An electron microscope investigation of electrolytic copper powders

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The size and nature of copper powders deposited in conditions close to those found in production units are investigated with a scanning electron microscope. It is shown that an increase in the current density or the concentration of sulphuric acid decreases the size of the particles and makes their dendritic structure more pronounced. In contrast, an increase of copper ion concentration or agitation increases the size of the particles and obscures their dendritic character. It is shown that the changes in the particle size and type are primarily dependent on cathode potential. A change from $-100\,mV$ to $-900\,mV$ versus SCE causes a decrease in the powder size from 80–$100\,\mu m$ to 5–$10\,\mu m$ and a successive appearance of the following types of particles: (a) round particles or dendrites with round tips, due to electrocrystallization in one plane (a compact deposition); (b) a transient structure, apparently a change to polycrystal growth on the pyramidal tips; (c) particles with pyramidal tips and (d) dimeric and trimeric dendrites.

1. Introduction

Many authors have investigated the possibility of depositing different crystal structures, such as single crystals, dendrites and compact deposits, by varying the electrolysis conditions [1–6]. Some of these papers deal especially with copper dendrites and their formation. In particular, Ogburn [7] has studied the formation of dimeric[†] copper dendrites from aqueous solutions and Saltikova *et al.* [8–10] have studied the nature and orientation of dendrites obtained from a molten CuCl bath. In all these cases electrolyses have been carried out at relatively low cathode overpotential to give large, well-formed dendrites suitable for studying their morphology and orientation. On the other hand, industrial copper powder, although also dendritic, has mainly been studied with respect to its technologically important properties: apparent density, flowability, sieve analysis, specific surface, etc. [11, 12]. There are only a few papers where the authors deal with the real form and size of the powder particles and relate these with the process of electrocrystallization. Horiuchi [13], however, has shown that

[†] Dimeric dendrites are dendrites with stem and branches in one plane.

there is a logarithmic dependence of powder size on the cathode polarization. Pick and Wilcock [14] have shown that a spiral growth may occur when copper is electrodeposited from a bisulphite electrolyte, and Gabe [15] has studied the conditions for dendritic growth.

In production units, copper powder is obtained under conditions which differ drastically from those in laboratories where single, well-shaped crystals are the goal. The two most important differences are: (a) the many-fold increase of cathode surface area during the electrolysis and (b) the much higher and changing cathode polarization. Due to these factors the final product represents a heterogeneous mixture of particles both in respect to size and type. However, for many purposes copper powders have to be homogeneous with a given structure and dimensions. In principle this can be achieved by controlling the process of electrolysis. Bearing this in mind the present paper reports the effect of different electrolysis parameters on the nature and size of the copper powders obtained under conditions close to those in production units. We have shown that there is a direct relationship between the size and type of the particles and the value of the cathode potential and that when the process is carried out
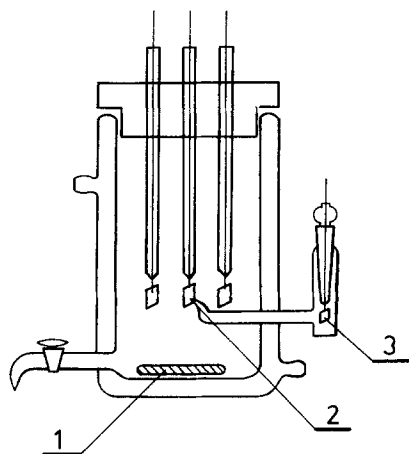
Fig. 1. Electrolytic cell. 1, magnet (magnetic stirrer);
2, Luggin capillary; 3, reference electrode.

at a controlled cathode potential, homogeneous
powders with the desired dendritic character can
be obtained.

2. Experimental

Specimens of electrolytic copper powders were
prepared in the electrolytic cell shown schematic-
ally in Fig. 1. The electrolytes were prepared from
'p.a.' grade reagents and used only once. The
temperature was kept constant at 40° C by an
ultra-thermostat U-3 (DDR). All experiments were
carried out in duplicate, with and without mech-
anical stirring at 250 rev min^{-1}. The desired
cathode current density was preset with a stabil-
ized transistor rectifier 3H-7 (Bulgaria). In order to
determine exactly the actual cathode current
density applied throughout a particular experi-
ment, a copper coulometer was included in the
circuit. Cathode potential was measured with a
WTW pH meter (Germany) and a saturated calomel
electrode as a reference. The electrolytic powder
was manually scraped down from the cathode,
washed with distilled water until there was a
negative test for copper ions in the wash waters
and then dried in a stream of warm air. The
electron micrographs were taken with a JEOL JXA
50 Å SEM at an original magnification of ×1000.

