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The effect of glue, LIX65N and chloride ion on the morphology of electrowon copper

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The combined effects of dissolved and entrained organic extractant, LIX65N, and the addition agents, glue and chloride ion on the morphology of electrowon copper were systematically investigated. The deposit morphology was assessed by optical microscopy techniques, scanning electron microscopy (SEM) and X-ray diffraction (XRD) measurements. The results indicated that the quality of copper deposits obtained in the presence of glue and LIX65N is considerably improved by the addition of chloride ion in concentration higher than 40 ppm.

1. Introduction

Organic addition agents such as glue and separan are used in copper electrodeposition to promote the growth of smooth deposits. These organic substances, usually containing amino or other electronegative groups, are supposed to adsorb at the peaks developed on the cathode due to higher charge density or thinner diffusion layers [1–3].

The influence of these additives on the crystallographic structure of cathodes produced during the commercial electrowinning of copper is important from a practical point of view particularly in their effects on the smoothness and subsequent properties of the deposit. The growth of nodules is particularly damaging to commercial operations since they initiate short circuits in the electrowinning cells. The nodular growth can be related directly to crystallographic preference in the rate of growth. In addition, the amount of impurity both codeposited and included in the final product is related to the structure of the deposit.

The addition of small amounts of inorganic substances such as chloride ion also have beneficial effects on the structure of copper deposits. Gurevich and Pomorov [4] have shown that the addition of low concentrations of chloride ion to copper sulphate electrolytes produced a marked depolarization effect and an increase in the limiting current density for copper deposition. Bockris and Enyo [5] have observed that the cathode double layer capacitance in chloride solutions is about twice that for sulphate solutions. Lakshmanan *et al.* [6] reported that the addition of chloride ion up to the 10 ppm level resulted in a substantial increase in the (022) orientation for copper deposits obtained at 40 A ft^{-2} (ASF). This indicated preferred ridge-type growth over pyramidal growth which resulted in smooth compact deposits.

The application of leaching–solvent extraction–electrowinning is now practised commercially as an alternative to the leaching–cementation–smelting route for the recovery of copper from its ores. The interaction of the solvent extraction and electrowinning unit processes requires detailed study. Hence, it was thought worthwhile to study the combined effects of dissolved and entrained solvent extractant and the additives normally used in copper electrodeposition.

In an earlier communication [7] the effects of LIX65N alone and in combination with various concentrations of chloride ion on the morphology of electrodeposited copper were reported. LIX65N at the 8 ppm level did not produce any harmful effects on the copper deposits. The tolerance limit for chloride ion in the presence of 8 ppm LIX65N

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was increased to 100 ppm. However, higher concentrations of LIX65N, 50 and 100 ppm, produced harmful effects on the copper deposits.

In the present communication the results obtained from a systematic investigation on the effect of glue, chloride ion and LIX65N are reported. Since recent developments in copper electrowinning indicate a trend towards higher current density operation [8–11] and because previous work by the authors [6] showed a more pronounced chloride ion effect at high current density, most of the results presented in this paper were obtained at 40 ASF rather than at the more conventional current density i.e. 20 ASF; however, for comparison, some results obtained at 20 ASF are also presented.

2. Experimental and apparatus

The electrowinning cell and electrode assembly have been described [6]. The electrolyte was prepared from anhydrous copper sulphate and ultra-pure sulphuric acid. The electrolysis solution contained $20\,g\,l^{-1}$ Cu^{2+} and $150\,g\,l^{-1}$ H_2SO_4. However, some tests were done with electrolytes containing 40 and $60\,g\,l^{-1}$ Cu^{2+} in order to assess the effect of Cu^{2+} concentration on the deposit morphology. The desired concentrations of chloride ion, LIX65N and glue in the electrolyte were obtained by adding the appropriate amount of their respective stock solutions. The volume of electrolyte used in each test was 300 ml. The LIX65N used in this work was purified by the method suggested by Ashbrook [9].

Most of the copper deposits were obtained at a current density of $40\,A\,ft^{-2}$ (ASF)* for a deposition time of 60 min although additional deposits were also obtained at 20 ASF. The electrolyte was maintained at $35 \pm 1°$ C and was agitated with a glass stirrer at a constant speed of 2100 rpm. This method of electrolyte circulation consistently provided compact, coherent copper deposits at 40 ASF. At the end of the designated deposition time the cathode was removed from the cell for stripping.

The surface morphology of sections of each deposit was examined in the SEM. Optical microscopy was used to observe and measure the cross-section of the polished specimens from each deposit. Sections of the deposits were examined by X-ray diffraction (XRD) to determine their preferred orientation relative to the ASTM standard for copper powder. Current–potential curves for copper deposition were obtained as a function of various glue–chloride ion concentrations using a Wenking potentiostat model 70HP10 driven at a rate of $1\,mV\,s^{-1}$ by a Wenking model VSG72 voltage scan generator.

*1 ASF = $10{\cdot}76\,A\,m^{-2}$.

