The effect of antimony, chloride ion, and glue on copper electrorefining

T. J. O'KEEFE

Materials Research Center, University of Missouri, Rolla, Missouri, USA

L. R. HURST

Homer Research Laboratory, Bethlehem Steel Company, Bethlehem, Pa, USA

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A study has been made to determine the effect of antimony, chloride ion, and glue on copper electro-refining. All deposits were made at a temperature of 65° C on a titanium cathode. Current densities of 398 A m^{-2} and 133 A m^{-2} were used. The deposits were analyzed by scanning electron microscopy (SEM) and X-ray diffraction (XRD) to determine morphology and crystal orientation. Atomic absorption (AA) and Auger spectroscopy (AES) were used to study the chemical composition of the deposits and a simple bend test was used to determine structural integrity. It was found that when the antimony concentration in the electrolyte exceeded 300 ppm, brittle deposits were produced containing considerable amounts of antimony. Very small amounts of chloride ion (1·5 ppm or above) decreased the codeposition of antimony greatly and produced ductile deposits. However, at a chloride ion level of 15 ppm or above, the back side of the deposit had a very rough, powdery appearance. The effect of glue was to counteract this and to produce a mirror-like finish on the deposit back.

1. Introduction

In copper electrorefining operations the presence of impurities in the electrolyte can have a great impact on both the process and the resulting deposit. Concentrations of these substances in the parts per million (ppm) range can affect the process and deposit in either a beneficial or detrimental fashion.

Two common impurities are chloride ion and antimony. The effect of chloride ion on the electrode processes has been the subject of considerable research [1–6]. It is generally agreed that it acts as a cathode depolarizer until its concentration exceeds a certain critical level, beyond which it acts as a cathode polarizer. The exact value of this critical level seems to be temperature-dependent and therefore varies, depending on experimental conditions.

Less work has been done on the effect of chloride ion on the quality of the copper deposit.

Gauvin and Winkler [1] reported that chloride ion additions up to 50 mg l^{-1} produced increasing hardness and reflectivity because of grain refinement. Additions beyond this caused detectable adsorption of CuCl in the deposit and lowered current efficiency. Lakshmanan *et al.* [6] reported that additions of chloride ion to the 10 ppm level promoted (022) orientated deposits. Additions beyond this amount favoured (111) growth.

Antimony is introduced into the electrolyte via the anodes. Its presence in the electrolyte can result in lowered cathode quality because of deposit contamination. Several researchers ascribe this contamination to entrapment of antimony precipitates [7–9].

Different organic substances are often added to the electrolyte for their beneficial effects on the refining operation. They are commonly used for grain refinement, deposit levelling and deposit brightening. Numerous investigations have been done on the effect of gelatin, animal glue and

protein on copper deposition [5, 10–14]. In commercial electrorefining, pure gelatin is seldom used, but glue is a very common additive.

In addition to impurities and additives in the electrolyte, the material used for the cathode and the operating current density can influence copper deposition [15, 16]. In recent years, the introduction of titanium blanks has represented a major advance in the industry. Titanium cathodes have two principal advantages over the traditional method of using copper starter sheets [15]. Copper cathodes are susceptible to corrosion in the acid sulphate environment found in electrorefining cells. The corrosion can be especially severe at the air–liquid interface. Titanium is made inactive by an oxide film in a manner similar to aluminium. This makes it very resistant to corrosion, and it is almost impervious to attack by chloride ion. Adhesion of the deposited copper to the copper starter blanks is another problem. Chemical parting agents must be applied to overcome this difficulty. With titanium, the oxide layer acts as a permanent, self-repairing parting agent and therefore oiling is avoided completely.

Another trend in copper electrorefining has been the use of higher current densities. This represents a technique for increasing production without corresponding increases in capital expenditure. However, the increase in production can only be made if cathode quality remains high and no serious decreases occur in current efficiency. Tuddenham et al. [16] investigated the effect of current density on cathode purity and current efficiency, and they reported that the purity of the cathodes produced at $430 \, A \, m^{-2}$ compared favourably with those produced at $215 \, A \, m^{-2}$. Thus, satisfactory deposits are possible as long as proper control is maintained.

Most previous studies were done using copper starter sheets and more or less conventional process parameters. Since antimony, chloride ion and glue were shown to affect the deposition process during these studies, it was desirable to determine the effects these additives would have at high current densities when a titanium electrode is used. The initial stages of deposition were thought to be the most critical because of direct interactions between the additives and the substrate titanium. For this reason, the deposition times used were relatively short and many of the features

that were thought to be important would occur during nucleation and the early stages of growth.

