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

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The effect of thiourea, LIX65N (a common organic extractant for copper) and chloride ion on the morphology of electrodeposited copper under different conditions is reported. The deposit morphology was assessed by optical microscopy techniques, scanning electron microscopy and X-ray diffraction measurements. The importance of controlling the concentration of these additives in electrowinning copper from electrolytes obtained from a solvent extraction separation process is indicated.

1. Introduction

Addition agents in copper electrodeposition have been developed for brightening, hardening, grain refining, surface smoothing, levelling the deposit and for increasing the limiting current density for the electrolysis. Their action has been associated with various properties, such as the ability to form complex ions, to become colloidally dispersed in the electrolyte or to adsorb on the cathode surface [1]. However, it may be assumed that addition agents which modify the physical and metallurgical properties of the deposit do so by virtue of their effect on the deposit microstructure and on the nature and distribution of the deposited impurities. Since these two factors are determined by the nucleation and growth of the deposit, it is the effect of the addition agents on these properties which should be looked into in detail [2]. The additives used can be organic molecules such as thiourea and/or glue or inorganic ions such as chloride. The effects of these additives in the electroplating and in the electrorefining industries have drawn considerable attention and have been subjected to detailed investigation [3].

In the field of copper extractive metallurgy with the application of leaching/solvent extraction/electrowinning as an alternative to the leaching/cementation/smelting route for copper recovery, the interaction of the solvent extraction and electrowinning unit processes requires detailed study. Hence the effect of dissolved and entrained solvent extractants together with the additives used in copper electrowinning on the structure of the deposit should be examined.

In earlier communications [4, 5] the effects of chloride ion and the solvent extracting reagent LIX65N on the morphology of the deposited copper was reported. It was found that the addition of chloride ion in concentrations up to 10 ppm resulted in a depolarization of the cathode reaction; polarization of the cathode was observed with further addition of chloride ion. The X-ray diffraction (XRD), scanning electron microscopy (SEM) and optical microscopy results suggested that for chloride concentrations up to 10 ppm a ridge type copper structure, (022) orientation, is favoured but with further increases in chloride ion concentration, pyramidal growth, (111) orientation, increases resulting in nodule formation. LIX65N at the 8 ppm level did not produce any harmful effects on the copper deposits. The tolerance of chloride ion in the presence of LIX65N was found to be higher than 10 ppm. However, higher concentrations of LIX65N, caused the electrodeposit to deteriorate. In the present communication the results obtained from a systematic investigation of the effect of thiourea, chloride ion and LIX65N on the structure of copper deposits is reported.

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2. Experimental

2.1. *Materials and apparatus*

The electrowinning cell and the electrode assembly have deen described [4, 5]. The electrolyte was prepared from anhydrous copper sulphate and ultrapure sulphuric acid. The electrolytic solution contained 20 g l^{-1} Cu^{2+} and 150 g l^{-1} H_2SO_4. The desired concentrations of chloride ion, LIX65N and thiourea in the electrolyte were obtained by adding the appropriate amounts of their respective stock solutions. The volume of electrolyte used in each test was 300 ml. The LIX65N was purified by the method suggested by Ashbrook [6].

2.2. *Experimental*

Copper deposits were obtained at a current density of 40 A ft^{-2} (ASF) for a deposition time of 60 min. The electrolyte was maintained at 35 ± 1° C and was agitated with a glass stirrer at a constant speed of 2100 rev min^{-1}. 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. X-ray diffractometry was used to determine the preferred crystallographic orientations of each deposit. The samples were scanned over the seven most intense lines for copper. A sample of copper dust was scanned in order to obtain peak values for randomly oriented copper. Any departure from these values indicates the type and degree of preferred orientation in the specimens.

Table 1. Crystallographic orientations of copper deposits obtained at 40 ASF as a function of thiourea concentration

Thiourea (ppm)	*Peak height* (0.01 inch) (111)	(002)	(022)
0	125	41	60
3	46	24	100
12	19	11	508
18	22	5	523

Current–potential curves for copper deposition from solutions containing 12 ppm thiourea and 0–40 ppm chloride ion were obtained using a Wenking potentiostat model 70HP10 driven at a rate of 1 mV s^{-1} by a Wenking model VSG72 voltage scan generator.

