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Factors affecting the structure of copper deposits electrowon from aqueous chloride electrolyte

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The effect of various organic additives on the structural characteristics of copper deposits electrowon at 161 A m^{-2} from aqueous chloride electrolyte using a diaphragm cell featuring electrolyte agitation by vibrating the cathode has been evaluated. The addition of 0.25–0.5 mg l^{-1} Jaguar C13 to the electrolyte improved the quality of the deposit whereas other additives such as glue and gelatin were less effective. The effects of CuCl concentration, the relative proportions of NaCl and HCl and the presence of Na_2SO_4 in the electrolyte on the copper deposits have also been determined.

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1. Introduction

Hydrometallurgical chloride processes for treating copper ores or concentrates eventually result in solutions containing cuprous chloride, ferrous chloride and sodium chloride (used as a solubilizing agent) in various proportions from which copper metal can be recovered by electrowinning. Copper electrowinning from aqueous chloride solutions is potentially attractive since the energy required can be decreased by a factor of between 2 and 4 compared to conventional copper sulphate electrowinning. This energy saving arises because the copper ions discharged at the cathode in the chloride system are monovalent rather than divalent and the overall cell voltage including diaphragms is much lower than in the sulphate system. An additional benefit is that under properly controlled operating conditions the leachant is regenerated at the anode. A disadvantage of the chloride system is that copper tends to deposit as a crystalline powder which can be difficult to collect and handle and it is easily oxidized; also cell design for coping with powder deposits can be complex. The development of techniques capable of forming compact copper deposits should, therefore, enhance the development of chloride leaching processes.

Most of the previous studies on the nature of copper deposits from aqueous chloride electrolyte were carried out using an electrolyte composition similar to that of Gokhale [1], i.e. 70 g l^{-1} CuCl, 0.5 N HCl and 4 N NaCl. Although some of the early workers, notably Gokhale [1], reported a smooth tenacious deposit at current densities of 54–86 A m^{-2} that became rough and nodular at current densities > 100 A m^{-2}, most workers [2–5] obtained powdery deposits. Olsen *et al.* [6] reported deposits which ranged from a spongy mass to leafy dendrites, and they noted that the particle size of the copper was smaller at lower copper concentrations. Haver and Wong [2] found that the electrode spacing had a substantial effect on the nature of the copper deposit; close electrode spacing (2.5–3.75 cm) gave a spongy deposit which would not settle readily whereas a 7.5 cm spacing resulted in a powdery deposit (-28 + 325 mesh) which settled quickly. Andrianne *et al.* [7] showed that the copper deposit tended to become increasingly powdery as the current density increased. In the current density range 54–108 $\mathrm{A\,m^{-2}}$ the deposited crystals grew with holes between them and the number of holes increased with increasing temperature. At 161–215 $\mathrm{A\,m^{-2}}$, the number of holes decreased and this was considered to be the optimum current density range. Langer *et al.* [3] observed that the copper crystals which formed at a current density of 323 $\mathrm{A\,m^{-2}}$ were easily brushed from the cathode surface. Winter *et al.* [8] found that if the outlet catholyte concentration of Cu(I) decreased to 0.115 M, the deposit was loose with only about 7% being adherent to the cathode. Maintaining the outlet catholyte level at 0.392 M produced a dramatic increase in the deposit adherence.

Some attempts have been made to electrowin smooth, compact, even deposits from aqueous chloride electrolyte. Gokhale [1] found that the addition of small amounts ($\sim 20\ \mathrm{mg\,l^{-1}}$) of gum arabic or gelatin inhibited nodule formation and improved the texture and smoothness of the deposit; gum arabic was comparatively more effective than gelatin. Cathro [9] found that the addition of gelatin was effective in promoting compact deposits. He observed that at a gelatin concentration of 0.5 $\mathrm{g\,l^{-1}}$ the copper deposit changed from a coarsely crystalline uneven texture to a finer, even deposit which, however, showed severe nodular growth at the electrode edges. To eliminate these nodules, Cathro found it necessary to increase the gelatin concentration to 2 $\mathrm{g\,l^{-1}}$. Long-term tests (10–100 h) using this high gelatin concentration, however, resulted in deposits which were quite brittle. It is interesting to note that the concentration of addition agent which produces equivalent effects in sulphate electrolyte is only 20 $\mathrm{mg\,l^{-1}}$.

Albert and Winand [10] examined several additives or inhibitors necessary to obtain a non-porous and adherent copper deposit. Their experiments were performed at 215 $\mathrm{A\,m^{-2}}$, 30° C for 24–48 h in a 'Gokhale electrolyte'. They reported that Jaguar in the concentration range 25–250 $\mathrm{mg\,l^{-1}}$ had only a small effect on the deposit morphology; it reduced the grain size and changed the type of crystallization but had no levelling effect. Thiourea in concentrations of 1–100 $\mathrm{mg\,l^{-1}}$ had no effect on the electrolytic deposition of copper from chloride solutions. Gelatin was examined in concentrations ranging from 50–1000 $\mathrm{mg\,l^{-1}}$. At concentrations up to 200 $\mathrm{mg\,l^{-1}}$ gelatin, the surface of the copper deposits was partly covered by dendrites; at 300 $\mathrm{mg\,l^{-1}}$ gelatin, a deposit 3 mm thick without pores or cracks was obtained. Gelatin was observed to decrease the deposit grain size and also to increase grain cohesion, resulting in a compact deposit.