3. Results and discussion

3.1. *Glue–chloride ion effects*

The effects of various combinations of glue and chloride ion on the crystallographic orientations of the copper deposits are summarized in Table 1; the various peak intensities are presented as ratios to the ASTM standard for copper powder. The (111), (002), and (022) peak height values obtained as a function of glue (0–45 ppm) and chloride ion (0–100 ppm) concentrations are

Table 1. Crystallographic orientation of copper deposits as a function of glue and chloride ion concentrations at 40 ASF (electrolysis conditions: Cu^{2+} content = $20\,g\,l^{-1}$, H_2SO_4 = $150\,g\,l^{-1}$; T = 35° C)

Glue (ppm)	Cl^- (ppm)	Surface orientation (ratio to ASTM standard)* Orientation (111)	(002)	(022)
15	0	1·7	1·3	1·3
	2	0·3	0·2	1·8
	5	2·0	0·3	1·0
	10	3·1	0·7	1·0
	40	4·8	0·3	0·7
	100	4·2	0·5	1·3
30	0	0·2	0·4	1·7
	2	0·5	0·6	1·7
	5	3·2	0·4	1·0
	10	4·6	0·3	0·4
	40	6·6	0·2	0·5
	100	4·5	0·3	0·8
45	0	0·8	0·7	1·2
	2	1·7	0·1	0·04
	5	3·0	0·1	1·0
	10	3·2	0·5	1·0
	40	4·5	0·1	0·04
	100	4·5	0·3	0·6

* (111) 100; (002) 46; (022) 20

compared. The data show that for no added chloride ion, the preferred orientation is (022) as the glue concentration is increased from 15–45 ppm. The most notable changes occur in the (111) peak height values as the chloride ion concentration is increased for each value of glue concentration. For each glue concentration, the (111) peak height reaches a maximum at 40 ppm chloride ion, and, for a chloride ion concentration > 2 ppm, the (111) peak height values are generally highest for the 30 ppm glue addition. It is also noted that, with few exceptions, the changes effected by the glue–chloride ion combinations on the other peak height values listed in Table 1 are not as significant when compared to those for the (111) orientation.

The preferred ridge structure, (022) orientation, observed previously [6] for chloride concentrations ⩽ 10 ppm does not prevail in the presence of glue. The only exceptions are the 15 ppm glue–2 ppm Cl^- and 30 ppm glue–2 ppm Cl^- combinations which, according to Table 1, indicate preferred (022) orientation. These results are supported by the data obtained from the polarization measurements. A series of plots of current (current density) versus glue concentrations for a range of cathode potentials is shown in Fig. 1. The decrease in current, which occurs with the addition of glue for all values of the cathode potential, indicates an increase in cathode polarization. However, in spite of this increase in cathode polarization, the deposit orientation remains (022) preferred (Table 1). The addition of chloride ion in concentrations > 5 ppm to an electrolyte containing 30 ppm glue results in a substantial increase in copper deposition polarization as indicated in Fig. 2 which shows a series of plots of current (current density) versus chloride ion concentration for a range of cathode potentials. Deposits obtained under these conditions had a preferred (111) orientation (Table 1). The change in deposit orientation from (022) to (111) may be related to this additional increase in cathode polarization since it has been reported [12, 13] that the (111) orientation is favoured by an increase in deposition overpotential. For chloride ion concentration < 5 ppm, there is a decrease in cathode polarization and the deposit orientation remains (022).

The plots in Fig. 2 indicate that the polarization generally reaches a maximum at about 40 ppm chloride ion concentration. This is precisely the condition for which the (111) orientation was observed to be at a maximum (Table 1). However, although both glue and chloride ion promote pyramidal growth at high chloride ion concentration, the result is a fairly smooth compacted deposit which may be attributed to the grain refining effect of glue.

The surface morphology of copper deposits obtained for several glue–chloride ion combinations is shown in Fig. 3 in a series of SEM photomicrographs. Fig. 3a 15 ppm glue–2 ppm Cl^-, reveals clusters of large rounded nodules growing out of relief on the fine-grained base deposit. At 10 ppm chloride ion concentration the deposit becomes increasingly powdery and non-crystalline (Fig. 3b). However, increasing the chloride ion concentration to 100 ppm results in a crystalline and compact deposit (Fig. 3c). The SEM photomicrograph for the deposit obtained at 30 ppm glue–0 ppm Cl^- is shown in Fig. 3d and reveals a smooth, compacted deposit, having a much finer grain size than the glue-free deposit previously

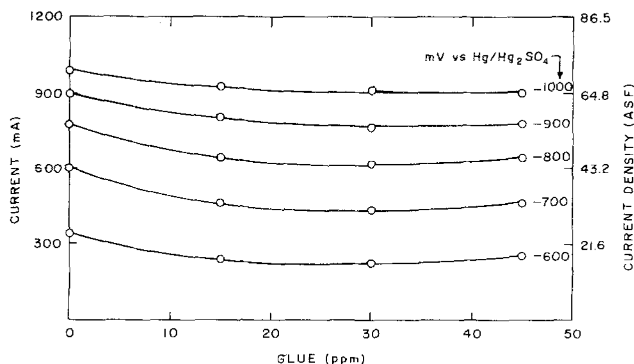


Fig. 1. Plot showing the effect of glue concentration on the current for copper deposition at various cathode potentials.

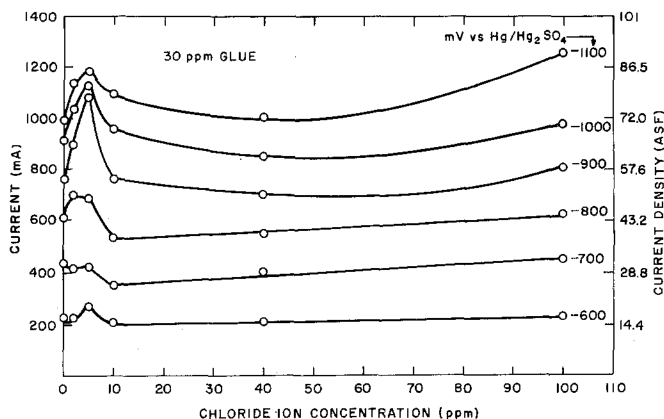


Fig. 2. Plot showing the effect of chloride ion concentration on the current for copper deposition at various cathode potentials for 30 ppm glue.

obtained under similar conditions [6]. The SEM photomicrograph presented in Fig. 3e is typical of the copper deposit morphology obtained for chloride ion concentrations ⩾ 40 ppm in the presence of glue. These structures are again compact but the grain size is larger than for the glue-only case, indicating the prominence of the pyramidal growth structure. The powdery deposit obtained for 45 ppm glue–10 ppm Cl^- is shown in Fig. 3f.