3. Results and discussion

3.1. *Crystallographic orientation*

The effects on the crystallographic orientations of the copper deposits of thiourea alone and in the presence of LIX65N and chloride ion both individually and together were studied by X-ray diffractometry. Of the seven lines which were scanned only three; namely (111), (002) and (022) showed any significant change in their respective peak heights. The results are summarized in Table 1.

The results presented in Table 1 show that the (022) peak height values increase substantially whereas both the (111) and (002) peak height values decrease as the thiourea concentration is increased to 18 ppm. As was discussed in previous communications [4, 5], an increase in the (022) peak height with corresponding decrease in the (111) peak height suggests preferred ridge type growth resulting in compact deposits. Billen [7] and Scheers [8] studied the influence of thiourea on the electrocrystallization of copper. In the concentration range of 1–5 ppm thiourea they found (002) rather than (022) oriented structures. However, their results indicated that any increase in thiourea concentration above this level reduced the grain size. At these concentrations the overvoltage is reduced [9] and this gives rise to preferentially (022) oriented deposits as the crystallization overvoltage for (022) is less than that for (002) [10].

Limiting current density values for various thiourea concentrations were obtained from the current–potential curves for copper deposition and are listed in Table 2. They indicate that increasing thiourea concentration to 18 ppm results in an increase in the limiting current density for copper deposition. This result, as discussed previously for the effect of chloride ion concentration on the structure of copper deposits [4], tends to favour (022) oriented deposits. This is in agreement with

Table 2. Effect of thiourea concentration on the limiting current density for copper deposition

Thiourea (ppm)	*Limiting current density* (ASF)
0	72
3	72
12	77
18	79

the orientation measurements (Table 1) which show an increase in (022) peak height values as the thiourea concentration is increased to 18 ppm.

The results presented in Table 3 show that increasing the chloride ion concentration beyond 2 ppm in the presence of 12 ppm thiourea causes an increase in both pyramidal (111) and planar (002) growth. However, for chloride concentration ⩽ 2 ppm substantial ridge type growth occurs as indicated by the (022) peak height values listed in Table 3. This result is confirmed by the polarization curves obtained for copper deposition from solutions containing 12 ppm thiourea and various concentrations of chloride ion. The results of these polarization studies are presented in Fig. 1 at various cathode potentials as plots of current (current density) as a function of chloride ion concentration. These plots indicate substantially less polarization for copper deposition from a solution containing 2 ppm chloride ion than from one

Table 3. Crystallographic orientations of copper deposits obtained at 40 ASF and 12 ppm thiourea as a function of chloride ion and LIX65N concentrations

	Peak height (0.01 inch)		
	Orientation		
	(111)	(002)	(022)
Cl^- (ppm) at 0 ppm LIX65N			
0	19	11	508
2	55	12	285
10	370	111	22
100	348	284	10
Cl^- (ppm) at 8 ppm LIX65N			
0	60	26	334
2	89	29	142
10	141	46	35
100	339	129	56
Cl^- (ppm) at 50 ppm LIX65N			
0	331	67	79
2	122	37	16
10	196	59	22
100	213	75	37
Cl^- (ppm) at 100 ppm LIX65N			
0	387	94	46
2	–	–	–
10	–	–	–
100	–	–	–