3. Results

This paper describes the effect of the plating
variables copper ion concentration, sulphuric acid
concentration, cathode current density and stirring,

as well as the resulting cathode potential, on the
size and form of electrolytic copper powders. All
powder specimens were obtained as a result of the
same amount of charge (0.4 A h). The experiments
were done this way to compensate at least partially
for the different rates of cathode surface increase
during the course of different experiments and to
eliminate the charge factor on the particle size.

3.1. Effect of copper ion concentration

To assess the effect of copper ion concentration
on the size and structure of the particles, baths
containing from 0.0635 to 0.3810 mol dm^{-3}
Cu^{2+} were examined. The sulphuric acid concen-
tration was fixed at 1.66 mol dm^{-3}. The powders
shown in Figs. 2 and 3 are obtained at 50 A dm^{-2}
cathode current density, with and without stirring
respectively. It is seen that the copper ion con-
centration has a pronounced effect on both the
size and form of the particles. The examples of
powders obtained from stirred electrolytes are
coarser and the influence of the different copper
ion concentration is more clearly expressed. Thus
the increase from 0.0635 to 0.3810 mol dm^{-3}
causes an increase in particle size from 5–10 μm
to 50 μm and more. It should be noted that at the
higher copper ion concentration the particles are
not easy to distinguish, as particles that appear to
be aggregates apparently originate from a single
dendrite. Moreover, the nature of the particles
also changes. The tiny dimeric dendrites obtained
at $C_{Cu^{2+}} = 0.0635$ mol dm^{-3} (Fig. 2A) change
into trimers branched in different directions at
$C_{Cu^{2+}} = 0.1270$ mol dm^{-3} (Fig. 2B). With a further
increase of the copper ion concentration to 0.1905
mol dm^{-3} (Fig. 2C) crystals with pyramidal tips
appear. The tips of the particles obtained from
the baths with the next two concentrations, 0.2540
mol dm^{-3} and 0.3810 mol dm^{-3} (Fig. 2D and
Fig. 2E), loose their pyramidal form and become
round. On these round tips the electrocrystalliz-
ation occurs in a plane and compact polycrystal-
line deposits are formed.

When powders are prepared from unstirred
electrolytes (Fig. 3), trimeric† dendrites appear at
every copper ion concentration used. With its
increase in the range 0.0635–0.3810 mol dm^{-3}

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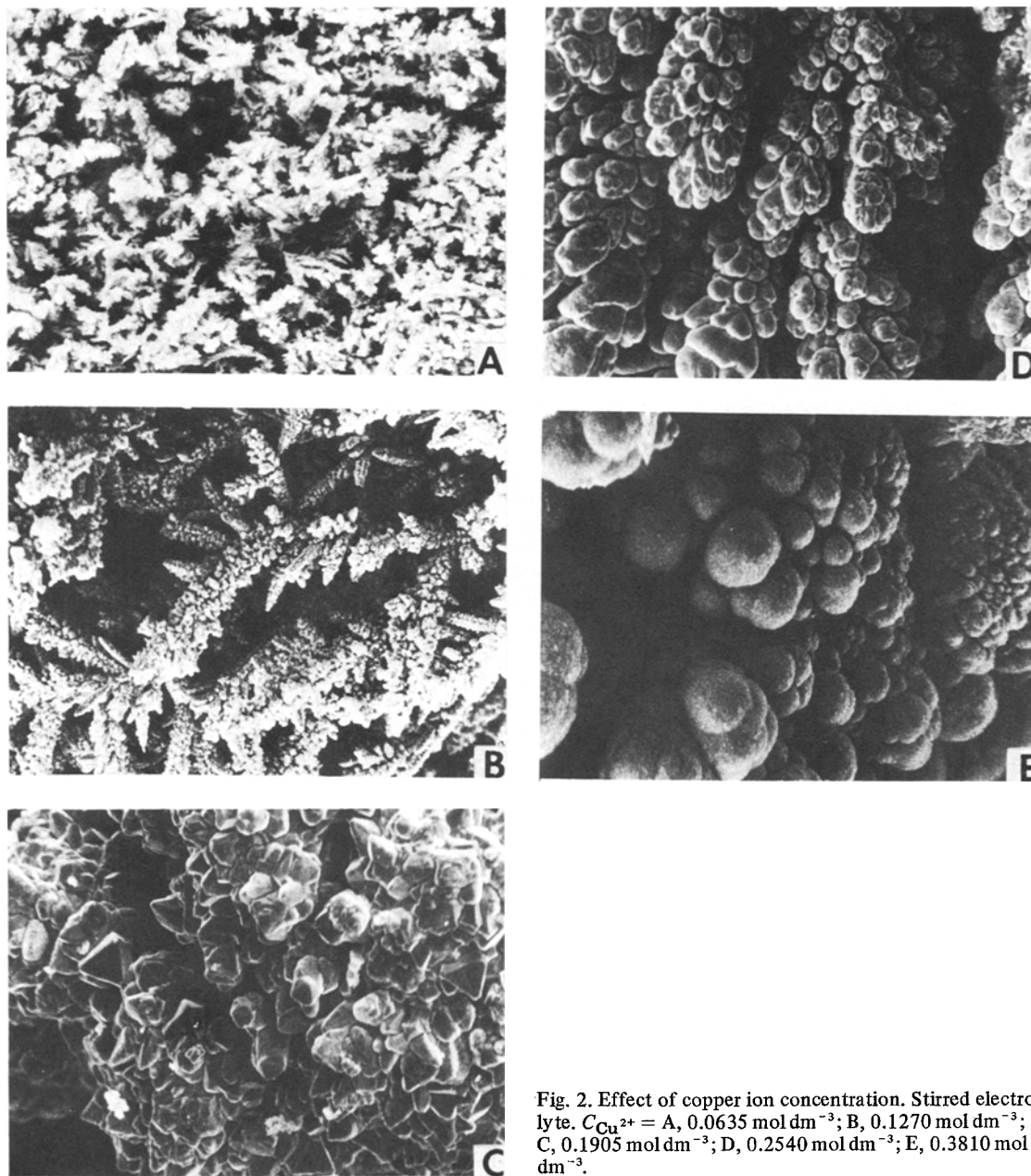† Trimeric dendrites are dendrites with stem and branches
in more than one plane.

