JOURNAL OF APPLIED ELECTROCHEMISTRY 13 (1983) 429–438

Nodulation of electrodeposited copper due to suspended particulate

T. N. ANDERSEN

Kennecott, Process Technology, Salt Lake City, Utah

C. H. PITT, L. S. LIVINGSTON

Department of Metallurgy and Metallurgical Engineering, University of Utah, Salt Lake City, Utah

Received 28 July 1982

Cathode nodulation was studied by electrodepositing copper at 38 mA cm^{-2} from acid sulphate baths which contained 0.5 g dm^{-3} of various suspended particulate. The conductive particulates, such as copper and graphite, produced dense nodulation at temperatures of 50° C and less. Antimony and silver powders caused pitting as well as nodulation. Non-conducting powders such as lead sulphate, lead dioxide, and gypsum produced no nodulation, and correspondingly were occluded only to a very small extent. Once formed, the nodules occluded very large concentrations of any particulate present. The nodulation decreased markedly with an increase in temperature, particularly from 50° to 70° C. With increasing Cu^{2+} ion concentration, the nodulation decreased nominally. These effects and characteristics of the nodulated deposits are discussed.

1. Introduction

Rough deposits are detrimental to electrorefined and electrowon copper, as they tend to cause short circuits in the electrolytic process cells and, even more important, foster contamination of the cathodes by promoting occlusion of electrolyte and suspended particulate. The particulate in electrorefining usually originates from the anode slimes [1, 2], and contains several elements (e.g., selenium and tellerium) which are particularly deleterious to the fabricating and annealing of the copper [3]. Particulate in electrowinning cells usually contains lead compounds which arise from corrosion of the lead-based anodes [4]; lead, too, reduces the fabricability of copper [3]. Cathode quality, which is critical in all tankhouses, is controlled through the plating parameters (e.g., current density, temperature, and electrolyte composition) as well as through the introduction into the cells of trace levels of 'addition agents' such as chloride ions, animal glue, thiourea and other organics [1, 5, 6]. It is usually considered that control of the above parameters prevents coarse-grained and other porous growth patterns as well as preventing the accelerated growth of dendrites [7, 8]. Rarely has the literature implicated the particulate as being a primary cause of surface roughness. It has been noted, however, that floating slimes in copper electrorefining cause irregular growth [5]. The most direct involvement of particulate has been identified by workers at the University of Louvain [8–10], who found that electrically conducting and semi-conducting particulates caused 'nodules' on copper cathodes whereas non-conducting particulate did not. These 'nodules' are distinguished [10] from dendrites, which form from the selective development of particular crystal orientations.

In the present work nodulation by particulate is explored further. Several types of particulate were suspended at concentrations of 500 mg dm^{-3} in a copper electrodeposition cell to verify the effect of particulate conductivity on nodulation and to characterize the nodulation. Also, the effect of temperature and copper ion concentration on nodulation was studied as was impurity entrap-

0021-891X/83 $03.00 + .12.

ment by the nodules. Observations of previous workers [9, 10] were re-emphasized and several additional phenomena were noted.

2. Experimental procedure

2.1. *Apparatus*

Copper was electroplated in the presence of suspended particles and the cathode deposit was studied by various means to determine the degree and nature of the nodulation and, in some cases, the impurity entrapment.

Details of the equipment used are given elsewhere [11]. A 500 cm ^{3} covered Pyrex cylindrical jar served as the cell. This contained two vertical electrodes, a 5 cm x 11.4 cm x 0.3 cm thick titanium cathode blank and a 5 cm x 10.2 cm x 0.6 cm thick piece of electrolytic copper as the anode. The back and edges of the cathode were coated with a lacquer such that only a 5.4 cm x 3.0 cm 'face' of the titanium was exposed to the solution; this prevented excessive edge growth. The electrodes were attached to and suspended from the cell cover at a separation of 4.5 cm. Suspension of test particulates was effected with a plastic turbine impeller, 5 cm in diameter, powered by a laboratory mixer with speed control. The cell was immersed in a constant-temperature bath. In most tests the anode was enclosed in a dacron-cotton bag to prevent any anode particulate contacting the cathode. Some tests were, however, performed without this bag for comparison.

The electrolyte was made up of reagent grade sulphuric acid (adjusted to 198 g dm^{-3} H_2SO_4) and copper sulphate (usually at 50 g dm^{-3} Cu^{2+} but varied in some tests). A wide variety of powders was used for suspended particulate, including some substances found in commercial electrorefining and electrowinning cells. Commercial powders used 'as-received' included graphite, lead dioxide, selenium, silver, gypsum ($CaSO_4 \cdot 2H_2O$), and beryllium oxide. Antimony and cuprous selenide were purchased as chunks and ground to size. Copper powder was prepared by electrowinning from a 10 g dm^{-3} Cu^{2+} solution ($CuSO_4$–H_2SO_4) onto a titanium cathode at 38 mA cm^{-2}. The lead anode was bagged in this case to prevent cathode contamination. The powdered copper was scraped off the cathode, washed, dried and kept in an airtight container. Lead sulphate was precipitated from a lead nitrate solution with sulphuric acid. The mean particle diameter for most of the materials was 10–25 μm as determined microscopically. The lead sulphate and beryllium oxide particle diameters were 42 and 110 μm, respectively, and the lead dioxide was oblong shaped at roughly 10 μm x 65 μm.

