Influence of Chloride Ion On Electrocrystallization of Copper

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A study was made to determine the effect of chloride ion during electrodeposition of copper, using an open-channel cell. Electrolysis parameters, such as current density, copper concentration, temperature, and circulation rate were varied in the presence of chloride ion to determine their effect. The deposits were examined by scanning electron microscopy (SEM) and X-ray diffractometry (XRD) to determine morphology and crystallographic orientations. It was observed that chloride ion affects the quality of the deposit surface, crystallographic orientations and deposit morphology of cathode copper. These are further affected by changing the electrolysis parameters.

The effect of various operating conditions on the structure and properties of copper deposits from acid sulfate electrolyte is very important to commercial operations.^{1,2} The most attention has been paid to the effect of bath composition on the structure of the deposits, because it governs critical properties such as purity, surface smoothness and hardness. Recognition of the factors that influence the structure is important, therefore, because this often permits prediction of those conditions or changes that will yield a product having



Fig. 1—Effect of Cu^{*2} concentration on copper deposit in the presence of chloride ion: (a) 17 g/L; (b) 27 g/L; (c) 37 g/L. H₂SO₄, 152 g/L; chloride ion, 500 mg/L; current density, 300 A/m²; temp, 60 °C; circulation rate, 0.08 m³/min/m² of cathode. 10X.

certain desirable properties.

It is known that during the process of electrodeposition of metal, certain inevitable foreign species generally present in the electrolyte, as well as the anion, may be codeposited or absorbed at the cathode.³⁻

⁶ Growth during electrodeposition can be seriously affected by these codeposited materials and may eventually influence the physical and mechanical properties of the deposits.

During their studies on the mechanism and kinetics of copper deposition, Bockris and Enyo⁷ assumed that one of the factors influencing growth is the blocking of deposition sites by adsorption of anions. In view of the role of adsorbable additives in practical plating processes,⁸ it is reasonable to expect that such specific adsorption, the effect of which varies with anion size, can result in modifications of the external form and internal structure of electrodeposits.

The effect of chloride ion has been studied by Arndt,⁹ Rouse and Aubel,¹⁰ Motorin,¹¹ Yao,¹² Gurevich and Pomosov,^{13,14} Byallozor,¹⁵ and Gauvin and Winkler.¹⁶ These studies mainly discuss the effect of chloride ion on cathode polarization during copper deposition. The effect of chloride ion on the electrocrystallization of copper has been reported by Nageswar and Setty,¹⁷ Barnes,³ Hardesty,¹⁸ Lakshmanan, Mackinnon and Brannen,²⁰ and Carneval and Cusminsky.²¹ These studies were carried out on laboratory scale, using either a static or stirred bath. The information on the cathode copper characterization available seems to be incomplete for the amount of data required for an industrial operation. In order to generate such information, the current study was undertaken where an open-channel cell was scaled down to simulate an industrial cell.

Experimental Procedure *Structure Evaluation Cell*

For this study, an open-channel cell, geometrically similar to an industrial cell, was employed to simulate the industrial operation. The cell was made of perspex, having dimensions $6.3 \times 6.0 \times 10.0$ cm. The cell was provided with an inlet and



Fig. 2—Effect of chloride ion concentration on copper deposit: (a) 0 mg/L; (b) 25 mg/L; (c) 100 mg/L. Cu², 37 g/L; H₂SO₄, 152 g/L; current density, 300 A/m²; temp, 40 °C; circulation rate, 0.08 m³/min/m² of cathode. 10X.

outlet, each having a diameter of 0.6 cm at the heights of 2.0 and 8.0 cm, respectively, from the bottom of the cell. A thermostat was used to preheat the electrolyte to the required temperature, then the electrolyte was fed to the cell at the desired circulation rate by a metering pump. The working cell contained two lead-antimony anodes (Sb 0.7%) and one stainless steel cathode.

Materials

The electrolyte was prepared from reagent grade sulfuric acid and cupric sulfate, using distilled water. The stock chloride solution was prepared from reagent grade sodium, potassium and magnesium chlorides. The chloride ion addition to the copper electrolyte was made by addition of an appropriate amount of the respective reagents from the stock solutions.



Fig. 3*a*—cjject of chioride ton concentration (500 mg/L) on copper deposit: Cu^{2} , 37 g/L; H₂SO₄, 152 g/L; current density, 300 A/m²; temp, 40 °C; circulation rate, 0.08 m³/min/m² of cathode. 10X. 3b,c—Effect of temperature on copper deposit in the presence of chloride ion (100 mg/L): (b) 30 °C; (c) 50 °C. Cu²², 37 g/L; H₂SO₄, 152 g/L; current density, 300 A/m²; circulation rate, 0.08 m³/min/m² of cathode. 10X.