The above observations are further illustrated in the photomicrographs of the copper deposit cross-sections presented in Fig. 4. The deposits obtained for glue alone or in combination with chloride ion concentration ⩾ 10 ppm are compact and even (Figs. 4a, c and d) whereas that for the low chloride ion–glue combination is thin and nodular, (Fig. 4b). However, increased glue additions at 2 ppm Cl^- improves the copper deposits (Figs. 4e and f).

3.2. *Glue–LIX65N effects*

The combined effects of glue and LIX65N on the crystallographic orientations of the copper deposits are summarized in Table 2 in terms of the observed variations in the (111), (0002) and (022) peak intensity ratios to the ASTM standard for copper powder. The data show that the addition of 8 ppm LIX65N alone or with 15 ppm glue results in an increase in the ridge-type over the pyramidal-type growth. This is indicated by the decrease in the (111) and (002) peak height and the simultaneous increase in (022) peak height values. However, increasing the glue to 30 and 45 ppm at 8 ppm LIX65N, results in a substantial increase in the pyramidal and planar growth structures. This is attributed to the significant increase in both the (111) (pyramidal growth) and (002) (planar growth) peak height values and to the simultaneous decrease in the (022) (ridge growth) peak height values.

At 50 and 100 ppm LIX65N, with increasing glue concentration, there is an increase in both

Table 2. Crystallographic orientation of copper deposits as a function of glue and LIX65N concentrations at 40 ASF (electrolysis conditions: Cu^{2+} content = 20 g l^{-1}, H_2SO_4 = 150 g l^{-1}; T = 35° C)

LIX65N (ppm)	Glue (ppm)	Surface orientation (ratio to ASTM standard)*		
		Orientation		
		(111)	(002)	(022)
0	0	1·3	0·9	3·0
	15	1·7	1·3	1·3
	30	0·2	0·4	1·7
	45	0·8	0·7	1·2
8	0	0·7	0·6	6·2
	15	0·1	0·2	6·2
	30	1·9	1·5	1·3
	45	1·9	1·5	1·1
50	0	0·7	0·5	0·7
	15	1·9	1·7	1·1
	30	2·0	1·7	1·1
	45	1·9	1·2	1·1
100	0	0·4	0·4	0·5
	15	1·1	0·9	1·1
	30	1·9	1·4	1·3
	45	1·1	0·9	0·4