Current was supplied by means of a constant current power supply.

2.2. *Procedure*

The electrolyte was brought to the desired temperature; a weighed amount of particulate was mixed with a small quantity of electrolyte to wet the particles and then added to the cell. The stirrer was set at 60 rpm, which was the minimum speed capable of keeping the particles suspended. A low level of agitation was desired so as to qualitatively simulate commercial electrorefining cells. At higher rates of stirring, copper selenide was found to leave erosion marks on the copper deposit. Other particulate may have behaved similarly, but were not tested at high stirring speeds. Finally, current was passed for the desired time, which was 2 hours in most cases. Temperatures employed were 25°, 50°, and 70° C. The cathode current density, i, was set at 38 mA cm^{-2} for most tests which provided mixed rate control by both charge transfer and mass transfer under the applied agitation conditions. The deposition time, t, was usually two hours, but was eight hours in some cases.

Because a particular set of conditions were used in most tests, these shall be termed 'the standard conditions' to save repetition; i.e., the standard conditions = 198 g dm^{-3} H_2SO_4, 50 g dm^{-3} Cu^{2+}, 0.5 g dm^{-3} particulate, $i = 38$ mA cm^{-2} and $t = 2$ h.

After each test the copper deposit was peeled off the titanium starter sheet, rinsed with water and dried. When the deposit was to be analysed for impurities, the washing step included other reagents to ensure that no particulate remained on the surface, e.g., ammonium acetate solution was used to remove any surface lead sulphate. Deposits were examined with a stereomicroscope to determine the nodule populations, diameters, and characteristics. A light section microscope was used to measure the heights of the nodules. The resolution was 0.5 micrometers and the maximum height measureable was 300 micrometers, which was surpassed by the nodule height in many cases. The heights of taller nodules could be estimated with a divider and rule. Surface features and nodule populations were examined under low magnification (e.g., 20x) and cross-sections, polished with 0.05 μm diamond grit, were examined under 75–100x using an M15C Vickers microscope. Some features were examined with a scanning electron microscope.

Crystal orientation was determined by means of X-ray diffraction, with the growth plane facing the X-ray beam. Chemical analyses were performed on some of the deposits to determine the lead or selenium content. Lead assays were determined by emission spectrography and selenium by a wet chemical method.

3. Results

3.1. *Effect of particulate conductivity*

The particulates fell into two groups, those that produced nodules and those that did not. The individual substances tested are categorized as follows:

Nodule producers: Cu, C, Sb, Se, Ag.

Non-producers of nodulues: $PbSO_4$, PbO_2, BeO, Cu_2Se, $CaSO_4 \cdot 2H_2O$.

The deposit surface appeared smooth in the case of all powders which did not cause nodulation and when no particulate was present. The high and low points on the surface differed by approximately 10 μm.

Only the electrical conductors and good semiconductors produced nodules, as earlier investigators [9, 10] found. The surfaces produced and the nodules themselves were very different, however, depending on the type of powder and the plating conditions, as the next section describes.

3.2. *Variations in nodulation with temperature and composition of particulate*

With variations in particles and temperatures, the deposits ranged from smooth to heavily nodulated to pitted with or without nodulation. The heavily nodulated surfaces were often darker than the smooth surfaces. The nodules ranged from the size of the particulate (0.02 mm diameter) to 1 mm diameter, and varied from smooth to coarse and bushy. Table 1 indicates individual characteristics of the surface and nodules with different plating conditions. Figure 1 shows some of the features described.

Nodule populations and sizes are needed along with Table 1 to characterize the surfaces. These are shown in Figs. 2 and 3, respectively, as a function of temperature. Values shown are averages for all replicate tests at the indicated conditions; copper particulate nodule populations varied by ± 30%, from up to six replicates. For antimony there was only one replicate and for carbon no

Table 1. Surface characteristics of deposits grown at various temperatures and with various particulates present (the standard conditions were applied)

Particulate	*Temperature*		
	25° C	*50° C*	*70° C*
Cu	Very rough nodules.	Rough to moderately smooth, rounded nodules.	Very few nodules; smoother than at 50° C.
C	Very rough nodules.	Very rough nodules.	Nodules rounded and moderately rough.
Sb	Very rough nodules.	Moderately rough nodules; surface pitted.	Nodules quite smooth and rounded; many pits.
Se	Smooth round nodules.	Nodules round and very smooth	Nodules round and very smooth.
Ag	Smooth round nodules.	No nodules; surface slightly pitted.	No nodules; surface moderately pitted.

