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Electrodeposition from a fluidized bed electrolyte. III. Electrodeposit structure

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Copper electrodeposits grown from a fluidized bed electrolyte appear to be unaffected by mechanical action of the inert particles. Additions of thiourea to the electrolyte caused some improvement in levelling at lower current densities but, at the limiting value, additions of up to 10^{-2} M gave no improvement.

Micrographic evidence is presented to suggest that a simultaneous dissolution process may account for the transition from nodular to powder growths at the limiting current density.

1. Introduction

In many applications of fluidized bed electrolytes which are being considered at the present time, properties and quality of the electrodeposit are not of prime consideration. However, it is possible to envisage applications in which the effects of inert particles on the mechanical properties of the electrodeposit might be of concern, and also the manner in which dendritic growth tendencies might be modified. A metallographic study of the deposits produced by fluidized bed electrolysis was therefore thought to be timely.

Previous work [1,2] has shown that for acid copper sulphate solutions, dendrites or nodules appear never to form at current densities less that $0{\cdot}4\ i_L$ where i_L is the limiting value in the prevailing conditions. Above $0{\cdot}7\ i_L$, nodules develop rapidly and may lead to powdery growths, i.e. nodules having poor adhesion to the substrate. The critical value of current density, $0{\cdot}4\ i_L$, at which nodular growth may be first observed, can be attributed to the change from activation to mass transport controlled growth [3] and clearly is specific to the particular solution and metal investigated. Ibl [4–6] has extensively reviewed the literature relating to dendritic and powdery deposit formation and has pointed out that powder formation is always to be expected when deposition takes place at the limiting current density ($i/i_L = 1{\cdot}0$). Factors encouraging powder formation therefore include increased current density, concentration of support electrolyte and viscosity and decreased metal ion concentration, temperature and agitation. The copious evolution of hydrogen has sometimes been suggested as a criterion for powder formation but while it may ensure that the limiting current density for metal deposition is attained, it does not imply that a hydrogen reduction mechanism of metal deposition is important. A much more satisfactory theory due to Despic and Popov [7] and Ibl [4–6] suggests that under concentration polarization control the diffusion distance for depositing ions to surface protrusions is less than that to the surface and leads to disproportionate deposition rates. Such disproportionality reaches a maximum when the concentration gradient is greatest, i.e. at the limiting current. Specific nucleation may not be necessary as surface irregularities may be adequate as preferential growth sites. Ibl [4–6] also pointed out that a predominance of activation polarization will lead to surface levelling.

The initiation time t_p for powders to form has been

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attributed [4] to the establishment of steady state diffusion conditions at the limiting current density.

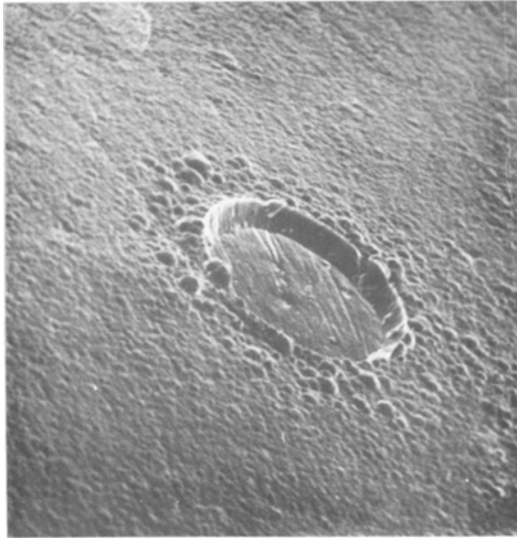

Fig. 1. Pore probably caused by particle adhesion SEM × 52.