2. Experimental

2.1. Electrolysis

All experiments were performed galvanostatically using a Hewlett–Packard Model 3284 A power supply. The current density for all of the experiments was $398 \, A \, m^{-2}$, except for a limited number of tests which were made at $133 \, A \, m^{-2}$. A Precision Scientific controlled water bath was used to maintain an electrolyte temperature of $65 \degree C$ ($\pm 2 \degree C$). The electrolyte was prepared from Fisher certified grade cupric sulphate pentahydrate and Fisher reagent grade sulphuric acid; respective concentrations being $36 \cdot 4 \, g \, l^{-1}$ copper ion and $163 \cdot 8 \, g \, l^{-1}$ sulphuric acid. A total of 750 ml of this solution was used for each run, with a cylindrically shaped Nalgene beaker serving at the cell. Deposition time for all experiments was 6 h, except for a few 24 h deposits which were used for Auger spectroscopy studies.

Electrolytically refined copper served as the soluble anodes for the experiments. Before each experiment the anodes were prepared by soaking in a 40% HNO_3 solution, then rinsing with tap water, followed by distilled water, and finally acetone. They were then immediately dried in a hot air stream. The cathodes were commercial titanium with working dimensions of 3·6 cm × 4·2 cm. They were prepared by abrading with 400 grit metallography grade paper and then rinsing with tap water, distilled water, acetone and finally drying with hot air. Teflon edge strips were used to prevent edge growth during electrolysis and to facilitate deposit removal. Two anodes and one cathode were used, and a slotted plexiglass top cover maintained a cathode to anode distance of 3·5 cm. The individual stock solutions for reagent additions consisted of 10 000 ppm antimony added as potassium antimony tartrate, 4000 ppm chloride ion added as potassium chloride, and 1000 ppm Swift's TCP-5V glue. The glue stock solution was refrigerated to prevent deterioration. When more than one reagent was added the order of addition was antimony, chloride ion and then glue. The concentrations of the reagents in the electrolyte were varied from 0 to

600 ppm antimony, 0 to 30 ppm chloride ion and
0 to 60 ppm glue.

The electrodes were removed from the cell
at the end of each experiment and treated as
described above for their preparation. The copper
deposits were carefully removed from the titanium
by a sharp knife.

2.2. *Deposit analysis*

A number of different tests were performed on
the deposited copper in an effort to determine
various effects of the process parameters. The
deposit's morphology and crystal orientation were
determined by scanning electron microscopy (SEM)
and X–ray diffraction (XRD). The ductility was
measured on a relative basis by subjecting the
deposits to a series of 180° bends until fracture
occurred. The antimony content of the deposits
was determined by atomic absorption (AA) and
Auger spectroscopy (AES). For the AES cross-
section tests, 24 h copper deposits were used.
The process variables, except time, were the same
in all aspects as used to produce the 6 h deposits.

3. Results

All of the results to be presented were obtained
from deposits made at 398 A m^{-2} unless otherwise
specified.

3.1. *Scanning electron microscope analysis*

Morphologies of the deposits made from solutions
containing various concentrations of antimony,
chloride ion, and/or glue were determined using
SEM techniques. Deposits made from additive free
electrolyte were flat and smooth with both front
and back sides having a cohesive appearance with
no obvious crevices, pits, or separations between
the crystals (Figs. 1 and 2).

The addition of antimony increased the
crystallite size with individual crystals taking on a
nodular shape. Crevices or lack of continuous
growth were visible on both the front and back of
the cathode, with an apparent lack of cohesion
between the grains (Figs. 3 and 4). The separation
between the crystals became more pronounced as
the concentration of antimony in the electrolyte
increased. The increase in crystallite size is gradual
up to 200 ppm antimony with an abrupt change
occurring between this concentration and 300 ppm
antimony. The 600 ppm antimony deposit was an
extreme example of this condition with the pres-
ence of a myriad of cracks which, for the most part,
appeared to be intergranular. Cross-section micro-
graphs of the 600 ppm antimony deposit showed
that the separations extended continuously through
the deposit and were not limited to the front and
back surfaces (Figs. 5 and 6).
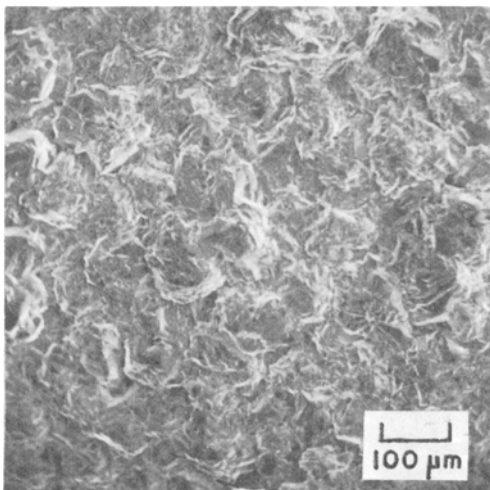
The presence of chloride ion reduced the crystal