Fig. 44—Ljject of lempetature of chloride ion: Cu⁻², 37 g/L; H₂SO₄, 152 g/L; circulation rate, 0.08 m²/min/m² of cathode; current density, 300 A/m²; temp, 60 °C. 10X. 4b,c—Effect of current density on copper deposit in the presence of chloride ion: (b) current density, 50 A/m²; (c) current density, 150 A/m². Cu⁺², 37 g/L; H₂SO₄, 152 g/L; temp, 40 °C; circulation rate, 0.08 m²/min/m² of cathode; chloride ion conc., 100 mg/L. 10X.

Operation

All the deposits were made by applying constant current from a regulated power supply (0-30 V, 0-10 A). A precision voltmeter and ammeter were incorporated in the cell circuit for recording the cell voltage and current. Unless otherwise specified, all the experiments were carried out under the following conditions: copper concentration, 37 g/L; H_2SO_4 concentration, 152 g/L; current density, 300 A/m²; electrolyte circulation rate, 0.08 m³/min/m² of cathode; bath temperature, 40 °C; electrolysis time, 2 hr, with sodium chloride as the source of chloride ions.

Deposit Examination

The cathode copper deposits were photographed under an optical microscope (10X) for determination of the quality of the deposit's surface. The surface morphology of sections of each cathode was also examined by scanning electron microscope. The crystallographic orientations of each deposit were determined by X-ray diffractometry.

Results and Discussion

Nature of Deposit Surface

The effect of various electrolysis parameters in the presence of chloride ion was studied to assess their effect on current efficiency and nature of the deposits. It was observed that current efficiency remained close to 100 percent, with variation of parameters such as current density, cell temperature, chloride ion concentration and electrolyte circulation rate,

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Table 1Effect of Copper ConcentrationConc. chloride, 500 mg/L; Temp, 60 °

Conc. of copper, g/L	CE, %
10	90
17	95
27	98
37	100

Table 2Crystallographic OrientationsAs a Function of Chloride Ion Concentration

Conc. of chloride		Peak inter	sity ratio,	(I/I _{max}), %	6
ion, mg/L	(111)	(200)	(220)	(311)	(222)
0	68.93	35.54	30.13	22.60	11.78
5	11.98	6.0	52.8	9.3	5.22
10	28.31	12.27	50.3	16.48	8.87
25	—	42.37	32.37	29.71	13.68
50	40.66	12.96	59.37	21.68	11.25
100	100	50.22	28.78	38.71	17.34

Table 3Crystallographic OrientationsAs a Function of Current DensityConc. chloride ion, 100 mg/L

Current densi	Peak int	Peak intensity ratio(I/I _{max}), %			
A/m2	(111)	(200)	(220)	(311)	(222)
50	54.43	31.67	17.93	19.07	8.94
150	100	45.36	33.41	35.36	16.27
300	79.50	39.93	22.88	30.77	13.79
450	99.33	42.86	36.17	33.97	16.09
700	10.56	5.62	38.66	1.75	2.86

except variation in copper concentration. The results of the effect of copper concentration in the presence of 500 mg/L chloride ion at 60 °C are given in Table 1. Current efficiency increased from ~90 to ~100 percent when Cu^{+2} concentration was raised from 10 to 27 g/L. Concentration of 17 g/L Cu^{+2} produced a lacy (*i.e.*, surface coverage was not uniform) copper deposit (Fig. 1a). On increasing the copper concentration, the copper deposit improved slightly (Fig. 1b), but at 37 g/L Cu^{+2} , the surface of the copper deposit became a little rough (Fig. 1c).

Variation of chloride ion concentration in the range 5 to 500 mg/L resulted in remarkable changes in the nature of surface deposits. In the absence of chloride ion, the surface deposit was smooth (Fig. 2a). Addition of chloride ion produced a smooth, but lacy copper deposit until a NaCl concentration of 100 mg/L was reached (Figs. 2b,c). The surface became comparatively rough (Fig. 3a) at higher concentration. The effect of cell temperature was studied in the range of 30 to 60 °C at 100 mg/L chloride ion. Surface roughness became more pronounced with increase in temperature from 30 to 60 °C (Figs. 2c, 3b-c, 4a). Further, lacy copper deposition began at 40 °C and above (Figs. 2c, 3c, 4a). Such copper deposits were also reported by O'Keefe and Hurst²² and Toth.²³ Lower current density (50 to 150 A/m²) at 100 mg/L chloride ion also produced similar deposits (Figs. 4b,c). Though bright and smooth, lacy copper deposits resulted until current density increased to 300 A/m² (Fig. 2c).