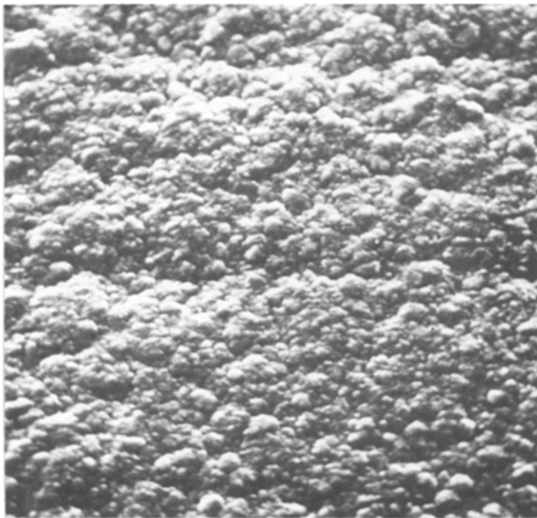

Fig. 2. Copper electrodeposit. SEM × 1200. 0·07 M $CuSO_4$; 21·5°C; 354 μm particles; 1·5 bed expansion, 50 μm thickness; i/i_L = 0·25.

In the absence of convection the Sand equation gives the time for the diffusion boundary layer to be established as:

$$It^{\frac{1}{2}} = \frac{nF(1-t^{+})\ (C_b - C_s)}{2} \ \frac{(D)^{\frac{1}{2}}}{(\pi)}$$

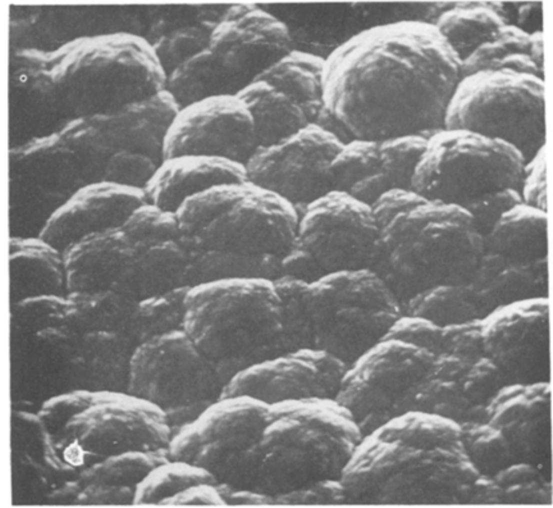

Fig. 3. As Fig. 2, but 0·25 bed expansion; i/i_L = 0·70.

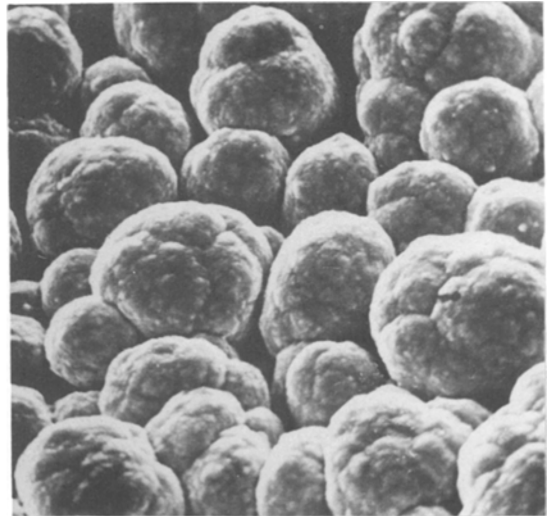

Fig. 4. As Fig. 2, but 0·05 bed expansion; i/i_L = 0·85.

where C_b and C_s are the bulk and surface concentrations respectively and D is the diffusion coefficient of the depositing ion. It follows that at the limiting current $I_L, I_L t^{\frac{1}{2}} = kC_b$ because $C_s \rightarrow 0$. Experimental evidence for 0·1 to 0·3 M $CuSO_4$ solutions has shown that a graph of log t_p against log I gave a straight line of slope [8] and a graph of $It_p{}^{\frac{1}{2}}$ against concentration also gave a linear relationship [4]. However Ibl [4] has been unable to show that the Sand transient time t is effectively identical with the initiation time for powder growth t_p.