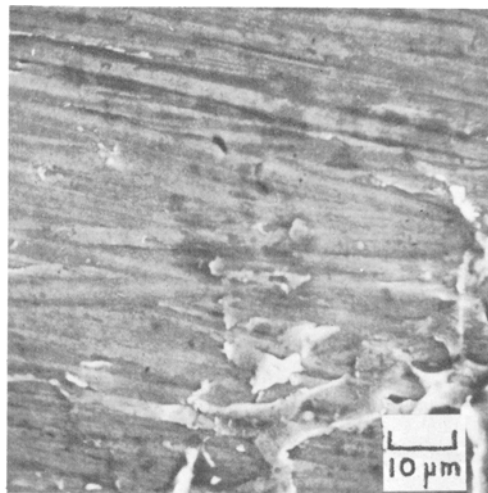

Fig. 1. Cu deposit, front side with no additives (× 100).

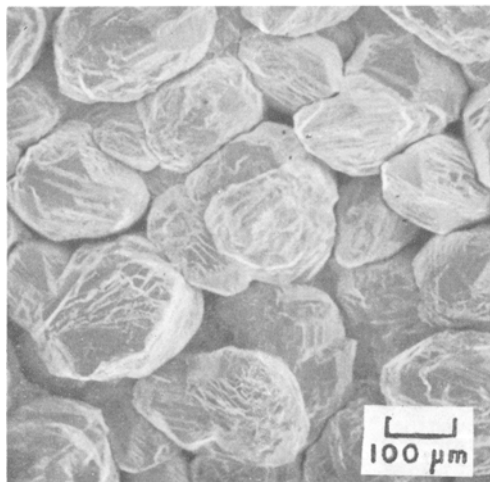

Fig. 2. Cu deposit, back side with no additives (× 1000).

Fig. 3. Cu deposit, front side with 300 ppm Sb (× 100).

Fig. 5. Cu deposit, cross-section of next to front side, with 600 ppm Sb (× 300).

size. The back of the deposit was very rough and irregular with a powdery, faceted appearance when the chloride ion concentration was 15 ppm or greater (Fig. 7).

Glue decreased the crystal size at a concentration of 7·5 ppm, but the crystal size increased as the concentration was raised to 30 ppm. The deposits appeared to be cohesive on both front and back side (Figs. 8 and 9).

The addition of chloride ion to high antimony electrolytes, i.e. 600 ppm, reduced the crystal size compared to that in which there was only 600 ppm antimony and eliminated the grain boundary separations on the front of the deposit (Fig. 10).
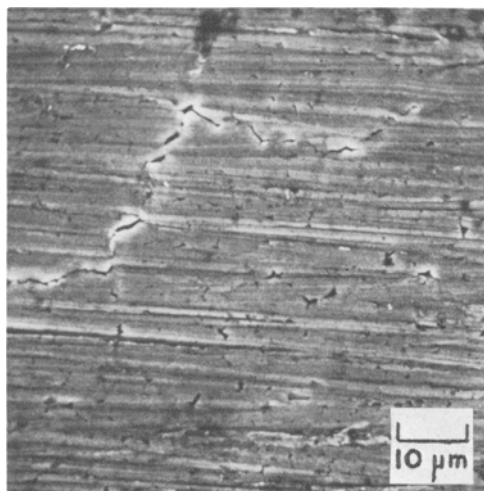
Separations were not visible when the deposit was viewed in cross-section. However, when the chloride ion concentration equalled or exceeded 15 ppm the back appeared to be very powdery and did not produce a surface identical with the initial cathode surface commonly obtained when no additives were present. The appearance of the back side was similar to that obtained when chloride ion was the only reagent added.