In the present study, the effects of various addition agents on the structure and characteristics of copper deposits electrowon from aqueous chloride electrolyte were evaluated. The effects of CuCl concentration in the cell, the relative proportions of HCl and NaCl in the electrolyte and the presence of Na_2SO_4 on the deposit structure were also studied.

2. Experimental details

2.1. *Electrolyte composition*

The electrolyte was prepared from reagent grade materials. The cell solution contained 0.5 M CuCl ($\sim 30\ \mathrm{g\,l^{-1}}$ Cu^+), 3.0 M NaCl and 1.0 M HCl. The feed solution to the cell contained 0.7 M CuCl ($\sim 45\ \mathrm{g\,l^{-1}}$ Cu^+), 3.0 M NaCl and 1.0 M HCl. The various addition agents were added to both the cell and feed electrolyte as aliquots from the respective stock solutions.

2.2. *Electrowinning cells*

The cell, constructed from polycarbonate, consisted of three compartments: two anode compartments which were separated from a central cathode compartment by Nafion membranes. The cathode was a stainless steel sheet (approximate surface area 64.5 $\mathrm{cm^2}$) and DSA anodes were used. Vigorous agitation of the catholyte, which was maintained under a N_2 atmosphere, was achieved by vibrating the cathode at 60 Hz.

2.3. *Experimental procedure*

The electrolysis cell and electrolyte circulation system were set up as shown schematically in Fig. 1. The feed electrolyte was stirred over copper powder and sparged with N_2 to maintain

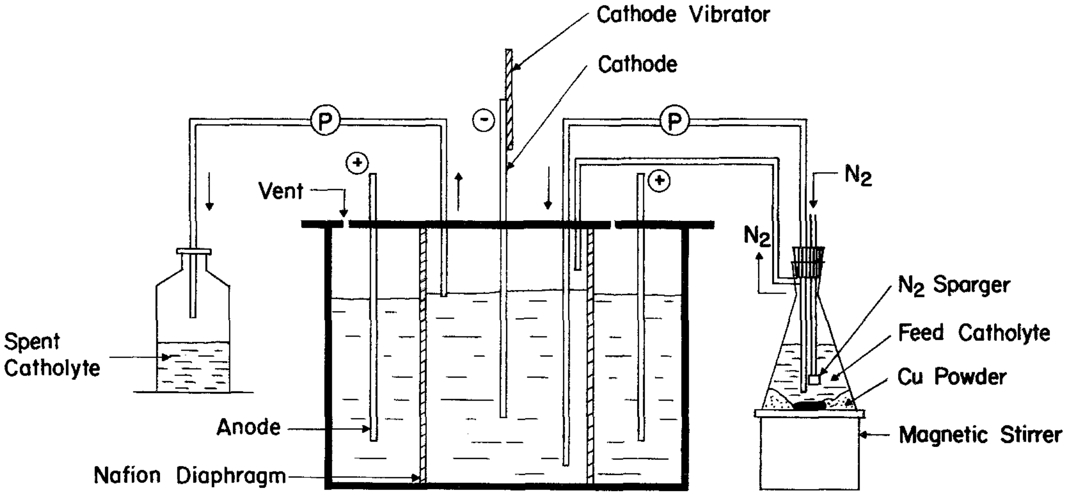

Fig. 1. Schematic drawing of the electrowinning cell and electrolyte recirculation system.

the copper in the Cu^+ state. Feed electrolyte was pumped into the cathode compartment of the cell at a rate sufficient to maintain the copper concentration of the cell electrolyte constant at $30\,g\,l^{-1}$ Cu^+. The catholyte was maintained at a constant volume by pumping spent catholyte from the cell via a glass tube placed at a fixed height which thus controlled the catholyte level. Because the emphasis in this work was on the structure and characteristics of the copper deposits, the anolyte was not circulated or replaced during the electrolysis.

2.4. *Electrowinning conditions*

Most of the experiments were performed at $161\,A\,m^{-2}$ current density at room temperature. Electrolysis time varied from 6 to 24 h.

2.5. *Deposit examination*

Sections of the deposits were examined by X-ray diffraction (XRD) to determine their preferred orientation relative to the ASTM standard for copper powder and by scanning electron microscopy (SEM) to determine their surface morphology.

3. Results and discussion

3.1. *The effect of addition agents*

Several addition agents including glue, gelatin, gum arabic, Percol 351, tetrabutylammonium chloride, Separan NP10 and Jaguar C13 were evaluated for their effectiveness in levelling the copper deposit electrowon from aqueous chloride electrolyte. The initial tests were carried out using $2\,mg\,l^{-1}$ of each addition agent and the duration of the electrolysis was 6 h.