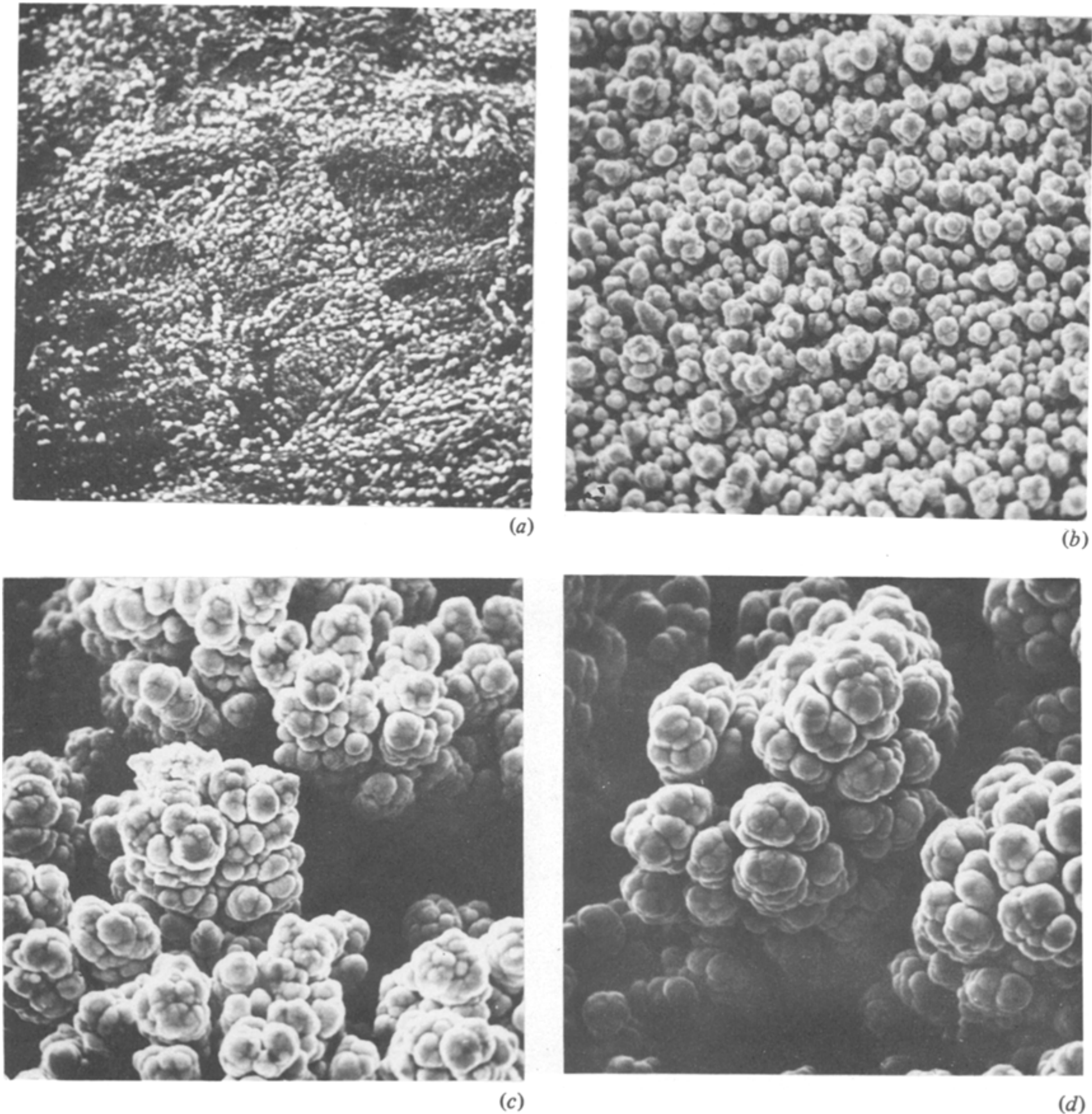

Fig. 5. As Fig. 2, but 0·5 bed expansion; i/i_L = 1·0. (a) 1 μm thickness; (b) 5 μm thickness; (c) 20 μm thickness; (d) 50 μm thickness.

The solution depletion model thus appears to give a fairly satisfactory explanation of why coarse or nodular growths occur, but is unable to show why the growths become loosely adherent to the surface thereby becoming powdery. Probably some additional factor or process must be taken into account.