Fig. 2. Effect of copper ion concentration. Stirred electrolyte. $C_{Cu^{2+}} =$ A, 0.0635 mol dm^{-3}; B, 0.1270 mol dm^{-3}; C, 0.1905 mol dm^{-3}; D, 0.2540 mol dm^{-3}; E, 0.3810 mol dm^{-3}.

(Figs. 3A–C) the powders become coarse and at the highest concentration particles with round tips are observed together with trimeric dentrites and pyramid-tipped particles.

3.2. Effect of sulphuric acid concentration

Electron micrographs of copper powders obtained from electrolytes containing from 1 to 2 mol dm^{-3} of sulphuric acid with and without stirring are shown in Figs. 4 and 5 respectively. The current density is 50 A dm^{-2} and the copper ion concentration 0.2540 mol dm^{-3}. It is seen from the micrographs that the sulphuric acid concentration has a much less pronounced effect on the powders than the copper ion concentration. Nevertheless, with an increase in the sulphuric acid concentration and when the experiments were carried out in stirred
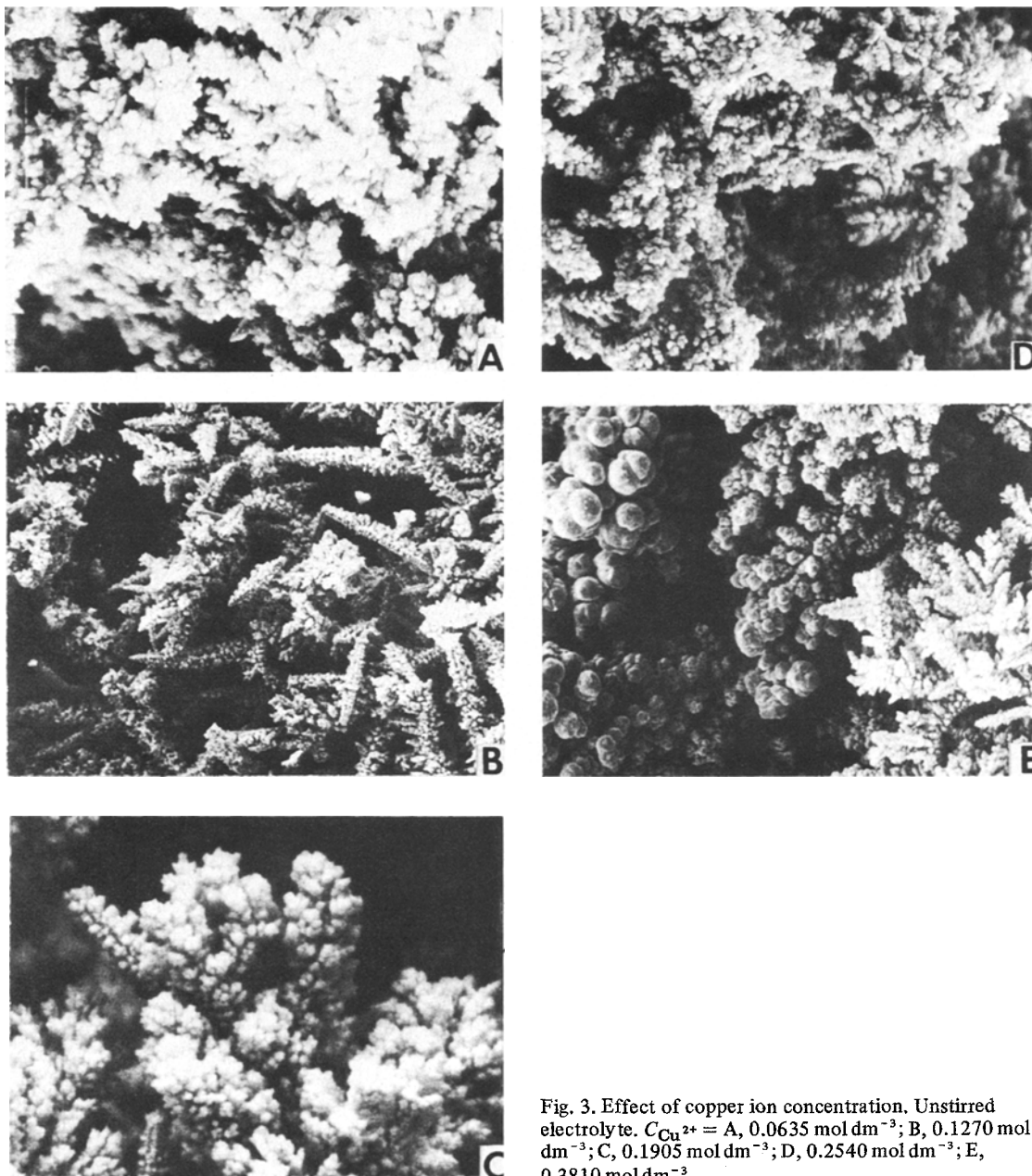
Fig. 3. Effect of copper ion concentration. Unstirred electrolyte. $C_{Cu^{2+}}$ = A, 0.0635 mol dm^{-3}; B, 0.1270 mol dm^{-3}; C, 0.1905 mol dm^{-3}; D, 0.2540 mol dm^{-3}; E, 0.3810 mol dm^{-3}.