Additions of glue to 600 ppm antimony electrolyte reduced the crystal size, though not as much as chloride ion had. Separations between the crystals
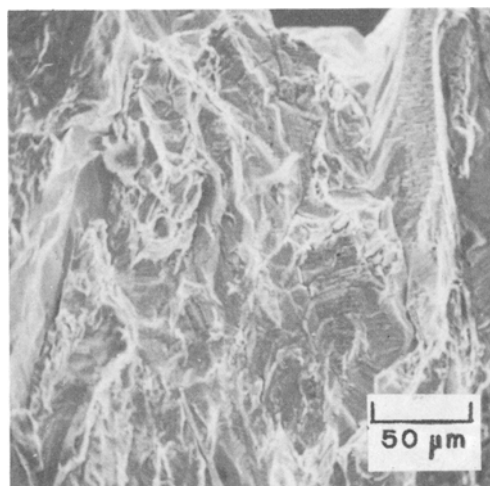

Fig. 4. Cu deposit, back side with 300 ppm Sb (× 1000).

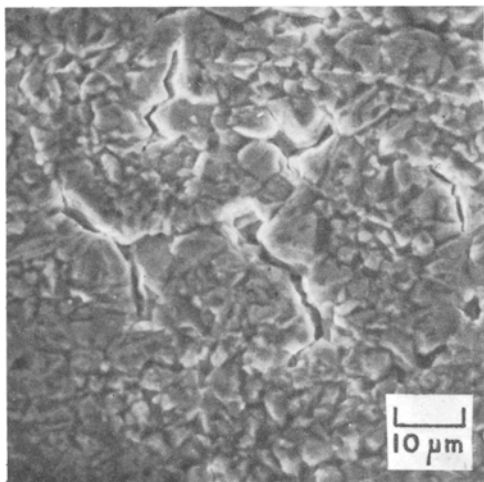Fig. 6. Cu deposit, cross-section of next to back side, with 600 ppm Sb (× 300).

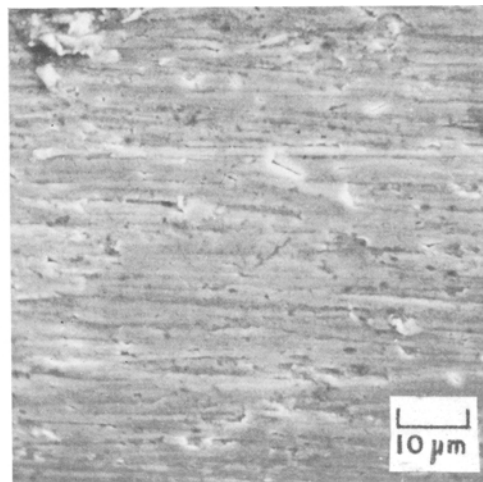Fig. 7. Cu deposit, back side with 30 ppm Cl⁻ (× 1000).

Fig. 9. Cu deposit, back side with 30 ppm glue (× 1000).

were less pronounced but were still evident. The back of the deposit had a similar appearance to deposits made without additives.

Chloride ion and glue together produced a deposit similar to glue alone, but with slightly more pitting on the back side.

With all three reagents present, the deposit had a very fine crystal structure and the back side was almost devoid of separation and pitting. At least this was true for the concentrations used during this study.

3.2. *X-ray diffraction analysis*

The results of the XRD analyses are summarized in Table 1. With no additives present in the electrolyte the (220) orientation was predominant, with some indications of (331) and (420) orientations.

Additions of antimony produced marked changes in the deposit orientation. For antimony levels of 100 and 200 ppm the (111) orientations predominated but reverted back to the (220) orien-

Fig. 8. Cu deposit, front side with 30 ppm glue (× 100).

Fig. 10. Cu deposit, front side with 600 ppm Sb/30 ppm Cl⁻ (× 100).