The structural details of the 6-h copper deposits electrowon from chloride electrolyte containing the various addition agents are compared in the series of SEM photomicrographs (Fig. 2). In the absence of an addition agent, the typical copper deposit morphology (Fig. 2a) consists of large elongated crystals protruding into the electrolyte; voids occur between the individual crystals. A similar morphology was reported by Albert and Winand [10].

As indicated by the photomicrographs in Fig. 2, all the addition agents were effective to various degrees in refining the deposit grain size. A comparison of the various morphologies suggests that Jaguar C13 is the most effective additive in refining the grain size and smoothing the deposit surface. Qualitatively, the various addition agents can be ranked as follows: Jaguar C13 > glue > gelatin ~ Percol 351 > Separan NP10 > gum arabic ~ tetrabutylammonium chloride (TBACl).

The effect of the various addition agents on the current efficiency (CE) and on the preferred orientation of the 6-h copper deposits is summarized in Table 1. In all cases the CE was $\geqslant 90\%$ and the addition agents generally had no

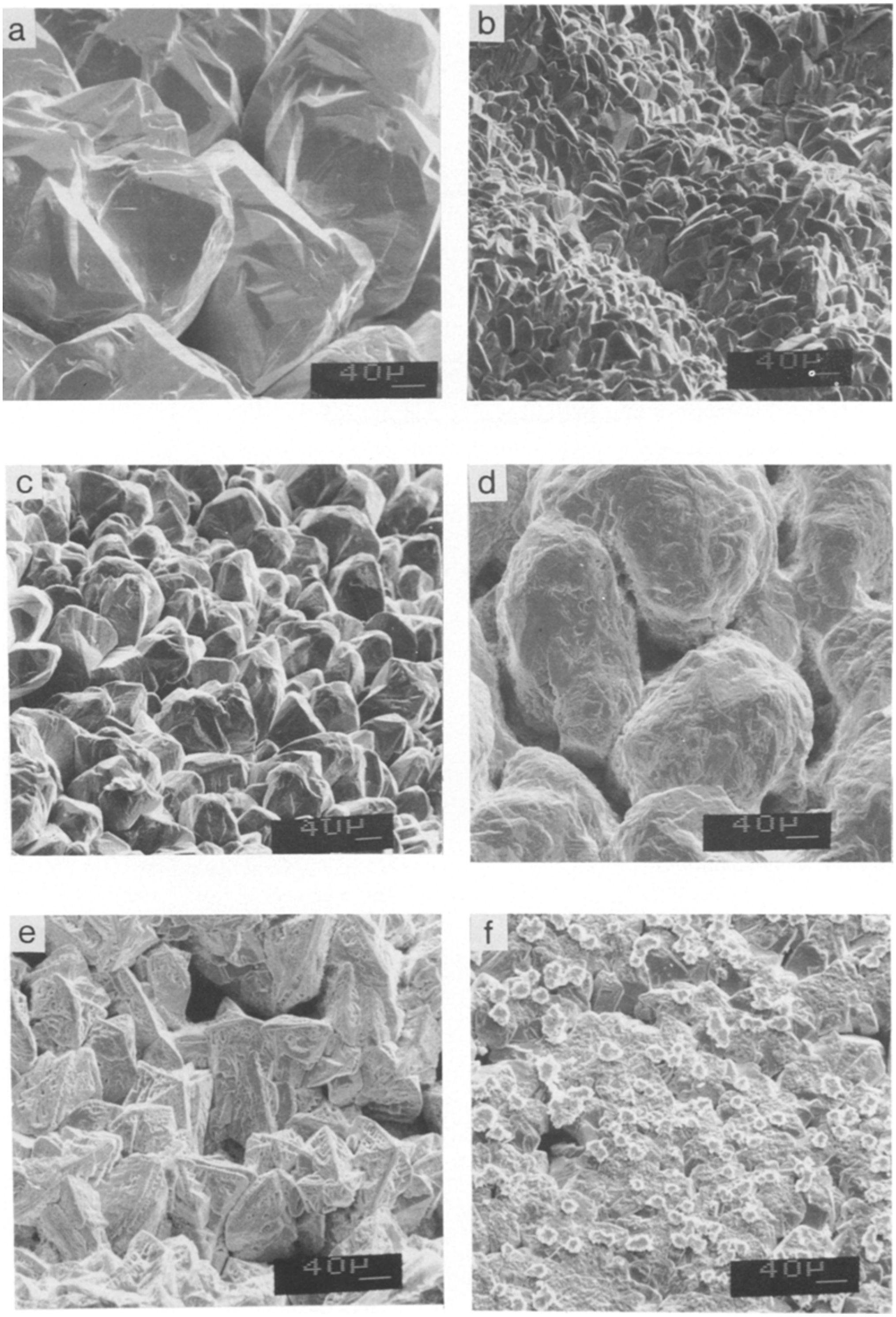

Fig. 2. SEM photomicrographs showing the effect of various addition agents (2 mg l^{-1}) on the morphology of 6-h copper deposits electrowon at 161 A m^{-2}: (a) addition-free, (b) Jaguar C13, (c) animal glue, (d) gum arabic, (e) TBACl, (f) gelatin, (g) Separan NP20, (h) Percol 351.