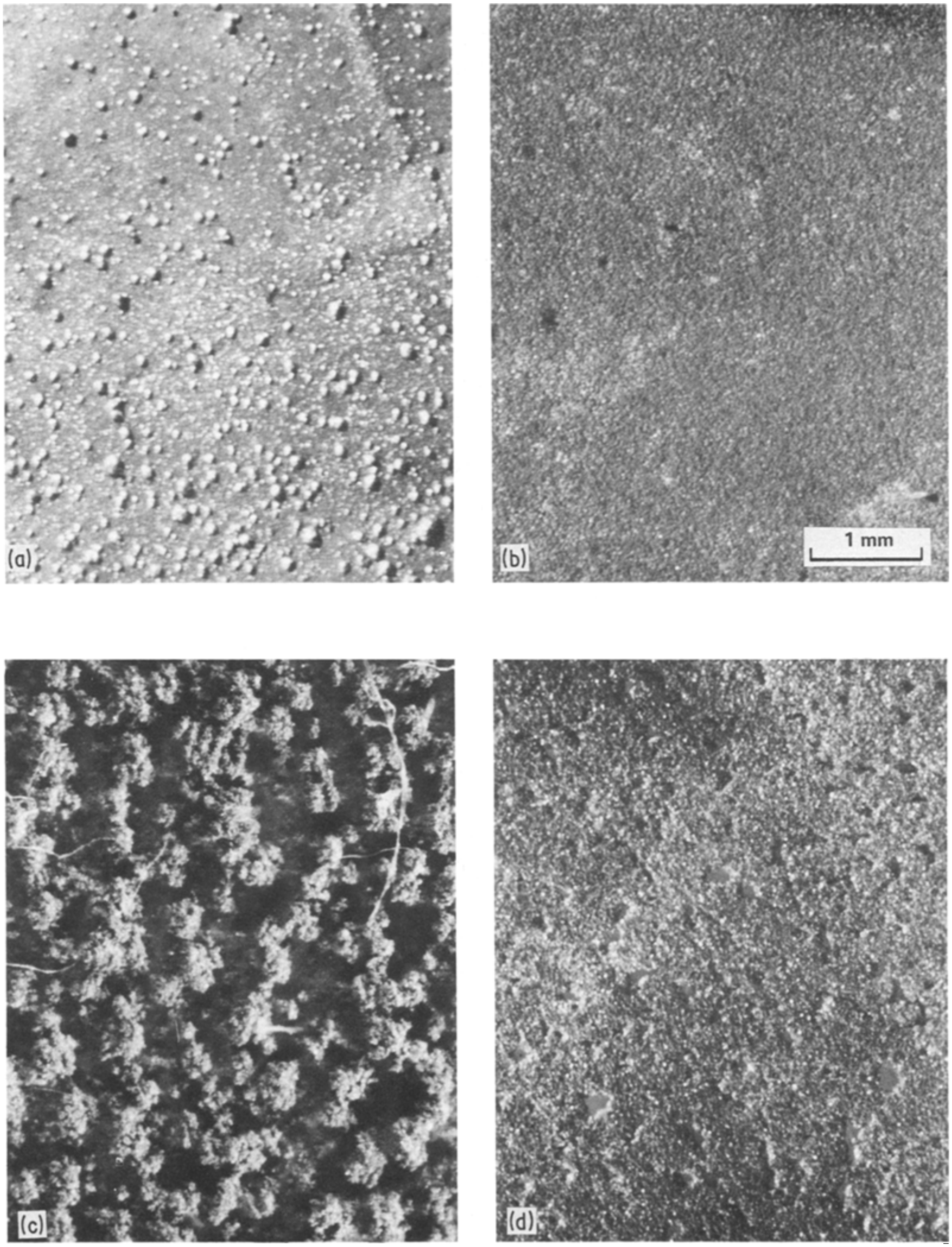

Fig. 1. Cathode faces grown under the standard conditions but with various particulates and at various temperatures. a, 25° C, silver particulate; b, 70° C, graphite particulate; c, 25° C, antimony particulate; d, 70° C, antimony particulate.

replicates. Therefore the differences with carbon and antimony are questionable.