Table 1. X-ray diffraction orientation data

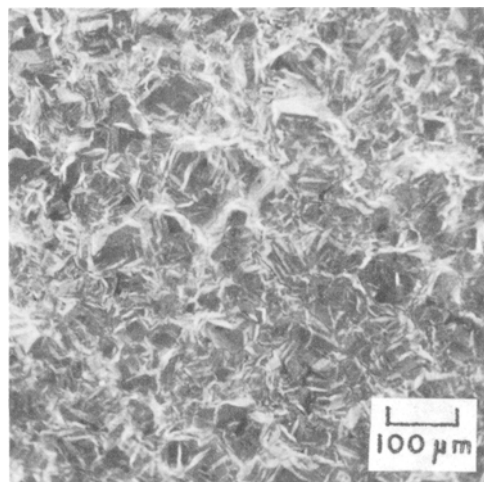| Entry	Addition (ppm)	(111)	(200)	(220)	(311)	(222)	(400)	(331)	(420)
1	Random Orientation	100	46	20	17	5	3	9	8
2	No additives	0	0	100	0	0	0	13	6
3	Sb 60	3	0	100	0	0	0	12	1
4	Sb 100	100	44	59	35	6	2	13	9
5	Sb 200	100	16	86	22	5	3	37	16
6	Sb 300	31	12	100	28	3	2	30	14
7	Sb 600	44	13	100	24	4	3	21	10
8	glue 7·5	25	11	100	16	2	0	7	3
9	glue 15	60	23	100	77	4	6	63	6
10	glue 30	8	1	100	8	0	0	4	1
11	Cl⁻ 7·5	3	1	100	2	0	0	20	14
12	Cl⁻ 15	17	5	100	6	0	0	33	22
13	Cl⁻ 30	41	4	100	4	0	0	17	12
14	Sb 600, glue 7·5	14	2	100	2	0	0	18	9
15	Sb 600, glue 15	10	14	100	11	3	3	27	13
16	Sb 600, glue 30	8	6	100	6	0	1	38	5
17	Sb 600, glue 60	44	15	100	15	0	0	39	7
18	Sb 600, Cl⁻ 1·5	0	0	100	0	0	0	10	2
19	Sb 600, Cl⁻ 3·5	0	0	100	0	0	0	6	4
20	Sb 600, Cl⁻ 7·5	0	0	100	0	0	0	16	2
21	Sb 600, Cl⁻ 15	0	1	100	0	0	0	6	2
22	Sb 600, Cl⁻ 30	0	1	100	0	0	0	18	3
23	Cl⁻ 30, glue 7·5	0	0	100	0	0	0	1	1
24	Cl⁻ 30, glue 15	1	0	100	0	0	0	1	1
25	Cl⁻ 30, glue 30	0	0	100	0	0	0	5	0
26	Sb 600, Cl⁻ 7·5, glue 7·5	7	0	100	1	0	0	2	1
27	Sb 600, Cl⁻ 30, glue 30	0	0	100	1	0	0	1	0

tation for concentrations of 300 and 600 ppm antimony.

For additions of glue or chloride ion alone, (220) was the predominant orientation. With increasing chloride ion concentration the occurence of (111) orientation also increased.

Varying concentrations of glue or chloride ion were added to electrolyte containing 600 ppm antimony. The results of antimony and glue mixtures were similar to those of 600 ppm antimony alone. Additions of 7·5, 15, and 30 ppm glue did tend to reduce the level of (111), (200), and (311) orientations.

Chloride ion and 600 ppm antimony produced very different results from 600 ppm antimony alone. The (220) was the principal orientation and the (331) and (420) were always visible, but all other orientations were missing or present at very low levels. The orientations were similar to those of deposits produced with no additives.

When chloride ion and glue were added together the orientation was predominantly (220). All other orientations were missing or barely visible. Similar results to this were obtained when varying amounts of chloride ion and glue were added in combination to electrolyte containing 600 ppm antimony.

3.3. Bend test

The degree of ductility or brittleness of a deposit was measured by the number of 180° bends it could withstand without fracturing. The results of this test are summarized in Table 2. The term brittleness is used here in a relative context to indicate structural instability. This rather inexact

Table 2. Bend test data

Addition (ppm)	Number of 180° bends before fracture
No additives	9
Sb 60	8
Sb 100	9
Sb 200	6
Sb 300	3
Sb 600	0
glue 7·5	9
glue 15	6
glue 30	3
Cl⁻ 7·5	11
Cl⁻ 15	12
Cl⁻ 30	10
Sb 600, glue 7·5	0
Sb 600, glue 15	0
Sb 600, glue 30	0
Sb 600, glue 60	0
Sb 600, Cl⁻ 1·5	10
Sb 600, Cl⁻ 3·5	10
Sb 600, Cl⁻ 7·5	10
Sb 600, Cl⁻ 15	9
Sb 600, Cl⁻ 30	8
Cl⁻ 30, glue 7·5	7
Cl⁻ 30, glue 15	6
Cl⁻ 30, glue 30	6
Sb 600, Cl⁻ 7·5, glue 7·5	8
Sb 600, Cl⁻ 30, glue 30	10

qualitative test was used to indicate the general ability of the deposit to withstand the physical handling associated with commercial operations such as automatic stripping.

As the antimony concentration in the electrolyte increased, brittleness increased correspondingly. At 600 ppm antimony the deposit was extremely brittle and fractured before one bend was complete.

The presence of glue produced a similar trend. Increasing concentrations reduced the number of bends required for fracture.

The addition of chloride ion did not reduce ductility. The deposit produced with 15 ppm chloride ion withstood the largest number of bends of all the deposits tested.