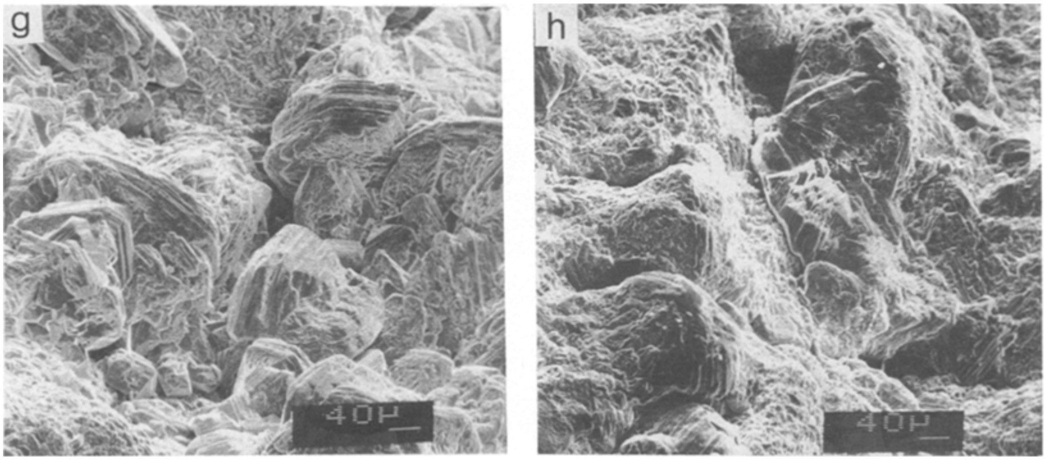

Fig. 2 continued.

effect on the preferred deposit orientation; all the deposits showed a predominant [1 3 3] [0 2 2] preferred orientation similar to the addition-free case. The major exception was Percol 351 where the [0 0 4] and [2 2 2] orientations were also prominent and Separan NP10 where the [0 2 2] orientation was not significant.

The effectiveness of Jaguar C13 in producing smooth compact copper deposits was investigated in more detail. Experiments were performed in which the concentration of Jaguar C13 was varied between 0 and 2 $\mathrm{mg\,l^{-1}}$ for copper deposition times of 24 h. The results indicated that Jaguar C13 concentrations as low as 0.25 $\mathrm{mg\,l^{-1}}$ were effective in maintaining a smooth, compact copper deposit over a 24-h period. Fig. 3 compares the morphologies of 24-h copper deposits electrowon at 161 $\mathrm{A\,m^{-2}}$ in the presence (0.25 $\mathrm{mg\,l^{-1}}$) and absence of Jaguar C13. In the absence of Jaguar C13, the morphology of the 24-h copper deposit (Fig. 3a) is similar to that of the 6-h deposit (cf. Fig. 2a), i.e. featuring elongated crystals and large voids. The presence of 0.25 $\mathrm{mg\,l^{-1}}$ Jaguar C13 in the electrolyte resulted in a smooth, compact 24-h deposit, having a refined grain size (Fig. 3b). The preferred deposit orientation was [133].

Table 1. The effect of various addition agents on the current efficiency and preferred orientation of 6-h copper deposits

*Addition agent**	*CE (%)*	*Preferred orientation†*
Addition-free	91.2	[1 3 3] [0 2 2]
Jaguar C13	93.9	[1 3 3] [0 2 2]
Glue	90.0	[1 3 3] [0 2 2]
Gelatin	90.3	[1 3 3] [0 2 2]
Percol 351	92.3	[0 0 4] [1 3 3] [2 2 2] [0 2 2]
Separan NP10	92.9	[1 3 3]
Gum arabic	90.9	[1 3 3] [0 2 2]
TBACl	90.1	[0 2 2] [1 3 3]

* Addition agent concentration = 2 $\mathrm{mg\,l^{-1}}$.
† Relative to ASTM standard for copper powder.

3.2. *Effect of electrolyte composition*

3.2.1. CuCl concentration. The effect of reducing the copper concentration in the cell from 0.5 M CuCl to 0.2 M CuCl on the structure and quality of the copper deposits was determined. The morphology of 6-h copper deposits electrowon at 161 $\mathrm{A\,m^{-2}}$ for solutions containing 0.5, 0.3 and 0.2 M CuCl is shown in the SEM photomicrographs of Fig. 4. As indicated, the copper crystals are less well-defined and the deposits become more porous as the copper concentration in the cell is decreased. The current efficiency decreased from 99.2% at 0.5 M CuCl to 96.7% at 0.2 M CuCl.