Nodule diameters on each cathode ranged from approximately 0.02 mm (the starting particulate) to 0.1–1 mm. The heights of these nodules were roughly comparable to the diameters. Because of the variations in size, Fig. 3 shows the diameters of the largest nodules in each case. These diameters

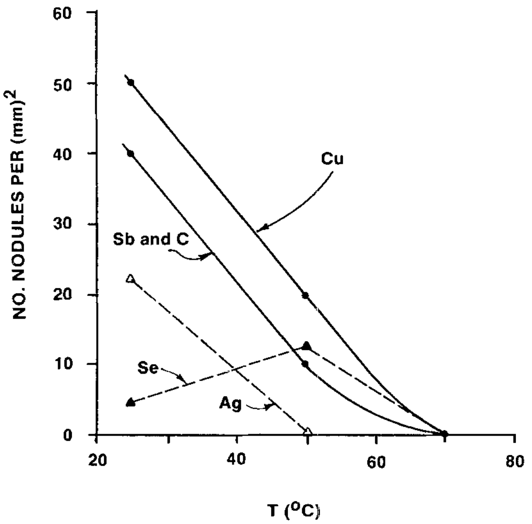

Fig. 2. Nodule population versus temperature for deposits plated under the standard conditions.

varied from test to test (sometimes by ± 60%), so the averages of replicate tests are shown in the figure.

Although the large nodules had the most profound affect on surface roughness, as judged visually and by touch, the small nodules weighed heavily in the populations. The surfaces of the most nodulated cathodes (i.e., those plated with carbon and antimony at 25° C) were like a forest with the smaller nodules fitting into the interstices between the larger nodules. This 'crowding' effect explains why the smoother, smaller nodules produced from copper particulate were more numerous than their larger, rougher counterparts produced from carbon and antimony. The smaller numbers of nodules produced from silver particulate appears to relate to the pitting, as is discussed in a later section.

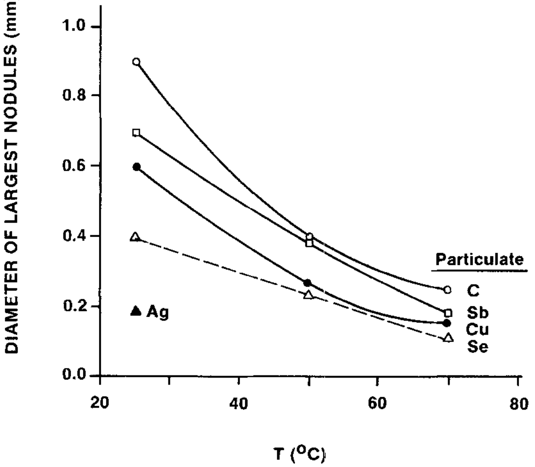

Fig. 3. Diameters of largest nodules versus temperature for deposits plated under the standard conditions.

The large rough nodules contained many particles which were occluded during the growth (see the cross-section of Fig. 4). Renucleation started at each of these particles, which results in a tree-like structure.

Even with substantial nodulation the particulate made up an insignificant fraction of the deposit weight. Weighing the test coupons failed to show a significant difference between smooth and nodular ones; most corresponded roughly to the faradaic charge. In some cases the weights of the roughest deposits were slightly less than that corresponding to the charge because some of the nodules apparently broke off (as they easily did during handling). Spectrographic analysis showed the antimony content in the roughest deposits to be of the order of 500 ppm (0.05%), which is in line with the particulate weight's being insignificant.

3.3. *Effect of copper ion concentration*

The deposits became noticeably rougher as the Cu^{2+} ion concentration was decreased from 50 g dm^{-3} to 5 g dm^{-3} (independent of whether or not the ionic strength was held constant with $ZnSO_4$). This was most apparent when nodule size was considered (Fig. 5). Nodule population showed little if any trend with the Cu^{2+} ion concentration as shown in Table 2. However, this appeared to be due in part to crowding effects. The large, branched nodules were so crowded that incoming particulates could not get to the substrate. Thus at 5 g dm^{-3} Cu^{2+} ions, the small nodules were noticeably absent.

3.4. *Characteristics of nodules*

As the surface changed from smooth to heavily nodulated, the texture and grain character of the deposit changed, as the scanning electron microscope (SEM) micrographs of Fig. 6 show. The deposit of Fig. 6a shows the bare surface and nodules grown under the standard conditions with Cu particulate and at 50° C, whereas Fig. 6b shows the heavily nodulated surface grown under the

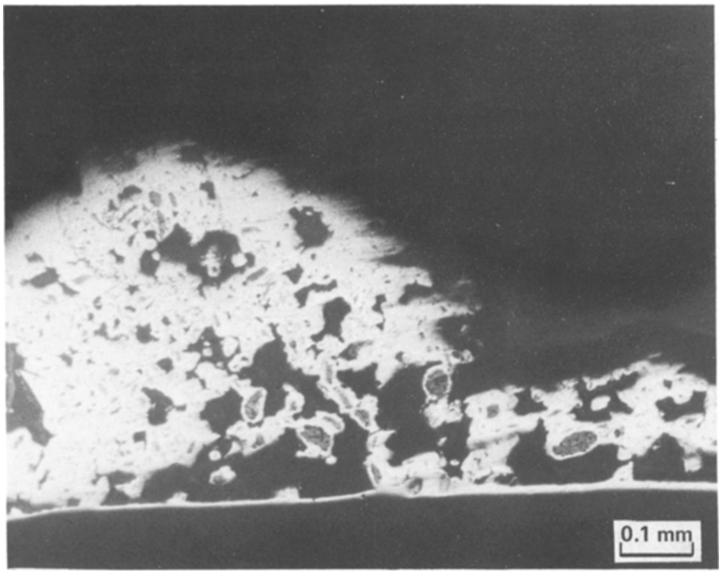

Fig. 4. Cross-section of copper deposit grown in the presence of carbon showing multiple nodulation and rimming of C (gray particles). (The standard conditions and 25° C were applied).