* (111) 100; (002) 46; (022) 20

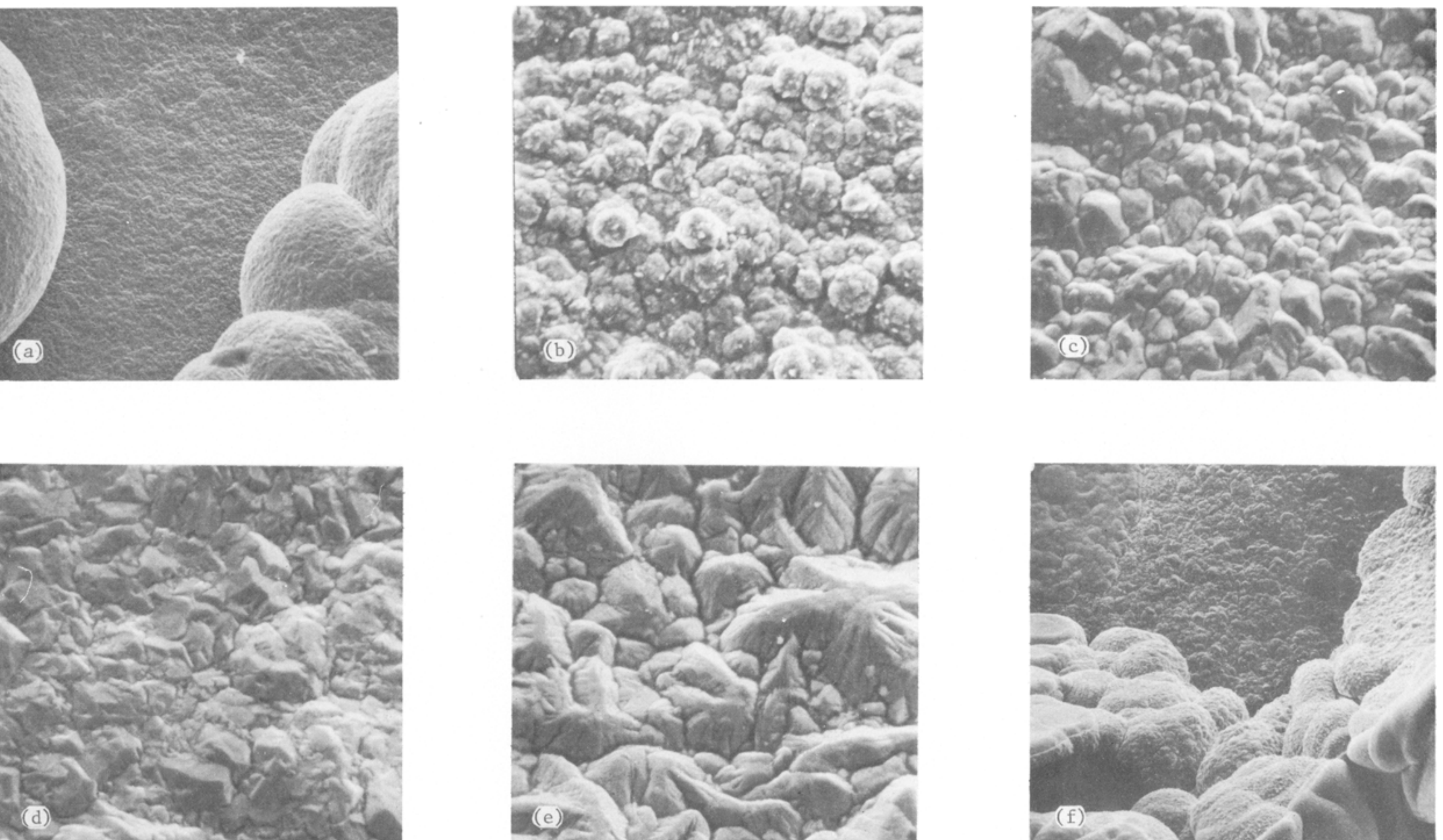
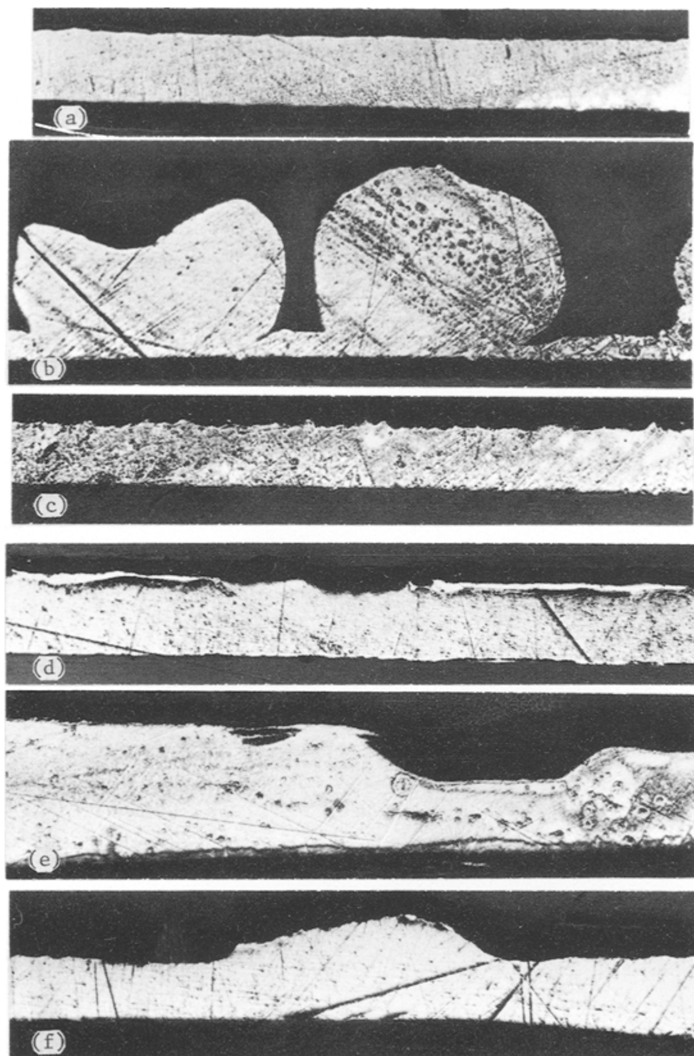


Fig. 3. SEM photomicrographs showing the effect of glue and chloride ion concentrations on the morphology of copper deposits obtained at 40 ASF; (a) 15 ppm glue, 2 ppm Cl^-, × 275; (b) 15 ppm glue, 10 ppm Cl^-, × 1100; (c) 15 ppm glue, 100 ppm Cl^-, × 1100; (d) 30 ppm glue, × 1100; (e) 30 ppm glue, 40 ppm Cl^-, × 1100; (f) 45 ppm glue, 10 ppm Cl^-, × 275.



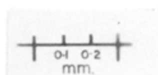


Fig. 4. Effect of glue and chloride ion concentrations on the cross-sections of copper deposits obtained at 40 ASF; (a) 15 ppm glue; (b) 15 ppm glue, 2 ppm Cl^-; (c) 15 ppm glue, 10 ppm Cl^-; (d) 15 ppm glue, 100 ppm Cl^-; (e) 30 ppm glue, 2 ppm Cl^-; (f) 45 ppm glue, 2 ppm Cl^-.

pyramidal and planar growth with a maximum occurring at 30 ppm glue.

An examination of the deposit cross-sections obtained at the various glue–LIX65N additions generally supports the crystallographic orientation data presented in Table 2. At 8 ppm LIX65N concentration and for all values of the glue concentration the deposits are very metallic in appearance and their cross-sections are even and compact as indicated by the representative photomicrograph in Fig. 5a. At 50 and 100 ppm LIX65N, the deposits become increasingly powdery and their cross-sections are rough and nodular in appearance. Fig. 5b shows a photomicrograph of the cross-section of a deposit obtained at 100 ppm LIX65N–15 ppm glue.