2. Experimental

A full description of the apparatus and procedure has been given previously [9] but for the metallographic investigation the 0·07 M copper sulphate solution at 21·5°C received most attention. After the complete polarization curve was established by a potentiodynamic technique samples were deposited to nominal thicknesses of 1, 5, 20 and 50 μm at various currents calculated as fractions of the limiting value. Each test was potentiostatically controlled and any change in current was monitored by means of the potentiometric recorder.

All specimens were examined in the 'Mark II Stereoscan' scanning electron microscope using a modified support stub to accommodate the cylindrical

electrode and enable it to be fully rotated and tilted. Selected samples were cold mounted in 'Araldite' epoxy resin under vacuum which was adequate to protect the more powdery electrodeposits. Following transverse sectioning the samples were polished with silicon carbide paper and diamond paste and then etch-polished on ferric-chloride impregnated cloth to reveal grain structures.

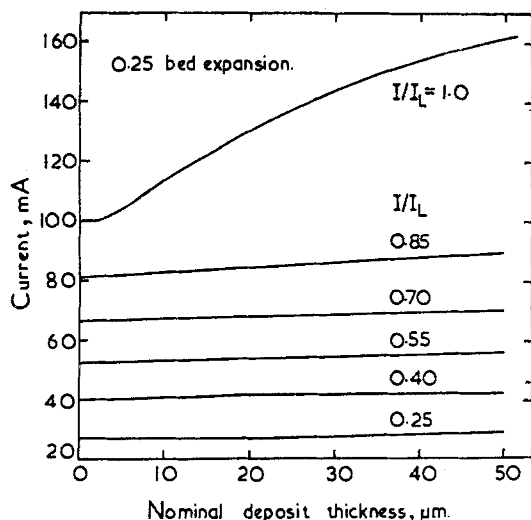

Fig. 6. Variation of current with deposit thickness at constant electrode potential at various values of i/i_L and 0·25 bed expansion.

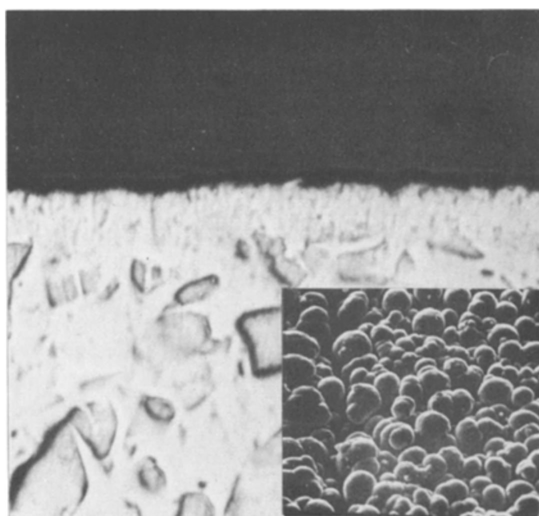

Fig. 7. Copper electrodeposit in section. Optical micrograph × 400 (inset: surface SEM × 400) i/i_L = 0·85; 20 μm thickness

A previous investigation [2] suggested that additions of thiourea to 0·7 M $CuSO_4$ had little effect on the tendency for powders to form. Nevertheless, additions of thiourea to the 0·07 M solution were made and the deposit structures examined.

3. Results

Approximately 200 samples were examined by scanning electron microscopy after which it was clear that the fluidizing particles produced no visible damage to the electrodeposit surface and only in one isolated case was porosity observed (Fig. 1) which could be attributed to particle adhesion or entrapment – the pore is about 200 μm in diameter and occurred when 350 μm particles were being used.

