Results and discussion

3.1. Bending tests

Moment (M) *versus* bending angle curves were plotted up to a bending angle of 50°, which is probably higher than the typical wedge angle, using Zn deposits obtained from organic-free electrolyte and solutions containing 50 mg L^{-1} of organics, as shown in Fig. 3. All the samples were tested using $L_H = 12$ mm. It can be seen that the profile of all curves, except those for samples produced from electrolytes with Organic 3 (at $L_H = 12$ mm), exhibits a similar behavior: the bending moment increases parabolically with the angle, and then display increasing oscillations as the testing angle increases. These oscillations, observed for angles above about 40°, are probably associated with the friction between the punch and the sample, as the horizontal component of the bending force (F_H) increases with the bending angle. The surface roughness caused by the porosity has a direct influence on the friction between the punch and the specimen, making it difficult to assign a specific meaning to these oscillations.

The curve obtained from solution containing the collector of impurities (Organic 3, Fig. 3) reached a peak at about 3.5° and then decreased, which was caused by the cracking of the sample. This indicates that the deposit produced from electrolytes containing this impurity presents a very low ductility, leading to the early cracking of the product. Therefore, Zn deposits produced in electrolytes containing such organic should present severe stripping problems, tending to crack before being stripped from the Al cathodes. The bending tests also indicated that the Zn deposit obtained from solution containing the lubricating oil (Organic 4, Fig. 3) displayed quite low values of moment along the full bending cycle, and it may be associated with a slow cracking of the sample, as visually observed (Fig. 4), which, however, did not lead to its complete breakage. This behavior may suggest that even under this situation stripping could proceed without major problems.

It is difficult to explain the differences in the magnitude of the moment measured for the various samples (or net force F that causes bending), since it depends closely on the material strength that is affected by crystallographic texture, grain size, thickness and stress concentrators in the specimens, as caused by porosity. As better discussed elsewhere (Majuste et al., 2017), some Zn deposits exhibited dual changes (*e.g.* decrease of the crystallite size and porosity), making it more complex to evaluate stress concentration and average thickness as well as the relative, individual or combined effects of these features on the measured M values. These authors showed that samples are very porous and have irregular surfaces (as shown by SEM images), which causes severe stress concentration at certain points. Moreover, as Zn has hexagonal (HCP) atomic structure, differences in crystallographic texture should have a strong effect on Zn slip and brittleness: the preferential slip systems in HCP metals are on the basal plane and, depending on the mismatch between the slip planes and the stress state applied to the metal, brittle fracture may be favored over plastic deformation (Dieter, 1988). Complex computer models are required to take into account the effects of stress concentration, combined with differences in crystallographic texture.

3.2. Fracture surface analysis

Morphological analyses revealed that the sample obtained from solution containing the Organic 3 are the ones exhibiting the highest level of porosity, among all the other samples (Majuste et al., 2017). The importance of this porosity was thus analyzed considering the fracture surface of the various samples. In order to observe the fractured surfaces, all bent samples were submitted manually to further bending till they fractured. The SEM images of the fracture surfaces

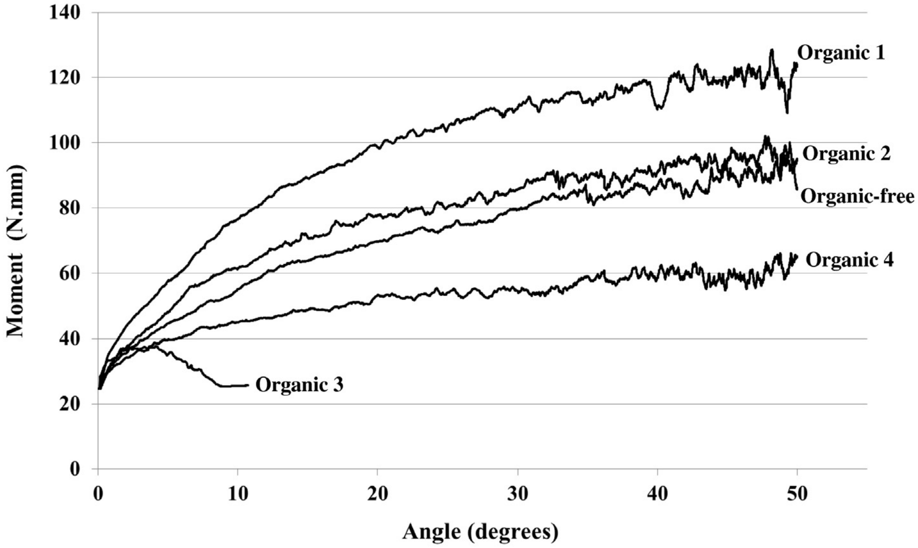

Fig. 3. Moment *versus* bending angle curves for Zn deposits obtained from organic-free and organic-containing solutions (50 mg L^{-1}).