3.2.2. Effect of $FeCl_2$. The addition of 1 M $FeCl_2$ to an electrolyte containing 3 M NaCl + 1 M HCl + 0.5 M CuCl + 0.5 $\mathrm{mg\,l^{-1}}$ Jaguar C13 had a detrimental effect on the 6-h copper deposit electrowon at 161 $\mathrm{A\,m^{-2}}$. As indicated by SEM photomicrographs (Fig. 5a), the deposit is poorly crystalline and porous, similar to that

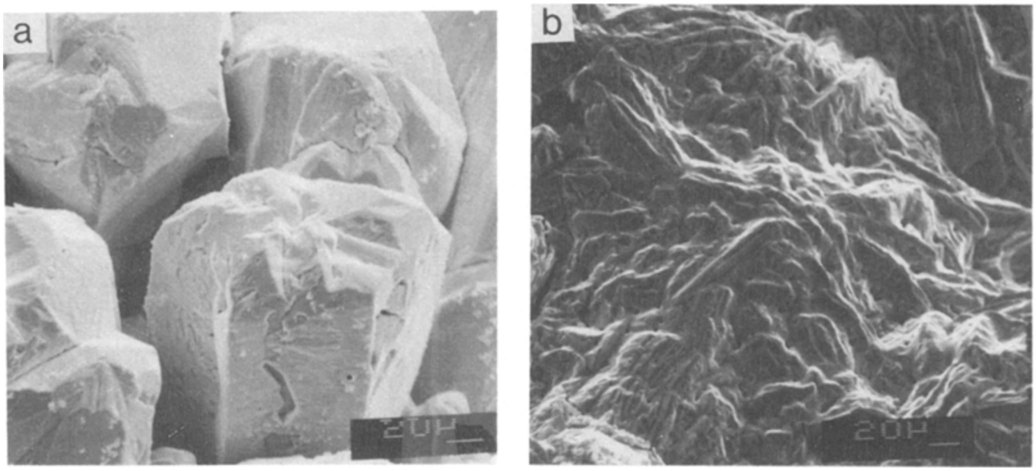

Fig. 3. SEM photomicrographs showing the effect of Jaguar C13 on the morphology of a 24-h copper deposit electrowon at 161 A m^{-2}: (a) addition-free, (b) 0.25 mg l^{-1} Jaguar C13.

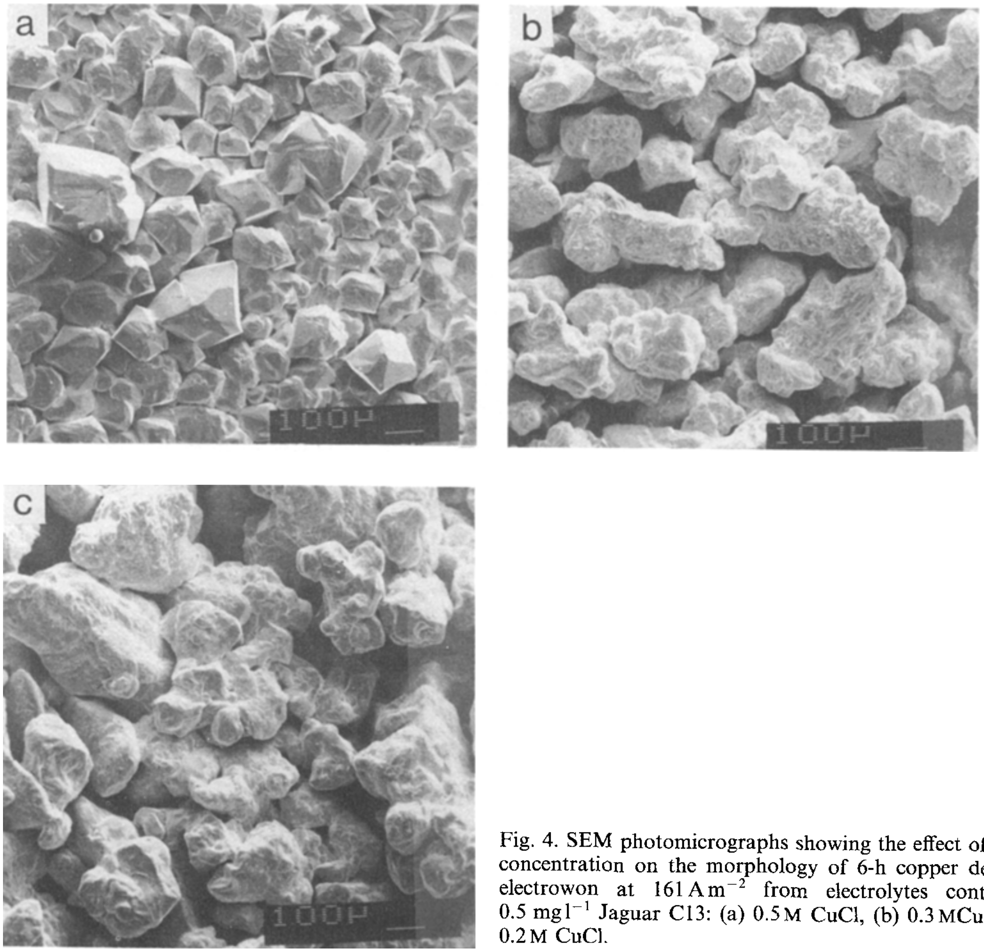

Fig. 4. SEM photomicrographs showing the effect of CuCl concentration on the morphology of 6-h copper deposits electrowon at 161 A m^{-2} from electrolytes containing 0.5 mg l^{-1} Jaguar C13: (a) 0.5 M CuCl, (b) 0.3 M CuCl, (c) 0.2 M CuCl.

