The Physical Characteristics of Electrorefined Copper Starter Sheet Material

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Abstract The interaction of anode and electrolyte chemistry in copper electrorefining is complex. This is especially true with regard to the behavior of Group 15 elements (As, Sb, and Bi). To better understand this system, laboratory electrorefining experiments were conducted using commercial anodes with As/(Sb + Bi) molar ratios of 0.54 and 3.8 and an electrolyte collected from a commercial refinery. The effect of adding thiourea during plating was also examined. Twenty-one hour copper deposits were produced in the laboratory to simulate starter sheet production. The mechanical properties of the electrodeposited copper as measured by an industrially relevant empirical bend test and a one-point bend test developed by UFMG are reported. The crystal structures of the samples were also examined.

Keywords Copper · Electrorefining · Starter sheet · Ductility · Bending

Introduction

Approximately 25% of the world's copper electrorefineries produce and use starter sheets for their operations [1]. While starter sheet technology has been employed for many decades, situations arise where their production can be problematic [2]. Specifically, the ductility of the starter sheet material can become compromised which leads to loop breakage.

The ductility of starter sheet material is measured in a plant setting using a simple bend test [2]. In a bend test, material is placed in a vice and bent, evenly, at 90° in each direction. Each motion is counted as one bend, and the total number of

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bends to failure is recorded. A higher number of bends indicates a sample with more ductility. This method was used by O'Keefe and Hurst [3] when they showed that antimony in electrolyte produced brittle copper electrodeposits but chloride and glue additions counteracted this effect. Laforest and Moats [4, 5] also employed a bend test while examining the effects of anode chemistry and thiourea on deposit ductility and electrolyte chemistry.

While ductility of copper starter sheet material is important, the reporting of physical characterization using quantified and reproducible methods was not found in the open literature. Ductility of electrodeposited copper for other applications has been measured, but the copper deposits are thinner than those produced in this study [6–9]. Therefore, the ductility of copper starter sheet materials was measured using a one-point bending test. Comparisons of the one-point bending test results to crystal structure and bend test values were made.

Experimental

Starter Sheet Materials

Two sets of starter sheet materials were evaluated by bend testing and the UFMG one-point bending test. The first set was commercial starter sheet samples. The second set was laboratory starter sheet samples. The commercial starter sheet samples were produced by two facilities and selected to provide a range of bend test values. The laboratory starter sheet samples were produced during an earlier investigation with details reported elsewhere [4, 5, 9].

One-Point Bending Test

A one-point bending test was developed by researchers at Universidade Federal de Minas Gerais to simulate the stress that would be imposed upon copper and zinc electrodeposits produced by electrowinning during removal from permanent cathodes. The test was developed as part of the AMIRA P705 series of projects.

Cu samples (25 mm width × 55 mm length) were subjected to a one-point bending test in a customized device, which reproduces the bending of the metal sheet during the stripping stage. The device was placed on a universal testing machine (INSTRON 5582) using a 100 N load cell, where a controlled vertical force is applied to the punch of the device. One end of the sample is fixed by a lock 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 horizontal distance between the punch and the support was kept constant during the tests at 10 mm. The punch's weight was considered in the calculations. This approach takes into account all geometric factors related to the experimental set-up. The variables measured here were the vertical displacement of the punch and the vertical force. In order to calculate the angle θ between the bent sample and its original position, the geometry of the test system was simplified: the sample was assumed to be straight.

X-ray Diffraction

The crystalline structure of the Cu deposits was analyzed by X-ray diffraction (XRD), using a PANalytical (Empyrean) X-ray diffractometer, with Cu Kα1 ($\lambda = 1.5406$ Å) radiation. The XRD patterns were measured in 2θ range from 30 to 100° using a step size of 0.02°. The patterns were identified using an ICDD (International Centre for Diffraction Data) file as reference (04-0836). The texture of the electrodeposited metal was discussed semi-quantitatively on the basis of the relative peak intensities.

Results and Discussion

Commercial Starter Sheets

Four commercial starter sheet samples were provided by an industrial partner. Selected impurity concentrations for the samples are provided in Table 1 along with the average number of bends to failure. The data indicate no correlation between these impurities and the bends to failure.

Specimens of the commercial samples were measured using the UFMG one-point loading test. Force versus deformation curves for the four commercial samples are shown in Fig. 1. No correlation was observed. The commercial samples were of differing thickness as indicated in Table 1. Once the force was normalized to account for the deposit thickness, a correlation between the average number of bends to failure and the maximum normalized deformation force was observed as shown in Fig. 1. It is not totally unexpected that samples which were stronger were also less ductile.