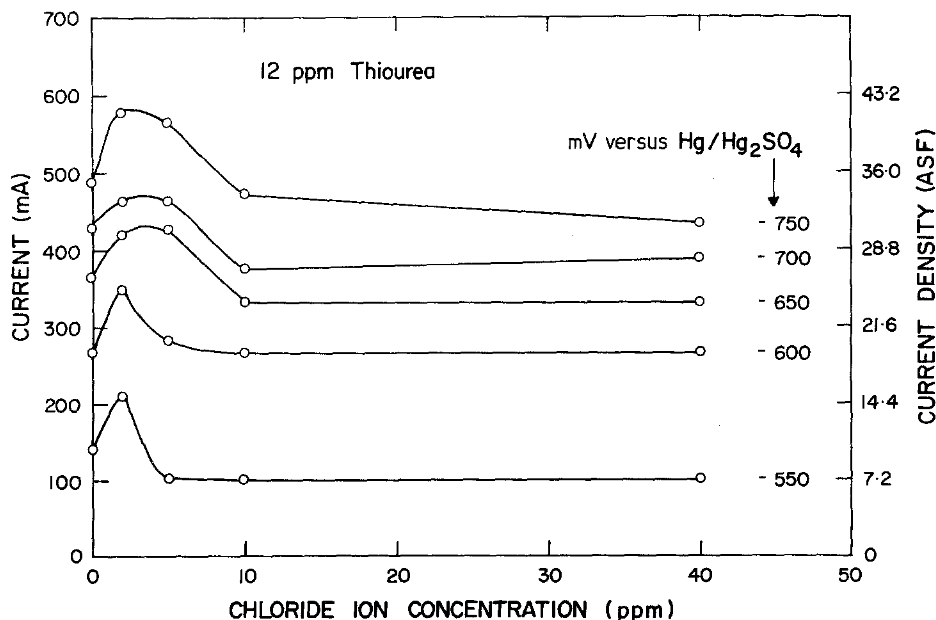

Fig. 1. Plots of current (current density) versus chloride ion concentration for copper deposition at various cathode potentials at 12 ppm thiourea.

containing 10 ppm chloride ion. The decrease in polarization obtained in the presence of 2 ppm chloride ion should favour (022) rather than (111) oriented deposits as discussed previously [4].

The results obtained from the combined effect of 12 ppm thiourea at LIX65N concentrations varying from 0–100 ppm are also shown in Table 3. It can be seen that the addition of LIX65N causes a decrease in the (022) peak height; however, under these conditions the peak heights obtained for (111) and (002) show a progressive increase. These results indicate a steady fall in ridge growth and an increase in planar and pyramidal growth.

The combined effect of thiourea, LIX65N and chloride ion on the preferred orientation of the deposits can be obtained from Table 3. Thiourea concentration was maintained at 12 ppm; LIX65N concentrations were either 8 or 50 ppm and the chloride ion concentration was varied between 0–100 ppm. The particular concentrations of LIX65N were chosen because the 8 ppm level is less than the maximum solubility of LIX65N in aqueous solutions and the 50 ppm level includes both dissolved and entrained LIX65N. At the 8 ppm LIX65N level, (111) and (002) peak heights increase as the concentration of chloride ion is varied from 0 to 100 ppm. However, the (022) peak height shows a minimum value at 10 ppm level and increases to a higher value at 100 ppm chloride. This agrees with our earlier results when the effect of LIX65N and chloride ion on the orientation of copper deposits was studied [5].

At 50 ppm LIX65N concentration, all the peak height values reduce to a minimum at the 2 ppm chloride level and then show a progressive increase as the chloride ion concentration is increased. This results in porous nodular deposits as will be seen from the cross-section and SEM photomicrographs presented in the following sections.

3.2. *Deposit cross-sections*

The effect of various concentrations of LIX65N and chloride ion in the presence of 12 ppm thiourea on the copper deposit cross-sections was examined and some typical examples are shown in Fig. 2. Increasing the thiourea concentration from 3 to 18