The addition of glue to electrolyte containing 600 ppm antimony did not alter the ductility. All samples tested fractured on the first bend. The addition of chloride ion to electrolyte of this antimony concentration did increase ductility. Chloride ion concentrations as low as 1.5 ppm were sufficient to restore ductility to a value comparable to those from additive-free solutions.

With mixtures of chloride ion and glue present the ductility was always lower than that obtained when chloride ion alone was present. At low concentrations of glue the ductility was lower than might be predicted when examining results produced from each additive alone. However, as the glue concentration was increased the chloride ion enhanced deposit ductility from that obtained for glue alone.

3.4. Atomic absorption analysis

Because of the changes in the copper cathodes observed when antimony was added to the electrolyte it was desirable to determine if the impurity was taken into the metal. Samples were dissolved in 50% HNO_3 and analyzed by AA spectroscopy to determine their antimony content.

When antimony alone was added to the solution, its concentration in the deposit increased as the quantity of antimony in the electrolyte was raised. A critical point appeared to occur between 200 and 300 ppm where a twentyfold increase in antimony in the deposit occurred, rising from 0·0058% to 0·12%. At 600 ppm the antimony content of the deposit was approximately 0·3%.

The additions of glue to the 600 ppm antimony electrolyte seemed to result in a slight increase in the antimony concentration in the deposit. The maximum antimony content was found with an electrolyte concentration of 600 ppm antimony and 15 ppm glue.

With chloride ion additions to the 600 ppm antimony electrolyte, a decrease of about two orders of magnitude in the antimony content of the copper was noted. A chloride ion concentration as low as 1·5 ppm was sufficient to reduce the antimony content to 0·0027%. When all three reagents were added this same reduction was still noticeable.

These results are summarized in Table 3.

3.5. Auger spectroscopy analysis

Two 24 h deposits were made to provide a sufficient thickness for analysis of the cathode cross-section

Table 3. Atomic absorption analysis

Addition (ppm)	% Antimony in deposit
Sb 60	0.0023%
Sb 100	0.0033%
Sb 200	0.0058%
Sb 300	0.12%
Sb 600	0.30%
Sb 600, glue 7·5	0.26%
Sb 600, glue 15	0.37%
Sb 600, glue 30	0.35%
Sb 600, glue 60	0.31%
Sb 600, Cl⁻ 1·5	0.0027%
Sb 600, Cl⁻ 3·5	0.0038%
Sb 600, Cl⁻ 7·5	0.0023%
Sb 600, Cl⁻ 15	0.0035%
Sb 600, Cl⁻ 30	0.0027%
Sb 600, Cl⁻ 7·5, glue 7·5	0.0023%
Sb 600, Cl⁻ 30, glue 30	0.0029%

with AES. The electrolyte for one test contained 600 ppm antimony, and the other had 600 ppm antimony and 30 ppm chloride ion. The front faces of three of the 6 h deposits were analyzed using AES. The electrolyte from which these deposits were produced contained 600 ppm antimony, 600 ppm antimony and 1·5 ppm chloride ion, and 600 ppm antimony and 30 ppm chloride ion respectively.

The 24 h deposit produced at 398 A m^{-2} using antimony as the only additive in the electrolyte showed a peak of 454 eV which indicated the presence of antimony. After sputtering into the sample to an approximate depth of 50 Å the peak at 454 eV was still present and the relative intensity of antimony to copper increased slightly after sputtering. The analysis of the antimony only 6 h deposit also showed the presence of antimony.

The AES scan from the antimony and 30 ppm chloride ion 24 h deposit showed a peak of 181 eV corresponding to chlorine. However, no peak appeared at 454 eV indicating an absence of antimony. After sputtering to a depth of 50 Å, chlorine was still present but the relative intensity of chlorine to copper decreased sharply. Front side analysis of the 6 h deposit with the same additive also showed the presence of chlorine.

The front side scan of the 600 ppm antimony and 1·5 ppm chloride ion deposit was almost identical to the 600 ppm antimony and 30 ppm chloride ion scan. No peak at 454 eV appeared and the relative intensity of chlorine to copper was the same.

These results are summarized in Table 4.

