Lead-Based Anodes for Copper Electrowinning: Effect of Grain Size on Mechanical and Anticorrosion Properties

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The aim of this paper was to study the effect of the grain size of lead-based anodes for copper electrowinning on their mechanical and anticorrosion properties. Aged anodes were cold rolled to different thicknesses, achieving reductions varying from their standard 50% up to 75%. The grain size, yield stress, and corrosion behavior of the different rolled samples was evaluated by galvanostatic polarization essays. It was found that by lowering the grain size, the yield stress of the anodes increased up to 66 MPa and the improved anodes maintained a higher yield stress with time and throughout temperature operation in cells, as compared with the currently used anodes. Also, a significant diminution of the corroded mass, up to 30%, was observed as cold reduction increased due to the formation of a more compact and less permeable PbSO₄ at lower grain size. [doi:10.2320/matertrans.M2017356]

(Received November 27, 2017; Accepted January 22, 2018; Published March 25, 2018)

Keywords: lead-based anodes, yield stress, grain size, corrosion behavior, working life

1. Introduction

Lead-based alloys (Pb-0.07% Ca-1.3% Sn), with 1 m × 1 m sections and 6, 7.5 or 9 mm thickness are used as anodes in copper electrowinning. These anodes have limited working life due to material loss, and consequent thickness reduction, caused by oxidation from the electrowinning process; if the thickness reduction is combined with a low yield stress, the anodes are much more likely to suffer premature deformations in the cells.

Regarding the yield stress of 6 mm thick anodes, a minimum value of 58 MPa is required to guarantee a working life of 4–5 years under a typical current density of 300–350 A/m². To reach this value, the aged anodes must be subjected to a 50% cold rolling thickness reduction, from their initial thickness of 12 mm, which is in turn reached through a previous hot rolling of a slab of 30 mm thick. If the thickness reduction during the cold rolling goes beyond 50%, the grain size of the anodes will decrease further and as a consequence, it is expected that the yield stress of the aged anodes will increase. This trend is interesting from the point of view of the copper industry as it illustrates a simple way to produce anodes with extended working life, provided that the corrosion rate does not vary significantly as the grain size diminishes with the reduction in thickness.

The yield stress of the anodes also depends on precipitation hardening. In this regard, several studies have dealt with the effect of cooling and aging on the precipitation behavior of Pb–Ca–Sn alloys, showing that stable values of ageing are obtained after 30–45 days.

In addition to the yield stress of the anodes, another factor that affects their working life is the corrosion process occurring in the cells, which depends on operating conditions, such as current density and electrolyte composition, and anode characteristics such as the shape, grain size, and the location and distribution of the precipitates. Regarding the effect of the grain size on the corrosion of the anodes, there is little agreement between results presented in studies from different investigators. Some studies claim that large grains can reduce the corrosion rate, while others indicate that a fine grain structure, characteristic of cold rolling and dependent on the percentage of area reduction, reduces the corrosion of the anodes.

The main objective of this work was to study the extent to which the yield stress, σ₀, of the anodes can be increased by reducing their grain size, and determine if the yield stress achieved is maintained under the operating conditions of the cells (time and temperature), and whether the grain size is related to differences on the corrosion behavior. The final aim was to obtain anodes with a longer working life.

To accomplish the proposed objective, we cold rolled 6 mm thick anodes to reach thickness reductions varying from their standard 50% to 75% reduction in thickness. The anodes were then analyzed in order to determine the grain size and yield stress by plane compression tests. The shape and size of the grains were determined by metallographic analysis and the Hollomon curve as well as the Hall-Petch constants were obtained. In addition, the evolution of the yield stress with time and with the electrolyte temperature of the cold rolled anodes whose area had been reduced by 70% was studied. Finally, the corrosion behavior of the samples was determined by galvanostatic assays. The study of the corrosion layer was performed by scanning electron microscopy (SEM) and by X-ray diffraction (XRD).