electrolyte, the particles size decreased from 40–60 μm to 15–20 μm. Also, with the increase of sulphuric acid, the form of the particles gradually changed from round-tipped dendrites to coarse pyramid-tipped crystals. In the course of this change a characteristic transient structure is observed (Fig. 4C) which could be accounted for by a growth in macro-steps over the pyramid-tipped particles.

The micrographs in Fig. 5 show that the size of the particles obtained from unstirred electrolyte is unaffected by the change in the sulphuric acid concentration. In all of the specimens the same mixture of dimeric and trimeric dendrites is seen. The only difference is that in the powders obtained from electrolytes with the two highest concentrations (Figs. 5C and D) the dimeric structure is predominant.
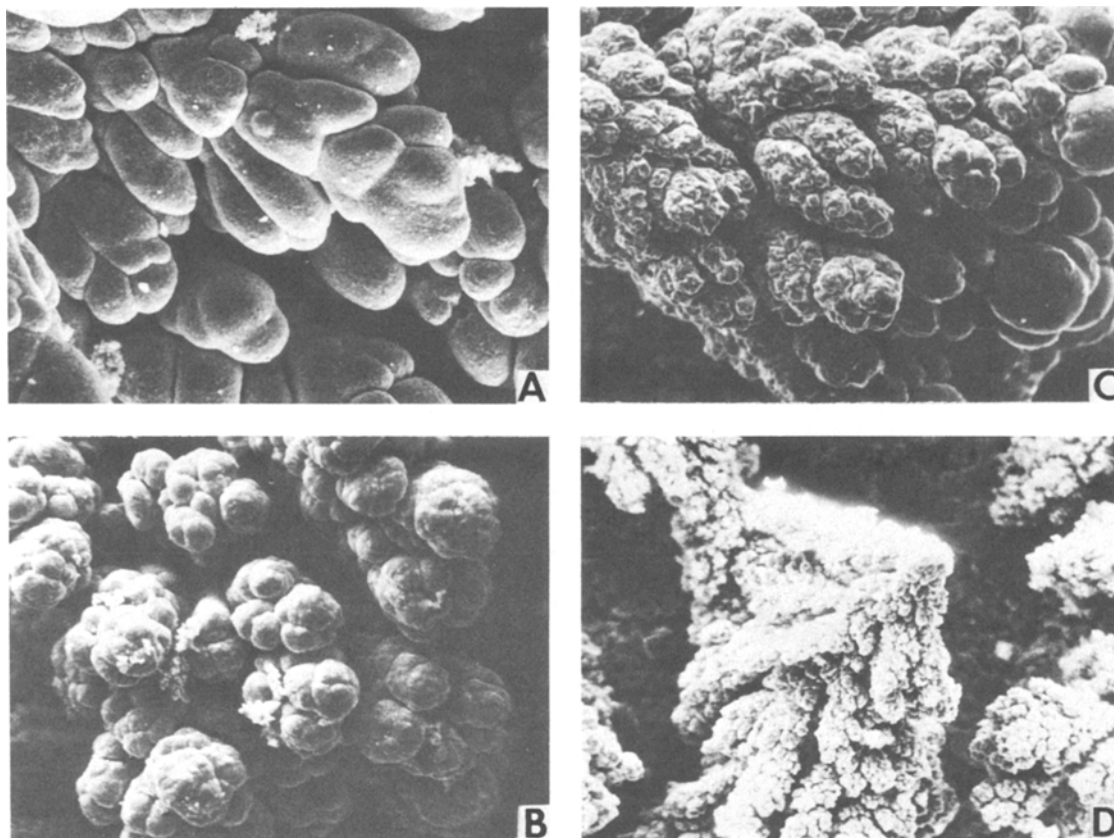
Fig. 4. Effect of sulphuric acid concentration. Stirred electrolyte. $C_{H_2SO_4}$ = A, 1 mol dm^{-3}; B, 1.33 mol dm^{-3}; C, 1.66 mol dm^{-3}; D, 2 mol dm^{-3}.