Laboratory Starter Sheets

To understand the effect of anode composition and thiourea on starter sheet ductility, laboratory electrorefining experiments were conducted. Sections of commercial anodes and cathodes were employed along with commercial electrolyte. Details of the electrorefining experiments were previously reported [4, 5, 9].

Table 1 Selected concentrations and average bends to failure for commercial starter sheet samples

Sample	As (ppm)	Bi (ppm)	Sb (ppm)	Pb (ppm)	Ag (ppm)	S (ppm)	Ave bends to failure	Thickness (mm)
Comm 1	3.0	0.1	0.7	0.2	1.7	23.0	2.6	0.60
Comm 2	6.7	0.2	1.2	0.6	3.3	15.3	4.0	0.39
Comm 3	1.1	<0.1	0.3	0.1	6.6	3.1	5.6	0.57
Comm 4	0.8	<0.1	0.1	0.3	2.4	18.4	11.5	0.22

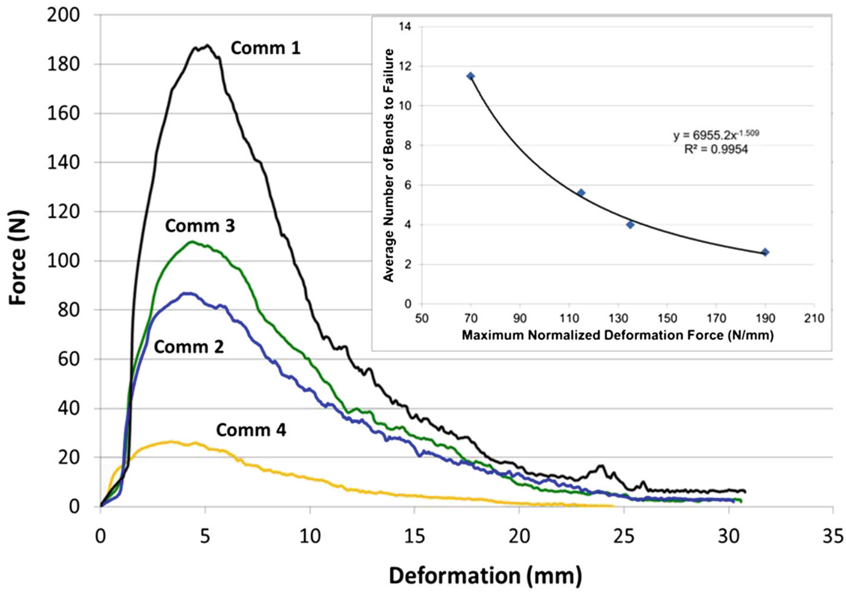

Fig. 1 Force versus deformation curves from one-point loading test for commercial samples. *Insert* Average number of bends to failure versus maximum normalized deformation force

Three experimental series were conducted. The conditions for each series and the average bends to failure are provided in Table 2. With 95% confidence, Series 2 (high molar ratio anodes) produced more ductile starter sheets than Series 3 (low molar ratio anodes with thiourea), which in turn was more ductile than Series 1 (low molar ration anodes).

Fourteen or fifteen electrorefining tests were conducted in each series. Four electrodeposits were produced in each test. Two deposits were subjected to the bend to failure test. Two were available for other characterization. From these extra samples, three specimens were selected from each series and sent to UFMG one-point bending measurement. The samples are identified as Lab with the series number and an arbitrary letter (A through C).

Figure 2 shows normalized load (N) versus deformation (mm) curves obtained for each lab produced Cu sample. Load was normalized based on differences in sample thickness. The range of thickness was 1.627–1.95 mm. An initial fracture (not complete breakage) was observed for samples Lab 1A, Lab 1B, Lab 3A, and Lab 3B during the one point bending test, thereby indicating that such samples are less ductile. This correlates well with the bend test values where Series 1 and 3 were less ductile than Series 2.