2. Experimental Procedure

The raw materials for this work were 6 mm thick anodes, aged for at least 30 days and finished by cold rolling with a 50% thickness reduction. The chemical composition of the anodes has been previously determined by EPMA microprobe and has been found to vary slightly around the following average values: Pb = 98.5%; Ca = 0.075% and Sn = 1.3%. Six of these anodes were cold rolled in our laboratory, using a reversible Joliot mill, to final thicknesses of 5.5, 5.0, 4.5, 4.0, 3.5 and 3.0 mm, i.e., with a maximum cold reduction of 75%. From these rolled anodes, samples of 25 mm width and 100 mm length were cut and machined to a 3 mm thickness under abundant refrigeration. The yield stress of these 3 mm thick samples was determined by plane
compression tests through an Instron machine, using steel indenters of 50 mm length and 6.25 or 5 mm width and lubricated with grease in the area in contact with the indenters. Details of the plane compression test and the determination of the friction coefficient in correspondence of the zone of contact between samples and indenters have been previously reported. The cold rolled samples with different reductions were polished, etched using acetic acid and hydrogen peroxide in a 3:1 ratio, and observed by optical microscopy to determine their shape and average grain size, D, using the Heyn method. The data of the yield stress, the effective strain \[\varepsilon_{\text{eff}} = 1.15 \ln (12/\text{final thickness})\] and the grain size of the samples, were used to obtain the Hollomon law and the constants of the Hall-Petch equation.

Furthermore, the evolution of the yield stress with temperature (20°, 35°, 50°, and 80°C) and with operating times up to 1.5 years was evaluated for the currently used anodes and for the cold rolled anodes with 70% area reduction. The data for the currently used anodes was obtained from a copper industry after 6, 12 and 18 months of operation in electrowinning cells.

Finally, the corrosion behavior of samples of 6, 5 and 3 mm final thickness (average grain sizes range: 0.039–0.014 mm) was determined by galvanostatic polarization assays with a VERSA STAT 3 potentiostat. The cell contained a circular electrode obtained from the three different rolled samples, with an overall working area of 1 cm², a Pt counter electrode, and a saturated calomel electrode as reference. The electrolyte contained 200 g/L of sulfuric acid at 40°C, a typical concentration and temperature in a copper electrowinning process. A stirring rate of 200 rpm was used. An oxidation current density of 350 A/m² for the anodic polarization at 4, 8 and 12 h and a discharging current density of 7 A/m² were used in all tests. By recording the times associated with the reduction step it was possible to compare the corrosion behavior of the different samples. To study the corrosion layers, SEM and EDS analyses were performed using a JeoJSM-6380 and XRD spectra were measured with a Rikoku 3070 instrument.

All the plane compression tests and corrosion assays were repeated at least twice.

3. Results and Discussions

Figure 1 shows the average grain size and the yield stress of the samples for increasing degrees of cold reduction. It should be noted that \(\sigma_0\) increased from 58 MPa for the currently used anodes (50% cold rolling reduction) to 66 MPa for samples with 70%–75% cold rolling reduction, and the average grain size diminished from 0.039 mm-ASTM 6 (currently used anodes) to 0.014 mm-ASTM 9 (75% area reduction). Increasing the cold reduction above 70%–75% did not yield any further enhancement of yield stress because of saturation of dislocation density.

When plotting the yield stress of the rolled samples as a function of the effective strain, the following Hollomon law, \(\sigma_0 = 59.7 \varepsilon_{\text{eff}}^{0.13}\) MPa is obtained.

The Hall-Petch law results from the average grain size and the yield stress of the anodes reported in Fig. 1: \(\sigma_0 = 48.9 + 1.82 \times D^{-0.5}\) MPa.

Figure 2 shows the yield stress of the currently used and improved anodes with a 70% cold rolling area reduction as a function of operating times up to 1.5 years.

In both cases, a decrease in the yield stress of the anodes was observed over time, particularly during the first year of operation. This was due to some partial recuperation process. Note that the precipitation of the CaSn₃ particles occurs at higher temperature, 225 up to 630°C, than of the cell of 40 to 50°C. Anodes with lower mechanical quality, with a yield stress below 48 MPa, are deformed after a few months of operation in the cells, a period in which they also release the residual stresses induced during their cold rolling fabrication.

Figure 3 shows the evolution of the yield stress of the currently used and improved anodes as a function of temperature.