100 mg/L) on copper deposit: (a) KCl; (b) MgCl₂ Cu⁺², 37 g/L; H₂SO₄, 152 g/L; temp, 40 °C; circulation rate, 0.08 $m^3/$ A/m^2 , 10X.

Fig. 5-Effect of current density on copper deposit in the presence of chloride ion (conc., 100 mg/L): (a) current density, 450 A/m²; (b) current density, 750 A/ m²; (c) current density, 750 A/m², chloride ion conc., 500 mg/L. Cu+2, 37 g/L; H,SO, 152 g/L; temp, 40 °C; circulation rate, 0.08 m³/min/m² of cathode. 10X.

min/m² of cathode; current density, 300

The surface began roughening at 450 A/m^2 and above (Figs. 5a,b). The color of the deposits also changed with surface roughness. On increasing chloride ion concentration at 750 A/m² from 100 to 500 mg/L, a dark-colored granular deposit was obtained (Fig. 5c).

Electrolyte circulation rate also affected the deposit in the presence of chloride ion. With 100 mg/L chloride ion and no circulation, the surface of the deposit was rough, but became smooth when the electrolyte was circulated at a rate of 0.08 m³/min/m² of cathode. In addition to NaCl, other chloride salts, such as KCl, NH₂Cl and MgCl₂ were also used to evaluate the effect of corresponding cations. Although there was no change in current efficiency, noticeable effect on surface deposits was observed on changing the cations (Figs. 2c, 6a,b).

Crystallographic Orientation

The effect of chloride ion on the crystallographic orientation of cathode deposits was obtained under the influence of different electrolysis parameters. Of the seven copper lines scanned in the diffractometer, only five, namely (111), (200), (220), (311) and (222) showed any significant change in peak intensities. The results of the effect of variation in chloride concentration are summarized in Table 2. With no chloride ion addition, the most preferred crystal plane was (111) and the order of preference of different planes was (111) > (200)>(220)>(311)>(222). Upon addition of 5 mg/L chloride ion, the most preferred plane shifted from (111) to (220). Further, the growth in the direction of the (200) plane was reduced, whereas in the case of (311), it was favored. Increase in chloride concentration, further improved crystal growth in the direction of all the planes under consideration and the (220) plane remained most preferred. Postl, Eichkorn and Fisher²³ explained that addition of chloride ion to the copper



Fig. 7-SEM photomicrograph of cathode copper showing effect of chloride ion concentration: (a) 0 mg/L; (b) 5 mg/L; (c) 25 mg/L; (d) 100 mg/L. Cu⁺², 37 g/L; H₂SO₄, 152 g/L; temp, 40 °C; circulation rate, 0.08 m³/min/m² of cathode; current density, 300 A/m². 1300X.

electrolyte changes the overvoltage values for copper deposition because of its adsorption on the cathode. It forms an intermediate complex of the type $Cu^{+2} - Cl^{-} - e(Cu)$ at lower chloride concentration, where it causes decrease in overvoltage. This situation favors electrocrystallization of copper in the direction of the (220) plane (*i.e.*, ridge-type growth), which also results in even deposition. This trend continued until chloride ion concentration reached 50 mg/L, where the degree of orientation was in the order (220) > (111) > (311)>(220)>(222). Addition of 100 mg/L chloride ion drastically changed the orientation of crystal planes shown at lower levels. In this case, the most preferred plane again became

Table 4 **Crystallographic Orientations** As a Function of Temperature Conc. chloride ion, 100 mg/L

Temp					
°C	(111)	(200)	(220)	(311)	(222)
30	100	45.22	43.12	41.93	20.79
40	99.77	50.10	28.72	38.62	17.30
50	59.61	29.05	44.66	25.50	13.34
60	78.36	39.08	20.71	22.61	11.58

Table 5 Comparison of the Effect of Chloride Ion At Different Temperatures

°C	Chloride	Pea (111)	k Intens (200)	ity ratio (220)	, (I/I _{max}), (311)	% (222)
30	0	37.45	34.40	20.57	27.73	8.38
	100	100.00	45.22	43.12	41.93	20.79
40	0	68.77	35.45	30.06	22.55	11.65
	100	99.77	50.10	28.72	38.62	17.30
60	0	13.13	5.68	67.46	11.16	7.0
	100	78.42	39.08	20.71	22.69	11.58



Fig. 8a—SEM photomicrograph of cathode copper showing effect of chloride ion concentration (500 mg/L): Cu^{*2} , 37 g/L; H_2SO_4 , 152 g/L; temp, 40 °C; circulation rate, 0.08 m³/min/m² of cathode; current density, 300 A/m². 1300X. 8b,c,d—SEM photomicrograph of cathode copper showing effect of current density: (b) 50 A/m²; (c) 150 A/m²; (d) 450 A/m². Cu^{*2} , 37 g/L; H_2SO_4 , 152 g/L; temp, 40 °C; circulation rate, 0.08 m³/min/m² of cathode; chloride ion conc., 100 mg/L. 1300X.