thus obtained show that the sample obtained from electrolyte with Organic 3 (Fig. 5a) is extremely porous and displays regions where the thickness of the sample is almost zero. The Zn sample obtained from solution with Organic 2 (Fig. 5c) has a regular pattern of conical pores that span across the whole thickness of the sample; cleavage marks seem to be present on the fracture surface. The analysis of Zn sample obtained from electrolyte containing Organic 4 (Fig. 5b) displays some porosity, which is however much lower than that observed for the specimen obtained from solution with Organic 3, as shown in Majuste et al. (2017). Higher magnifications suggest the presence of cleavage (Fig. 6), considered as a possible fracture mechanism due to the crystallographic orientation of some of its crystallites.

Taking into account the main findings of this work, it can be concluded that 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 process, with serious implications in the electrowinning performance. Simple control and optimization procedures were implemented in an industrial operation in order to minimize the detrimental effects caused by organic contamination, namely better control of the use of lubricating oils in all the machinery; installation of trays below the tankhouse cranes for collection of oil droplets; optimization of the organic dosage in the flotation stage or even the use of a different technology to remove carbonates from the zinc ore.

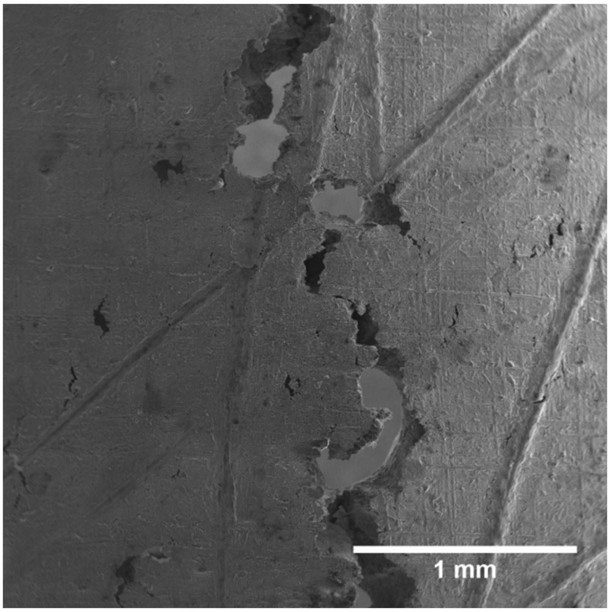

Fig. 4. Early cracking observed in the outer surface of the Zn deposit obtained from electrolyte containing 50 mg L^{-1} of lubricating oil (Organic 4).

4. Conclusions

The role of some organic compounds on the quality of Zn electrodeposits is discussed with original approach that involves product characterization by morphology, crystallographic texture and bending behavior. The individual additions of a flocculant, a collector for zinc, a collector for impurities and a lubricating oil to the sulfate electrolyte changed the features of the metal deposit. These changes affected the mechanical behavior of the material, as confirmed by means of bending tests using a customized device. Zn deposits produced from solutions containing the collector for impurities suffered complete fracture during the bending tests, which can be explained by their high level of porosity. Deposits produced from solutions containing the lubricating oil presented fissures, but did not break during the bending tests. These results may be used to predict the behavior of the deposits during the industrial stripping process. Early fracture during bending tests is a probable indicator of severe stripping problems, while fracture at large bending angles is probably an indicator of occasional stripping problems.

Acknowledgements

The authors would like to thank Votorantim Metais – Zinc for providing technical support and Laboratory of Ceramic Materials/UFMG (Prof. Eduardo H.M. Nunes and Prof. Wander L. Vasconcelos) for the SEM 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) is acknowledged as well.