The powdery, non-crystalline nature of the deposits obtained in the presence of LIX65N and glue at high LIX65N concentrations is shown in the SEM photomicrographs presented in Figs. 6a

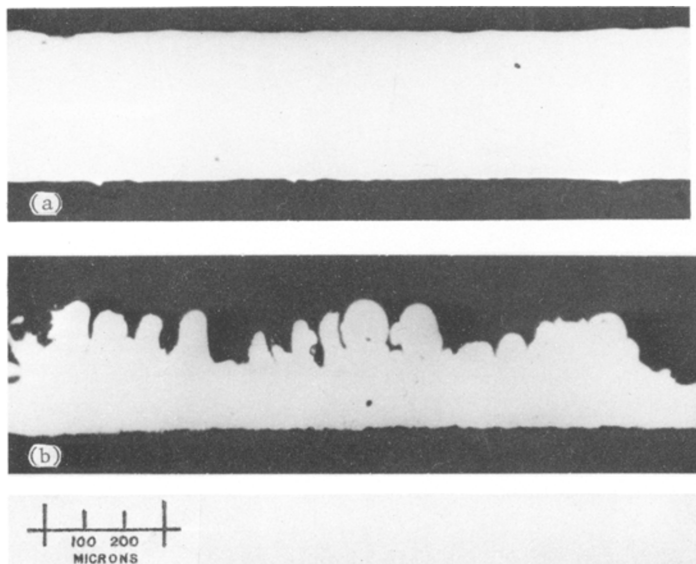


Fig. 5. Effect of glue and LIX65N on the cross-sections of copper deposits obtained at 40 ASF; (a) 30 ppm glue, 8 ppm LIX65N; (b) 15 ppm glue, 100 ppm LIX65N.

and b, for LIX65N–glue combinations of 100 ppm –30 ppm and 100 ppm–45 ppm respectively.

3.3. *Combined effects of glue, LIX65N and chloride ion*

The peak intensity ratios to the ASTM standard for copper powder for the (111), (002) and (022) orientations obtained as a function of LIX65N and chloride ion concentrations at 30 ppm glue and 40 ASF are presented in Table 3. In general, the pyramidal growth structure which was observed for the glue–chloride ion additions persists in the presence of LIX65N. However, at chloride ion concentrations > 5 ppm, there is a reduction in the (111) peak height values and a slight increase in the (022) peak height values in the presence of 8 ppm LIX65N indicating an increase in ridge growth for these conditions; however, the pyramidal growth structure remains predominant.

Photomicrographs of the cross-sections of some representative copper deposits obtained under a variety of glue–Cl^-–LIX65N additions are presented in Fig. 7. Figs. 7a and b compare two cross-sections obtained at 30 ppm glue–2 ppm Cl^- and at 8 and 50 ppm LIX65N respectively, and clearly illustrate the adverse effect of the high LIX65N concentration under these conditions. Fig. 7c shows the cross-section of a deposit

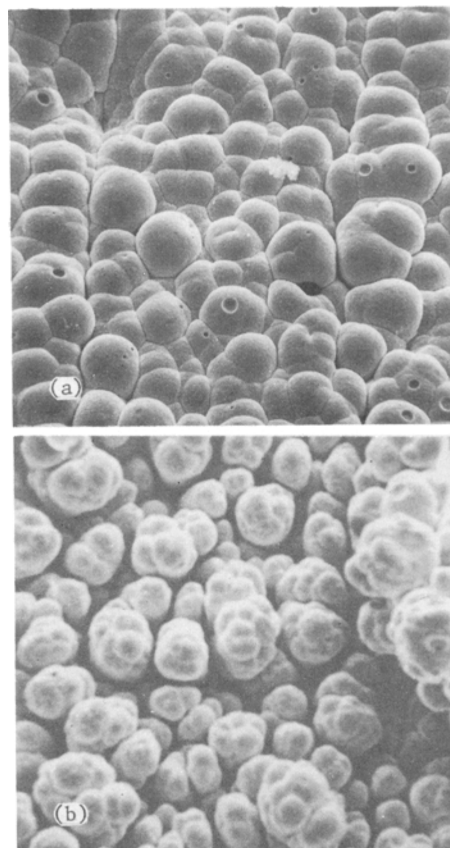


Fig. 6. SEM photomicrographs showing the effect of glue and entrained LIX65N on the morphology of copper deposits obtained at 40 ASF; (a) 30 ppm glue, 100 ppm LIX65N, × 275; (b) 45 ppm glue, 100 ppm LIX65N, × 275.

Table 3. Crystallographic orientation of copper deposits obtained at 40 ASF as a function of chloride ion and LIX65N concentrations at 30 ppm glue (electrolysis conditions: Cu^{2+} content = 20 g l^{-1}, H_2SO_4 = 150 g l^{-1}; T = 35° C)

LIX65N (ppm)	*Cl⁻* (ppm)	*Surface orientation (ratio to ASTM standard)** *Orientation* (111)	(002)	(022)
0	0	0·2	0·4	1·7
	2	0·5	0·6	1·7
	5	3·2	0·4	1·0
	10	4·6	0·3	0·4
	40	6·6	0·2	0·5
	100	4·5	0·3	0·8
8	0	1·9	1·5	1·2
	2	3·2	0·5	0·4
	5	1·1	0·3	1·2
	10	3·1	0·5	0·8
	40	4·4	0·3	0·5
	100	4·3	0·5	1·2
50	0	0·7	0·5	0·7
	2	1·0	0·8	0·7
	5	3·2	0·8	1·1
	10	3·3	0·7	1·5
	40	4·3	0·4	0·8
	100	4·3	0·5	1·3
100	0	0·4	0·4	0·5
	2	1·9	1·0	1·1
	5	0·7	0·5	0·8
	10	1·2	0·4	0·8
	40	4·3	0·4	0·7
	100	4·3	0·5	1·3

* (111) 100; (002) 46; (022) 20.

obtained at 30 ppm glue–10 ppm Cl^-–8 ppm LIX65N. Compared to the deposit shown in Fig. 7a increasing the chloride ion concentration from 2–10 ppm has resulted in a more nodular, thinner deposit. Figs. 7d and e compare two copper deposit cross-sections obtained at 30 ppm glue–100 ppm Cl^- at 8 and 100 ppm LIX65N, respectively. It can be seen that these cross-sections are quite similar, both being fairly smooth and compact. This result again suggests, as was mentioned in a previous publication [7], that reasonably good deposits can be obtained from electrolytes containing entrained LIX65N provided the chloride ion concentration is sufficiently high.