Table 4. Auger analysis of copper deposits

Addition (ppm)	Area analysed	Elements	Peak to peak distance (cm)	Relative intensity
Sb 600	cross-section before sputtering	Cu	7·4	100
		Sb	2·4	32
Sb 600	cross-section after sputtering	Cu	4·7	100
		Sb	1·7	36
Sb 600	front side	Cu	5·7	100
		Sb	0·7	12
Sb 600, Cl⁻ 30	cross-section before sputtering	Cu	8·0	100
		Cl	4·3	54
		Sb	0·0	0
Sb 600, Cl⁻ 30	cross-section after sputtering	Cu	12·8	100
		Cl	1·4	11
		Sb	0·0	0
Sb 600, Cl⁻ 30	front side	Cu	2·3	100
		Cl	1·6	70
		Sb	0·0	0
Sb 600, Cl⁻ 1·5	front side	Cu	6·4	100
		Cl	4·5	70
		Sb	0·0	0

Fig. 11. 'Lacy' Cu deposits on Ti Cathode.

3.6. Low current density tests

It has been reported [5] that under certain conditions it was possible to produce a 'lacy' copper deposit, i.e. one that did not completely cover the titanium cathode. One set of conditions that yielded this was low current density (133 $A\,m^{-2}$), high temperature and the presence of chloride ion. Fig. 11 shows an example of this type of deposit. Tests made during this study indicated that a titanium surface abraded with 600 grit paper showed a complete deposit cover despite the above conditions.

On a smooth titanium surface, where the only preparation was acetone cleaning, reagent-free solution gave complete deposition. However, the addition of 30 ppm chloride ion resulted in 'lacy' deposits. The addition of 30 ppm glue to an electrolyte containing chloride ion was able to counteract this effect and give complete coverage of the titanium.

4. Discussion

The results presented previously have shown that each of the additives (antimony, chloride ion, and glue) has a distinctive effect on the electrocrystallization of copper with titanium as the substrate. Even more important, there were interactions between the additives which tended to minimize the ill effects that were caused by each individually.

Some of the possible causes for the embrittling effect of antimony and the ability of chloride ion to cancel this, as well as the role of glue in modifying the spotty or powdery deposition caused by chloride ion, and the importance of these to insuring high quality copper cathodes will be discussed in the subsequent sections.

4.1. Antimony contamination

The problem of antimony contamination of electrorefined copper deposits has been studied previously [9], and it was stated that the formation of antimony arsenates played the major part in deposit contamination. The mechanism in this case was felt to be the physical inclusion of the particles into the copper. In this study the electrolyte was doped using reagent grade chemicals, whereas tankhouse electrolyte was used in the previous study. The antimony was introduced here in an oxidation state of +3, whereas with the tankhouse conditions the antimony would have been introduced via the oxidation process at the anode. The final state of the antimony in these two cases could differ and this would have to be taken into account when evaluating its behaviour. The very large increase in the amount of antimony in the deposit that occurred when its concentration in the electrolyte was raised from 200 to 300 ppm indicates that the mechanism for its inclusion goes from physical entrapment to codeposition.

The degree of brittleness exhibited by the deposit increased with increasing antimony content but not in a directly proportional manner. The antimony in the deposit is probably not, per se, the only reason for the brittleness. It has been reported [17] that antimony will only cause a slight reduction in the ductility of cast copper up to a level of 0·5%. The lack of ductility in the copper as it is deposited is probably the result of the extensive separations between the crystals and the distinct lack of coherence at the grain boundaries noted in the high antimony deposits. The fact that the lateral growth of the crystals is incomplete is readily apparent from the high degree of faceting observed on the cross-sections. This morphology is very comparable to a deposition surface and is probably not a result of fracturing. This structural defect is probably the major contributor to the lack of integrity and strength of the deposits.

Hospadaruk and Winkler [4] reported that the addition of 25 ppm gelatin appeared to increase antimony inclusion in copper deposits. Results gathered during this study are inconclusive on this point. However, any increase was at best marginal, especially when compared to the very large increases that occurred when the antimony concentration of the electrolyte was raised from 200 to 300 ppm.

The use of chloride ion to reduce antimony contamination has long been practised by commercial copper refiners. Original theories attributed this to the precipitation of antimony oxychlorides, but there is now considerable speculation about the actual mechanism involved. Results from this study show that in an electrolyte containing 600 ppm antimony the addition of 1·5 ppm chloride ion reduced the codeposition by a factor of 100. If stoichiometric proportions are necessary, then the oxychloride theory is unlikely for the conditions used in this research.