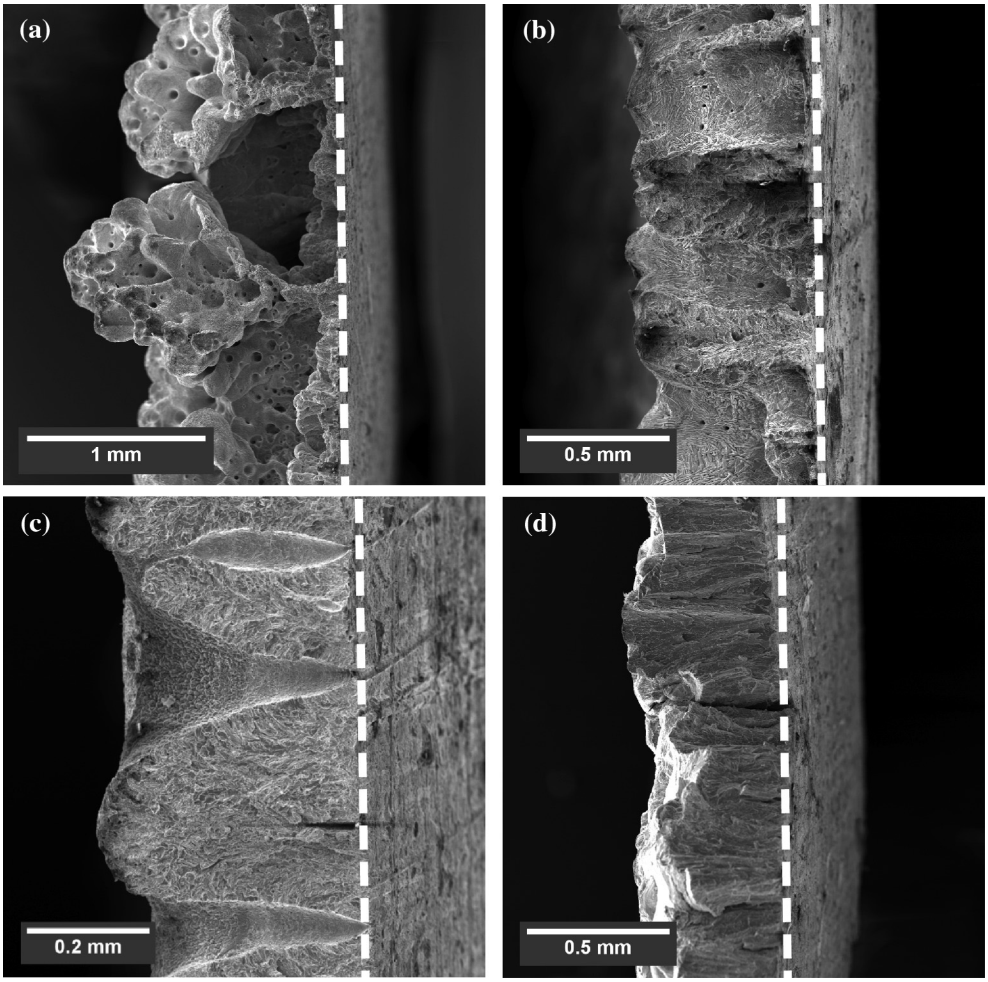

Fig. 5. Fracture surface of Zn deposits obtained from electrolytes containing 50 mg L^{-1} of (a) collector for impurities (Organic 3); (b) lubricating oil (Organic 4); (c) collector for zinc (Organic 2); and (d) flocculant (Organic 1), under low magnification. The white dashed lines in the images mark the limit between the fracture surface (left) from the projection of the surface originally in contact with the electrode (right).

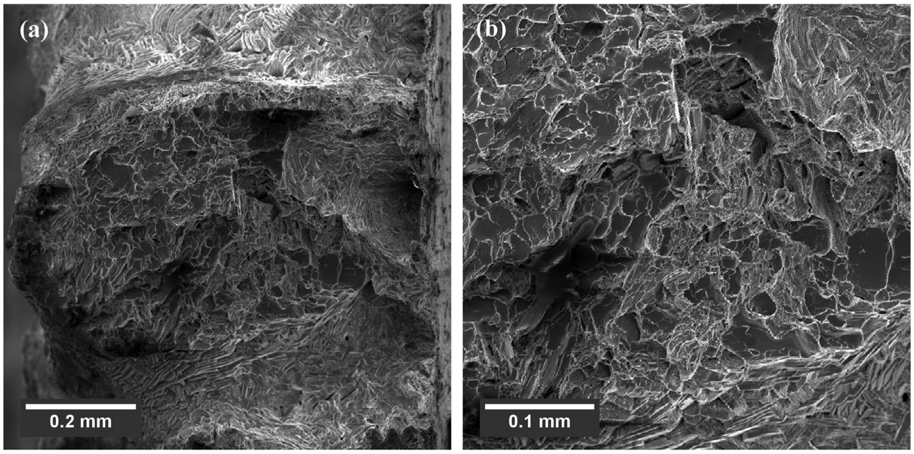

Fig. 6. Fracture surface of Zn deposit obtained from solution with 50 mg L^{-1} of lubricating oil (Organic 4), under higher magnification. Marks on the surface suggest that cleavage is likely the mechanism responsible for fracture.

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