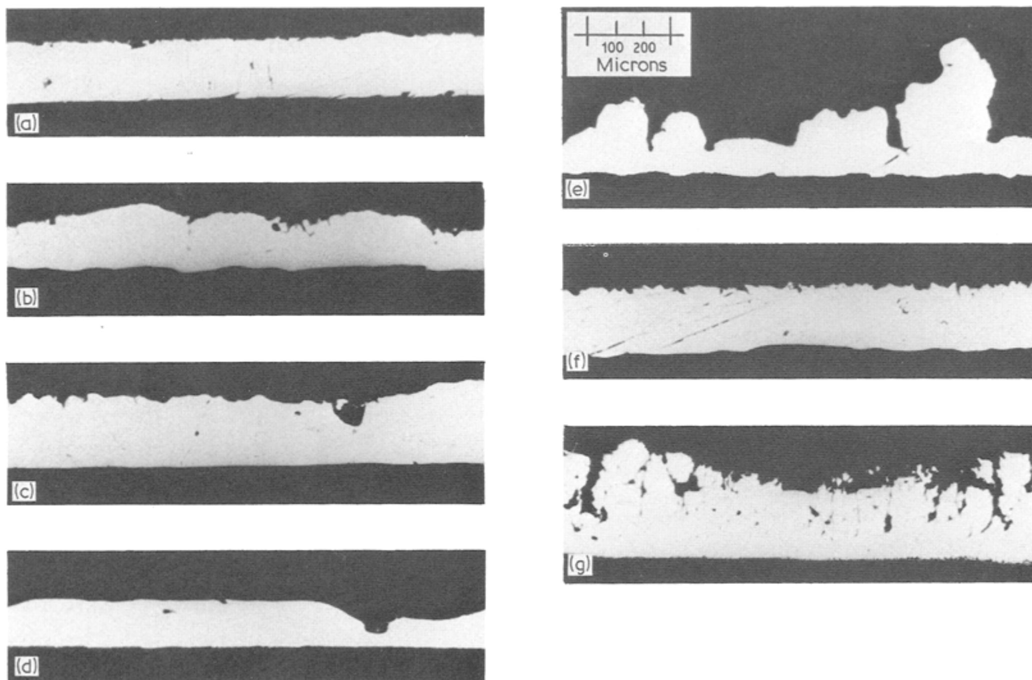

Fig. 2. Photomicrographs of copper deposit cross-sections showing the effect of the addition of chloride ion and LIX65N concentrations at 40 ASF and 12 ppm thiourea: (a) no addition; (b) 10 ppm Cl^-; (c) 100 ppm Cl^-; (d) 8 ppm LIX65N; (e) 8 ppm LIX65N and 10 ppm Cl^-; (f) 8 ppm LIX65N and 100 ppm Cl^-; (g) 50 ppm LIX65N and 100 ppm Cl^-.

ppm reduced the thickness of the electrodeposit by 10%. This confirms the orientation data above which showed an increase in the (022) peak which should result in a thinner more compact deposit [11]. The cross-section of a copper deposit obtained in the presence of 12 ppm thiourea is shown in Fig. 2(a) and indicates an even and compact deposit typical of those favouring ridge type growth, (022) orientation.

As indicated by the data in Table 3, the combined addition of 12 ppm thiourea and various concentrations of chloride ion changes the orientation of the copper deposits from (022) at $\leqslant 2$ ppm Cl^- to preferred (111) and (002) orientations at $Cl^- \geqslant 10$ ppm. The maximum pyramidal growth, (111) orientation, occurs for the 12 ppm thiourea – 10 ppm Cl^- additions giving rise to a nodular deposit as indicated by the photomicrograph of the cross-section shown in Fig. 2(b). At higher chloride ion concentrations, e.g., 100 ppm, however, planar growth, (002) orientation, has increased considerably in proportion to pyramidal growth, producing a much smoother deposit cross-section, Fig. 2(c).

The combined addition of 12 ppm thiourea and 8 ppm LIX65N resulted in a slight increase in pyramidal growth as indicated by the data in Table 3. This is confirmed by the cross-section shown in Fig. 2(d) which indicates the beginning of nodule formation on the surface of the deposit. The addition of various amounts of chloride ion to electrolytes containing 12 ppm thiourea and 8 ppm LIX65N resulted in extremely nodular copper deposits at 10 ppm Cl^- [Fig. 2(e)] but produced very smooth compact copper deposits at 100 ppm Cl^- [Fig. 2(f)]. This is in excellent agreement with previous results obtained for the effect of LIX65N and Cl^- on the structure of copper deposits [5]. The even deposit obtained for the 100 ppm Cl^- addition in the presence of 8 ppm LIX65N and 12 ppm thiourea [Fig. 2(f)] may be attributed to the large increase in planar growth, (002) orientation, observed under these conditions (see Table 3).