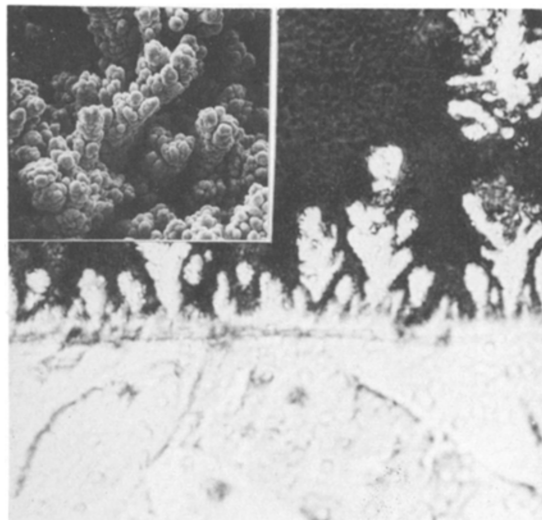

Fig. 8. As Fig. 7, but × 800. i/i_L = 1·0 μm thickness.

For each of six i/i_L ratios examined, four bed expansions were used and no changes in structure could be attributed to this variable. By varying the i/i_L value systematically, however, clear trends in growth may be seen. At i/i_L = 0·25, the deposit was smooth even up to 50 μm thickness (Fig. 2). At i/i_L = 0·4, small nodules first appeared at about 1 μm thickness growing from about 1 μm diameter to about 3 μm diameter at a total thickness of 50 μm. At i/i_L = 0·7, nodules tended to develop slowly but continuously (Fig. 3), but at i/i_L = 0·85, nodule coarsening was marked until at 50 μm

the nodules were 15 – 30 μm in diameter although still relatively smooth (Fig. 4). At the limiting current (i/i_L = 1·0), a large number of small nodules were apparent at 1 μm thickness which grew with thickness until at 20 μm some sub-nucleation appeared to take place and the characteristic powdery nature became apparent (Fig. 5). Such powders tended to be removed by the scrubbing action of the fluidized particles and the eroded debris was entrained with the electrolyte or trapped in the bed.

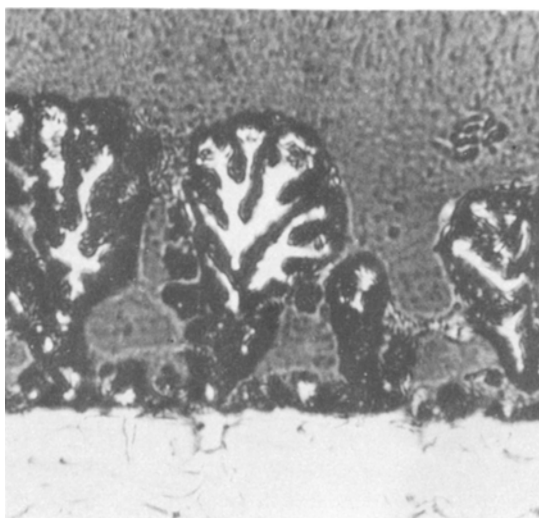

Fig. 9. Copper electrodeposition in section. Optical Micrograph × 400. 50 μm thickness; 0·25 bed expansions; i/i_L = 1·0.

Such dendritic or powdery growth development must necessarily be accompanied by an increase in cathode surface area, and this was recognised by an increase in cathode current for constant potential control. Typical current-thickness curves are given in Fig. 6, and it was noted that the increase was particularly marked when powdery growth developed rather than nodular growth, i.e. at $i/i_L > 0{\cdot}85$.

The development of nodular growth forms was examined by means of optical microscopy of cross sections which could be related directly to the surface structures already observed. Fig. 7 shows a deposit grown to a thickness of 50 μm at i/i_L = 0·85. Deposits grown at the limiting current density and having powdery characteristics appeared to have developed by a marked lateral growth after nucleation (Fig. 8) which in some instances suggests that some dissolution may have taken place near the deposit/substrate interface (Fig. 9). These micrographs illustrate clearly why the powdery deposits are much less adherent than the nodular deposits grown at lower current densities.