These results are substantiated by the SEM photomicrographs of the surface morphology of the copper deposits shown in Fig. 8. Fig. 8a shows the surface morphology of the copper deposit obtained at 30 ppm glue–10 ppm Cl^-–8 ppm LIX65N. The growth of isolated clusters of nodules on the surface is clearly visible and this results in the nodular cross-section shown in Fig. 7c. Figs. 8b and c are SEM photomicrographs of the copper deposits obtained at 30 ppm glue–100 ppm Cl^- and 8 and 100 ppm LIX65N, respectively. They indicate that the 8 ppm LIX65N structure is relatively more compact and crystalline than the 100 ppm LIX65N structure.

3.4. *The effect of current density*

Because in plant typical operating current densities are 16–25 ASF, several tests were done at 20 ASF for various chloride ion, glue and LIX65N combinations in order to determine if the results would be significantly different than those obtained at 40 ASF.

The peak intensity ratios of the ASTM standard for copper powder for the (111), (002) and (022) orientations obtained as a function of chloride ion concentration at 30 ppm glue are compared in Table 4 at current densities of 40 and 20 ASF.

Table 4. Crystallographic orientation of copper deposits as a function of chloride ion concentration and current density (electrolysis conditions: Cu^{2+} content = 20 g l^{-1}, H_2SO_4 = 150 g l^{-1}, glue = 30 ppm; T = 35° C)

Current density (ASF)	*Cl⁻* (ppm)	*Surface orientation (ratio to ASTM standard)** *Orientation* (111)	(002)	(022)
40	0	0·2	0·4	1·7
	2	0·5	0·6	1·7
	5	3·2	0·4	1·0
	10	4·6	0·3	0·5
	40	6·6	0·2	0·5
20	0	0·1	0·3	3·6
	2	1·0	0·2	2·5
	5	3·7	0·3	0·8
	10	7·8	0·3	–
	40	4·6	0·2	0·4

* (111) 100; (002) 46; (022) 20

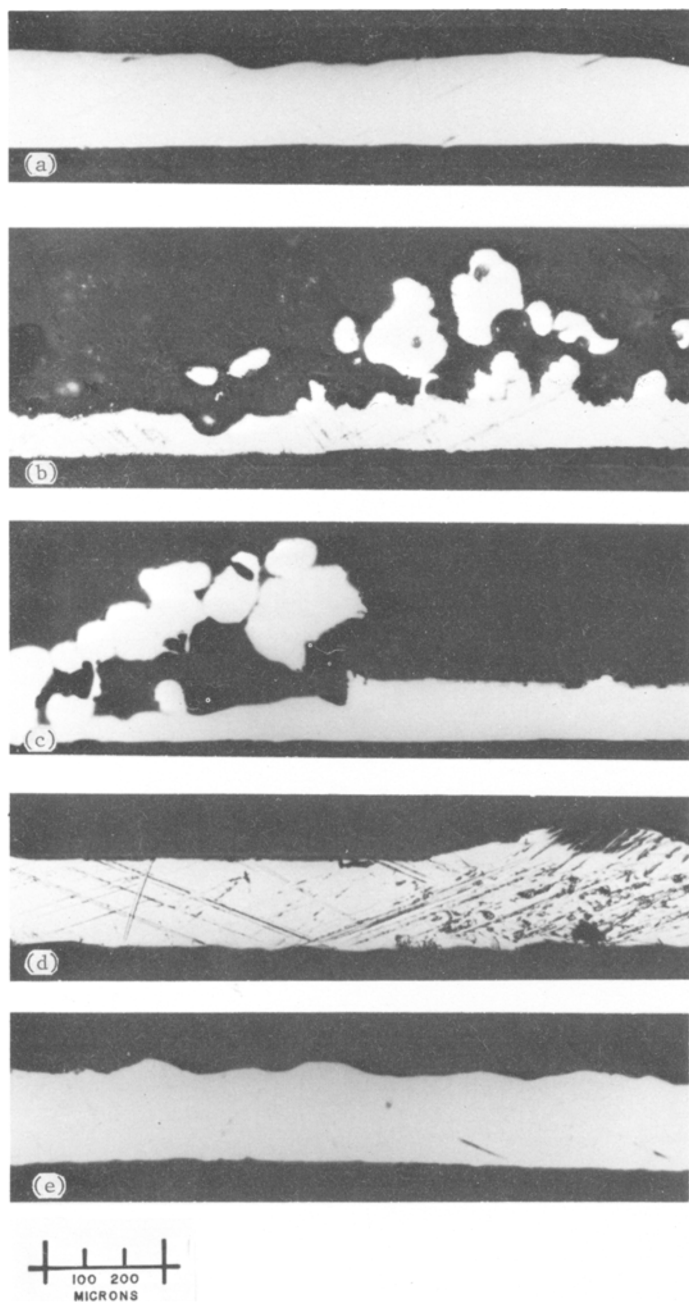


Fig. 7. Effect of chloride ion and LIX65N concentrations on the cross-sections of copper deposits obtained at 40 ASF and in the presence of 30 ppm glue;
(a) 2 ppm Cl^-, 8 ppm LIX65N;
(b) 2 ppm Cl^-, 50 ppm LIX65N;
(c) 10 ppm Cl^-, 8 ppm LIX65N;
(d) 100 ppm Cl^-, 8 ppm LIX65N;
(e) 100 ppm Cl^-, 100 ppm LIX65N.