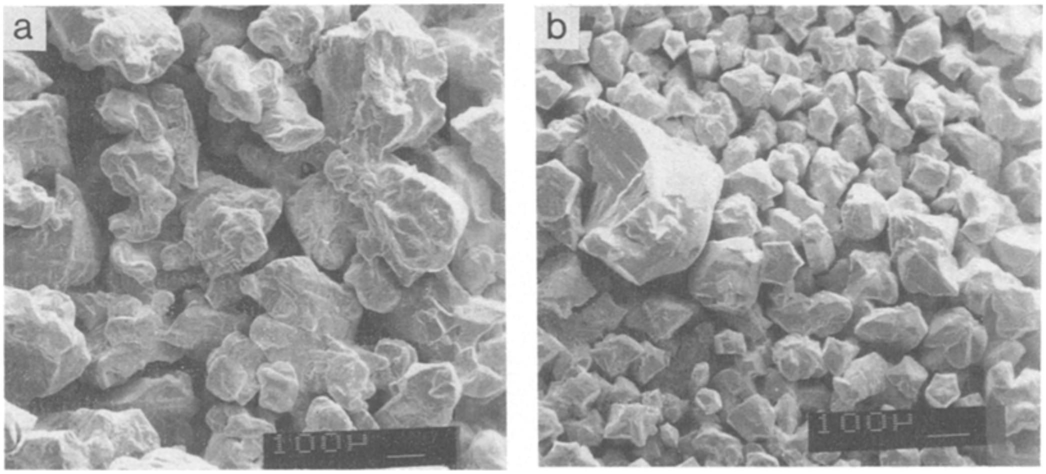

Fig. 5. SEM photomicrographs showing the effect of $FeCl_2$ on the morphology of 6-h copper deposits electrowon at $161\ A\,m^{-2}$ from electrolytes containing $0.5\ mg\,l^{-1}$ Jaguar C13: (a) 1 M $FeCl_2$ + 3 M NaCl, (b) 1 M $FeCl_2$ + 2 M NaCl.

obtained when the copper concentration in the electrolyte was decreased (cf. Fig. 4c).

The deposit improved in the presence of 1 M$FeCl_2$ when the NaCl concentration was reduced to 2 M. The SEM photomicrograph (Fig. 5b) indicates that this deposit consists of well-defined crystals and is less porous than that shown in Fig. 5a. In fact, the morphology of this deposit is similar to that electrowon under standard conditions (cf. Fig. 4a).

3.2.3. Effect of variations in NaCl and HCl concentrations. The effect of various NaCl and HCl concentrations on the morphology of 6-h copper deposits electrowon at $161\ A\,m^{-2}$ was determined and compared to the standard conditions, i.e. 0.5 M CuCl + 3 M NaCl + 1M HCl + 0.5 $mg\,l^{-1}$ Jaguar C13. The results are shown in the SEM photomicrographs, Fig. 6. Changing the solution composition from 3 M NaCl + 1 M HCl to 2 M NaCl + 2 M HCl resulted in a more compact deposit with a reduced crystal size (cf. Fig. 6a, b). The 6-h deposit electrowon from 3 M NaCl + 2 M HCl (Fig. 6c), was similar to that obtained from 2 M NaCl + 2 M HCl (Fig. 6b). The combination of 4 M NaCl + 1 M HCl also produced a compact deposit with a further refinement in crystal size (Fig. 6d).

The effect of other organic additives in these electrolytes was also examined. The 6-h deposit electrowon from 3 M NaCl + 2 M HCl without Jaguar C13 is shown in the SEM photomicrograph, Fig. 7a. The copper morphology depicted here is very similar to that obtained when this electrolyte contains 0.5 $mg\,l^{-1}$ Jaguar (cf. Fig. 6c). The addition of 10 $mg\,l^{-1}$ glue to the electrolyte containing 3 M NaCl + 2 M HCl resulted in deterioration in the deposit morphology (Fig. 7b). The deposit became less compact with larger, less distinct crystals. The deposit was brittle and difficult to strip from the stainless steel cathode. A similar effect was observed when the electrolyte contained 10–50 $mg\,l^{-1}$ gelatin.