(111) and the order of preference altered to (111) > (200) >(311) > (220) > (222). Gurevich and Pomosov¹³ explained that this may be attributed to the fact that at higher chloride ion concentration, CuCl is formed and adsorbed on the cathode, resulting in decrease of the active surface area and increase in local current density, thereby increasing overvoltage. Accordingly, growth of the (220) plane is suppressed, consequently promoting electrocrystallization of copper in the direction of the (111) plane (*i.e.*, pyramidal growth dominates, causing nodular deposition. This is in contradiction to the observations made by Lakshmanan *et al.*,¹⁹ who reported the (220) plane to be the most preferred in the similar range of chloride ion concentration.

The results of the effect of current density are given in Table 3. At a current density of 50 A/m², crystal growth in the direction of the (111) plane was most prominent and the degree of preference was in the order (111) > (200) > (311) > (220) > (222). Almost same trend continued until the current density approached 750 A/m², where the most prominent plane shifted from (111) to (220) and the order of preference of crystal growth shifted to (220) > (111)> (200) > (222) > (311). Such changes in the orientation were also reflected in surface deposits, where a nodular deposit was obtained.

The crystallographic orientations of cathode copper at different temperatures are given in Table 4. At 30 °C, the (111) plane was the most preferred and the order of preferred growth of different planes was (111) > (200) > (220) > (311) > (222). When the temperature was raised to 40 °C, the order of preferred planes remained the same. The growth of the (311) plane was favored simultaneously suppressing growth of (220) plane. On increase in temperature to 50 °C, growth of the (200) plane was suppressed while growth of the (220) plane was promoted. This caused a shift in the order of preference to (111) > (220) > (200) > (311) > (222). At 60 °C, the order of preferred planes was the same as at 40 °C.

Table 5 shows a comparison of crystallographic orientations of cathode copper obtained without and with addition of 100 mg/L of chloride ion at different temperatures. With no



Fig. 9a,b—SEM photomicrograph of cathode copper showing effect of current density; (a) current density, 750 A/m², chloride ion conc., 100 mg/L; (b) current density, 750 A/m², chloride ion conc., 500 mg/L. Cu⁺², 37 g/L; H₂SO_q 152 g/L; temp, 40 °C; circulation rate, 0.08 m³/min/m² of cathode. 1300X. 9c,d—SEM photomicro-graph of cathode copper showing effect of temperature: (c) 50 °C; (d) 60 °C. Cu⁺², 37 g/L; H₂SO_q, 152 g/L; chloride ion conc., 100 mg/L; circulation rate, 0.08 m³/min/m² of cathode; current density, 300 A/m². 1300X.

addition, the order of preferred crystal planes was (111) > (200) > (220) > 311) > (222) up to 40 °C, but in the case of 60 °C, the most dominant plane was (220) instead of (111), as observed at lower temperatures. Upon addition of 100 mg/L chloride ion, the peak intensity ratio (I/I_{max}) increased for each crystal plane except (220) at 40 °C and above.

The results of the effect of variation in chloride salts are given in Table 6. It can be seen that with all the salts considered, the (111) crystal plane dominated, but the order of preferred planes differed. In the case of NaCl, the order was (111) > (200) > (311) > (220) > (222), whereas in the case of KCl, the order changed to (111) > (311) > (220) > (200) > (222). The order of preferred planes in the case of MgCl₂ was completely different from those of NaCl and KCl and was (111) > (200) > (221) > (311) > (222). Such changes were also evident in surface deposits (Figs. 2c, 6a,b).