The copper deposits obtained in the presence

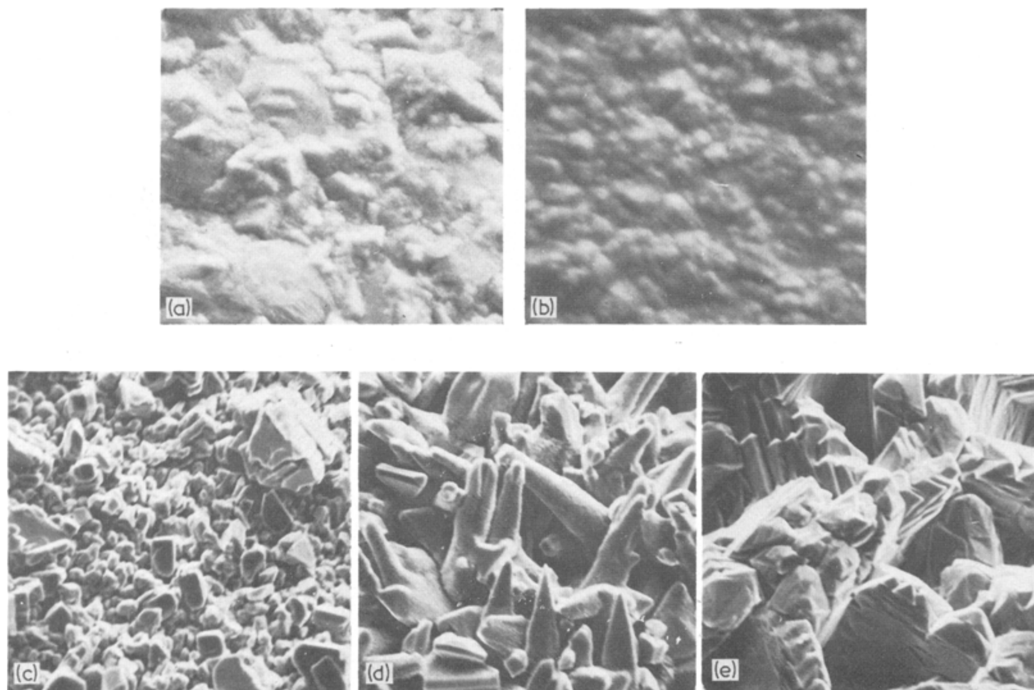

Fig. 3. SEM photomicrographs showing the effect of thiourea alone and in combination with chloride ion on the morphology of copper deposits obtained at 40 ASF. (a) 3 ppm thiourea. × 3500; (b) 12 ppm thiourea. × 3500; (c) 12 ppm thiourea and 2 ppm Cl^-. × 1400; (d) 12 ppm thiourea and 10 ppm Cl^-. × 1400; (e) 12 ppm thiourea and 100 ppm Cl^-. × 1400.

of 12 ppm thiourea and 50 ppm LIX65N with and without chloride ion addition were extremely powdery and nodular. However, the copper deposit obtained in the presence of 100 ppm chloride ion [Fig. 2(g)] was much improved over those obtained at lower chloride ion concentrations.

3.3. *Surface morphology*

The surface morphology of the copper deposits obtained at 40 ASF in the presence of either thiourea alone or thiourea in combination with chloride ion was examined in the SEM. Some typical SEM photomicrographs are presented in Fig. 3. As the thiourea concentration is increased from 3 to 12 ppm [Fig. 3(a) and (b)], the grain size of the deposit decreased considerably. These results are in agreement with Billen [7] and Scheers [8] who reported a decrease in the grain size as thiourea concentration was increased above the 5 ppm level.

The morphology of the copper deposits obtained at 40 ASF and 12 ppm thiourea in the presence of chloride ion concentrations of 2, 10 and 100 ppm are presented in Fig. 3(c), (d) and (e), respectively. They indicate that the poorest morphology is that obtained for 12 ppm thiourea and 10 ppm chloride ion, Fig. 3(d) which agrees with the orientation and cross-section data. The deposit obtained at 100 ppm chloride ion is more coarsely crystalline, an observation which is in agreement with the cross-section shown in Fig. 2(c).

The morphology of the copper deposits obtained at 40 ASF and 12 ppm thiourea in the presence of various concentrations of LIX65N and chloride ion are presented in Fig. 4. The addition of 8 ppm LIX65N produces circular depressions in the surface of the deposit, Fig. 4(a). The addition of chloride ion in the presence of 8 ppm LIX65N results in powdery, nodular deposits at $Cl^- \leqslant 10$ ppm, Fig. 4(b) and (c). The deposits become more crystalline at higher (100 ppm) chloride ion concentrations, Fig. 4(d), in agreement with the cross-section shown in Fig. 2(f). Increasing the LIX65N concentration to 50 ppm results in a powdery porous deposit even in the presence of 100 ppm Cl^-, Fig. 4(e).