Note that a reduction of the yield stress of the anodes took place with increasing temperature as a consequence of recuperation processes and not due to recrystallization, since this temperature varied between 130°–150°C, depending on the composition of the anodes.

In both Figs. 2 and 3, which show the variation of the yield stress of the anodes with time and with temperature, respectively, the improved anodes have a higher yield stress than the currently used anodes.
Figure 4 shows a typical curve obtained from galvanostatic polarization assays of a Pb–Ca–Sn anode, in this case corresponding to 12 h oxidation for the current anode with 50% cold reduction.

All the curves obtained for the samples with different degrees of cold reduction exhibited a similar behavior in the reduction zone. In the early stage of the reduction process a typical plateau corresponding to the reduction of PbO₂ was observed²¹ (see insert in Fig. 4). After this plateau, the potential decreased continuously as long as the reduction current was applied, suggesting that the oxidized layer was composed of a mix of corroded compounds.²²

Figure 5 shows a SEM image and the corresponding EDS analysis (red, oxygen; blue, lead) of the cross section of a 3 mm thick anode after 12 hours of oxidation. The outside layer corresponded to PbSO₄, which due to its permeability permitted the diffusion of the electrolyte towards the Pb²³ where oxidation to lead oxide occurred (black zone).

Figure 6 shows the XRD results for oxidized anodes, where the presence of different corroded compounds, PbO, PbSO₄, and Pb₃O₄ was clearly seen. The presence of lead oxide in correspondence of the Pb–PbSO₄ interface with the associated mismatch of the lattice parameters of the
compounds\(^{21}\) was responsible for cracking and mass loss in the anodes as the oxidation time increased.

Table 1 indicates the reduction times for the three samples tested (6, 5 and 3 mm thickness) for each one of the three oxidation times: 4, 8 and 12 h.

Note that the reduction time, and correspondingly the corroded mass, decreased with decreasing grain size of the samples, which was associated with highest cold rolling deformations. The reduction time, averaged for the three oxidation times tested, was at least 30\% lower for the 5 and 3 mm thick anodes than for the 6 mm anode. Thus, considering Faraday’s law, a significant reduction of the corroded mass was obtained from the improved anodes. At lower grain size, more nucleation sites were available for the formation of PbSO\(_4\) and the corroded layer was more compact, as shown by the SEM micrographs of the surface of the corroded anodes of Fig. 7-a (6 mm, less compact) and 7-b (3 mm, more compact). This effect has been previously noted\(^{24}\) and it was found that large PbSO\(_4\) crystals increased the distance across which the Pb\(^{2+}\) ions must diffuse to reach the reaction surface extend, while small PbSO\(_4\) crystals impeded the diffusion of SO\(_4^{2-}\) ions through the micro pores, thus increasing the corrosion resistance of the anodes at highest cold reduction.

The yield stress, \(\sigma_0\), of the anodes and their lowest useful thickness in operation, \(h_{\text{min}}\), were related by the formula \(\sigma_0h_{\text{min}}^3 = C\), where C was a constant depending on the standard operating conditions adopted during the electrowinning process, and also of the over voltages and short circuits.\(^{3}\) If, as demonstrated in this work, reducing the grain size caused an increase in the yield stress of the anodes from 58 to 66 MPa and a decrease up to 30\% of their corrosion rate within the cells, the useful life of the anodes increased from their standard 4–5 years to at least 5–6 years.

### 4. Conclusions

Increasing the cold rolling reduction of the anodes diminished their grain size from ASTM 6 to ASTM 9 and the yield stress of the anodes increased from the current value of 58 MPa up to 66 MPa for a cold rolling reduction of 70–75\%. The decrease of the grain size also produced a reduction in the corrosion of the anodes, because the corroded layer was more compact. The improved anodes showed higher yield stress than the currently used anodes under different conditions of temperature and operating time. Thus, to increase the working life of 6 mm thick lead based anodes for copper electrowinning, a possible alternative would be to cold roll it from 20 to 6 mm instead of 12 to 6 mm as currently done. This practice would lead to a double benefit: increase in the anode yield stress, and reduce their corrosion rate.

### Acknowledgments

The authors wish to acknowledge the support and financial contribution of Conicyt, under grant Fondecyt 1150005.

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