3.2.4. Effect of sulphate ion. The effect of sodium sulphate on the morphology of 6-h copper deposits was examined using an electrolyte containing 4 M NaCl + 1 M HCl + 0.5 M CuCl without an addition agent. The results are shown in a series of SEM photomicrographs (Fig. 8) and indicate that sodium sulphate concentration to 20 $g\,l^{-1}$ had no significant effect on the morphology of the 6-h copper deposits. These concentrations of Na_2SO_4 also had no significant effect on the current efficiency.

4. Conclusion

Smooth, compact 24-h copper deposits were electrowon at $161\ A\,m^{-2}$ from 3 M NaCl + 1 M HCl + 0.5 M CuCl electrolyte using a dia-

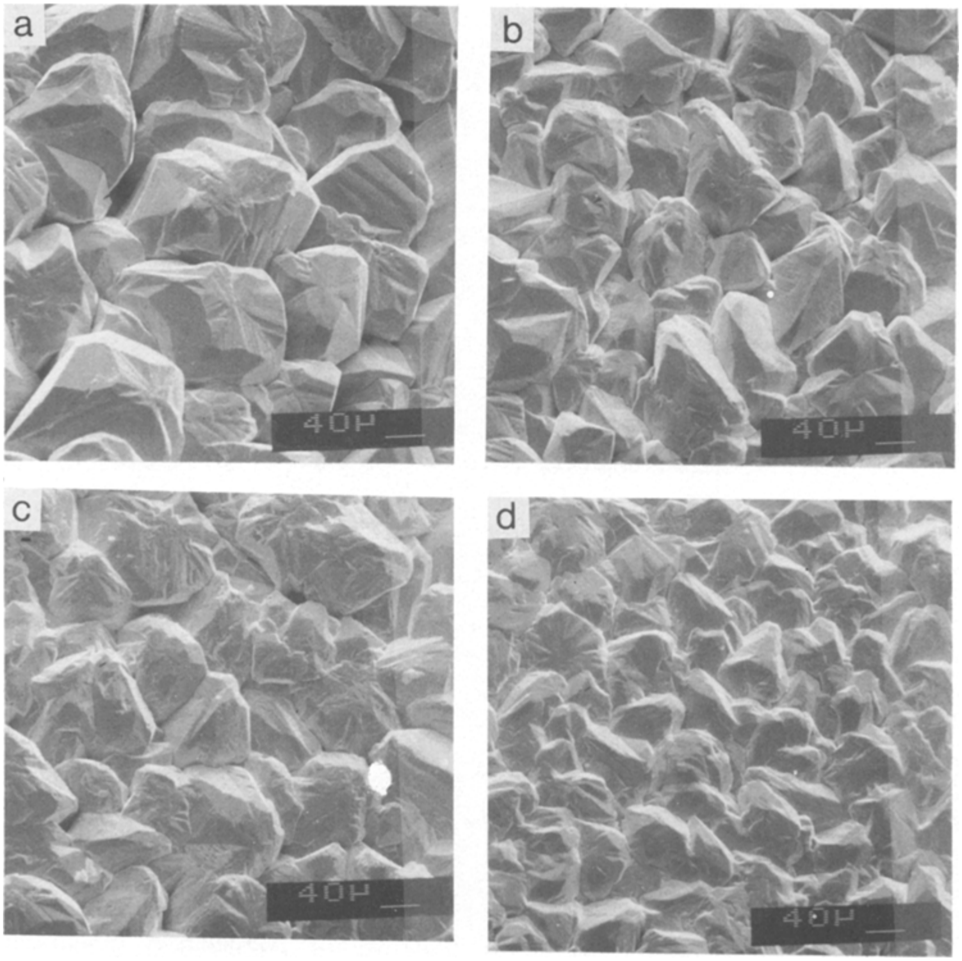

Fig. 6. SEM photomicrographs showing the effect of the relative proportion of NaCl and HCl on the morphology of 6-h copper deposits electrowon at 161 A m^{-2} from electrolytes containing 0.5 mg l^{-1} Jaguar C13: (a) 3 M NaCl + 1 M HCl, (b) 2 M NaCl + 2 M HCl, (c) 3 M NaCl + 2 M HCl, (d) 4 M NaCl + 1 M HCl.

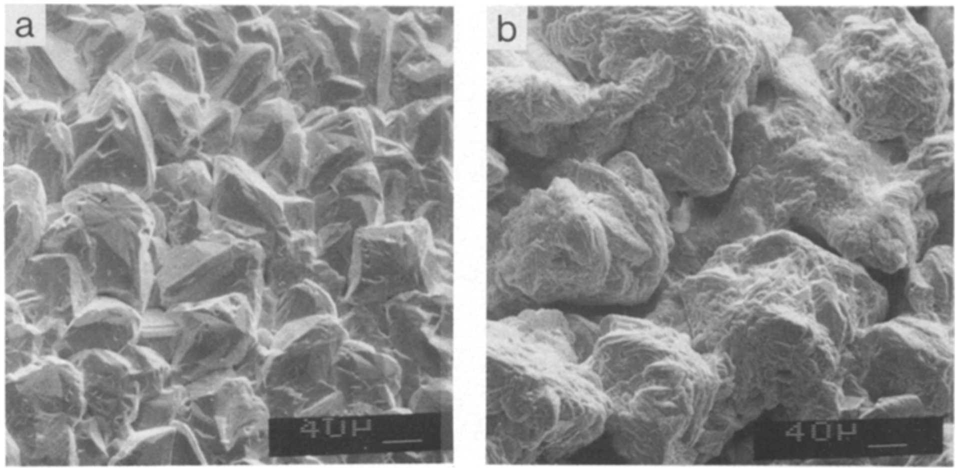

Fig. 7. SEM photomicrographs showing the morphology of 6-h copper deposits electrowon at 161 A m^{-2} from 3 M NaCl + 2 M HCl in the presence and absence of glue: (a) no additive, (b) 10 mg l^{-1} glue.