3.3. Effect of cathode current density

To study this effect electrolysis was carried out in baths containing 0.1905 mol dm^{-3} of copper and 1.66 mol dm^{-3} of sulphuric acid at 12.5, 25 and 50 A dm^{-2}, which cover the current density range used commercially.

Fig. 6 shows typical powders obtained from stirred electrolyte. Increase in the cathode current density obviously decreases the particle size. The form of the particles is also changed: at the lowest current density (12.5 A dm^{-2}) their tips are round and almost accreted together and the electrocrystallization occurs in a plane, giving a polycrystalline, compact deposit (Fig. 6A). At the highest cathode current density (50 A dm^{-2}) the particles reveal a crystal form of multi-edged prisms with pyramidal tips (Fig. 6C). The transition between these two structures becomes obvious at the medium cathode current density of

25 A dm^{-2} (Fig. 6B). The dendrites on this micrograph show both round tips due to polycrystalline growth and tips due to growth in macrosteps. From this it can be concluded that with increasing surface area of the cathode deposit the transient structure at the tips of the dendrites changes into a compact deposit. The particles with macrosteps, which in some cases show spiral character, are smaller and consequently have not grown enough to change their form, while those with round tips are bigger and are the result of a longer growing time.

The powders obtained from unstirred electrolytes are of almost equal size and have a pronounced dendritic character at all the cathode current densities examined (Fig. 7).

3.4. Effect of cathode potential

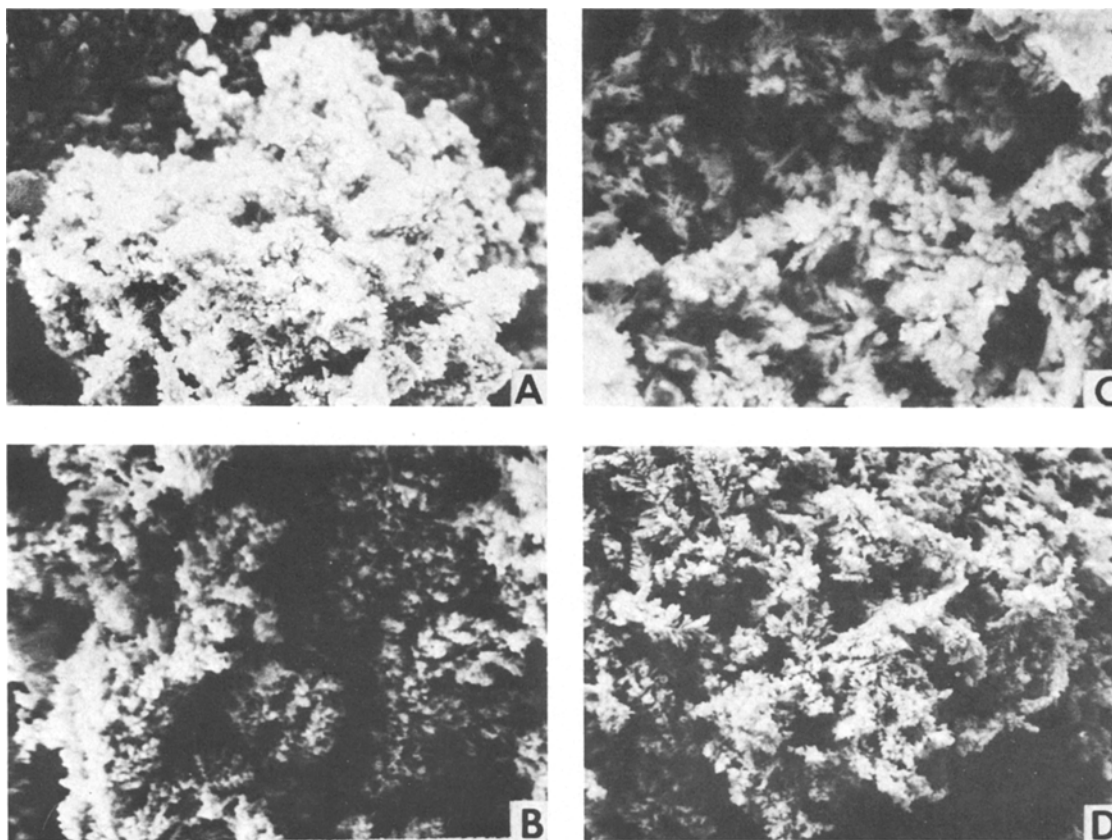The results described so far show that all the