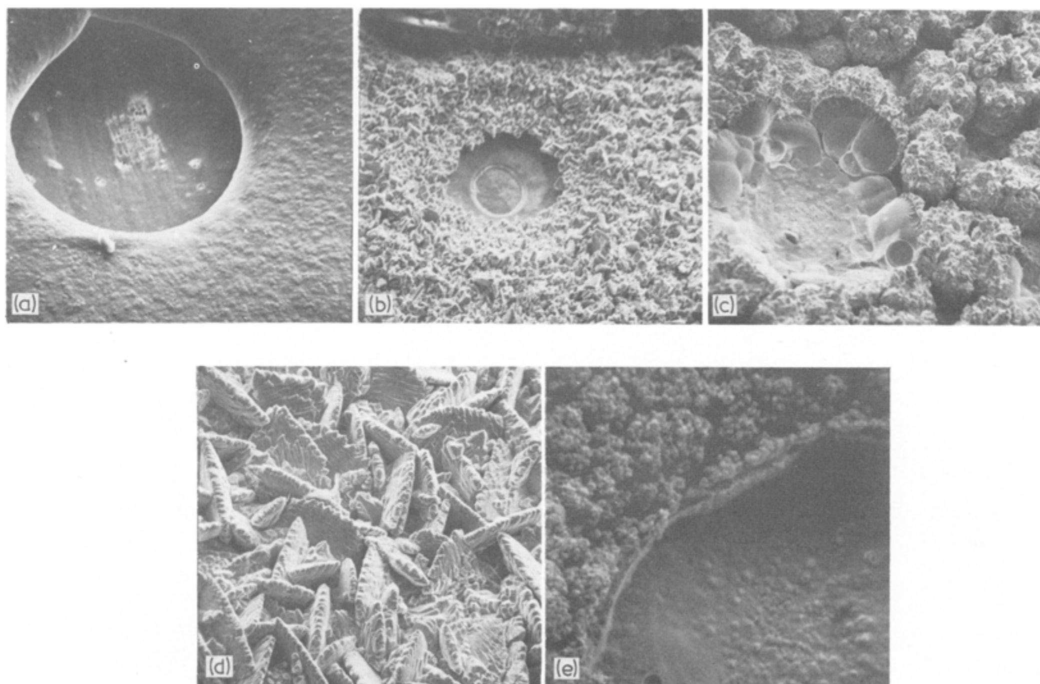

Fig. 4. SEM photomicrographs showing the effect of LIX65N and chloride ion on the morphology of copper deposits obtained at 40 ASF and 12 ppm thiourea. (a) 8 ppm LIX65N. × 350; (b) 8 ppm LIX65N and 2 ppm Cl^-. × 350; (c) 8 ppm LIX65N and 10 ppm Cl^-. × 140; (d) 8 ppm LIX65N and 100 ppm Cl^-. × 350; (e) 50 ppm LIX65N and 100 ppm Cl^-. × 350.

4. Conclusions

(1) The presence of thiourea in concentrations to 18 ppm promotes ridge type growth (022) and produces fine-grained deposits.

(2) In the presence of 12 ppm thiourea increasing chloride concentrations in the range of 2–100 ppm increases pyramidal (111) and planar (002) growths which yield a compact deposit.

(3) In the presence of 12 ppm thiourea and 8 or 50 ppm LIX65N, pyramidal growth is favoured leading to nodular deposits.

(4) At 12 ppm thiourea and 8 ppm LIX65N, increasing concentrations of chloride ion (0–10 ppm) produce a significant increase in pyramidal growth. However, at 100 ppm chloride ion concentration an even compact deposit was obtained.

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References

[1] G. G. Storey and S. C. Barnes, *J. Inst. Metals* **90** (1961) 336.
[2] A. Brennar, V. Zenderland and C. W. Jennings *Plating* 38 (1952) 865.
[3] D. J. MacKinnon and V. I. Lakshmanan, Canmet Scientific Bulletin, CM76–10, (1976).
[4] V. I. Lakshmanan, D. J. MacKinnon and J. M. Brannen, *J. Appl. Electrochem.* 7 (1977).
[5] D. J. MacKinnon, V. I. Lakshmanan and J. M. Brannen, *Trans. Inst. Mining & Metallurgy, Section C* 85 (1976) in press.
[6] A. W. Ashbrook, *J. Chromatog.* 105 (1975) 141.
[7] J. Billen, Ph.D. Thesis, University of Louvain, (1969).
[8] P. H. Scheers, Ph.D. Thesis, University of Louvain, (1969).
[9] C. LaHousse, Ph.D. Thesis, University of Louvain, (1969).
[10] D. Poste, G. Eickhorn and H. Fischer, *Z. phys. Chem.* 77 (1972) 138.
[11] J. B. Cuminsky, *Electrochim. Acta* 15 (1970) 73.