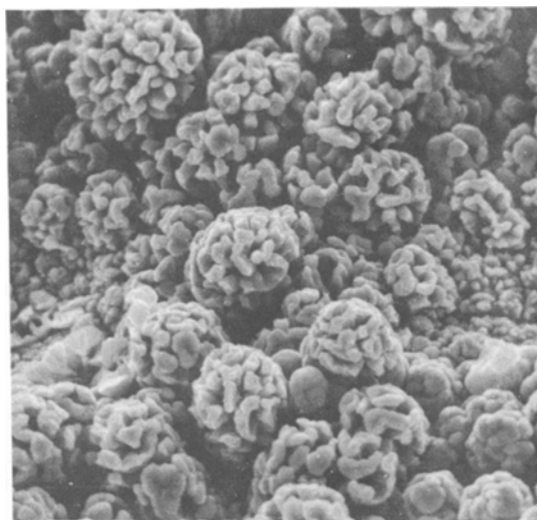

Fig. 10. Copper electrodeposit, SEM × 1200. Addition of 5 × 10^{-3} M thiourea to 0·07 M $CuSO_4$ at 21·5°C; 20 μm thickness.

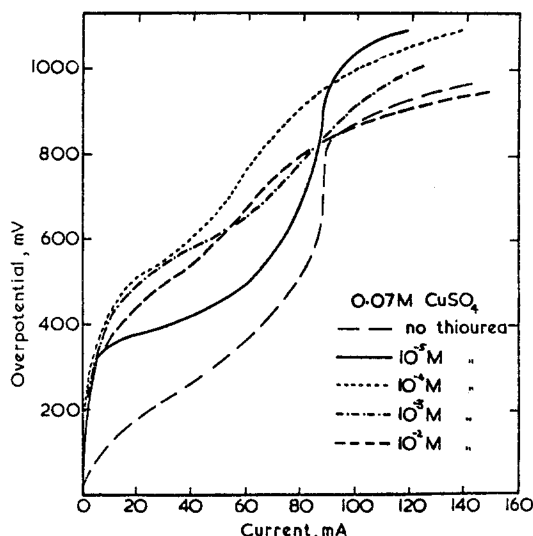

Fig. 11. The effect of various concentrations of thiourea on the polarization curve for copper electrodeposition. 0·07 M $CuSO_4$; 22·8°C; 354 μm particles.

Additions of thiourea less than 5 × 10^{-3} M

appear to have little effect but above this concentration (Fig. 10) some cracking of the deposits occurs, finer nodules form and at 10^{-2} M a spongy contaminated deposit results. The effect on the polarization curves can be seen in Fig. 11 where the limiting current portion of the curve becomes less well-defined, and at the limiting current value (i/i_L = 1·0) pronounced surface roughening is indicated by the current-thickness measurements (Fig.12).

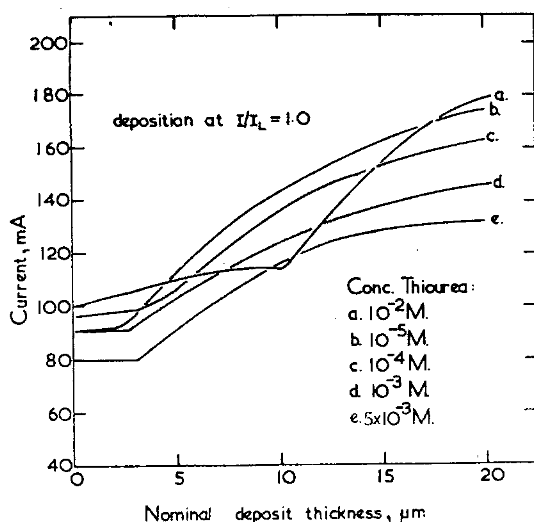

Fig. 12. Variation of current with deposit thickness, at constant electrode potential, for 0·07 M $CuSO_4$ at i/i_L = 1·0 and various additions of thiourea.