Surface Morphology

The surface morphology of the various copper deposits was examined by scanning electron microscope (SEM). The effect of chloride ion on the morphology of cathode copper is shown in Figs. 7a to 8a. As observed from these figures, chloride ion has a marked effect on the surface morphology of the deposited copper. With no chloride ions, there appeared long triangular blocks showing pyramidal growth. The addition of 5 mg/L chloride ion abruptly changed the morphology. The triangular blocks disappeared and the shape

Table 6Crystallographic OrientationsAs a Function of Different Chloride SaltsConc. chloride ion, 100 mg/L

Salt	Peak Intensity ratio, (I/I _{max}), %				
	(111)	(200)	(220)	(311)	(222)
NaCl	87.98	44.18	25.32	34.06	15.26
KC1	100	33.76	36.86	37.32	17.26
$MgCl_2$	79.99	44.27	41.63	32.97	15.08



Fig. 10a—SEM photomicrograph of cathode copper showing effect of temperature: Chloride ion conc., 0 mg/L; 60 °C; Cut³, 37 g/L; H₂SO₂, 152 g/L; circulation rate, 0.08 m³/min/m² of cathode; current density, 300 A/m². 1300X. 10b—SEM photomicrograph of cathode copper showing effect of circulation rate: 40 °C. Cut³, 37 g/L; H₂SO₂, 152 g/L; chloride ion conc., 500 mg/L; no circulation; current density, 300 A/ m². 1300X. 10c,d—SEM photomicrograph of cathode copper showing effect of chloride salt: (c) MgCl₃; (d) KCl; 40 °C; Cut³, 37 g/L; H₂SO₄, 152 g/L; chloride ion conc., 100 mg/L; circulation rate, 0.08 m³/min/m² of cathode; current density, 300 A/ m². 1300X.

and size of crystal planes changed. Such changes were also marked in the crystallographic orientations, where preferred growth direction changed from the (111) to the (220) plane. The deposit obtained upon addition of 25 mg/L chloride ion showed similar morphology, as observed in the case of 5 mg/ L chloride ion. But upon increase of the chloride concentration to 100 or 500 mg/L, the morphology changed again to triangular shape, showing pyramidal growth. Similar observations were also reported by Lakshmanan et al.¹⁹

The photomicrographs (Figs. 7d, 8b-d, 9a) show the morphology of cathode copper in the presence of 100 mg/L chloride ion in the current-density range of 50 to 750 A/m². Figure 9b shows the morphology of cathode copper in the presence of 500 mg/L chloride ion at a current density of 750 A/m². The deposit at 50 A/m² shows very poor morphology. This was clearly indicated by the quality of the surface deposit (Fig. 4b). Upon increasing the current density, the morphology appeared to improve until a current density of 300 A/m² (Figs. 8c and 7d) was attained. At 450 A/m² (Fig. 8d) or above (Fig. 9a), nodular growth formation was observed. When chloride ion concentration was increased from 100 to 500 mg/L at 750 A/m², the nodule size decreased, permitting formation of a greater number of smaller nodules.

The SEM photographs (Figs. 7d, 9c,d) show the morphology of copper deposits at temperatures in the range of 40 to 60 °C. From these figures, it is clear that temperature had a noticeable effect on the surface morphology of cathode copper in the presence of chloride ion. The crystallites became flat and irregular in shape and size with increase in temperature. Addition of chloride ion largely decreased the crystallite size, but produced a more compact deposit (Figs. 9d and 10a).

Figures 8a and 10b show the effect of electrolyte circulation rate on the morphology of cathode copper. Nodular growth morphology was observed with deposits obtained with a stagnant electrolyte. This was also evident from visual examination of the deposit surface and crystallographic orientations where a ridge-type structure was favored. The surface morphology of copper obtained with variation of chloride salts is shown in Figs. 7d and 10c,d. The morphology upon addition of NaCl or MgCl₂ appeared similar, but a relatively different morphology was obtained when KCl was added. Such changes were also shown in the crystallographic orientations where, besides (111) crystal planes, other planes, such as (311), (220) and (200) were equally favored.

Conclusions

- 1. At lower chloride ion concentration, although the deposit is smooth and bright, a lacy type of deposit forms. The unevenness of the copper deposit is enhanced at higher chloride ion concentration.
- 2. Electrolysis parameters, such as current density, temperature, circulation rate, etc., have a remarkable effect on copper deposits.
- 3. Chloride ions have a significant effect on crystallographic orientations of a copper deposit. At lower concentrations, the (220) plane is predominant, whereas at higher concentrations the (111) plane is preferred. The transformation of preferred crystal planes takes place from (111) to (220) then (200) and finally becomes the (111) plane at higher chloride ion concentration.
- 4. The crystallographic orientations also show variations with change in electrolysis parameters.
- 5. The presence of chloride ions significantly changes the microscopic morphology of cathode copper, which shows further variations upon changing the electrolysis parameters.

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