The data show that for no addition of chloride ion, the deposit obtained at 20 ASF is (022) oriented, in agreement with the earlier result for 40 ASF. The trend toward increasing (111) orientation with increasing chloride ion concentration which was observed at 40 ASF, also occurs when the current density is reduced to 20 ASF. A similar trend in the crystallographic orientations is observed for current density variations when the electrolyte contains 30 ppm glue and 8 ppm LIX65N. These results are summarized in Table 5.

The effect of varying the initial copper ion concentration at 40 and 20 ASF on the crystallographic orientation of copper deposits obtained from electrolytes containing 30 ppm glue and 40 ppm Cl^- is shown in Table 6. The data show

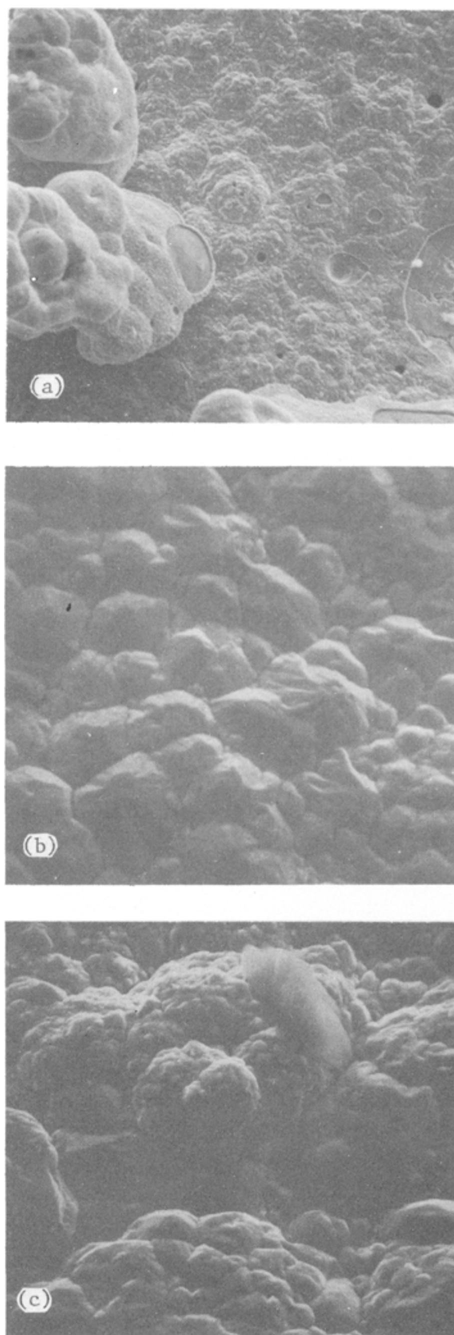


Fig. 8. SEM photomicrographs showing the effect of chloride ion and LIX65N concentrations on the morphology of copper depostis obtained at 40 ASF in the presence of 30 ppm glue; (a) 10 ppm Cl^-, 8 ppm LIX65N, × 275; (b) 100 ppm Cl^-, 8 ppm LIX65N, × 1100; (c) 100 ppm Cl^-, 100 ppm LIX65N, × 1100.

Table 5. Crystallographic orientation of copper deposits as a function of chloride ion concentration and current density (electrolysis conditions: Cu^{2+} content = $20\,g\,l^{-1}$, H_2SO_4 = $150\,g\,l^{-1}$, glue = 30 ppm, LIX65N = 8 ppm; T = 35° C)

Current density (ASF)	Cl^- (ppm)	Surface orientation (ratio to ASTM standard)* Orientation (111)	(002)	(022)
40	0	1·9	1·5	1·3
	2	3·2	0·5	0·4
	5	1·1	0·3	1·2
	10	3·1	0·5	0·8
	40	4·4	0·3	0·5
20	0	–	–	–
	2	2·9	0·4	0·4
	5	6·7	0·2	0·4
	10	6·1	–	–
	40	2·0	0·4	0·8

* (111) 100; (002) 46; (022) 20

that these variations have no significant effect on the preferred deposit orientation which remains (111).

These results are further confirmed by the SEM data shown in Fig. 9 in which the surface morphologies of the copper deposits obtained in the presence of 30 ppm glue and 40 ppm Cl^- at current densities of 20 and 40 ASF, copper ion concentrations of 20 and $60\,g\,l^{-1}$ and LIX65N

Table 6. Crystallographic orientation of copper deposits as a function of copper ion concentration and current density (electrolysis conditions: glue content = 30 ppm, Cl^- = 40 ppm, H_2SO_4 = $150\,g\,l^{-1}$; T = 35° C)

Current density (ASF)	Cu^{2+} ($g\,l^{-1}$)	Surface orientation (ratio to ASTM standard)* Orientation (111)	(002)	(022)
40	20	6·6	0·2	0·5
	40	3·9	0·3	0·8
	60	5·4	0·2	0·4
20	20	4·6	0·2	0·4
	40	5·1	0·2	0·4
	60	5·2	0·2	0·4