same conditions but at 25° C. At 50° C the deposit shows oriented layers which give the effect of 'smoothing' the nodule surfaces. At 25° the layers are not seen, but rather the deposit is growing randomly in all directions, which leaves many voids and a rough surface. Some tiny crystals were noted in SEM's of a few coarse nodules but the unoriented growth of Fig. 6b was more the rule at the low temperatures and copper concentrations. X-ray diffraction of the surfaces further substantiated this trend. The smooth deposits were (220) textured, whereas the rough nodules tended toward random orientation (Table 3). The data in Table 3 represent more than 30 different cathode coupons.

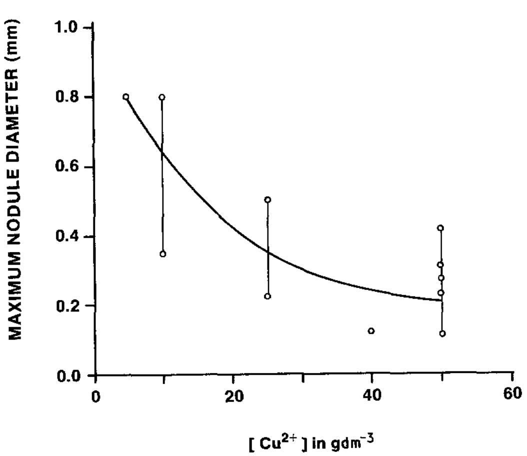

Fig. 5. Diameters of largest nodules as a function of copper ion concentration of the electrolyte. (The standard conditions were applied except for $C_{Cu^{2+}}$; $T = 50°$ C.)

3.5. *Effect of addition agents*

When addition agents, such as those used in electrorefining, were added to the particulate-containing cell, definite effects were observed. For example, 20 mg dm^{-3} Cl$^-$ ions and 100 or 200 mg dm^{-3} thiourea prevented nodulation from electrolyte containing copper powder in tests at the standard conditions. The deposits were smooth but also very brittle, as is typical for copper electrodeposited at too high concentrations of thiourea. When 100 mg dm^{-3} of an ammonium lignosulphonate (trade name, Orzan A) was added to the bath in place of thiourea, the nodulation was impeded, although to a lesser extent than with thiourea. When copper was grown in the presence of non-nodule producing powders (e.g., $PbSO_4$)

Table 2. Effect of copper ion concentration on nodule population (Cu particulate and the standard conditions applied)

[Cu^{2+}] g dm^{-3}:	5	10	25	40	45	50
Number of nodules per mm^2:	12	26*	10	10	29	9
		37	13			10
						11
						13

* Each value represents one test.

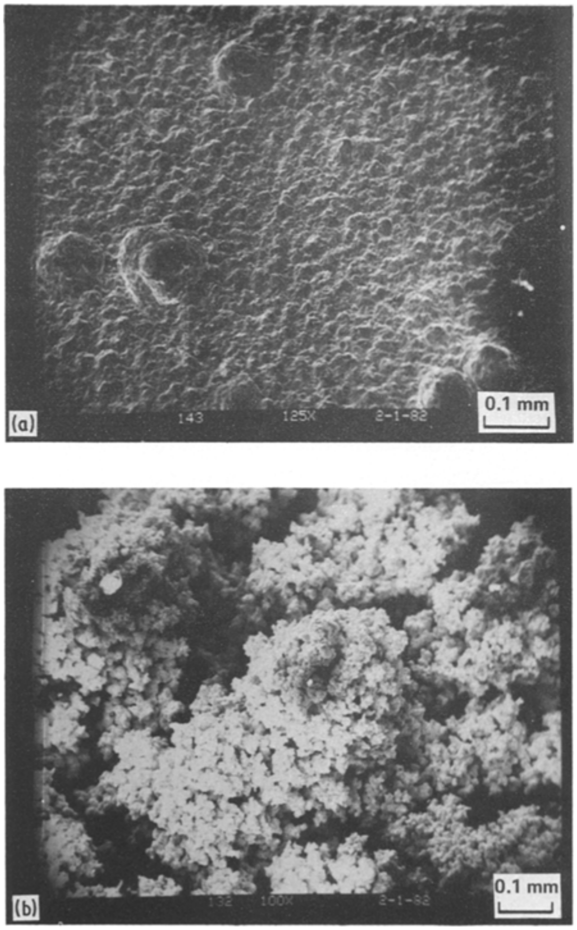

Fig. 6. SEM photographs of surfaces produced at standard conditions and with Cu particulate (a) at 50° C and (b) at 25° C.

and addition agents, the deposits were smooth, as in the case of no addition agents.