Fig. 5. Effect of sulphuric acid concentration. Unstirred electrolyte. $C_{H_2SO_4} = $ A, $1 \, mol \, dm^{-3}$; B, $1.33 \, mol \, dm^{-3}$; C, $1.66 \, mol \, dm^{-3}$; D, $2 \, mol \, dm^{-3}$.

electrolysis parameters studied have a definite effect on the structure of the deposit. The exact relationships between them, however, remain obscure until we express the size and the form of the particles as a function of the cathode potential (Fig. 8).

Fig. 8 is composite: on its four parts the same potential–current density relationship is drawn to show the influence of the different plating variables investigated. On the right side of the figure the effect of the cathode potential on the size of the particles is shown, as well as the approximate cathode potential range in which each particular structure is obtained. A clear dependence of particle type emerges, indicating that the process of electrocrystallization primarily depends on the cathode potential, which in turn is a function of the concentration of the copper ion and the sulphuric acid, the current density, stirring, etc.

4. Discussion

All crystal forms observed by SEM examination of the copper powders fall into four categories: (a) dimeric and trimeric dendrites, the former representing composite crystals with two parallel twin planes and lamellae between them, while the latter are monocrystals; (b) particles with pyramidal tips, similar to the 'hollow needles' (prisms with pyramidal tips) which were observed by Saltikova *et al.* as a result of fourfold twinning [8–10]; (c) a transient form which is a result of growth in macrosteps over the pyramid-tipped particles (some of the steps may be accounted for by a spiral growth process) and (d) round particles or dendrites with round tips on which a compact deposit is formed. All these crystal forms show a good coincidence with those described by other authors [7–10]. An exception is the transient
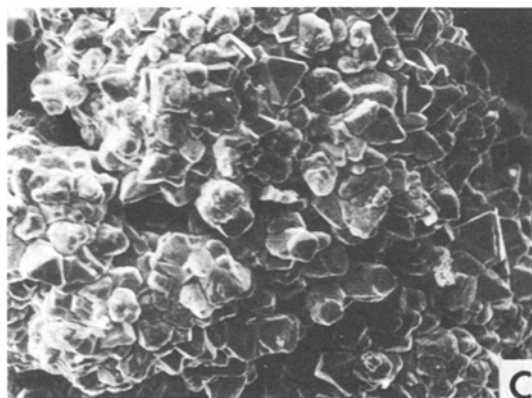
Fig. 6. Effect of cathode current density. Stirred electrolyte. I = A, 12.5 A dm^{-2}; B, 25 A dm^{-2}; C, 50 A dm^{-2}.
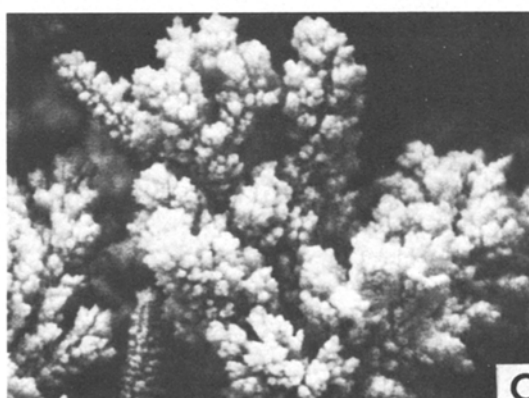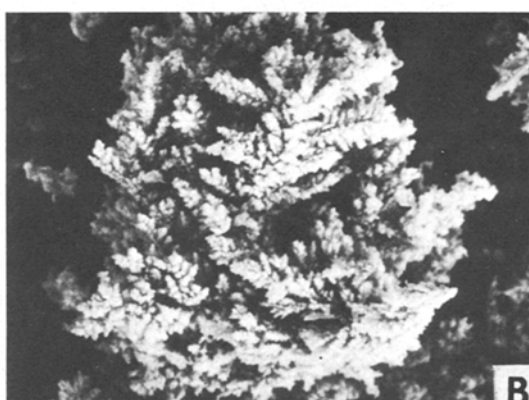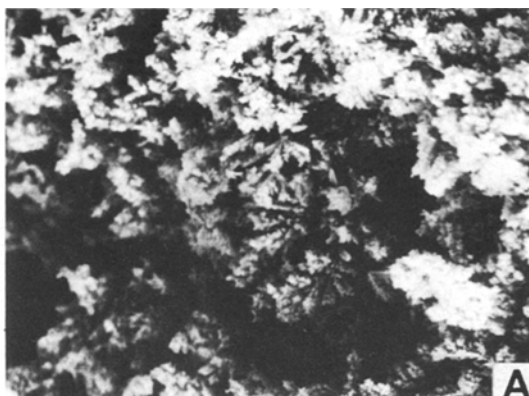