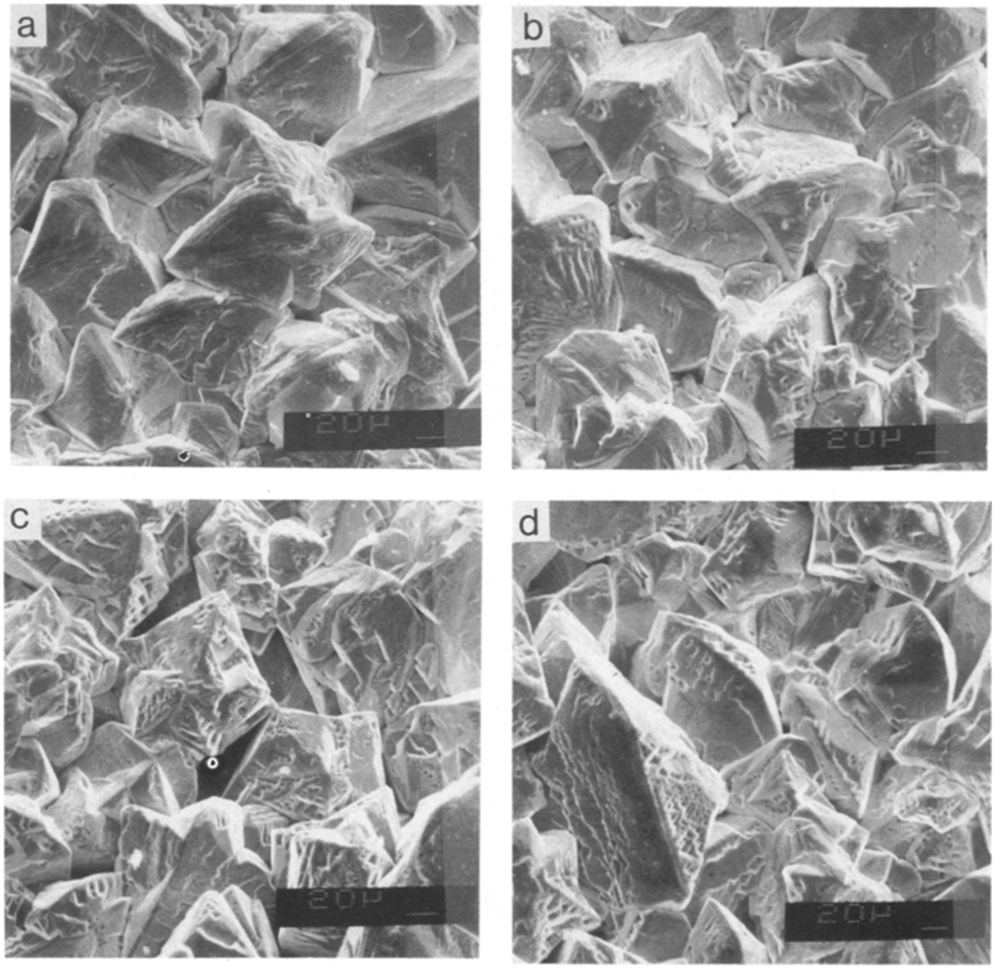

Fig. 8. SEM photomicrographs showing the effect of Na_2SO_4 on the morphology of 6-h copper deposits electrowon at 161 A m^{-2} from 4 M NaCl + 1 M HCl: (a) no Na_2SO_4, (b) 5 g l^{-1} Na_2SO_4, (c) 12 g l^{-1} Na_2SO_4, (d) 20 g l^{-1} Na_2SO_4.

phragm cell featuring electrolyte agitation by vibrating the cathode. The cathode quality was further improved by adding 0.25–0.5 mg l^{-1} Jaguar C13 to the electrolyte. Other additives such as glue and gelatin were not as effective and in some cases were actually detrimental to cuprous chloride electrolysis.

The copper deposit became more porous when the CuCl concentration in the electrolyte was < 0.5 M. Variations in the relative proportions of NaCl and HCl in the electrolyte, e.g. 3 M NaCl + 2 M HCl and 4 M NaCl + 1 M HCl improved the compactness of the copper deposits. The presence of Na_2SO_4 up to 20 g l^{-1} had no significant effect on the structure of the copper deposits.

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