AES scans show that the chlorine to copper intensity does not decrease as the chloride ion content of the electrolyte is decreased from 30 ppm to 1·5 ppm with 600 ppm antimony also present. This suggests that in the range of chloride ion concentrations considered here, its concentration in the double layer or the adsorbed concentration remains fairly constant regardless of the content in the bulk solution. If so, this could explain why a very low amount of chloride ion greatly reduces antimony codeposition and no further decreases are noted as the chloride ion concentration is increased to 30 ppm. The chloride ions in the double layer could act to complex antimony ions and prevent their deposition onto the cathode by altering the overvoltages required for reduction. Further evidence in support of this idea is Raub's work [18] on the electrodeposition of copper–antimony alloys. He showed that in alkaline baths, the percentage of each metal deposited was highly dependent on the complexing anion present. It is also possible that specific adsorption of the chloride ion at the cathode could influence or poison antimony deposition and this could account for the effectiveness of the very low anion concentrations. However, it becomes readily apparent that the behaviour of the antimony ion is probably very complex and an exact explanation would require additional study.

4.2. Deposit morphology

The morphologies of the high antimony deposits were distinguished principally by their large crystallite size. Hospadaruk and Winkler [4] reported that antimony acts as a polarizer in copper electrolytes. This fact along with the experimental conditions of high current density and no bath agitation would seem to favour fine crystal size because of increased nucleation. This increased polarization could cause a shift from the more common lateral growth mode observed for copper to an outward mode which is characteristic of metals with higher crystallization overpotentials. This would also partly account for the incomplete growth noted at the crystal grain boundaries, since a fibrous-type growth was being approached.

With the 300 and 600 ppm antimony deposits, there were very distinct intergranular separations visible as noted previously. The exact origin of this condition is not known. There are indications that they occurred during deposition and were a result of incomplete lateral growth of the crystallites which yielded boundary separations of greater magnitude than usual. However, it is not known whether the separations observed on the back face of the deposits were present initially, thus they may well have been induced by stresses incurred during sample preparation.

The decreased crystal size noted when glue additions were made is consistent with results reported by other researchers. Lorenz [13] noted that glue worked best as a grain refiner when it was used alone in concentrations of 5 to 10 ppm. Results obtained here agree with his findings.

The crystal size of the copper was reduced when the chloride ion was present in the electrolyte. AES scans show chlorine to be present in the deposits made from chloride ion-bearing electrolyte. Winkler and Gauvin [1] stated that when chloride ion is present in a deposit it will be in the form of CuCl. If so, the finely divided CuCl may represent a barrier to grain growth and increase nucleation which would explain the decrease in crystal size.

Each additive individually tended to increase the relative amounts of orientations other than (220), especially (111). For the 100 and 200 ppm antimony tests the (111) was the predominant orientation. At 300 ppm antimony, and above, the principal orientation shifted back to (220). This

shift occurred in the same range that the antimony content of the deposit changed drastically, thus giving additional evidence that the mechanism was altered at this point.

Chloride ion, when used in combination with either or both of the other reagents, produced a deposit orientation very similar to that of no additives deposit. Chloride ion, apparently, counteracted the effects of both antimony and glue, but in the process its effect on the orientation was also eliminated.

4.3. Chloride ion and glue effects

The incomplete deposition of copper on the titanium that was noted under certain process conditions has important implications for commercial operations. It can be a serious problem since such cathodes are difficult to handle and unnecessary losses may result from electrode fragmentation and breaking.

The principal conditions leading to incomplete deposition appeared to be low current density, a smooth titanium surface and the presence of chloride ion. The condition disappeared when any one of these were eliminated.

The effect of the first two is understandable. Low current density does not favour the creation of a large number of nuclei and a smooth titanium surface offers few places for the nuclei to form. The effect of the chloride ion is more difficult to elucidate. Copper electrolytes containing chloride ion have also been shown to result in a copper deposit with a powdery appearance on its back face. It is possible that these two phenomena are related; the appearance of powder on the deposit could lead to, under special circumstances, incomplete deposits. When process conditions which produced the powdery and the incomplete deposits were repeated, but with the addition of 30 ppm glue, both of these effects were eliminated. Commercial copper refiners have also used, with some success, the addition of glue to combat incomplete deposits in their tankhouse.

5. Conclusions

(1) Deposits become more brittle with increasing concentrations of antimony or glue in the electrolyte.

(2) Copper deposits made with excess antimony are brittle because of incomplete lateral growth and intergranular separations between the growing crystallites.

(3) The presence of chloride ion will counteract the embrittling action of antimony.

(4) Chloride ion affects the initial nucleation on the titanium giving a rough or powdery and faceted initial deposit.

(5) Under certain process conditions excessive chloride ion can result in discontinuous or 'lacy' deposits.

(6) Glue additions to the electrolyte can eliminate the undesirable effects of the chloride ion.

(7) The morphology and orientation of the cathode copper are dependent on which additives are dominant during deposition.

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