3.6. *Impurity entrapment*

Although some particulate was entrapped in most cases, the extent of this entrapment depended much more on the deposit quality than on the availability of contaminating particulate. Table 4 shows the lead content of the copper deposit at various levels of $PbSO_4$ when it was the only particulate present and when both lead sulphate and copper particulate were present. The smooth deposits obtained with only $PbSO_4$ present showed only a small tendency to occlude the particles. But when nodules were produced from copper particulate, occlusion of very significant amounts of lead sulphate occurred. This trend also was found with other substances.

Either PbO_2 or Cu_2Se, when present as the only particulate at 500 ppm, resulted in a smooth cathode and only 80 ppm Pb or 40 ppm Se, respectively, at 50° C. When 500 ppm Cu and 260 ppm Cu_2Se particulate were present together, the Se level was greater than 500 ppm.

Selenium particulate, at the 500 ppm level and at 25° C, resulted in 40 ppm Se in the cathode. At 70° C, the cathode contained fewer nodules and 1.4 ppm Se. Antimony particulate produced much heavier nodulation than selenium and correspondingly was found in the deposit at 500 ppm at 50° C.

4. Discussion

4.1. *Surface initiation*

The high concentration of particulate and the stirring in these tests assured a more or less constant rate of collision with time between the particles and surface. When the particulate is sufficiently conductive and inert toward the copper, its surface takes on the same potential as the cathode while it is in contact with the latter. Therefore, Cu^{2+} ions may deposit at the particulate surface as well as at the planar cathode surface. Although the rates of

Table 3. Ratios of XRD peak heights for deposits showing effect of nodulation

Deposit/plating conditions	*Ratio of (111)/(220) peaks*	*Ratio of (200)/(220) peaks*
(Random Orientation ASTM)	5	2.3
Smooth/non-conductive particulate at 70° C	0.03–0.5	0.03–0.5
Mostly smooth with scattered nodulation/conductive particulate at 50° C	0.25–1.2	0.2–0.6
Very nodulated/conductive particulate at 25° or at 50° C and low Cu^{2+} ion concentrations	2.3–12	0.4–5

Table 4. Lead entrapment by copper deposit plated under the standard conditions and at 50° C but with variable particulate

Particulate in solution	*Deposit quality*	*Pb in cathode* (ppm*)
None	smooth, no nodules	0–5
37 ppm $PbSO_4$	smooth, no nodules	2, 3, 4, 19
75 ppm $PbSO_4$	smooth, no nodules	71
147 ppm $PbSO_4$	smooth, no nodules	10, 33, 44
293 ppm $PbSO_4$	smooth, no nodules	18
293 ppm $PbSO_4$ + 500 ppm Cu	very nodulated	860, 1600

* Multiple values represent replicate tests.

electrodeposition on the two surfaces are not necessarily equivalent, they occur sufficiently that the two growing deposits meet and may 'cement' the particulate to the cathode. This is exemplified by the 'encapsulation rims' around occluded antimony (Fig. 7) and graphite (Fig. 4) particles.

Nonconductive particulate is also occluded in metal deposits, as shown by Table 4 and previous in-depth studies [12–15], but the occlusion mechanism differs from that for conductive particulate, as the differences in nodulation and amount of occluded impurities demonstrate. The difference is due to lack of deposition onto the outer layers of nonconductors. These latter particles are buried by the growing substrate without renucleation and nodulation with its subsequent enhanced impurity entrapment.

Particles of intermediate conductivity would be expected to induce intermediate nodulation, and this appears to be manifest by selenium, antimony, and carbon particulate causing fewer nodules than the more conductive copper, when surface crowding is not a limiting factor (at 50° C).

When the conductive particulate is different from copper, there is a tendency for galvanic effects between the dissimilar substances in addition to nodulation. These effects appear as pitting or erosion–corrosion when the galvanic currents are large as in the cases of antimony, silver, and selenium. Oxidation and reduction of carbon are too slow to cause such effects. A competition between the galvanic corrosion and nodulation is evidenced by the change in the surface with temperature (Table 1). At the lowest temperature,