* (111) 100; (002) 46; (022) 20

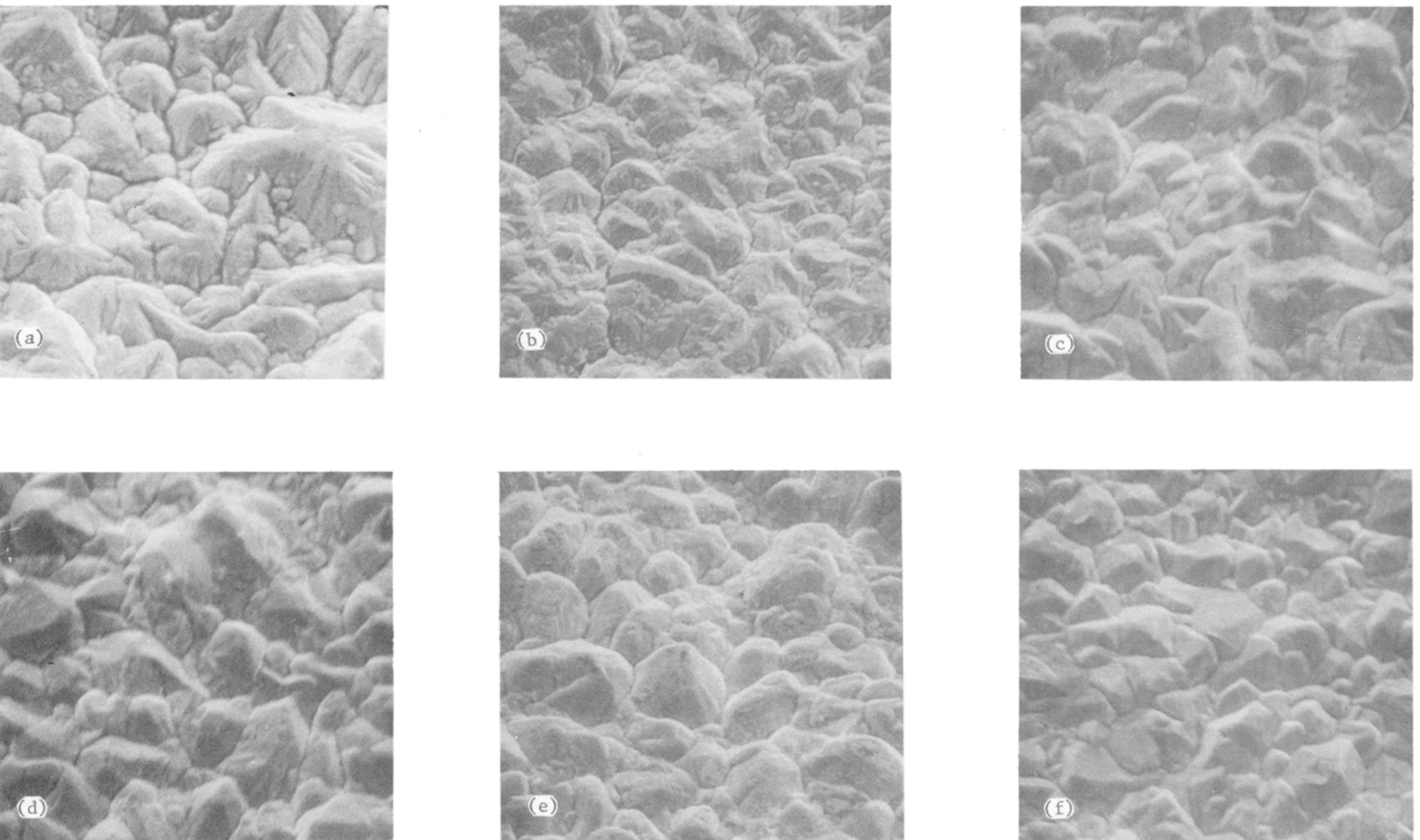


Fig. 9. SEM photomicrographs showing the effect of current density, copper ion and LIX65N concentrations on the morphology of copper deposits obtained in the presence of 30 ppm glue and 40 ppm chloride ion; (a) 40 ASF, 20 g l^{-1} Cu^{2+}, × 1100; (b) 40 ASF, 20 g l^{-1} Cu^{2+}, 8 ppm LIX65N, × 550; (c) 40 ASF, 60 g l^{-1} Cu^{2+}, × 1100; (d) 20 ASF, 20 g l^{-1} Cu^{2+}, × 1100; (e) 20 ASF, 20 g l^{-1} Cu^{2+}, 8 ppm LIX65N, (f) 20 ASF, 60 g l^{-1} Cu^{2+}, × 1100.

concentrations of 0 and 8 ppm are compared. As indicated by the SEM photomicrographs in Fig. 9, the deposit morphologies obtained under these experimental conditions are very similar to one another.

4. Conclusions

The combined effects of chloride ion and glue on the structure of electrodeposited copper result in a distinct preference for (111) orientation. This results in pyramidal growth, which in the presence of chloride ion alone at concentrations $\geqslant 40$ ppm leads to the formation of large nodules [6]; the addition of glue, however, results in grain refinement such that even at chloride ion concentrations up to 100 ppm, reasonably smooth, compact copper deposits are obtained at 40 ASF.

The combined effects of glue and LIX65N for LIX65N concentrations > 8 ppm result in powdery non-crystalline copper deposits as observed in the previous study [7] on the effect of LIX65N on the morphology of copper deposits obtained at 40 ASF.

Chloride ion concentrations $\geqslant 40$ ppm in the presence of glue and LIX65N resulted in improved copper deposits at 40 ASF in agreement with previous results which indicated that the adverse effect of entrained LIX65N can be compensated for by the presence of sufficient chloride ion [7].

In the presence of glue and chloride ion, variations in current density, copper ion concentration and the addition of 8 ppm LIX65N produced no significant effect in the preferred deposit orientations or surface morphologies.

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