Moment (M) versus bending angle curves were plotted up to a bending angle of 60º (Fig. 3). The maximum angle of the test is likely greater than the typical wedge angle during stripping. It can be seen that the curves exhibit similar behavior: the bending moment increases parabolically with angle, and then displays increasing

Table 2 Summary of each series experimental conditions and average bend test results

Lab series	Anode As/(Sb + Bi) molar ratio	Daily glue (g/tonne)[a]	Avitone (g/tonne)	Thiourea (g/tonne)	Average bends per mm thickness	Std dev. of bends/mm
1	0.54	240	27	0	4	2
2	3.82	240	27	0	8	4
3	0.54	240	27	240	6	2

[a]Prior to each plating cycle 1800 g/tonne of top glue was added to the electrolyte

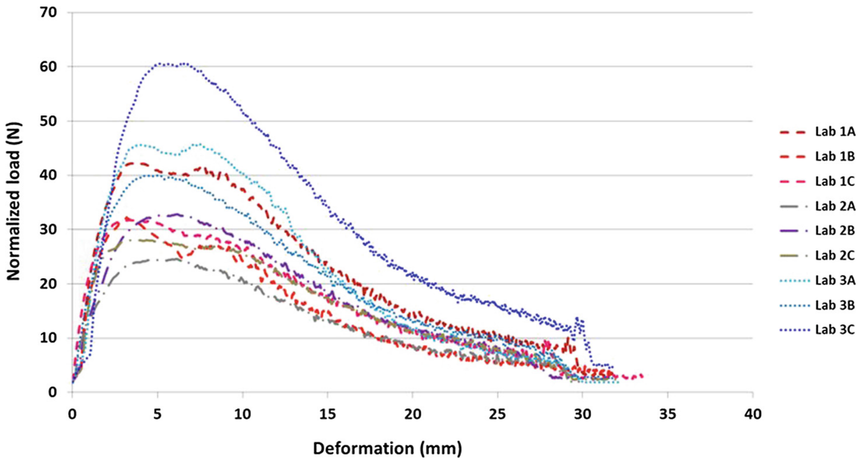

Fig. 2 Normalized load versus deformation curves obtained for the lab Cu samples

oscillations as the testing angle increases. These oscillations, which were observed for angles above about 40º, are probably associated with the friction between the punch and the sample, as the horizontal component of the bending force increases with the bending angle. The surface roughness has a direct influence on the friction between the punch and the specimen, making it difficult to assign a specific meaning to these oscillations. Figure 3 also reveals that the curve obtained for samples Lab 1A, Lab 1B, and Lab 3B reached a peak at about 48°, 51° and 59°, respectively, and then decreased, which was caused by the fracture of the corresponding sample. Again, this indicates that these Cu deposits present a relatively lower ductility and, therefore may present problems during loop making.

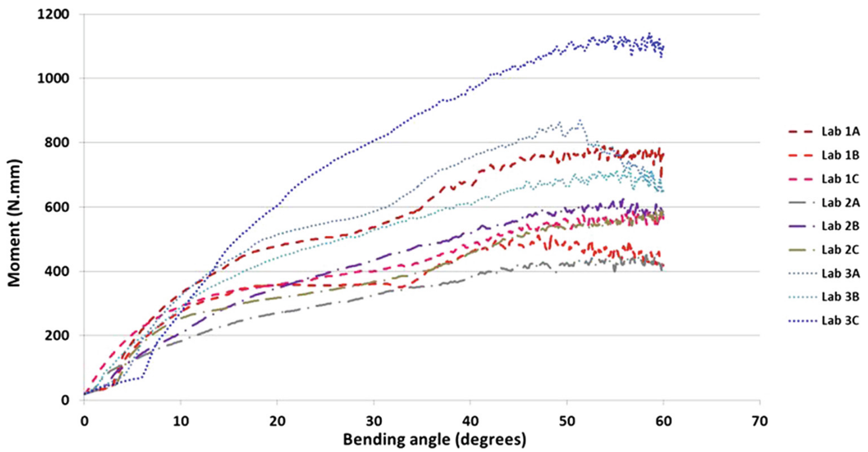

Fig. 3 Moment versus bending angles curves obtained for the Cu samples plotted with normalized data

All bent samples were submitted manually to further bending (about 180°)—one cycle, in an attempt to simulate the preparation of loops. The samples Lab 1B, Lab 3A, and Lab 3B broke, while a severe fracture was observed for samples Lab 1A and Lab 1C. This again correlates well with the bend test values where Series 1 and 3 were less ductile than Series 2.

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 the crystallographic texture, grain size, thickness and stress concentrators in the specimens. Considering the testing of non-porous Cu samples (as visualized), the behavior observed here would be probably related to the crystallite orientation and size. A careful polishing and metallographic analysis should be performed to generate additional information.