Fig. 7. Effect of cathode current density. Unstirred electrolyte. I = A, 12.5 A dm^{-2}; B, 25 A dm^{-2}; C, 50 A dm^{-2}.

structure, which has not been previously reported with sulphuric acid baths. In our experiments it appeared regularly and was clearly expressed in all cases as an intermediate between dendritic growth and electrocrystallization in a plane. Although the mechanism of formation of this structure cannot be considered proved, it can be

concluded from the micrographs in Fig. 9 that it is a change to polycrystalline growth over the already formed particles.

Our experiments show that the appearance of these four crystal forms, as well as the size of the particles, entirely depends on the cathode potential and indicates that it is possible to obtain the same
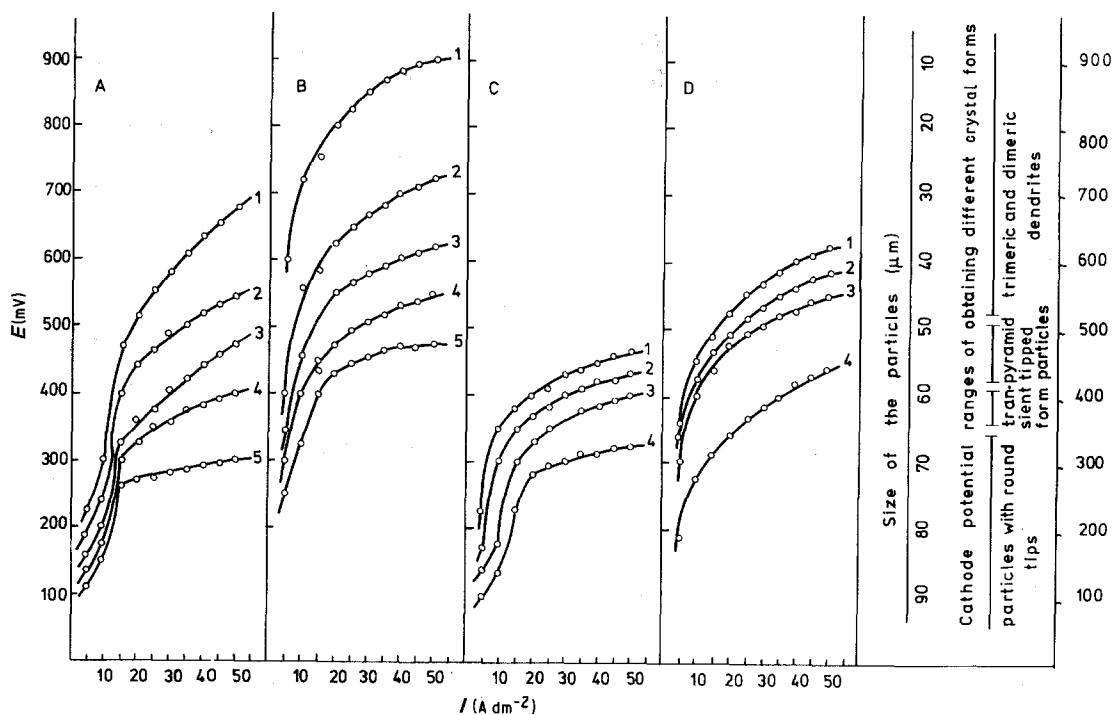
Fig. 8. The effect of plating variables on the cathode potential (recorded as minus cathode potential, referred to the SCE) and their effect on particle size and structure. Effect of copper ion concentration: A, stirred electrolyte; B, unstirred electrolyte; $C_{Cu^{2+}} = 1$, 0.0635 mol dm^{-3}; 2, 0.1270 mol dm^{-3}; 3, 0.1905 mol dm^{-3}; 4, 0.2540 mol dm^{-3}; 5, 0.3810 mol dm^{-3} ($C_{H_2SO_4} = 1.66$ mol dm^{-3} fixed). Effect of sulphuric ion concentration: C, stirred electrolyte; D, unstirred electrolyte. $C_{H_2SO_4} = 1$, 1 mol dm^{-3}; 2, 1.33 mol dm^{-3}; 3, 1.66 mol dm^{-3}; 4, 2 mol dm^{-3} ($C_{Cu^{2+}} = 0.2540$ mol dm^{-3} fixed).