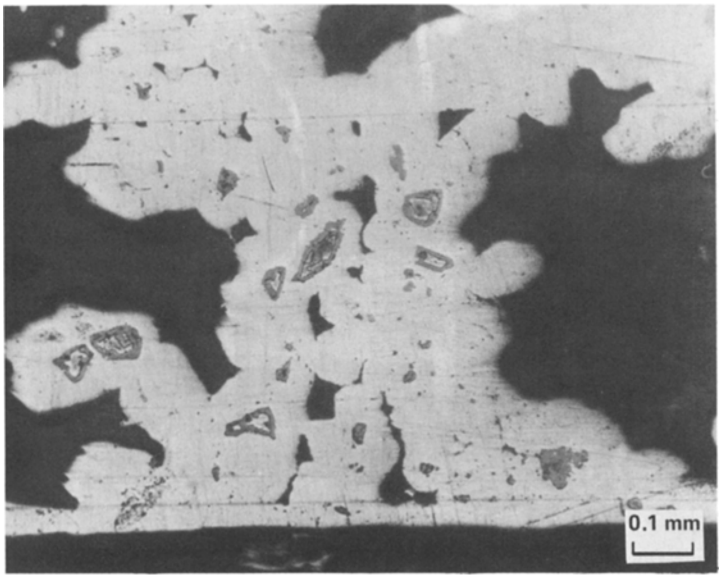

Fig. 7. Cross-section of copper deposit grown in the presence of antimony particulate showing rimming around dark antimony grains. (The standard conditions were applied except the electrolyte contained 25 g dm^{-3} Cu^{2+} and 10 g dm^{-3} Zn^{2+} as $ZnSO_4$.

nodulation is the most intense while galvanic action is at its lowest rate. This results in the particulate getting buried in the deposit with resultant nodulation. At higher temperatures galvanic action is accelerated with resultant dissolution of either the particulate or the surrounding copper (depending on which is anodic). The net result is nonadherence of the particulate and formation of pits. For antimony at 50° C, the rates must be competitive, as both nodules and pits result.

4.2. *Nodule growth and effects of parameters thereon*

The effects of temperature and Cu^{2+} ion concentration on nodule population and size appear to be effects on nodule growth after particle attachment rather than effects on particulate attachment to the surface. Furthermore, these effects, which were examined in the absence of inhibitors, appear to be mass-transport controlled. Similar effects are observed in powder formation [16] and, although perhaps less dramatically, in electrocrystallization without the presence of suspended particulate [17].

In the present agitation/curent density regime the deposition is partially mass transport limited. The diffusion layer thickness at the flat substrate, δ, may be estimated to be roughly 0.1 mm (between that of rapid forced convection and natural convection, see [18]), such that the limiting current density for Cu^{2+} ions, i_L would be roughly twice the applied current density of 38 mA cm^{-2}. This conclusion is drawn from calculating i_L from Equation 1.

$$i_L = 2FDC_{bulk}/\delta \qquad (1)$$

Here F is Faraday's constant, D is the diffusion coefficient of the Cu^{2+} ions (about 5×10^{-6} cm^2 s^{-1}, δ is taken as 0.1 mm, and C_{bulk} is the bulk concentration of the Cu^{2+} ions. As the initial particulate diameters (~ 0.02 mm) are somewhat smaller than δ, the diffusion to these particles would be faster than that to the flat surface, both because of the thinner diffusion layer above them [19] and because of their small size which allows faster spherical diffusion to them. As the particles grow and sharp corners of edges protrude through the diffusion layer of the substrate into the bulk solution, deposition at these sharp regions may be enhanced greatly compared to that at the flat surface [19]. This is because the rate of diffusion of Cu^{2+} ions is then proportional to the reciprocal of the radius of curvature, r, rather than to $1/\delta$, and r at corners may be substantially less than δ. Three-dimensional nucleation is a natural consequence of the high local current densities [8, 20], and accounts for the change in the X-ray diffraction patterns with nodulation.

Increasing the temperature decreases the solution viscosity (the decrease is about 50% with a temperature increase from 25° to 75° C [21]) and increases the diffusion coefficient by about 2% per degree. This increases i_L (cf. Equation 1) and decreases the relative importance of diffusion in the deposition process, (cf. Equation 2).

$$i \simeq i^0(1 - i/i_L)\exp(-\alpha F\eta/RT) \qquad (2)$$

(Here i is the exchange current density, α is the charge transfer coefficient, η is the overvoltage, R is the gas constant and T is the temperature.) This results in more charge-transfer control which does not favour deposition at the particulate peaks. Increasing the copper ion concentration likewise increases i_L (by a direct increase in C_{bulk}) and thereby decreases the importance of the $(1 - i/i_L)$ term.

Cell voltage decreased approximately 200 mV (at the standard current density of 38 mA cm^{-2}) as the temperatures increased from 25° to 70°, independent of the degree of cathode nodulation. This voltage change is also in line with the changes in electrolyte resistance, anodic overvoltage and cathodic overvoltage [1, 21], as opposed to changes in inhibition.

In the case of adding thiourea, the cell voltage at constant current density increased with a decrease in nodulation, thus exemplifying that the role of thiourea was different than that of temperature and copper ion concentration. Nodulation was stopped by inhibition, because the thiorea diffuses to and covers the peaks to a greater extent than it covered the flat substrate [7].