Comparison of the results from the industrial bend test and one-point bending test did not produce a strong correlation as seen with the commercial samples. On average, the Lab 2 samples which had the highest number of bends to failure needed the least amount of force to deflect the samples. The best commercial

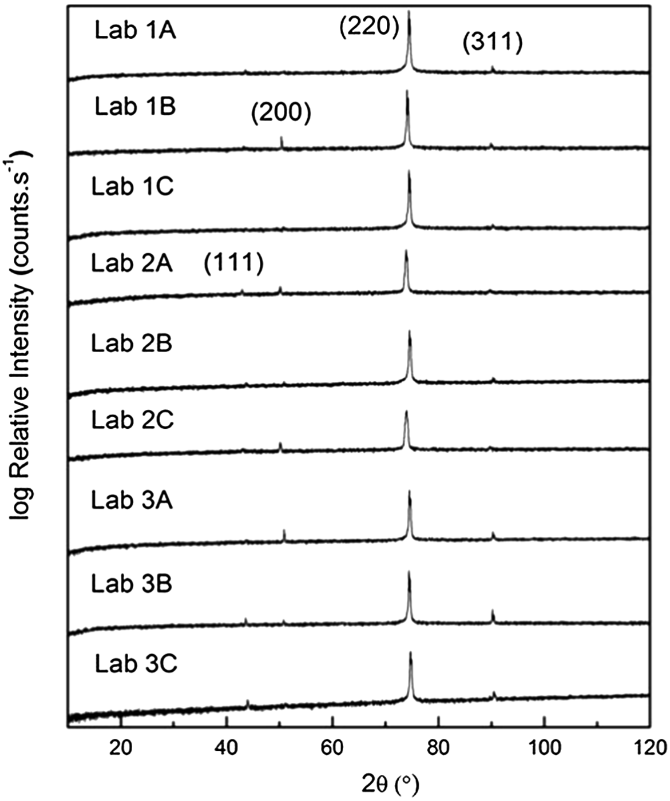

Fig. 4 XRD patterns for laboratory starter sheet deposits

Table 3 Relative intensity of the XRD peaks detected for the lab samples

Sample	Relative intensity			
	(111)	(200)	(220)	(311)
Lab 1A	–	–	1	0.008
Lab 1B	–	0.017	1	0.010
Lab 1C	–	–	1	–
Lab 2A	0.034	0.043	1	–
Lab 2B	–	0.011	1	0.016
Lab 2C	–	0.061	1	–
Lab 3A	–	0.035	1	0.028
Lab 3B	0.016	0.014	1	0.038
Lab 3C	0.014	–	1	0.031

sample also needed the least amount of force. The one-point bending test seems to indicate that starter sheets need to be weaker and more ductile to perform better in the industrial bend test.

In an attempt to understand the root causes of the bend and one-point bending measurements, XRD was performed on the laboratory Cu deposits. Figure 4 shows the XRD patterns. The relative intensity of the peaks is given in Table 3. Only peaks ascribed to Cu crystallites were detected. As can be seen, the preferred orientation detected in all samples was the (220). It can also be observed that the relative intensity of orientation (200) was magnified for samples Lab 1B, Lab 2A, Lab 2B, Lab 2C, Lab 3A and Lab 3B. The increased presence of the (200) plane was also detected during our previous investigation [4, 5, 9] and correlated to improved bend test results. These XRD data appear to confirm this correlation.

It therefore appears that Sb(V) in the electrolyte promotes the orientation of the deposit in favor of the (220) plane parallel to the surface. Change in anode chemistry decreases Sb(V) and promotes the growth of grains not completely orientated with the (220) plane. Thiourea at the dosage used also promotes this trend, but not as effectively as the change in anode chemistry. As stated previously, a detailed investigation on the crystallite size and type of growth (via cross-section analysis) may help us to further explain the observed trends.

Conclusions

Physical characterization of commercial and laboratory produced copper starter sheet materials was conducted. One point bending tests provided complimentary data about the strength and ductility of the electrodeposits. The one point bending test data revealed that, in general, samples that perform well in an industrial bend test require less force for deformation.

XRD analysis confirmed previous observations that samples produced with a higher molar ratio anode or in the presence of thiourea exhibits grains with more (200) orientation. The number of bends appears to be a function of the relative intensity of (200) plane. Anode chemistry appears to affect electrolyte chemistry and the deposit structure of starter sheets. The detrimental ductility efforts associated with using low molar anodes can be mitigated to some extent by the addition of thiourea. However, the use of anodes with a molar ratio greater than two is highly recommended based on the literature.

To further understand the root causes of the physical characterization reported in this report, detailed microstructural and textural analysis should be conducted.

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