type of deposit at quite different electrolysis parameters, provided cathode potential remains constant. This finding is important, because it allows the preparation of homogenous powders with controlled characteristics and also permits variation, within a given range of the electrolysis conditions, without any effect on the characteristics of the powder.

The best from a practical point of view are the trimeric dendrites with size about 10–30 μm, which are obtained at cathode potentials over — 450 mV versus SCE.
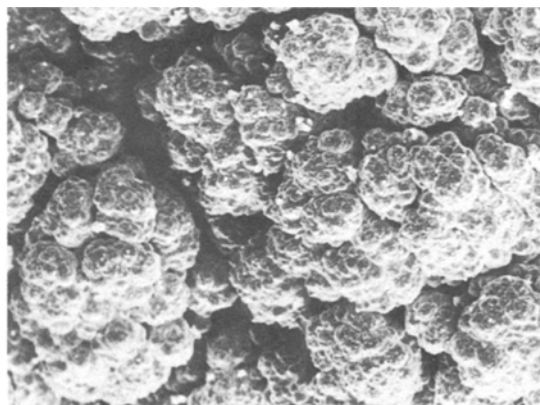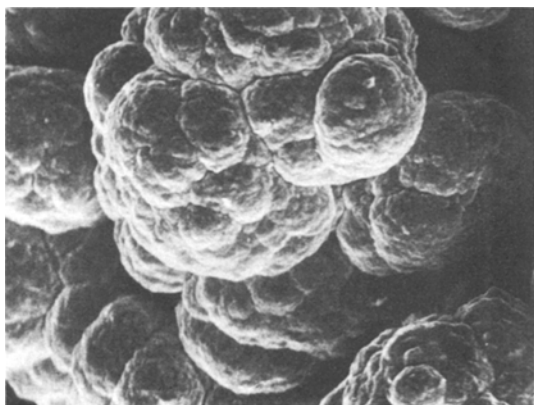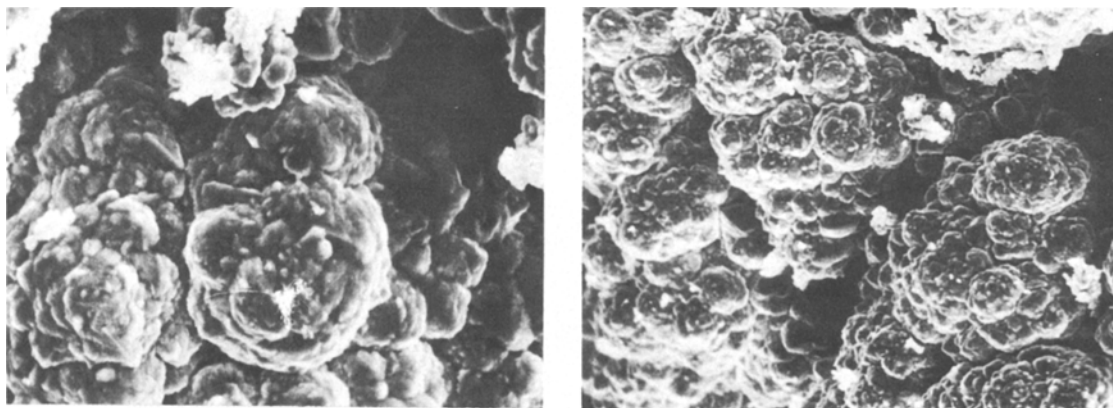

Fig. 9. Typical examples of the transient form.

Fig. 9(cont.). Typical examples of the transient form.

Acknowledgements

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