4. Discussion

Experimental observations strongly suggest that powdery deposits only develop at the limiting current where deposits show poor adhesion to the substrate. For most conditions where $i/i_L > 0{\cdot}4$, small nodules appear at nominal thicknesses as low as 1 μm and these appear to be the nuclei for subsequent nodular growths, although they may not develop markedly. Within the range $0{\cdot}4 < i/i_L < 0{\cdot}7$, activation and concentration polarization contributions appear to be comparable in magnitude and within this range nodular growth is not marked, supporting the views of Ibl [4,5,10] and Wranglen [11]. However, when $i/i_L > 0{\cdot}7$, surface roughness becomes more pronounced and nodules grow in size as the deposit thickens thus corresponding to the current region in which concentration polarization predominates. These values of current density ratio, which were suggested by earlier work [2,3], must necessarily be characteristic for copper and this type of electrolyte because the degree of activation over-potential has been ignored. The greater the activation over-potential and the lower the value of the exchange current density i_0 the less likely is nodular growth to develop.

It is interesting that mechanical action of the fluidized particles appears to have little levelling effect in the higher current regions. In the case of nickel deposited from a Watts-type solution, inert fluidized beads appear to improve deposit quality making some addition agents superfluous [12] but this electrodeposition reaction is predominantly activation-controlled. Furthermore, Eisner *et al.* [13–16] have reported that mechanical abrasion effects by particles may almost eliminate concentration polarization, thereby increasing deposition rates by several orders of magnitude. They found little evidence of powdery growth and fears of detrimental mechanical damage to the deposit surfaces, when using particles, appear to be unfounded.

Thiourea is a known levelling agent which is believed to operate by a mass transfer control mechanism [17]. It does not, however, appear to be capable of producing flat surfaces when concentration polarization predominates although some significant structural modifications have been observed. Ibl *et al.* [6,17] have claimed that smoothing occurred with additions of $2{\cdot}5 \times 10^{-3}$ M, smoothing being measured by means of a stylus-type profilometer and impedance measurements. While some macroscopic smoothing must have taken place, direct observations by scanning-electron microscopy suggests that while early stages of nodular growth may be suppressed by concentrations $> 10^{-4}$ M, powdery growth merely becomes spongy and at 10^{-2} M concentration quite inferior. The polarization curves (Fig. 11) suggest some increase in the activation component which would in itself account for some suppression of nodular growth tendencies at currents well below the limiting value.

Micrographs of sections of the powder deposits all indicate some degree of thinning at the deposit-substrate interface and, as such, offer support for the depletion-dissolution theories of powder formation. At the limiting current density, nodules grow outwards into the electrolyte and possibly reach the limit of the diffusion layer (~ 20 μm at 0·5 bed

expansion) when subnucleation may take place. One important characteristic of these nodular growths is that they remain individual whereas nodules grown at lower currents grow together and offer mutual cohesion.

One shortcoming of the solution depletion theory as described by Ibl [4] is that it does not predict that powders form specifically at the limiting current but merely that the tendency towards powder growth is greatest at that value. It appears to be increasingly likely that some other process also occurs and the dissolution concept of Wranglen [11] must attract some support. Wranglen observed simultaneous deposition at a dendrite tip and dissolution at its stem, the combined effect being most pronounced at the limiting current when the surface ion concentration is virtually zero. Under such circumstances a concentration cell might exist around the dendrite or nodule such that the cell potential is given by:

$$\Delta E = \frac{RT}{nF} \ln \left(\frac{C_t}{C_s}\right)$$

where C_t and C_s are the concentrations of metal ion at the tip and stem of the dendrite respectively. The value of E will be greatest when the tip protrudes beyond the diffusion layer ($C_t \rightarrow C_b$) and $C_s \rightarrow 0$ and must be sufficient to exceed the applied overpotential. The overpotential at the limiting current for 0·07 M $CuSO_4$ at 22°C was found to be about 0·7 V; by substituting this value for ΔE and assuming $C_t \rightarrow C_b = 0{\cdot}7$ M, we may find that $C_s \doteq 10^{-11}$ M. Thus dissolution may only take place when $C_s < 10^{-11}$ M which is a condition satisfied at the limiting current density.

It may also be possible to test the model of Ibl [4] by measuring the initiation time t_p for the onset of powder formation and relate this to the transient time t_L for the diffusion layer to form as predicted by the Sand equation. By using short pulses of length $t_L/2$ in agitated solution, it might then be possible to grow deposits at the limiting current density without any powder formation. Some recent reports suggest that this is feasible [18,19].

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