4.3. *Application to copper electrorefining*

The present results suggest that conductive particulate is a prime cause of nodule initiation and, correspondingly, of the ensuing contamination with insoluble impurities. (Other modes of contamination such as impurity codeposition and crystallization from solution are also present [2] but are outside the scope of this study). Previous investigators [9, 10] identified specific conductors and semiconductors in copper anode slimes which should or do cause nodulation i.e., Cu, Ag_2Te, Cu_2Se, CuS, Cu_2O, $SbAsO_4$ and Sb_2O_5. Some of the semiconductors are apparently not as effective nodule producers as copper, based on our results for copper as compared to copper selenide.

Even high purity copper anodes produce enough copper slimes to cause substantial nodulation without any other particulates being present. This was observed in plating tests under the standard conditions at 50° C which used electrolytic copper (99.98% pure) as the anode but in which the anode bag was removed. No particulate was added to the cell. In a series of eight-hour tests severe nodulation was observed on the cathodic deposit, many of the nodules being more than 1 mm high. Current densities of both 22 and 54 mA cm^{-2} were applied.

Some of the tests include the presence of $10\ \text{mg dm}^{-3}$ glue, thiourea, Orzan or various combinations thereof. Although the nodule size varied with the addition agents used, nodules arose during most of the tests. No effort was made to balance the concentrations of addition agents so as to eliminate nodulation.

From the results of this work it is apparent that the conventional methods used to produce smooth cathodes are nodule suppressants, i.e., electrolyte composition, temperature, current density, and electrolyte agitation are controlled to maximize the throwing power of the solution and to prevent enhancement of mass transport to the peaks of small profiles. Organic addition agents inhibit nodule growth through levelling. Membranes, although used less frequently than the above means, prevent contact between the cathode and nodule-producing or contaminating particulate.

References

[1] C. W. Eichrodt and J. H. Schloen, in 'Copper – The Science and Technology of the Metal, Its Alloys and Compounds', (edited by A. Butts), Reinhold Publishing Corp., New York, (1954) Ch. 8.

[2] T. B. Braun, J. R. Rawling and K. J. Richards, in 'Extractive Metallurgy of Copper – International Symposium', Vol. 2, AIME, New York, (1976) pp. 511–24.

[3] 'Kirk-Othmer: Encyclopedia of Chemical Technology', Vol. 6, 3rd edn., John Wiley and Sons, Inc. New York (1979) pp. 859–62.

[4] W. R. Hopkins, G. Eggett and J. B. Schuffham, in 'International Symposium on Hydrometallurgy', (edited by D. J. I. Evans and R. S. Shoemaker) AIME, New York, (1973) pp. 127–54.

[5] J. M. Steele, in 'Industrial Electrochemical Processes', (edited by A. T. Kuhn) Elsevier Publ. Co., New York, (1971) Ch. 7.

[6] J. H. Schloen, S. S. Forbes and S. B. Tuwiner, in 'Extractive Metallurgy of Copper, Nickel and Cobalt', AIME Interscience, New York, (1960).

[7] J. O'M. Bockris and G. A. Razumney, 'Fundamental Aspects of Electrocrystallization', Plenum Press, New York, (1967) Chs. 11 and 12.

[8] R. Winand, *Trans. Instn. Mining Metall. C* **84**, (1975) C67.

[9] L. Pauwels, PhD Thesis, University of Louvain, Louvain (1966).

[10] Cl. Feneau and R. Breckpot, *Ind. Chim. Belge* **32** (1967) 241.

[11] L. S. Livingston, M.S. Thesis, University of Utah, Salt Lake City, Utah (1980).

[12] F. K. Sautter, *J. Electrochem. Soc.* **110** (1963) 557.

[13] E. S. Chen, G. R. Lakshminarayanan and F. K. Sautter, *Met. Trans.* **2** (1971) 937.

[14] M. Guglielmi, *J. Electrochem. Soc.* **119** (1972) 1009.

[15] J. P. Celis and J. R. Roos, *ibid.* **124** (1977) 1508.

[16] N. Ibl, in 'Advances in Electrochemistry and Electrochemical Engineering', Vol. 2 (edited by C. W. Tobias), Interscience Publishers, New York, (1966), Ch. 3.

[17] O. Kardos and D. G. Foulke, in *ibid.* 217.

[18] J. O'M. Bockris and A. K. N. Reddy, 'Modern Electrochemistry', Vol. 2, Plenum Press, New York, (1972) 1058.

[19] *Idem, ibid.* 1219.

[20] H. Fischer, 'Electrolytische Abscheidung and Electrokristallisation von Metallen', Springer Verlag, Berlin, (1954) 729.

[21] D. C. Price and W. G. Davenport, *Met. Trans. B,* **12B** (1981) 636.